MOLPRO

Users Manual
Version 2015.1

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Introduction to MOLPRO

MOLPRO is a complete system of *ab initio* programs for molecular electronic structure calculations, designed and maintained by H.-J. Werner and P. J. Knowles, and containing contributions from a number of other authors. As distinct from other commonly used quantum chemistry packages, the emphasis is on highly accurate computations, with extensive treatment of the electron correlation problem through the multiconfiguration-reference CI, coupled cluster and associated methods. The recently developed explicitly correlated coupled-cluster methods yield CCSD(T) results with near basis set limit accuracy already with double−ζ or triple−ζ basis sets, thus reducing the computational effort for calculations of this quality by two orders of magnitude. Using local electron correlation methods, which significantly reduce the increase of the computational cost with molecular size, accurate *ab initio* calculations can be performed for much larger molecules than with most other programs. These methods have recently been augmented by explicitly correlated terms, which strongly reduce both the basis set truncation errors and the errors of the local approximations.

The heart of the program consists of the multiconfiguration SCF, multireference CI, and coupled-cluster routines, and these are accompanied by a full set of supporting features. The package comprises

- Integral generation for generally contracted symmetry adapted gaussian basis functions (spd fgh i). There are two programs with identical functionality: the preferred code is SEWARD (R. Lindh) which is the best on most machines; ARGOS (R. M. Pitzer) is available as an alternative, and in some cases is optimum for small memory scalar machines. Also two different gradient integral codes, namely CADPAC (R. Amos) and ALASKA (R. Lindh) are available. Only the latter allows the use of generally contracted symmetry adapted gaussian basis functions.

- Effective Core Potentials (contributions from H. Stoll).

- Many one-electron properties.

- Some two-electron properties, e.g. $L_x^2$, $L_y^2$, $L_z^2$, $L_xL_y$ etc..

- Closed-shell and open-shell (spin restricted and unrestricted) self consistent field.

- Density-functional theory in the Kohn-Sham framework with various gradient corrected exchange and correlation potentials.

- Multiconfiguration self consistent field. This is the quadratically convergent MCSCF procedure described in J. Chem. Phys. 82 (1985) 5053. The program can optimize a weighted energy average of several states, and is capable of treating both completely general configuration expansions and also long CASSCF expansions as described in Chem. Phys. Letters 115 (1985) 259.


- Møller-Plesset perturbation theory (MPPT), Coupled-Cluster (CCSD), Quadratic configuration interaction (QCISD), and Brueckner Coupled-Cluster (BCCD) for closed shell systems, as described in Chem. Phys. Lett. 190 (1992) 1. Perturbative corrections for triple excitations can also be calculated (Chem. Phys. Letters 227 (1994) 321).


- An interface to the MRCC program of M. Kallay, allowing coupled-cluster calculations with arbitrary excitation level.

- Full Configuration Interaction. This is the determinant based benchmarking program described in Comp. Phys. Commun. 54 (1989) 75.

- Analytical energy gradients for SCF, DFT, state-averaged MCSCF/CASSCF, MRPT2/CASPT2, MP2 and QCISD(T) methods.

- Analytical non-adiabatic coupling matrix elements for MCSCF.

- Valence-Bond analysis of CASSCF wavefunction, and energy-optimized valence bond wavefunctions as described in Int. J. Quant. Chem. 65, 439 (1997).

- One-electron transition properties for MCSCF, MRCI, and EOM-CCSD wavefunctions, CASSCF and MRCI transition properties also between wavefunctions with different orbitals, as described in Mol. Phys. 105, 1239, (2007).

- Spin-orbit coupling, as described in Mol. Phys., 98, 1823 (2000). More recently, a new spin-orbit integral program for generally contracted basis sets has been implemented.

- Douglas-Kroll-Hess Hamiltonian up to arbitrary order and the eXact-2-Component (X2C) Hamiltonian.


- Some two-electron transition properties for MCSCF wavefunctions (e.g., $L_\alpha^2$ etc.).

- Mulliken population analysis and Natural Population Analysis (NPA)

- Orbital localization.

- Natural bond orbitals (NBOs).

- Distributed Multipole Analysis (A. J. Stone).

- Automatic geometry optimization as described in J. Comp. Chem. 18, (1997), 1473. Constrained optimization is also possible.

- Automatic calculation of vibrational frequencies, intensities, and thermodynamic properties.


- Efficient facilities to treat large lattices of point charges for QM/MM calculations, including lattice gradients.

- Various utilities allowing other more general optimizations, looping and branching (e.g., for automatic generation of complete potential energy surfaces), general housekeeping operations.
Geometry output in XYZ, MOLDEN and Gaussian formats; molecular orbital and frequency output in MOLDEN format.

Integral-direct implementation of all Hartree-Fock, DFT and pair-correlated methods (MP, CCSD, MRCI etc.), as described in Mol. Phys., 96, (1999), 719. At present, perturbative triple excitation methods are not implemented.


Parallel execution on distributed memory machines, as described in J. Comp. Chem. 19, (1998), 1215. At present, SCF, DFT, MRCI, MP2, LMP2, CCSD(T), LCCSD(T) energies and SCF, DFT gradients are parallelized. Most density fitted codes such as DF-HF, DF-KS, DF-LMP2, DF-LMP2 gradients, DF-LCCSD(T), DF-MP2-F12, DF-DFT-SAPT, and GIAO-DF-HF NMR shieldings are also parallelized.

Automatic embarrassingly parallel computation of numerical gradients and Hessians (mppx Version).

The program is written mostly in standard Fortran–90. Those parts which are machine dependent are maintained through the use of a supplied preprocessor, which allows easy interconversion between versions for different machines. Each release of the program is ported and tested on a number of systems. A large library of commonly used orbital basis sets is available, which can be extended as required. There is a comprehensive users’ manual, which includes installation instructions. The manual is available in PDF and also in HTML for mounting on a Worldwide Web server.

More recent methods and enhancements include:


14. Enhanced connections to other programs, including graphical display of output and 3-dimensional structures.
15. Support for Mac OS X


18. DMRG calculations through the BLOCK code of the Chan group.

Future enhancements presently under development include

- Analytical energy gradients for CCSD(T) and CCSD(T)-F12.
- Analytic second derivatives for DFT.
- New, more efficient MRCI methods for larger molecules.

These features will be included in the base version at later stages. The above list is for information only, and no representation is made that any of the above will be available within any particular time.

**MOLPRO on the WWW**

The latest information on MOLPRO, including program updates, can be found on the worldwide web at location http://www.molpro.net/.

**References**

All publications resulting from use of this program must acknowledge the following two references.


Some journals insist on a shorter list of authors; in such a case, the following should be used instead.

MOLPRO, version 2015.1, a package of *ab initio* programs, H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schütz, and others see http://www.molpro.net.
Depending on which programs are used, the following references should be cited.

**Integral evaluation (SEWARD)**

**Integral-direct Implementation**

MCSCF/CASSCF:
H.-J. Werner and P. J. Knowles, J. Chem. Phys. 82, 5053 (1985);

See also:
H.-J. Werner and W. Meyer, J. Chem. Phys. 73, 2342 (1980);
H.-J. Werner and W. Meyer, J. Chem. Phys. 74, 5794 (1981);

**Internally contracted MRCI:**
H.-J. Werner and P.J. Knowles, J. Chem. Phys. 89, 5803 (1988);
H.-J. Werner and E.A. Reinsch, J. Chem. Phys. 76, 3144 (1982);

**Excited states with internally contracted MRCI:**

**Internally contracted MR-ACPF, QDVPT, etc:**

The original reference to uncontracted MR-ACPF, QDVPT, MR-AQCC are:

**Multireference perturbation theory (CASPT2/CASPT3):**
H.-J. Werner, Mol. Phys. 89, 645 (1996);


**Analytical energy gradients and geometry optimization**
Geometry optimization: F. Eckert, P. Pulay and H.-J. Werner, J. Comp. Chemistry 18, 1473 (1997);

**Harmonic frequencies**

**Anharmonic frequencies (SURF, VSCF, VCI):**
G. Rauhut, J. Chem. Phys. 121, 9313 (2004);
G. Rauhut, T. Hrenar, Chem. Phys. 346, 160 (2008);

**Ring-polymer instantons**
J. O. Richardson and S. C. Althorpe, J. Chem. Phys. 131, 214106 (2009);

**Full Configuration Interaction Quantum Monte Carlo**
D. M. Cleland, G. H. Booth, and A. Alavi, J. Chem. Phys. 134, 024112 (2011);

**Møller-Plesset Perturbation theory (MP2, MP3, MP4):**
Closed-shell Møller-Plesset Perturbation theory up to fourth order [MP4(SDTQ)] is part of the coupled cluster code, see CCSD.

**Open-shell Møller-Plesset Perturbation theory (RMP2):**

**Coupled-Cluster treatments (QCI, CCSD, BCCD):**

**Quasi-Variational Coupled-Cluster (QVCCD, OQVCCD, BQVCCD):**

**Equation-of-Motion Coupled Cluster Singles and Doubles (EOM-CCSD):**

**Open-shell coupled-cluster (RCCSD, UCCSD):**

**Local MP2 (LMP2):**
See also references on energy gradients, density fitting, and explicitly correlated methods.

**Local Coupled Cluster methods (LCCSD, LQCISD, LMP4):**


See also references on energy gradients, density fitting, and explicitly correlated methods.

Local methods for excited states:


LCC2 response and ADC(2) orbital relaxed properties and nuclear gradients:


Density fitting methods:


Explicitly correlated MP2 methods:

A. J. May and F. R. Manby, J. Chem. Phys. 121, 4479 (2004);


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Explicitly correlated coupled-cluster methods:


T. B. Adler and H.-J. Werner, J. Chem. Phys. 130, 241101 (2009);


Explicitly correlated multi-reference methods:


Rangehybrid methods:

Full CI (FCI):
P. J. Knowles and N. C. Handy, Chem. Phys. Letters 111, 315 (1984);

Distributed Multipole Analysis (DMA):

Valence bond:
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M. Reiher, A. Wolf, JCP 121, 2037–2047 (2004);
M. Reiher, A. Wolf, JCP 121, 10945–10956 (2004);

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H.-J. Werner and W. Meyer, J. Chem. Phys. 74, 5802 (1981);

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1 HOW TO READ THIS MANUAL

This manual is organized as follows: The next chapter gives an overview of the general structure of MOLPRO. It is essential for the new user to read this chapter, in order to understand the conventions used to define the symmetry, records and files, orbital spaces and so on. The later chapters, which describe the input of the individual program modules in detail, assume that you are familiar with these concepts. The appendices describe details of running the program, and the installation procedure.

Throughout this manual, words in Typewriter Font denote keywords recognized by MOLPRO. In the input, these have to be typed as shown, but may be in upper or lower case. Numbers or options which must be supplied by the user are in italic. In some cases, various different forms of an input record are possible. This is indicated as [options], and the possible options are described individually in subsequent subsections.

2 RUNNING MOLPRO

On Unix systems, MOLPRO is accessed using the molpro unix command. The syntax is

molpro [options] [datafile]

MOLPRO’s execution is controlled by user-prepared data; if datafile is not given on the command line, the data is read from standard input, and program results go to standard output. Otherwise, data is taken from datafile, and the output is written to a file whose name is generated from datafile by removing any trailing suffix, and appending .out. If the output file already exists, then the old file is appended to the same name with suffix .out.1, and then deleted. This provides a mechanism for saving old output files from overwriting. Note that the above behaviour can be modified with the -o or -s options.

2.1 Options

Most options are not required, since sensible system defaults are usually set. Options as detailed below may be given, in order of decreasing priority, on the command line, in the environment variable MOLPRO_OPTIONS, or in the files ./molpro.rc, $HOME/.molprorc, and tuning.rc in the library files directory.

-d dir1:dir2:... where dir1:dir2:... is a list of directories which may be used for creating scratch files. Each of the directories should be writable by those who will use the program, and the directory specification may contain embedded environment variables in shell form, for example $TMPDIR or /tmp/$USER; these will be expanded at run time. If multiple scratch file systems are available, it is advantageous to present a list of directories of which there is one in each file system. Some parts of MOLPRO present extreme I/O demands, and it is therefore important to be careful in optimizing the provision and specification of scratch directories.

Note that in the building of bin/molpro, the environment variables $TMPDIR, $TMPDIR2, $TMPDIR3..., are used to construct the list of scratch directories for the -d option. Thus, these environment variables should at make time be filled with the names
of directories on each available scratch file system (cf. section A.2.3).

-o|--output outfile  specifies a different output file.

-x|--executable executable  specifies an alternative MOLPRO executable file.

-d|--directory directory1:directory2...  specifies a list of directories in which the program will place scratch files. For detailed discussion of optimal specification, see the installation guide.

--backup nfile  enables the saving of previous output files, up to a maximum of nfile. If nfile is omitted, it defaults to infinity. The names of the backup files are constructed by appending _ and a sequence number to the output file name, and both regular and xml-format files are processed, together with any log file.

-a|--append-backup  Previous output files are concatenated by appending, instead of being kept separate.

--directory-backup  Backup files are stored in a single separate subdirectory, named datafile_d, with subdirectories 01, 02,..., --directory-backup and --append-backup are mutually exclusive, and switching one of them on will force the other to be switched off.

--backup-directory dir  In the case of --directory-backup, use dir as the location of backup files instead of the default.

-s|--nobackup  disables the mechanism whereby an existing output file is saved.

-v|--verbose  causes the procedure to echo debugging information; --noverbose selects quiet operation (default).

-k key  where key is the licence key. This is normally not necessary since the key should be installed globally when installing MOLPRO.

-m|--memory memory  specifies the working memory to be assigned to the program, in 8-byte words. For details, see section 4.6.

-I|--main-file-repository directory  specifies the directory where the permanent copy of any integral file (file 1) resides. This may be a pathname which is absolute or relative to the current directory (e.g., . would specify the current directory). Normally, the -I directory should be equal to the -d working directory to avoid copying of large integral files, since after completion of the job the file will be copied to the directory given after -I. On some main frames, the scratch directory is erased automatically after a job has terminated, and in such cases a different -I directory, e.g., $HOME/int, can be specified (environment variables will be expanded at run time). In view of the large integral file sizes, this should be used with care, however. Note that in parallel runs with more than 1 processor the integral file will never be copied, and cannot be restarted.

-W|--wavefunction-file-repository directory is similar to --main-file-repository except that it refers to the directory for the wavefunction files (2,3 and 4). This determines the destination of permanent wavefunction (dump) files used for storing information like orbitals or CI-vectors etc. These files are essential for restarting a job. As explained for the integral files above, permanent wavefunction files will be copied to directory after completion of the job. The default for directory is $HOME/wfu.
-X | --xml-output  specifies that the output file will be a well-formed XML file suitable for automatic post-processing. Important data such as input, geometries, and results are tagged, and the bulk of the normal descriptive output is wrapped as XML comments. --no-xml-output switches off this behaviour and forces a plain-text output file to be produced.

-L | --library directory  specifies the directory where the basis set library files (LIBMOL*) are found.

-1 | --file-1-directory directory:directory:...  specifies the directory where the run-time file 1 will be placed, overriding --directory for this file only. -2, -3, -4, -5, -6, -7, -8 and -9 may be used similarly. Normally these options should not be given, since the program tries to use what is given in -d to optimally distribute the I/O.

-t | --omp-num-threads n  Specify the number of OpenMP threads, as if the environment variable OPENMP_NUM_THREADS were set to n.

--xml2txt  Convert Molpro XML output file to plain text. In this mode the input file should refer to a Molpro XML output file.

--no-flush6  Don’t flush the output, this might increase performance on some systems as the expense of being able to poll the output.

-g | --use-logfile  Use a separate logfile for more in-depth output.

--nouse-logfile  All output will be in the regular output file.

-E | --exclusive-file-implementation  Specify file implementation. This is mainly for debugging, eg. reproducing non-shared file problems on a system with shared files, normally the default should be used.

--init  Run the initialization job, this is called as part of the build process and should not be used directly.

-k | --licence-token  Specify licence token on the command line.

--version  Print Molpro version and exit

--sysid  For debugging when the getinfo.sh script does not give the correct sysid.

There are a number of other options, specific to parallel execution, which are summarized below and described in detail in the next section. All of the following options are ignored when using serial MOLPRO.

-n | --tasks tasks/tasks_per_node:smp_threads tasks  specifies the number of parallel processes to be set up.

-N | --task-specification user1:node1:tasks1,user2:node2:tasks2... node1, node2 etc.  specify the host names of the nodes on which to run.

-S | --shared-file-implementation method  specifies the method by which the shared data are held in parallel.

--multiple-helper-server nprocs_per_server  enables the multiple helper servers.

--node-helper-server  specifies one helper server on every node.

--single-helper-server  specifies only one single helper server for all processes.

--no-helper-server  disables the helper server.
--all-outputs produces an output file for each process when running in parallel.
--ga-debug activates GA debugging statements.
--check-collective check collective operations when debugging
--mpp run conventional parallel (default)
--mppx run identical independent tasks parallel (eg. for frequencies).
--gpu|--gpus n number of GPUs
--tuning-mincuda n minimum dimension for using GPUs (CUDA), currently unused
--nclearsp n for clearspeed, obsolete
--tuning-mpplat n mpp latency in microseconds
--tuning-mpps speed n mpp bandwidth in MB/sec
-G|--global-memory n total amount of GA space initially allocated
-M|--ga-stack n stack option to MA_init() call
--ga-heap n heap option to MA_init() call

There are a number of other options for tuning and system parameters, but these do not usually concern the general user.

Tuning parameters for blas routines (mxma, mxmb, mxva, mxvb):

--tuning-flopdgm n speed of dgemm in MFLOPS
--tuning-flopdgv n speed of dgemv in MFLOPS
--tuning-flopxmxm n speed of fortran mxma in MFLOPS
--tuning-flopxmv n speed of fortran mxva in MFLOPS
--tuning-mindgv n use dgemv from mxva/mxvb if matrix dimensions are ge. mindgv
--tuning-mindgm n use dgemm from mxma/mxmb if all matrix dimensions are ge. mindgm
--tuning-mindgc n use dgemm from mxma/mxmb if column dimension is ge. mindgc and other dimensions larger than mindgm2
--tuning-mindgr n use dgemm from mxma/mxmb if row dimension is ge. mindgr and other dimensions larger than mindgm2
--tuning-mindgl n use dgemm from mxma/mxmb if link dimension is ge. mindgl and other dimensions larger than mindgm2
--tuning-mindgf n for old Fujitsu machines, probably obsolete

Tuning parameters for fortran versions of mxma/mxmb:

--tuning-unroll n level of unrolling in (2,3, or 4)
-b|--matrix-block-link|--tuning-mxmbln n block dimension for link dimension
-B|--matrix-block|--tuning-mxmblk n block dimension for rows and columns of result matrix
-K|--cache|--tuning-cache n cache size in words. If the total size of the 3 matrices is smaller than this, no blocking.

It is not usually necessary to specify any of these options as there are sensible defaults. Sometimes installation dependent options can be found in the system configuration file molpro.rc in the same directory as the MOLPROlibrary files.
2.2 Running MOLPRO on parallel computers

MOLPRO will run on distributed-memory multiprocessor systems, including workstation clusters, under the control of the Global Arrays parallel toolkit or the MPI-2 library. There are also some parts of the code that can take advantage of shared memory parallelism through the OpenMP protocol, although these are somewhat limited, and this facility is not at present recommended. It should be noted that there remain some parts of the code that are not, or only partly, parallelized, and therefore run with replicated work. Additionally, some of those parts which have been parallelized rely on fast inter-node communications, and can be very inefficient across ordinary networks. Therefore some caution and experimentation is needed to avoid waste of resources in a multiuser environment.

MOLPRO effects interprocess cooperation through the ppidd library, which, depending on how it was configured and built, draws on either the Global Arrays parallel toolkit or pure MPI. ppidd is described in Comp. Phys. Commun. 180, 2673-2679 (2009). Global Arrays handles distributed data objects using whatever one-sided remote memory access facilities are provided and supported. In the case of the MPI implementation, there is a choice of using either MPI-2 one-sided memory access, or devoting some of the processes to act as data ‘helpers’. It is generally found that performance is significantly better, and competitive with Global Arrays, if at least one dedicated helper is used, and in some cases it is advisable to specify more. The scalable limit is to devote one core on each node in a typical multi-core cluster machine, but in most cases it is possible to manage with fewer, thereby making more cores available for computation. This aspect of configuration can be tuned through the *-helper-server options described below.

Molpro can be compiled in three different ways:

1. Serial execution only. In this case, no parallelism is possible at run time.
2. ‘MPP’: a number of copies of the program execute simultaneously a single task. For example, a single CCSD(T) calculation can run in parallel, with the work divided between the processors in order to achieve a reduced elapsed time.
3. ‘MPPX’: a number of copies of the program run in serial executing identical independent tasks. An example of this is the calculation of gradients and frequencies by finite difference: for the initial wavefunction calculation, the calculation is replicated on all processes, but thereafter each process works in serial on a different displaced geometry. At present, this is implemented only for numerical gradients and Hessians.

Which of these three modes is available is fixed at compilation time, and is reported in the job output. The options, described below, for selecting the number and location of processors are identical for MPP and MPPX.

2.2.1 Specifying parallel execution

The following additional options for the molpro command may be used to specify and control parallel execution.

-n | --tasks tasks/tasks_per_node:smp_threads tasks specifies the number of parallel processes to be set up, and defaults to 1. tasks_per_node sets the number of GA(or MPI-2) processes to run on each node, where appropriate. The default is installation dependent. In some environments (e.g., IBM running under Loadleveler; PBS batch job),
the value given by \(-n\) is capped to the maximum allowed by the environment; in such circumstances it can be useful to give a very large number as the value for \(-n\) so that the control of the number of processes is by the batch job specification. \textit{smp\_threads} relates to the use of OpenMP shared-memory parallelism, and specifies the maximum number of OpenMP threads that will be opened, and defaults to 1. Any of these three components may be omitted, and appropriate combinations will allow GA(or MPI-2)-only, OpenMP-only, or mixed parallelism.

\(-N\)\textbar\textit{--task-specification} user1\_node1\_tasks1, user2\_node2\_tasks2... \textit{node1, node2 etc.} specify the host names of the nodes on which to run. On most parallel systems, node 1 defaults to the local host name, and there is no default for node 2 and higher. On Cray T3E and IBM SP systems, and on systems running under the PBS batch system, if \(-N\) is not specified, nodes are obtained from the system in the standard way. \textit{tasks1, tasks2 etc.} may be used to control the number of tasks on each node as a more flexible alternative to \(-n / \textit{tasks\_per\_node}\). If omitted, they are each set equal to \(-n / \textit{tasks\_per\_node}\). user1, user2 etc. give the username under which processes are to be created. Most of these parameters may be omitted in favour of the usually sensible default values.

\(-S\)\textbar\textit{--shared-file-implementation} \textit{method} specifies the method by which the shared data are held in parallel. \textit{method} can be \textit{sf} or \textit{ga}, and it is set automatically according to the properties of scratch directories by default. If \textit{method} is manually set to \textit{sf}, please ensure all the scratch directories are shared by all processes. Note that for GA version of MOLPRO, if \textit{method} is set to \textit{sf} manually or by default, the scratch directories can’t be located in NFS when running \textit{molpro\_job} on multiple nodes. The reason is that the SF facility in Global Arrays doesn’t work well on multiple nodes with NFS. There is no such restriction for MPI-2 version of MOLPRO.

\textit{--multiple-helper-server} \textit{nprocs\_per\_server} enables the multiple helper servers, and \textit{nprocs\_per\_server} sets how many processes own one helper server. For example, when total number of processes is specified as 32 and \textit{nprocs\_per\_server} = 8, then every 8 processes(including helper server) will own one helper server, and there are 4 helper servers in total. For any unreasonable value of \textit{nprocs\_per\_server} (i.e., any integer less than 2), it will be reset to a very large number automatically, and this will be equivalent to option \textit{--single-helper-server}.

\textit{--node-helper-server} specifies one helper server on every node if all the nodes are symmetric and have reasonable processes (i.e., every node has the same number of processes, and the number should be greater than 1), and this is the default behaviour. Otherwise, only one single helper server for all processes/nodes will be used, and this will be equivalent to option \textit{--single-helper-server}.

\textit{--single-helper-server} specifies only one single helper server for all processes.

\textit{--no-helper-server} disables the helper server.

\(-t\)\textbar\textit{--omp\_num\_threads} \textit{n} Specify the number of OpenMP threads, as if the environment variable \textit{OPENMP\_NUM\_THREADS} were set to \textit{n}.
Note that options --multiple-helper-server, --node-helper-server, --single-helper-server, and --no-helper-server are only effective for MOLPRO built with MPI-2 library. In the cases of one or more helper servers enabled, one or more processes act as data helper servers, and the rest processes are used for computation. Even so, it is quite competitive in performance when it is run with a large number of processes. In the case of helper server disabled, all processes are used for computation; however, the performance may not be good because of the poor performance of some existing implementations of the MPI-2 standard for one-sided operations.

In addition, for MOLPRO built with GA library (MPI over InfiniBand), GA data structures can’t be too large (e.g., 2GB per node) when running molpro job on multiple nodes. In this case, setting environment variable ARMCI_DEFAULT_SHMMAX might be helpful. The number should be less than 2GB (e.g., to set 1600MB for ARMCI_DEFAULT_SHMMAX in bash: export ARMCI_DEFAULT_SHMMAX=1600). One can also use more computer nodes to run such jobs, thus allocated memory for GA data structures on each node becomes smaller. There is no such restriction for MPI-2 version of MOLPRO.
3 DEFINITION OF MOLPRO INPUT LANGUAGE

3.1 Input format

MOLPRO’s execution is controlled by an input file. In general, each input record begins with a keyword, which may be followed by data or other keywords. Molpro input contains commands, directives, options and data. The commands and directives are sequentially executed in the order they are encountered. Furthermore, procedures can be defined anywhere in the input, which can include any number of commands and directives. They are only executed when called (which may be before or after the definition in the input file).

The input file can be written in free format. The following conversions take place:

- , (comma) move to next tab stop, i.e. this delimits input fields
- ; (semicolon) end of record, i.e. a new record is started
- ! (exclamation mark) ignore rest of input line (useful for comments)
- --- (three dashes) end of file (rest of input is ignored)

Input may be given upper or lower case. The input processor converts all characters to upper case. All integers are appended with "." (only floating point numbers are read by the program).

Several logical input records can actually be typed on one line and separated by semicolons, i.e., a given input line may contain many actual commands (separated by semicolons), or just one, as you prefer. These basic command units (records) delimited by semicolons are also frequently referred to as cards throughout this manual.

Exception to these general rules are:

*** first data line always
INCLUDE include other input file
FILE definition of named files
TEXT prints text
TITLE defines a title for the run or a table
CON specifies orbital configurations
--- last line of input

These commands always occupy a whole line. Using INCLUDE it is possible to open secondary input files. If an INCLUDE command is encountered, the new input file is opened and read until its end. Input is then continued after the include card in the first file. INCLUDE’s may be nested.

A MOLPRO input record (card) contains a number of input fields. Input fields may be up to 256 characters wide and contain either expressions or strings. The fields can be separated by commas or blanks. We recommend the general use of commas in order to avoid unexpected results.

Each line may start with a label. A label is separated from the body of the line by a colon (:). The colon is part of the label. The length of the label must not exceed 6 characters (including the colon) and the labels must be unique. Labels may be useful with GOTO commands. Example:

GOTO, START:
...
START: CCSD(T)
3 DEFINITION OF MOLPRO INPUT LANGUAGE

Here \texttt{START}: is a label, and \texttt{CCSD(T)} is a command.

Strings containing blanks can be entered using quotes. For instance, \texttt{'This is a string'} is interpreted as one string, but \texttt{This is a string} is a sequence of four strings in four subsequent fields. Strings in quotes are not converted to upper case.

Input lines may be concatenated using \texttt{\backslash} at the end of the line(s) to be continued. Any number of lines may be concatenated up to a total length of 1024 characters (only 500 characters are possible on older IBM systems).

Filenames may be up to 31 characters long, provided that long filenames are supported by the Unix system used. An exception are older CRAY systems, which allow only 8 characters for the names of binary MOLPRO files.

3.2 Commands

A command invokes a particular program. It may be followed by local input for this program, enclosed in curley brackets\footnote{Depending on the parameter \texttt{STRICTCHECK} in file \texttt{lib/variable.registry} the program may tolerate directives given after commands without curley brackets. The program checks for ambiguities in the input. A directive is considered ambiguous if a command or procedure with the same name is known, and the directive is not in a command block (i.e., no curley brackets are used). \texttt{STRICTCHECK=0}: The input checker tolerates ambiguous directives if they are followed by a non ambiguous directive which is valid for the current command. \texttt{STRICTCHECK=1}: The input checker does not tolerate any ambiguous directives. \texttt{STRICTCHECK=2}: The input checker does not tolerate any directives outside curley brackets. The default is \texttt{STRICTCHECK=0}, which gives the maximum possible compatibility to previous Molpro versions.}.

The general format is either

\texttt{COMMAND, options}

or

\texttt{\{COMMAND, options}

\texttt{directives}

\texttt{data}

\texttt{\}}

Examples for commands are \texttt{HF}, \texttt{MP2}, \texttt{CCSD(T)}, \texttt{MCSCF}, \texttt{MRCI}. Examples for directives are \texttt{OCC}, \texttt{CLOSED}, \texttt{WF}, \texttt{PRINT}. Directives can be in any order, unless otherwise noted. Data can follow certain directives. For the format of options, directives and data see subsections \texttt{3.3}, \texttt{3.5}, and \texttt{3.6}, respectively.

In the following, such a sequence of input will be denoted a \textit{command block}. Special command blocks are the geometry and basis blocks.

The options given on the command line may include any options relevant to the current program. For instance, in DF-LMP2-R12 this could be options for density fitting, local, explicit, and/or thresholds. Alternatively, options can be specified on individual directives like

\texttt{DFIT, options}

\texttt{LOCAL, options}

\texttt{EXPLICIT, options}

\texttt{THRESH, options}

In these cases, only the options belong to the corresponding directive are valid; thus, if an option for \texttt{EXPLICIT} would be specified, e.g., on the \texttt{DFIT} directive, an error would result. This error would be detected already in the input prechecking stage.
As already mentioned, the use of curly brackets is normally compulsory if more than one input line is needed. In the case of one-line commands, curley brackets are needed as well if the next command or procedure has the same name as a directive valid for the current command.

Note: DIRECT and associated options cannot be specified on command lines any more.

### 3.3 Directives

Directives serve to specify input data and special options for programs. They start with a keyword, followed by data and/or options. The general format is

```
DIRECTIVE data options
```

The format of data and options is specified in the subsequent sections. Data must always be given before any options.

Examples for directives are

```
OCC,CORE, CLOSED, WF, LOCAL, DFIT, ... 
```

### 3.4 Global directives

Certain directives can be given anywhere in the input, i.e. either inside or outside command blocks. If they are given inside of command blocks, the specified options are valid only locally for the current program. However, if they are given outside a command block, they act globally, and are used for all programs executed after the input has been encountered. Local options have preference over global options.

The following directives can be either local or global:

- **Wavefunction definition**: OCC, CORE, CLOSED, FROZEN, WF
- **Thresholds and options**: LOCAL, DFIT, DIRECT, EXPLICIT, THRESH, PRINT, GRID

If such options are given outside a command block, a context can be specified

```
DIRECTIVE data, CONTEXT= context,
```

e.g.,

```
OCC,3,1,1, CONTEXT= HF
OCC,4,1,2, CONTEXT= MCSCF
```

**CONTEXT** can be any valid command name (or any valid alias for this), but internally these are converted to one of the following: HF (Hartree-Fock and DFT), MC (MCSCF and CASSCF), CC (single reference correlation methods, as implemented in the CCSD program), CI (multireference correlation methods, as implemented in the MRCI program). The directive will then be applied to one of the four cases. Several contexts can be specified separated by colon, e.g.,

```
CONTEXT=HF:CCSD
```

If only a single context is given (no colon), shortcuts for the specifying the CONTEXT option are obtained by postfixing context to the command name, e.g.,

```
OCC_HF,3,1,1
OCC_MCSCF,4,1,2
```

If no context is given, the default is HF. The default occupations for single reference methods (e.g., MP2, CCSD) are the ones used in HF, the defaults for multireference methods (e.g. RS2, MRCI) correspond to those used in MCSCF.
3.5 Options

Options have the general form \[\text{NAME}[=\text{value}]\]

where value can be a number, and expression, or a string. Several options are separated by comma or blank. \text{NAME} must begin with a character [A-Z]. If options are given on a COMMAND line or on directives within a command block, they are valid only for the corresponding program (see Sec. 3.3). If options are given in a procedure, they are valid only in the procedure and procedures called from the current procedure; whenever a procedure is terminated, the options of the previous level are restored.

Options can also be single keywords, like \text{SYM} or \text{NOSYM}. In this case, the option is switched on or off, depending whether or not the key begins with \text{NO}. Alternatively, such logical options can also be set or unset using \text{NAME=ON} or \text{NAME=OFF}. For instance, \text{SYM=OFF} is equivalent to \text{NOSYM}. Furthermore, \text{YES} and \text{NO} are aliases for \text{ON} and \text{OFF}, respectively.

3.6 Data

Data are defined as a sequence of numbers, expressions, or strings, separated by commas or blanks. Generally, the order of data is essential. Empty fields are interpreted as zeros. Strings and variables must begin with a character [A-Z]. If + or − follows blank and directly precedes a number or variable it is interpreted as sign and not a binary operator. If there are no blanks before and after such operators, or blanks follow them, they are interpreted as binary operators. For example:

\[
3 - 4 4 \quad \text{yields \([-1,4]\)}
\]

\[
3 -4 4 \quad \text{yields \([-1,4]\)}
\]

\[
3 -4 4 \quad \text{yields \([3,-4,4]\)}
\]

\[
3, -4 4 \quad \text{yields \([3,-4,4]\)}
\]

\[
3, -4, 4 \quad \text{yields \([3,-4,4]\)}
\]

Expressions (including numbers) may contain variables.

Examples for the use of data: geometry and basis input, \text{LATTICE, OCC, CLOSED, CORE, WF} directives.

In some cases several lines of data are needed for a certain command or directive; in such cases the data must follow directly the corresponding command|directive, and must be enclosed in square brackets:

\[\text{COMMAND, options [data]}\]

Normally, the input format of data is \text{MOLPRO} style, i.e., numbers are separated by commas, and variables as well as expressions can be used.

If data are included using external files, the input format of data is free format: no commas are needed, but no variables and expressions can be used.

3.7 Expressions

In any input field, data can be entered in the form of expressions. Numbers and variables are special cases of expressions. An expression is typed in Fortran style and may contain any number of nested parenthesis. The standard intrinsic functions are also available (see next section).
MOLPRO understands both arithmetic and logical expressions. The result of an arithmetic expression is a real (double precision) number. Internally, all integers are also converted to real numbers. The result of a logical expression is either .TRUE. or .FALSE.. Internally, .TRUE. is stored as a one (1.0), and .FALSE. as zero (0.0). Expressions may contain any number of variables.

The following standard operations can be performed:

- \( expr + expr \)  Addition
- \( expr - expr \)  Subtraction
- \( expr * expr \)  Multiplication
- \( expr / expr \)  Division
- \( expr \text{ .OR. } expr \)  Logical OR
- \( expr \text{ .AND. } expr \)  Logical AND
- \( expr \text{ .XOR. } expr \)  Exclusive OR
- \( .\text{NOT.} expr \)  Logical NOT
- \( expr \text{ .GT. } expr \)  Greater Than
- \( expr \text{ .EQ. } expr \)  Equal
- \( expr \text{ .LT. } expr \)  Less Than
- \( expr \text{ .GE. } expr \)  Greater Equal
- \( expr \text{ .LE. } expr \)  Less Equal
- \( expr \text{ .NE. } expr \)  Not Equal
- \( expr \text{ ** } expr \)  Exponentiation
- \( expr \text{ ^ } expr \)  Exponentiation
- \( (expr) \)  Parenthesis (no effect)
- \(-expr\)  Change sign
- \(+expr\)  Keep sign (no effect)

### 3.8 Intrinsic functions

Expressions may contain the following intrinsic functions:

- \( \text{ABS (expr)} \)  Absolute value
- \( \text{MAX (expr,expr, . . . )} \)  Largest value of arbitrary number of numbers or expressions
- \( \text{MIN (expr,expr, . . . )} \)  Smallest value of arbitrary number of numbers or expressions
- \( \text{EXP (expr)} \)  Exponential
- \( \text{LOG (expr)} \)  Natural Logarithm
- \( \text{LOG10 (expr)} \)  Common Logarithm
- \( \text{SQRT (expr)} \)  Square Root
- \( \text{NINT (expr)} \)  Next nearest integer
- \( \text{INT (expr)} \)  Truncate to integer
- \( \text{SIN (expr)} \)  Sine
3 DEFINITION OF MOLPRO INPUT LANGUAGE

\[
\begin{align*}
\text{COS}(\text{expr}) & \quad \text{Cosine} \\
\text{TAN}(\text{expr}) & \quad \text{Tangent} \\
\text{ASIN}(\text{expr}) & \quad \text{Arcsine} \\
\text{ACOS}(\text{expr}) & \quad \text{Arccosine} \\
\text{ATAN}(\text{expr}) & \quad \text{Arctangent} \\
\text{COSH}(\text{expr}) & \quad \text{Hyperbolic cosine} \\
\text{SINH}(\text{expr}) & \quad \text{Hyperbolic sine} \\
\text{TANH}(\text{expr}) & \quad \text{Hyperbolic tangent} \\
\text{MOD}(\text{expr1}, \text{expr2}) & \quad \text{Remainder: expr1-\text{INT}(expr1/expr2)\times expr2}
\end{align*}
\]

Note: all trigonometric functions use or produce angles in degrees.

3.9 Variables

3.9.1 Setting variables

Data and results can be stored in MOLPRO variables. Variables can be of type string, floating, or logical and may be used anywhere in the input.

The syntax for setting variables is

\[
\text{VARNAME1}=\text{expression} [\text{unit}], \text{VARNAME2}=\text{expression} [\text{unit}]
\]

where unit is optional. If a variable is undefined, zero is assumed.

Variables are useful for running the same input with different actual parameters (e.g. geometries or basis function exponents), and to store and manipulate the results. Arrays are variables with an index in parenthesis, e.g., \text{var}(1). The number of elements in an array \text{var} is \#\text{var}. The array length can be reset to zero by the \text{CLEAR} directive or simply by modifying \#\text{var}.

Variables and variable arrays may be displayed at any place in the output by the \text{SHOW} command, and whole tables of variables can be generated using the \text{TABLE} command. For more details about variables see section 8.

3.9.2 String variables

Special care is necessary when using strings. In order to avoid unexpected results, either a $ has to be prefixed whenever a string variable is set, or the string has to be given in quotes. Possible forms are

\[
\begin{align*}
\$\text{name}=\text{string} \\
\text{name}='\text{string}' \\
\text{name}=\text{string variable} \\
\$\text{name}=\text{string variable}
\end{align*}
\]

Examples:

\[
\begin{align*}
\text{string1}='\text{This is a string}' & \quad !\text{define a string variable. Text in quotes is not converted to upper case.} \\
\text{string2}=\text{string1} & \quad !\text{assign string variable string1 to a new variable.} \\
\$\text{string3}=\text{string1} & \quad !\text{equivalent to previous case.} \\
\$\text{string4}=\text{mystring} & \quad !\text{define a string variable. Since ‘’mystring’’ is not given in quotes, it will be converted to upper case.} \\
\text{string5}=\text{mystring} & \quad !\text{string5 will not be a string variable since $ is missing.}
\end{align*}
\]
3 DEFINITION OF MOLPRO INPUT LANGUAGE

yields

```
SETTING STRING1 = This is a string
SETTING STRING2 = This is a string
SETTING STRING3 = This is a string
SETTING STRING4 = MYSTRING
VARIABLE MYSTRING UNDEFINED, ASSUMING 0
SETTING STRING5 = 0.00000000
```

For more information concerning strings and string variables, see section 8.3

3.10 Procedures

3.10.1 Procedure definition

Procedures are sequences of commands and/or options. They can be defined anywhere in the input as

```
[PROC] procname={
command blocks
directives
}
or
PROC procname
command blocks
directives
ENDPROC
```

In order to avoid unexpected results, `procname` must differ from all known command names. Procedures must not contain geometry blocks.

Note that procedures are not executed when encountered in the input, but only when called. Procedure definitions must not be nested. Procedures can contain procedure calls up to a nesting level of 10.

3.10.2 Procedure calls

Procedures can be called anywhere in the input. The syntax is the same as for commands (cf. section 3.2), except that the procedure name replaces the command name.

```
PROCEDURE
```

No options are allowed on procedure calls. However, specific options may be set using directives within the procedure, and these are then valid for all programs within the procedure which follow the directive. When execution of the procedure is finished, the previous global options are restored. The hierarchy in which options are processed is as follows:

- Global options
- Options in procedures
- Command line options
- Options given on directives within a command block
4 GENERAL PROGRAM STRUCTURE

The last option set is then actually used. Thus, options specified on command lines or within command blocks have preference over procedure options, and procedure options have preference over global options.

4 GENERAL PROGRAM STRUCTURE

This chapter gives an overview of the most important features of MOLPRO. For the new user, it is essential to understand the strategies and conventions described in this section, in particular the meaning of files and records, and the use of symmetry. This chapter will focus on general aspects; detailed information about each command will be given in later chapters. Information about commands and parameters can also be obtained using the MOLPRO help facility (see section 4.13).

4.1 Input structure

A typical MOLPRO input has the following structure:

```plaintext
***,title !title (optional)
memory,4,m !memory specification (optional)
file,1,name.int !permanent named integral file (optional)
file,2,name.wfu !permanent named wavefunction file (optional)
gprint,options !global print options (optional)
gthresh,options !global thresholds (optional)
gdirect[,options] !global direct (optional)
gexpec,opnames !global definition of one-electron operators (optional)
basis=basisname !basis specification. If not present, cc-pVDZ is used
geometry={...} !geometry specification
var1=value,var2=value,... !setting variables for geometry and/or wavefunction definitions
{command,options !program or procedure name
directive,data,option !directives for command (optional)
...} !end of command block
--- !end of input (optional)
```

If the memory card is given, it should be the first card (after the optional title card). If any file cards are given, they should follow immediately. The order of basis, geometry, gprint, gdirect, gthresh, gexpec, and variable definitions is arbitrary. It is possible to call several programs one after each other. It is also possible to redefine basis set and/or geometry between the call to programs; the program will recognize automatically if the integrals have to be recomputed.

4.2 Files

MOLPRO uses three sequential text files, namely the input file, the output file, and the punch file. The punch file is a short form of the output which contains the most important data and results, such as geometries, energies, dipole moments, etc. The punch file can be processed by the separate program READPUN, which selects specific results by keywords and is able to produce ordered tables in user supplied format. Furthermore, there are up to 9 binary MOLPRO
files available, each one known to the program simply by its number (1 to 9). By default, they are temporary files, usually allocated dynamically by the program, but they can be connected to permanent files with the `FILE` command. Each file is direct access, and word addressable (word=64 bit usually), but is organised in records of any length. The name, address and length of each record is held in a directory at the start of the file.

File 1 is the main file, holding basis set, geometry, and the one and two electron integrals. By default, file 2 is the dump file and used to store the wavefunction information, i.e. orbitals, CI coefficients, and density matrices. File 3 is an auxiliary file which can be used in addition to file 2 for restart purposes. Often files 1 and 2 (and 3) are declared as permanent files (see `FILE`) to enable restarts. Storing the wavefunction information on file 2 is useful, since the integral file is overwritten at each new geometry, while the orbitals and CI coefficients of one calculation can be used as a starting guess for the next calculation at a neighbouring geometry. Files 4 to 8 are used as scratch space, e.g., for sorting the integrals, storage of transformed integrals and of the CI vectors. These files should normally not be made permanent.

Note that the file name appearing in molpro input is always converted to lower case on unix machines.

### 4.3 Records

Record names are positive integers, and are usually referred to in the format `record.file`, e.g., 2100.2 means the record called 2100 on file 2. Note that these names are quite arbitrary, and their numerical values have nothing to do with the order of the records in the file. Record names ≤ 2000 are reserved for standard quantities (e.g. integrals, properties etc.) and you should never use these in an input, unless you know exactly what you are doing. Some important default records to remember are:

- 2100: RHF dump record (closed and open-shell)
- 2200: UHF dump record
- 2140: MCSCF dump record
- 4100: CPHF restart information
- 5000: MCSCF gradient information
- 5100: CP-MCSCF gradient information
- 5200: MP2 gradient information
- 5300: Hessian restart information
- 5400: Frequencies restart information
- 6300: Domain restart information

If an input contains several wavefunction calculations of the same type, e.g., several MCSCF calculations with different active spaces, the record number will be increased by 1 for each calculation of the same type. Thus, the results of the first SCF calculation in an input are stored in dump record 2100.2, the second SCF in record 2101.2, the first MCSCF in 2140.2, the second MCSCF in 2141.2 and so on. Note that these numbers refer to the occurrence in the input and not on the order in which the calculations are performed in the actual run. If an input or part of it is repeated using `DO` loops, this ensures that each calculation will start with the orbitals from the corresponding orbitals from the previous cycle, as long as the order of the commands in the input remains unchanged. If for instance the first SCF would be skipped in the second cycle using some `IF/ENDIF` structure, the second SCF would still use record 2101.2. Thus, under
most circumstances the program defaults are appropriate, and the user does not have to specify the records.

After a restart this logic will still work correctly if the number and sequence of SCF and MCSCF commands is kept unchanged. Thus, if you want to skip certain parts of the input after a restart, it is recommended to use IF/ENDIF structures or the GOTO command rather than to delete or comment certain commands. If for some reason this is not possible, the START and ORBITAL directives can be used to specify explicitly the records to be used.

In general we recommend the use of program defaults whenever possible, since this minimizes the probability of input errors and frustration!

After completion of each program step, MOLPRO prints a summary of the records on each file.

4.4 Restart

Information from the permanent files is automatically recovered in subsequent calculations. This can be controlled using the RESTART directive.

4.5 Data set manipulation

It is possible to truncate files and rename or copy records using the DATA command. Several standard matrix operations can be performed with MATROP, e.g., printing records, linearly combining or multiplying matrices, or forming the trace of a product of two matrices.

4.6 Memory allocation

MOLPRO can allocate memory dynamically as required by the user. Thus it is not necessary to maintain different versions of the program with different memory sizes. There are two ways to specify the memory: (1) MEMORY card in MOLPRO input file; (2) option -m or --memory in MOLPRO command line. If memory is specified using both methods at the same time, MEMORY card will take precedence. If both ways are omitted, the program will use a default memory size (currently it is 8000000 words, i.e. 64000000 bytes). Please note that: (1) memory specification is in words. 1 word is 8 bytes (i.e., the memory size to store one double precision data). (2) memory specification is for each process.

4.6.1 Memory card in input file

MEMORY,n,scal;

If scale is given as K, n is multiplied by 1000; if scale is M, n is multiplied by 1 000 000; if scale is G, n is multiplied by 10^9. The scale is case insensitive. So there is no difference between M and m (K and k, or G and g).

Note: The MEMORY card must precede all FILE cards!

Examples:

MEMORY, 90000 requests 90 000 words of memory
MEMORY, 500, K requests 500 000 words of memory
MEMORY, 2, M requests 2 000 000 words of memory
MEMORY, 100, M requests 100,000,000 words of memory
memory, 100, m requests 100,000,000 words of memory
MEMORY, 1, G requests 10^9 words of memory

4.6.2 Memory option in command line

-m|--memory nscale

The scale (k, m, g and K, M, G) is case sensitive, lower case for decimal and upper case for binary. k, m, g stand for 1000, 1000,000 and 10^9; K, M, G stand for 2^{10}, 2^{20} and 2^{30}.

Examples:

-m 1k requests 1000 words of memory
-m 1K requests 1024 words of memory
-m 1m requests 1000000 words of memory
-m 1M requests 1048576 words of memory
-m 1g requests 10^9 words of memory
-m 1G requests 2^{30} words of memory

4.6.3 Memory in parallel

The memory specification is for each process. So the total requested memory in parallel calculation will be the specified memory amount multiplied by the number of compute processes. For example, specifying 100 \times 10^6 words for a job with 4 compute processes:

memory, 100, m in input file
-m 100m in command line

the total requested memory will be 100 \times 10^6 \times 8 \times 4 = 3.2 \times 10^9 bytes.

4.7 Multiple passes through the input

It is possible to perform loops over parts of the input using DO loops, very much as in FORTRAN programs. DO loops may be nested to any reasonable depth. This can be conveniently used, for instance, to compute automatically whole potential energy surfaces.

4.8 Symmetry

MOLPRO can use Abelian point group symmetry only. For molecules with degenerate symmetry, an Abelian subgroup must be used — e.g., C_2, or D_{2h} for linear molecules. The symmetry group which is used is defined in the integral input by combinations of the symmetry elements x, y, and z, which specify which coordinate axes change sign under the corresponding generating symmetry operation. It is usually wise to choose z to be the unique axis where appropriate (essential for C_2 and C_{2h}). The possibilities in this case are shown in Table [1].
Table 1: The symmetry generators for the point groups

<table>
<thead>
<tr>
<th>Generators</th>
<th>Point group</th>
</tr>
</thead>
<tbody>
<tr>
<td>(null card)</td>
<td>( C_1 ) (i.e. no point group symmetry)</td>
</tr>
<tr>
<td>( X ) (or ( Y ) or ( Z ))</td>
<td>( C_s )</td>
</tr>
<tr>
<td>( XY )</td>
<td>( C_2 )</td>
</tr>
<tr>
<td>( X Y Z )</td>
<td>( C_i )</td>
</tr>
<tr>
<td>( X, Y )</td>
<td>( C_{2v} )</td>
</tr>
<tr>
<td>( X Y, Z )</td>
<td>( C_{2h} )</td>
</tr>
<tr>
<td>( XZ, YZ )</td>
<td>( D_2 )</td>
</tr>
<tr>
<td>( X, Y, Z )</td>
<td>( D_{2h} )</td>
</tr>
</tbody>
</table>

Table 2: Numbering of the irreducible representations in \( D_{2h} \)

<table>
<thead>
<tr>
<th>No.</th>
<th>Name</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( A_g )</td>
<td>( s )</td>
</tr>
<tr>
<td>2</td>
<td>( B_{3u} )</td>
<td>( x )</td>
</tr>
<tr>
<td>3</td>
<td>( B_{2u} )</td>
<td>( y )</td>
</tr>
<tr>
<td>4</td>
<td>( B_{1g} )</td>
<td>( xy )</td>
</tr>
<tr>
<td>5</td>
<td>( B_{1u} )</td>
<td>( z )</td>
</tr>
<tr>
<td>6</td>
<td>( B_{2g} )</td>
<td>( xz )</td>
</tr>
<tr>
<td>7</td>
<td>( B_{3g} )</td>
<td>( yz )</td>
</tr>
<tr>
<td>8</td>
<td>( A_u )</td>
<td>( xyz )</td>
</tr>
</tbody>
</table>

Normally, MOLPRO determines the symmetry automatically, and rotates and translates the molecule accordingly. However, explicit symmetry specification is sometimes useful to fix the orientation of the molecule or to use lower symmetries.

The irreducible representations of each group are numbered 1 to 8. Their ordering is important and given in Tables 2-4. Also shown in the tables are the transformation properties of products of \( x, y, \) and \( z \). \( s \) stands for an isotropic function, e.g., \( s \) orbital, and for these groups, this gives also the transformation properties of \( x^2, y^2, \) and \( z^2 \). Orbitals or basis functions are generally referred to in the format \( \text{number.irrep} \), i.e. 3.2 means the third orbital in the second irreducible representation of the point group used.

4.9 Defining the wavefunction

In all program modules where such information is required, the total symmetry of the \( N \)-electron wavefunction is defined on \( \text{WF} \) (wavefunction) cards in the following way:
Table 3: Numbering of the irreducible representations in the four-dimensional groups

<table>
<thead>
<tr>
<th>No.</th>
<th>Name</th>
<th>Function</th>
<th>Name</th>
<th>Function</th>
<th>Name</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>A₁</td>
<td>s, z</td>
<td>Aₛ</td>
<td>s, xy</td>
<td>A</td>
<td>s</td>
</tr>
<tr>
<td>2</td>
<td>B₁</td>
<td>x, xz</td>
<td>Aᵤ</td>
<td>z</td>
<td>B₃</td>
<td>x, yz</td>
</tr>
<tr>
<td>3</td>
<td>B₂</td>
<td>y, yz</td>
<td>Bᵤ</td>
<td>x, y</td>
<td>B₂</td>
<td>y, xz</td>
</tr>
<tr>
<td>4</td>
<td>A₂</td>
<td>xy</td>
<td>B₇</td>
<td>xz, yz</td>
<td>B₁</td>
<td>xy</td>
</tr>
</tbody>
</table>

Table 4: Numbering of the irreducible representations in the two-dimensional groups

<table>
<thead>
<tr>
<th>No.</th>
<th>Name</th>
<th>Function</th>
<th>Name</th>
<th>Function</th>
<th>Name</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>A′</td>
<td>s, x, y, xy</td>
<td>A</td>
<td>s, z, xy</td>
<td>Aₛ</td>
<td>s, xy, xz, yz</td>
</tr>
<tr>
<td>2</td>
<td>A″</td>
<td>z, xz, yz</td>
<td>B</td>
<td>x, y, xz, yz</td>
<td>Aᵤ</td>
<td>x, y, z</td>
</tr>
</tbody>
</table>

WF, nelec, irrep, spin

or, alternatively

WF, [NELEC=nelec], [SYM[METRY]=irrep], [spin=spin], [CHARGE=charge]

where nelec is the total number of electrons, irrep is the number of the irreducible representation, and spin equals 2 × S, where S is the total spin quantum number. Instead of nelec also charge can be given, which specifies the total charge of the molecule. For instance, for a calculation in C₂ᵥ symmetry with 10 electrons, WF, 10, 3, 0 denotes a 1B₂ state, and WF, 10, 1, 2 a 3A₁ state. The charge can also be defined by setting the variable CHARGE:

SET, CHARGE=charge

This charge will be used in all energy calculations following this input. Note that SET is required, since CHARGE is a system variable (cf. section 8.4).

Although in principle each program unit requires a WF command, in practice it is seldom necessary to give it. The program remembers the information on the WF card, and so one might typically specify the information in an SCF calculation, but then not in subsequent MCSCF or CI calculations; this also applies across restarts. Furthermore, nelec defaults to the sum of the nuclear charges, irrep to 1 and spin to 0 or 1; thus in many cases, it is not necessary to specify a WF card at all.

If the WF directive is given outside an command input block, it is treated as global, i.e., the given values are used for all subsequent calculations. Setting the variables NELEC, SPIN, or SYMMETRY, has the same effect giving these on a global WF directive. If the global WF directive is given after the variable definition, the values of the variables are replaced by the values given on the WF directive. Vice versa, if a variable definition follows a global WF directive, the new value of the variable is used in the following. Note that WF input cards in command blocks have preference over global WF directives or input variables.
4.10 Defining orbital subspaces

In the SCF, MCSCF, and CI programs it may be necessary to specify how many orbitals in each symmetry are occupied (or internal in CI), and which of these are core or closed shell (doubly occupied in all CSFs). This information is provided on the OCC, CORE, and CLOSED cards in the following way:

OCC,$m_1,m_2,...,m_8$; CORE,$c_0_1,c_0_2,...,c_0_8$; CLOSED,$c_l_1,c_l_2,...,c_l_8$; FROZEN,$f_r_1,f_r_2,...,f_r_8$;

where $m_i$ is the number of occupied orbitals (including core/frozen and closed), $c_{0i}$ the number of core orbitals, and $c_{li}$ is the number of closed-shell orbitals (including the core orbitals) in the irreducible representation $i$. In general, $m_i \geq c_{0i}$, and $c_{li} \geq c_{0i}$. It is assumed that these numbers refer to the first orbitals in each irrep. FROZEN only exists in the MCSCF program and denotes frozen core orbitals that are not optimized (note that in older MOLPRO versions frozen core orbitals were denoted CORE).

Note that the OCC and CLOSED cards have slightly different meanings in the SCF, MCSCF and CI or CCSD programs. In SCF and MCSCF, occupied orbitals are those which occur in any of the CSFs. In electron correlation methods (CI, MPn, CCSD etc), however, OCC denotes the orbitals which are occupied in any of the reference CSFs. In the MCSCF, FROZEN orbitals are doubly occupied in all CSFs and frozen (not optimized), while closed denotes all doubly occupied orbitals (frozen plus optimized). In the CI and CCSD programs, core orbitals are those which are not correlated and closed orbitals are those which are doubly occupied in all reference CSFs.

OCC, CORE and CLOSED directives are generally required in each program module where they are relevant; however, the program remembers the most recently used values, and so the directives may be omitted if the orbital spaces are not to be changed from their previous values. Note that this information is also preserved across restarts. Note also, as with the WF information, sensible defaults are assumed for these orbital spaces. For full details, see the appropriate program description.

The orbital spaces may also be defined outside command blocks, and then the directive is treated as global, i.e., it is used in all subsequent programs. Spaces specific to certain wavefunction types can be defined by specifying the program name with a CONTEXT option, e.g.,

OCC, 4, 2, 1, CONTEXT=MULTI

Alternatively, the context can be appended to the directive name with an underscore. For example

OCC, MULTI, 4, 2, 1

is equivalent to the previous form.

Local input given within command blocks has preference over global input.

4.11 Selecting orbitals and density matrices (ORBITAL, DENSITY)

As outlined in section 4.3, the information for each SCF or MCSCF calculation is stored in a dump record. Dump records contain orbitals, density matrices, orbital energies, occupation numbers, fock matrices and other information as wavefunction symmetries etc. Subsequent calculation can access the orbitals and density matrices from a particular record using the ORBITAL and DENSITY directives, respectively. These input cards have the same structure in all programs. The general format of the ORBITAL and DENSITY directives is as follows:
where the (optional) specifications can be used to select specific orbitals or densities, if several different orbital sets are stored in the same record. If a specification is not given, it is not checked and the last written set that fulfills all other criteria is used. The meaning of the individual specifications are as follows:

*orbtype* Orbital type. This can be one of
- CANONICAL: canonical or pseudo-canonical orbitals;
- NATURAL: natural orbitals;
- LOCAL: localized orbitals;
- LOCAL (PM): localized Pipek-Mezey orbitals;
- LOCAL (BOYS): localized Boys orbitals;
- PROJECTED: projected virtual orbitals used in local calculations.

Without further specification, the most recently computed orbitals of the specified type are used. If the orbital type is not specified, the program will try to find the most suitable orbitals automatically. For instance, in MRCI calculations NATURAL orbitals will be used preferentially if available; MRPT (CASPT2) calculations will first search for CANONICAL orbitals, and local calculations will first look for LOCAL orbitals. Therefore, in most cases the orbital type need not to be specified.

*state* Specifies a particular state in the form istate.isym. For instance, 2.1 refers to the second state in symmetry 1. This can be used if density matrices or natural orbitals have been computed for different states in a state-averaged CASSCF calculation. If not given, the last written orbitals are used. A state-averaged density can be selected using STATE=AV[ERAGED]. The specification of isym is optional; it can also be defined using the SYMMETRY key.

*dentype* Density type. This can be one of
- CHARGE: charge density;
- SPIN: UHF spin density;
- TRANSITION: transition density matrix;

The default is CHARGE.

*symmetry* Specifies a particular state symmetry. Alternatively, the state symmetry can be specified using STATE (see above).

*spin* Spin quantum number, i.e. 0 for singlet, 1/2 for doublet, 1 for triplet, etc. Alternatively MS2 can be used.

*ms2* $2M_S$, i.e. 0 for singlet, 1 for doublet, 2 for triplet etc. Alternatively, SPIN can be used.

*nelec* Number of electrons.

*iset* Set number of orbitals. The orbital sets are numbered in the order they are stored.
In some cases (e.g. in MATROP) transition density matrices can be specified. In this case STATEB, SYMB, MS2B, SPINB refer to the bra state and STATEK, SYMK, MS2K, SPINK refer to the ket state. If bra and ket differ, TYPE=TRANSITION is implied, and SYMMETRY is automatically set to the product symmetry of bra and ket. If STATEK, SYMK, MS2K, SPINK are not given, they are assumed to be equal to the corresponding bra quantities. See section 65 for examples.

If OVL is specified, the starting orbitals are obtained by maximizing the overlap with previous orbitals. By default, this is used if the basis dimension of the previous orbitals is different than the current one. If OVL is specified this procedure is used even if the basis dimensions are the same, which is occasionally useful if the contraction scheme changed.

If NOCHECK is specified, some consistency checks for finding correct orbitals are skipped, and error messages like "ORBITALS CORRESPOND TO DIFFERENT GEOMETRY" are ignored.

If IGNORE_ERROR is specified, MPn or triples calculations can be forced with other than canonical orbitals. Note that this can lead to meaningless results! Note that in MULTI IGNORE_ERROR must be given on the START directive, since in this program ORBITAL is used to define the new orbitals.

If any of the above options are given, they must be obeyed strictly, i.e., the program aborts if the request cannot be fulfilled.

Examples:

<table>
<thead>
<tr>
<th>Command</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ORBITAL,2100.2</td>
<td>!Use SCF orbitals</td>
</tr>
<tr>
<td>ORBITAL,2140.2</td>
<td>!Use (state-averaged) MCSCF orbitals</td>
</tr>
<tr>
<td>ORBITAL,2140.2,CANONICAL</td>
<td>!use canonical MCSCF orbitals</td>
</tr>
<tr>
<td>ORBITAL,2140.2,NATURAL,STATE=2.1</td>
<td>!use natural MCSCF orbitals for second state in sym. 1</td>
</tr>
</tbody>
</table>

4.12 Summary of keywords known to the controlling program

This is a summary of all keywords presently implemented in the controlling program. Each module knows further keywords, which are described in the chapters about the individual programs. For detailed information about the use of the commands listed below, consult the following chapters.
Program control:

***
indicates start of a new calculation

MEMORY
allocates dynamic memory

PUNCH
opens a punch file

FILE
connects units to permanent files

RESTART
recovers file information

INCLUDED
includes other input files

BASIS
can be used to define default basis sets

GEOMETRY
can be used to specify the geometry

ZMAT
can be used to define the Z-matrix

PARALLEL
can be used to control parallelization

STATUS
checks status of program steps

PRINT,GPRINT
controls global print levels

THRESH,GTHRESH
controls global thresholds

DIRECT,GDIRECT
flags direct computation of integrals and for setting direct options

EXPEC,GEXPEC
controls computation of expectation values

TEXT
prints text

EXIT
stops execution

DO
controls do loops

ENDDO
end of do loops

IF
controls conditional actions

ELSEIF
controls conditional actions

ENDIF
end of IF block

GOTO
used to skip part of input and for loops over input

LABEL
no action

DATA
data set management

DELETE, ERASE
data set deletion

MATROP
performs matrix operations

GRID
Define grid

CUBE
Dump data to grid

CARTESIAN
Use cartesian basis functions

SPHERICAL
Use spherical harmonic basis functions

USER
calls user-supplied subroutine

---
last line of input

Variables:

SET
sets variables (obsolete)

SETI
sets variables or numbers to their inverse (obsolete)

SETA
sets variable arrays (obsolete)

CLEAR
clears variables
CLEARALL clears all variables
GETVAR recovers variables from file
SHOW displays the values of variables
TABLE prints tables

Wave function optimization:
INT calls the machine default integral program. This is optional and needs not to be given.
LSINT calls the spin-orbit integral program
SORT calls two-electron sorting program. This is called automatically and needs not to be given
CPP compute core polarization potential integrals
HF, RHF, HF-SCF, or RHF-SCF calls spin-restricted Hartree-Fock program (open or closed shell)
UHF or UHF-SCF calls spin-unrestricted Hartree-Fock program
DFT calls the density functional program
KS, RKS call the Kohn-Sham spin restricted density functional program
UKS call the Kohn-Sham spin-unrestricted density functional program
MULTI, MCSCF, or CASSCF calls MCSCF/CASSCF program
CASVB calls the CASVB valence bond program
CI, MRCI, or CI-PRO calls internally contracted MRCI program
MRCI-F12 calls the explicitly correlated internally contracted MRCI program
CIPT2 calls internally contracted CIPT2 program
ACPF, AQCC calls internally contracted MR-ACPF program
CEPA calls single-reference CEPA program (closed- or open-shell)
RS2, RS3 calls internally contracted multireference perturbation theory program
RS2-F12 calls the explicitly correlated multireference perturbation theory program
RS2C faster program for internally contracted multireference perturbation theory
MP2 calls closed-shell MP2 program
MP3 calls closed-shell MP3 program
MP4 calls closed-shell MP4 program
CISD calls closed-shell CISD program
CCSD calls closed-shell coupled cluster program
BCCD calls closed-shell Brueckner CCD program
QCI, QCSID calls closed-shell quadratic configuration interaction program
UCCSD calls spin-unrestricted open-shell coupled cluster program
RCCSD calls spin-restricted open-shell coupled cluster program
FCI or FULLCI calls determinant based full CI program

Local correlation methods:
LMP2 calls closed-shell local MP2 program
LMP3 calls closed-shell local MP3 program
LMP4 calls closed-shell local MP4 program
LCISD calls closed-shell local CISD program
LCCSD calls closed-shell local coupled cluster program

Explicitly correlated methods:

DF-MP2-R12 MP2-R12 program with density fitting
DF-MP2-F12 MP2-F12 program with density fitting
DF-LMP2-R12 Local MP2-R12 program with density fitting
DF-LMP2-F12 Local MP2-F12 program with density fitting

Orbital manipulation:

LOCALI calls orbital localization program
MERGE calls orbital manipulation program

Properties and wavefunction analysis:

POP calls population analysis program
DMA calls distributed multipole analysis program
PROPERTY calls properties program
DIP adds dipole field to $h$
QUAD adds quadrupole field to $h$
LATTICE read or disable lattice of point charges

Gradients and geometry optimization:

FORCES calls gradient program
OPTG performs automatic geometry optimization
MIN performs energy minimization with respect to some parameters
PUT print or write geometry to a file
HESSIAN calculate Hessian
FREQUENCY calculate vibrational frequencies
MASS define atomic masses
DDR evaluates approximate non-adiabatic coupling matrix elements

The command names for single reference coupled cluster methods QCISD, CCSD, LQCISD, LCCSD can be appended by (T) and then a perturbative correction for triple excitations will be computed (e.g., CCSD(T)).

HF, KS, MP2 and all local correlation methods can be prepended by DF- to invoke density fitting.

4.13 MOLPRO help

The help command can be used to obtain a short description of commands, input parameters, and variables. The syntax is:

HELP,set.name,[keys]
where *set* is either `COMMAND`, `VARIABLE`, or the name of the input set (e.g., `THRESH`, `PRINT`, `LOCAL`, `EOM`, `CFIT`), and *name* is the name of the parameter. If *name* is blank, all parameters of the set are shown. Optionally, *keys* can be specified to request specific information (e.g., `short_description`, `long_description`, `default_value`, `type`, `program`). If *keys* are not given, `short_description` is assumed.

Currently, help is only available for a limited number of parameters and commands. However, the database will be extended in the near future.

## 5 INTRODUCTORY EXAMPLES

This section explains some very simple calculations in order to help the new user to understand how easy things can be.

### 5.1 Using the molpro command

1. Perform a simple SCF calculation for molecular hydrogen. The input is typed in directly and the output is sent to the terminal:

   ```
   molpro <<!
   basis=vdz;
   geometry={angstrom;h1;h2,h1,.74}
   hf
   !
   ```

2. The same calculation, with the data taken from the file `h2.com`. The output is sent to `h2.out`. On completion, the file `h2.pun` is returned to the current directory and the file `h2.wf` to the directory `$HOME/wfu` (this is the default):

   ```
   molpro h2.com
   ```

   `h2.com` contains:

   ```
   ***,H2
   file,2,h2.wf,new;
   punch,h2.pun;
   basis=vdz;
   geometry={angstrom;h1;h2,h1,.74}
   hf
   ```

   [http://www.molpro.net/info/current/examples/h2.com](http://www.molpro.net/info/current/examples/h2.com)

3. As before, but the file `h2.wf` is sent to the directory `/tmp/wfu`:

   ```
   molpro -W /tmp/wfu h2.com
   ```

### 5.2 Simple SCF calculations

The first example does an SCF calculation for H$_2$O, using all possible defaults.
5 INTRODUCTORY EXAMPLES

In the above example, the default basis set (VDZ) is used. We can modify the default basis using a BASIS directive.

5.3 Geometry optimizations

Now we can also do a geometry optimization, simply by adding the card OPTG.

5.4 CCSD(T)

The following job does a CCSD(T) calculation using a larger (VTZ) basis (this includes an f function on oxygen and a d function on the hydrogens).

5.5 CASSCF and MRCI

Perhaps you want to do a CASSCF and subsequent MRCI for comparison. The following uses the full valence active space in the CASSCF and MRCI reference function.
5.6 Tables

You may now want to print a summary of all results in a table. To do so, you must store the computed energies in variables:

```plaintext
***,h2o !A title
r=1.85,theta=104 !set geometry parameters
geometry={o;
    h1,O,r;
    h2,O,r,H1,theta}
basis=vtz !use VTZ basis
hf !closed-shell scf
ccsd(t) !do ccsd(t) calculation
casscf !do casscf calculation
mrci !do mrci calculation
e(1)=energy !save scf energy in variable e(1)
method(1)=program !save the string ‘HF’ in variable method(1)
e(2)=energy !save ccsd(t) energy in variable e(2)
method(2)=program !save the string ‘CCSD(T)’ in variable method(2)
e(3)=energy !save casscf energy in variable e(3)
method(3)=program !save the string ‘CASSCF’ in variable method(3)
e(4)=energy !save mrci energy in variable e(4)
method(4)=program !save the string ‘MRCI’ in variable method(4)
table,method,e !print a table with results
title,Results for H2O, basis=$basis !title for the table
```

This job produces the following table:

```
Results for H2O, basis=VTZ

<table>
<thead>
<tr>
<th>METHOD</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>-76.05480122</td>
</tr>
<tr>
<td>CCSD(T)</td>
<td>-76.33149220</td>
</tr>
<tr>
<td>CASSCF</td>
<td>-76.11006259</td>
</tr>
<tr>
<td>MRCI</td>
<td>-76.31960943</td>
</tr>
</tbody>
</table>
```
5.7 Procedures

You could simplify this job by defining a procedure `SAVE_E` as follows:

```fortran
***,h2o !A title
proc save_e !define procedure save_e
  if(#i.eq.0) i=0 !initialize variable i if it does not exist
  i=i+1 !increment i
  e(i)=energy !save scf energy in variable e(i)
  method(i)=program !save the present method in variable method(i)
endproc !end of procedure

r=1.85,theta=104 !set geometry parameters
geometry={o;
h1,O,r;
h2,O,r,H1,theta}
basis=vtz !use VTZ basis
hf !closed-shell scf
save_e !call procedure, save results
ccsd(t) !do ccsd(t) calculation
save_e !call procedure, save results
casscf !do casscf calculation
save_e !call procedure, save results
mrci !do mrci calculation
save_e !call procedure, save results
table,method,e !print a table with results
title,Results for H2O, basis=$basis !title for the table
```

[http://www.molpro.net/info/current/examples/h2o_proce.com](http://www.molpro.net/info/current/examples/h2o_proce.com)

The job produces the same table as before.

5.8 Do loops

Now you have the idea that one geometry is not enough. Why not compute the whole surface? `DO` loops make it easy. Here is an example, which computes a whole potential energy surface for H$_2$O.
**5 INTRODUCTORY EXAMPLES**

***H2O potential***

* symmetry=x ! use cs symmetry

* geometry={
  o;
  h1,o,r1(i);
  h2,o,r2(i),h1,theta(i) }

* basis=vdz ! define basis set

* angles=[100,104,110] ! list of angles

* distances=[1.6,1.7,1.8,1.9,2.0] ! list of distances

* i=0 ! initialize a counter

do ith=1,#angles ! loop over all angles H1-O-H2
  do ir1=1,#distances ! loop over distances for O-H1
    do ir2=1,ir1 ! loop over O-H2 distances (r1.ge.r2)
      i=i+1 ! increment counter
      r1(i)=distances(ir1) ! save r1 for this geometry
      r2(i)=distances(ir2) ! save r2 for this geometry
      theta(i)=angles(ith) ! save theta for this geometry
      hf; ! do SCF calculation
      escf(i)=energy ! save scf energy for this geometry
      ccsd(t); ! do CCSD(T) calculation
      eccsd(i)=energy ! save CCSD energy
      eccsdt(i)=energy ! save CCSD(T) energy
    enddo ! end of do loop ir1
  enddo ! end of do loop ir2
enddo ! end of do loop ith

* {table,r1,r2,theta,escf,eccsd,eccsdt ! produce a table with results
  head, r1,r2,theta,scf,ccsd,ccsd(t) ! modify column headers for table
  save,h2o.tab ! save the table in file h2o.tab
  title,Results for H2O, basis $basis ! title for table
  sort,3,1,2} ! sort table

http://www.molpro.net/info/current/examples/h2o_pes_ccsdt.com

This produces the following table.

Results for H2O, basis VDZ

<table>
<thead>
<tr>
<th>R1</th>
<th>R2</th>
<th>THETA</th>
<th>SCF</th>
<th>CCSD</th>
<th>CCSD(T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.6</td>
<td>1.6</td>
<td>100.0</td>
<td>-75.99757338</td>
<td>-76.20140563</td>
<td>-76.20403920</td>
</tr>
<tr>
<td>1.7</td>
<td>1.6</td>
<td>100.0</td>
<td>-76.00908379</td>
<td>-76.21474489</td>
<td>-76.21747582</td>
</tr>
<tr>
<td>1.7</td>
<td>1.7</td>
<td>100.0</td>
<td>-76.02060127</td>
<td>-76.22812261</td>
<td>-76.23095473</td>
</tr>
<tr>
<td>...</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>1.9</td>
<td>110.0</td>
<td>-76.01128923</td>
<td>-76.22745359</td>
<td>-76.23081968</td>
</tr>
<tr>
<td>2.0</td>
<td>2.0</td>
<td>110.0</td>
<td>-76.00369171</td>
<td>-76.22185092</td>
<td>-76.22537212</td>
</tr>
</tbody>
</table>

You can use also use DO loops to repeat your input for different methods.
### 6 PROGRAM CONTROL

#### 6.1 Starting a job (***)

The first card of each input should be:

```plaintext
***, text
```

where `text` is arbitrary. If file 1 is restarted, `text` must always be the same. The effect of this card is to reset all program counters, etc. If the *** card is omitted, `text` assumes its default value, which is all blank.
6.2 Ending a job (---)

The end of the input is signaled by either an end of file, or a
---
card. All input following the --- card is ignored.

Alternatively, a job can be stopped at some place by inserting an EXIT card. This could also be in the middle of a DO loop or an IF block. If in such a case the --- card would be used, an error would result, since the ENDDO or ENDIF cards would not be found.

6.3 Restarting a job (RESTART)

In contrast to MOLPRO92 and older versions, the current version of MOLPRO attempts to recover all information from all permanent files by default. If a restart is unwanted, the NEW option can be used on the FILE directive. The RESTART directive as described below can still be used as in MOLPRO92, but is usually not needed.

RESTART,r1,r2,r3,r4,...;

The ri specify which files are restarted. These files must have been allocated before using FILE cards. There are two possible formats for the ri:

a) 0 < ri < 10: Restart file ri and restore all information.

b) ri = name.nr: Restart file nr but truncate before record name.

If all ri = 0, then all permanent files are restarted. However, if at least one ri is not equal to zero, only the specified files are restarted.

Examples:

RESTART; will restart all permanent files allocated with FILE cards (default)
RESTART,1; will restart file 1 only
RESTART,2; will restart file 2 only
RESTART,1,2,3; will restart files 1-3
RESTART,2000.1; will restart file 1 and truncate before record 2000.

6.4 Including secondary input files (INCLUDE)

INCLUDE,file[ECHO];

Insert the contents of the specified file in the input stream. In most implementations the file name given is used directly in a Fortran open statement. If file begins with the character `/`, then it will be interpreted as an absolute file name. Otherwise, it will be assumed to be a path relative to the directory from which the Molpro has been launched. If, however, the file is not found, an attempt will be made instead to read it relative to the system `lib/include` directory, where any standard procedures may be found.

If the ECHO option is specified, the included file is echoed to the output in the normal way, but by default its contents are not printed. The included file may itself contain INCLUDE commands up to a maximum nesting depth of 10.
6.5 Allocating dynamic memory (MEMORY)

MEMORY,n, scale;

Sets the limit on dynamic memory to \( n \) floating point words. For details, see section 4.6.

6.6 DO loops (DO/ENDDO)

DO loops can be constructed using the DO and ENDDO commands. The general format of the DO command is similar to Fortran:

\[
\text{DO variable} = \text{start, end} [\text{[, increment]}] [\text{[, unit]}]
\]

where start, end, increment may be expressions or variables. The default for increment is 1. In contrast to Fortran, these variables can be modified within the loop (to be used with care!). For instance:

\[
\begin{align*}
\text{DR} &= 0.2 \\
\text{DO } R &= 1.0, 6.0, \text{DR}, \text{ANG} \\
\text{IF (R.EQ.2) DR} &= 0.5 \\
\text{IF (R.EQ.3) DR} &= 1.0 \\
\ldots \\
\text{ENDDO}
\end{align*}
\]

performs the loop for the following values of \( R \): 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.5, 3.0, 4.0, 5.0, 6.0 Ångström. The same could be achieved as follows:

\[
\begin{align*}
\text{RVEC} &= [1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.5, 3.0, 4.0, 5.0, 6.0] \text{ ANG} \\
\text{DO } I &= 1, \#\text{RVEC} \\
\text{R} &= \text{RVEC}(I) \\
\ldots \\
\text{ENDDO}
\end{align*}
\]

Up to 20 DO loops may be nested. Each DO must end with its own ENDDO.

Jumps into DO loops are possible if the DO variables are known. This can be useful in restarts, since it allows to continue an interrupted calculation without changing the input (all variables are recovered in a restart).

6.6.1 Examples for do loops

The first example shows how to compute a potential energy surface for water.
6 PROGRAM CONTROL

***, H2O potential
symmetry,x
geometry={
o;
  h1,o,r1(i);
  h2,o,r2(i),h1,theta(i) }
basis=vdz
angles=[100,104,110]
distances=[1.6,1.7,1.8,1.9,2.0]
i=0

do ith=1,#angles
  do ir1=1,#distances
    do ir2=1,ir1
      i=i+1
      r1(i)=distances(ir1)
      r2(i)=distances(ir2)
      theta(i)=angles(ith)
      hf;
      escf(i)=energy
      ccsd(t);
      eccsdt(i)=energy
    enddo
  enddo
enddo

{table,r1,r2,theta,escf,eccsdt}
head, r1,r2,theta,scf,ccsd,ccsd(t)
save,h2o.tab
title,Results for H2O, basis $basis
sort,3,1,2}

http://www.molpro.net/info/current/examples/h2o_pes_ccsdt.com

The next example shows how to loop over many methods.

***, h2o benchmark
$method=[hf,fci,ci,cepa(0),cepa(1),cepa(2),cepa(3),mp2,mp3,mp4,\ qci,ccsd,bccd,qci(t),ccsd(t),bccd(t),casscf,mrci,acpf]
basis=dz
geometry={o,h1,o,r2,h2,o,r,h1,theta}
r1=1 ang, theta=104
$method(i);
e(i)=energy
endo
table,method,e,e-escf,e-efci
head,method,scf,ccsd,ccsd(t)
save,h2o.tab
title,Results for H2O, basis $basis
sort,3,1,2}

http://www.molpro.net/info/current/examples/h2o_manymethods.com

6.7 Branching (IF/ELSEIF/ENDIF)

IF blocks and IF/ELSEIF blocks can be constructed as in FORTRAN.

6.7.1 IF statements

IF blocks have the same form as in Fortran:
IF (logical expression) THEN

statements

ENDIF

If only one statement is needed, the one-line form

IF (logical expression) statement

can be used, except if statement is a procedure name.

ELSE and ELSE IF can be used exactly as in Fortran. IF statements may be arbitrarily nested. Jumps into IF or ELSE IF blocks are allowed. In this case no testing is performed; when an ELSE is reached, control continues after ENDIF.

The logical expression may involve logical comparisons of algebraic expressions or of strings. Examples:

IF(STATUS.LT.0) THEN

TEXT, An error occurred, calculation stopped

STOP

ENDIF

IF($method.eq.'HF') then

...

ENDIF

In the previous example the dollar and the quotes are optional:

IF(METHOD.EQ.HF) then

...

ENDIF

6.7.2 GOTO commands

GOTO commands can be used to skip over parts of the input. The general form is

GOTO, command, [n], [nrep]

Program control skips to the |n|th occurrence of command (Default: n = 1). command must be a keyword in the first field of an input line. If n is positive, the search is forward starting from the current position. If n is negative, search starts from the top of the input. The GOTO command is executed at most nrep times. The default for nrep is 1 if n < 0 and infinity otherwise. We recommend that GOTO commands are never used to construct loops.

Alternatively, one can jump to labels using

GOTO, label

Since labels must be unique, the search starts always from the top of the input. It is required that the label ends with a colon.

6.7.3 Labels (LABEL)

LABEL

This is a dummy command, sometimes useful in conjunction with GOTO.
6.8 Procedures (PROC/ENDPROC)

Procedures can be defined at the top of the input or in INCLUDE files as follows:

PROC name
statements
ENDPROC

Alternatively, one can use the form

PROC name [=] {statements}

In the latter case, it is required that the left curly bracket ({{ appears on the same line as PROC, but statements can consist of several lines. If in the subsequent input name is found as a command in the first field of a line, it is substituted by the statements. Example:

PROC SCF
IF (#SPIN.EQ.0.OR.MOD(SPIN,2).NE.MOD(NELEC,2)) SET,SPIN=MOD(NELEC,2)
IF (SPIN.EQ.0) THEN
      HF
ELSE
      RHF
ENDIF
ENDPROC

Alternatively, this could be written as

PROC SCF=
IF (#SPIN.EQ.0.OR.MOD(SPIN,2).NE.MOD(NELEC,2)) SET,SPIN=MOD(NELEC,2)
IF (SPIN.EQ.0) THEN; HF; ELSE; RHF; ENDIF

Procedures may be nested up to a depth of 10. In the following example SCF is a procedure:

PROC CC
SCF
IF (SPIN.EQ.0) THEN
      CCSD
ELSE
      RCCSD
ENDIF
ENDPROC

Note: Procedure names are substituted only if found in the first field of an input line. Therefore, they must not be used on one-line IF statements; please use IF / ENDIF structures instead.

If as first statement of a procedure ECHO is specified, the substituted commands of the present and lower level procedures will be printed. If ECHO is specified in the main input file, all subsequent procedures are printed.

Certain important input data can be passed to the program using variables. For instance, occupancy patterns, symmetries, number of electrons, and multiplicity can be defined in this way (see section 8.8 for more details). This allows the quite general use of procedures. For example, assume the following procedure has been defined at the top of the input:

PROC MRCI
IF (INTDONE.EQ.0) INT
IF (SCFDONE.EQ.0) THEN
      SCF
ENDIF
MULTI
CI
ENDPROC
This procedure can be used for a calculation of a vertical ionization potential of H₂O as follows:

```
R=1 ANG !Set bond distance
THETA=104 DEGREE !Set bond angle
BASIS=VTZ !Define basis set
GEOMETRY !Geometry input block
O !Z-matrix
H1,O,R
H2,O,R,H1,THETA
ENDG !End of geometry input
HF
MRCI !Compute mrci energy of water using defaults
EH2O=ENERGY !save mrci energy in variable EH2O
SET,NELEC=9 !Set number of electrons to 9
SET,SYMMETRY=2 !Set wavefunction symmetry to 2
HF
MRCI !Compute mrci energy of H₂O+ (2B2 state)
IPCI=(ENERGY-EH2O)*TOEV !Compute MRCI ionization potential in eV
```

Note: At present, all variables are *global*, i.e., variables are commonly known to all procedures and all variables defined in procedures will be subsequently known outside the procedures as well. The reason is that procedures are included into the internal input deck at the beginning of the job and not at execution time; for the same reason, variable substitution of procedure names is not possible, e.g. one cannot use constructs like

```
method=scf
$method !this does not work!
```

### 6.9 Text cards (TEXT)

TEXT,xxxxxx

will just print xxxxx in the output. If the text contains variables which are preceded by a dollar ($), these are replaced by their actual values, e.g.

```
r=2.1
text,Results for R=$r
```

will print

Results for R=2.1

### 6.10 Checking the program status (STATUS)

STATUS,[ALL|LAST|commands],[IGNORE|STOP|CRASH],[CLEAR]

This command checks and prints the status of the specified program steps. *commands* may be a list of commands for wavefunction calculations previously executed in the current job. If no *command* or LAST is specified, the status of the last step is checked. If ALL is given, all program steps are checked.
If \texttt{CRASH} or \texttt{STOP} is given, the program will crash or stop, respectively, if the status was not o.k. (\texttt{STOP} is default). If \texttt{IGNORE} is given, any bad status is ignored. If \texttt{CLEAR} is specified, all status information for the checked program steps is erased, so there will be no crash at subsequent status checks.

Examples:

\begin{verbatim}
STATUS, HF, CRASH; will check the status of the last HF-SCF step and crash if it was not o.k. (i.e. no convergence). CRASH is useful to avoid that the next program in a chain is executed.
STATUS, MULTI, CI, STOP; will check the status of the most previous MULTI and CI steps and stop if something did not converge.
STATUS, RHF, CLEAR; will clear the status flag for last RHF. No action even if RHF did not converge.
\end{verbatim}

Note that the status variables are not recovered in a restart.

By default, the program automatically does the following checks:

1.) If an orbital optimization did not converge, and the resulting orbitals are used in a subsequent correlation calculation, an error will result. This error exit can be avoided using the \texttt{IGNORE \_ERROR} option on the \texttt{ORBITAL} directive.

2.) If a \texttt{CCSD\_QCI\_BCC\_LMPn} calculation did not converge, further program steps which depend on the solution (e.g. Triples, CPHF, EOM) will not be done and an error will result. This can be avoided using the \texttt{NOCHECK} option on the command line.

3.) In geometry optimizations or frequency calculations no convergence will lead to immediate error exits.

\subsection*{6.11 Global Thresholds (\texttt{GTHRESH})}

A number of global thresholds can be set using the \texttt{GTHRESH} command outside the individual programs (the first letter \texttt{G} is optional, but should be used to avoid confusion with program specific \texttt{THRESH} cards). The syntax is

\begin{verbatim}
GTHRESH, key1=value1,key2=value2,\ldots
\end{verbatim}

\texttt{key} can be one of the following.

\begin{verbatim}
ZERO Numerical zero (default 1.d-12)
ONEINT Threshold for one-electron integrals (default 1.d-12, but not used at present)
TWOINT Threshold for the neglect of two-electron integrals (default 1.d-12)
PREFAC Threshold for test of prefactor in TWOINT (default 1.d-14)
LOCALI Threshold for orbital localization (default 1.d-8)
EORDER Threshold for reordering of orbital after localization (default 1.d-4)
ENERGY Convergence threshold for energy (default 1.d-6)
GRADIENT Convergence threshold for orbital gradient in MCSCF (default 1.d-2)
STEP Convergence threshold for step length in MCSCF orbital optimization (default 1.d-3)
\end{verbatim}
6 PROGRAM CONTROL

ORBITAL Convergence threshold for orbital optimization in the SCF program (default 1.d-5).
CIVEC Convergence threshold for CI coefficients in MCSCF and reference vector in CI (default 1.d-5)
COEFF Convergence threshold for coefficients in CI and CCSD (default 1.d-4)
PRINTCI Threshold for printing CI coefficients (default 0.05)
PUNCHCI Threshold for punching CI coefficients (default 99 - no punch)
SYMTOL Threshold for finding symmetry equivalent atoms (default 1.d-6)
GRADTOL Threshold for symmetry in gradient (default 1.d-6).
THROVL Threshold for smallest allowed eigenvalue of the overlap matrix (default 1.d-8)
THROORTH Threshold for orthonormality check (default 1.d-8)

6.12 Global Print Options (GPRINT/NOGPRINT)

Global print options can be set using the GPRINT command outside the individual programs (the first letter G is optional, but should be used to avoid confusion with program specific PRINT cards). The syntax is

GPRINT,key1=value1,key2=value2,...
NOGPRINT,key1,key2,...

Normally, value can be omitted, but values > 0 may be used for debugging purposes, giving more information in some cases. The default is no print for all options, except for DISTANCE, ANGLES (default=0), and VARIABLE. NOGPRINT,key is equivalent to PRINT,key=-1. key can be one of the following:

BASIS Print basis information
DISTANCE Print bond distances (default)
ANGLES Print bond angle information (default). If > 0, dihedral angles are also printed.
ORBITAL Print orbitals in SCF and MCSCF
ORBEN Print orbital energies in SCF
CIVECTOR Print CI vector in MCSCF
PAIRS Print pair list in CI, CCSD
CS Print information for singles in CI, CCSD
CP Print information for pairs in CI, CCSD
REF Print reference CSFs and their coefficients in CI
PSPACE Print p-space configurations
MICRO Print micro-iterations in MCSCF and CI
CPU Print detailed CPU information
IO Print detailed I/O information
VARIABLE Print variables each time they are set or changed (default).
6.13 One-electron operators and expectation values (GEXPEC)

The operators for which expectation values are requested, are specified by keywords on the global GEXPEC directive. By default, only dipole moments are computed. The first letter G is optional, but should be used to avoid confusion with program specific EXPEC cards, which have the same form as GEXPEC. For all operators specified on the GEXPEC card, expectation values are computed in all subsequent programs that generate the first-order density matrix. This is always the case for variational wavefunctions, i.e., HF, DFT, MCSCF, MRCI. For non-variational wavefunctions such as MP2, MP3, QCISD, QCISD(T), CCSD, or CCSD(T) the density matrix is not computed by default, since this requires considerable additional effort (solving z-vector equations). The GEXPEC directive does not affect such programs. In some cases (currently for MP2, MP3, QCISD, QCISD(T), and CCSD) the EXPEC directive that is specific to those programs can be used to request the property calculation.

For a number of operators it is possible to use generic operator names, e.g., DM for dipole moments, which means that all three components DMX, DMY, and DMZ are computed. Alternatively, individual components may be requested.

The general format is as follows:

\[ [G] \text{EXPEC,\textit{opname}[,\textit{icen},[x,y,z]]...} \]

where

- \textit{opname} operator name (string), either generic or component.
- \textit{icen} z-matrix row number or z-matrix symbol used to determine the origin (x,y,z must not be specified).
  If \textit{icen} = 0 or blank, the origin must be specified in \textit{x,y,z}

Several GEXPEC cards may follow each other, or several operators may be specified on one card.

Examples:

GEXPEC, QM computes quadrupole moments with origin at (0,0,0).
GEXPEC, QM1 computes quadrupole moments with origin at centre 1.
GEXPEC, QM, O1 computes quadrupole moments with origin at atom O1.
GEXPEC, QM, , 1, 2, 3 computes quadrupole moments with origin at (1,2,3).

The following table summarizes all available operators:

Expectation values are only nonzero for symmetric operators (parity=1). Other operators can be used to compute transition quantities (spin-orbit operators need a special treatment).

6.13.1 Example for computing expectation values

The following job computes dipole and quadrupole moments for H$_2$O.
### 6.13.2 Example for computing relativistic corrections

**H2O properties**

```plaintext
***, h2o properties
geometry={o;h1,o,r;h2,o,r,h1,theta} !Z-matrix geometry input
r=1 ang !bond length
theta=104 !bond angle
gexpec, dm, sm, qm !compute dipole and quadrupole moments
$methods=[hf, multi, ci] !do hf, casscf, mrci
do i=1,#methods !loop over methods
$methods(i) !run energy calculation
e(i)=energy !energy
dip(i)=dmz !save dipole moment in variable dip
quadxx(i)=qmxx !save quadrupole moments
quadyy(i)=qmyy
quadzz(i)=qmzz
smxx(i)=xx !save second moments
smyy(i)=yy
smzz(i)=zz
enddo
table, methods, dip, smxx, smyy, smzz !print table of first and second moments
table, methods, e, quadxx, quadyy, quadzz !print table of quadrupole moments
```

This Job produces the following tables:

<table>
<thead>
<tr>
<th>METHODS</th>
<th>DIP</th>
<th>SMXX</th>
<th>SMYY</th>
<th>SMZZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>0.82747571</td>
<td>-5.30079792</td>
<td>-3.01408114</td>
<td>-4.20611391</td>
</tr>
<tr>
<td>MULTI</td>
<td>0.76285513</td>
<td>-5.29145148</td>
<td>-3.11711397</td>
<td>-4.25941000</td>
</tr>
<tr>
<td>CI</td>
<td>0.76868508</td>
<td>-5.32191822</td>
<td>-3.15540500</td>
<td>-4.28542917</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>METHODS</th>
<th>E</th>
<th>QUADXX</th>
<th>QUADYY</th>
<th>QUADZZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>-76.02145798</td>
<td>-1.69070039</td>
<td>1.73937477</td>
<td>-0.04867438</td>
</tr>
<tr>
<td>MULTI</td>
<td>-76.07843443</td>
<td>-1.60318949</td>
<td>1.65831677</td>
<td>-0.05512728</td>
</tr>
<tr>
<td>CI</td>
<td>-76.23369821</td>
<td>-1.60150114</td>
<td>1.64826869</td>
<td>-0.04676756</td>
</tr>
</tbody>
</table>

6.13.2 Example for computing relativistic corrections

**Ar2**

```plaintext
***, ar2
geometry=(ar1;ar2,ar1,r) !geometry definition
r=2.5 ang !bond distance
(hf; !non-relativistic scf calculation
expec, rel, darwin, massv) !compute relativistic correction using Cowan-Griffin operator
e_nrel-energy !save non-relativistic energy in variable enrel
show, massv, darwin, erel !show individual contribution and their sum
dkroll=1 !use douglas-kroll one-electron integrals
hf; !relativistic scf calculation
e_dk-energy !save relativistic scf energy in variable e_dk.
show, massv, darwin, erel !show mass-velocity and darwin contributions and their sum
show, e_dk-e_nrel !show relativistic correction using Douglas-Kroll
```

This jobs shows at the end the following variables:

<table>
<thead>
<tr>
<th>MASSV / AU</th>
<th>DARWIN / AU</th>
<th>EREL / AU</th>
</tr>
</thead>
<tbody>
<tr>
<td>-14.84964285</td>
<td>11.25455679</td>
<td>-3.59508606</td>
</tr>
<tr>
<td>Generic name</td>
<td>Parity</td>
<td>Components</td>
</tr>
<tr>
<td>--------------</td>
<td>--------</td>
<td>------------------------------------------------</td>
</tr>
<tr>
<td>OV</td>
<td>1</td>
<td>Overlap</td>
</tr>
<tr>
<td>EKIN</td>
<td>1</td>
<td>Kinetic energy</td>
</tr>
<tr>
<td>POT</td>
<td>1</td>
<td>potential energy</td>
</tr>
<tr>
<td>DELTA</td>
<td>1</td>
<td>delta function</td>
</tr>
<tr>
<td>DEL4</td>
<td>1</td>
<td>( \Delta^4 ) one-electron Darwin term, i.e., ( \Delta ) with appropriate factors summed over atoms.</td>
</tr>
<tr>
<td>DARW</td>
<td>1</td>
<td>mass-velocity term, i.e., ( \Delta^4 ) with appropriate factor.</td>
</tr>
<tr>
<td>REL</td>
<td>1</td>
<td>total Cowan-Griffin Relativistic correction, i.e., ( \Delta ) with appropriate factors</td>
</tr>
<tr>
<td>DM</td>
<td>1</td>
<td>( \Delta^4 ) dipole moments and ( R^2 )</td>
</tr>
<tr>
<td>SM</td>
<td>1</td>
<td>second moments</td>
</tr>
<tr>
<td>TM</td>
<td>1</td>
<td>third moments</td>
</tr>
<tr>
<td>MLTP&lt;sub&gt;n&lt;/sub&gt;</td>
<td>1</td>
<td>all unique Cartesian products of order ( n )</td>
</tr>
<tr>
<td>QM</td>
<td>1</td>
<td>quadrupole moments and ( R^2 )</td>
</tr>
<tr>
<td>EF</td>
<td>1</td>
<td>electric field</td>
</tr>
<tr>
<td>FG</td>
<td>1</td>
<td>electric field gradients</td>
</tr>
<tr>
<td>DMS</td>
<td>1</td>
<td>diamagnetic shielding tensor</td>
</tr>
<tr>
<td>LOP</td>
<td>-1</td>
<td>Angular momentum operators ( \hat{L}_x, \hat{L}_y, \hat{L}_z )</td>
</tr>
<tr>
<td>LOP2</td>
<td>1</td>
<td>one electron parts of products of angular momentum operators.</td>
</tr>
<tr>
<td>VELO</td>
<td>-1</td>
<td>velocity</td>
</tr>
<tr>
<td>LS</td>
<td>-1</td>
<td>spin-orbit operators</td>
</tr>
<tr>
<td>ECPLS</td>
<td>-1</td>
<td>ECP spin-orbit operators</td>
</tr>
</tbody>
</table>
7 FILE HANDLING

7.1 FILE

The FILE directive is used to open permanent files, which can be used for later restarts. The syntax in MOLPRO94 and later versions is

FILE, file, name, [status]

file is the logical MOLPRO file number (1-9). name is the file name (will be converted to lower case). status can be one of the following:

UNKNOWN A permanent file is opened. If it exists, it is automatically restarted. This is the default.
OLD Same effect as UNKNOWN. No error occurs if the file does not exist.
NEW A permanent file is opened. If it already exists, it is erased and not restarted.
ERASE Same effect as NEW.
SCRATCH A temporary file is opened. If it already exists, it is erased and not restarted. After the job has finished, the file is no longer existent.
DELETE Same effect as SCRATCH.

Note that RESTART is now the default for all permanent files. All temporary files are usually allocated automatically where needed. I/O buffers are allocated at the top of the dynamic memory, and the available memory decreases by the size of the buffers. The MEMORY card must therefore be presented before the first FILE card!

Examples:

FILE, 1, H2O.INT allocates permanent file 1 with name H2O.INT. Previous information on the file is recovered.
FILE, 2, H2O.WFU, NEW allocates permanent file 2 with name H2O.WFU. All previous information on the file is erased.

Note that filenames are converted to lower case on unix machines.

7.2 DELETE

DELETE, file1, file2, . . .

Deletes the specified files. file refers to the logical MOLPRO file numbers as specified on the FILE card.

7.3 ERASE

ERASE, file1, file2, . . .

Erases the specified files. file refers to the logical MOLPRO file numbers as specified on the FILE card.
### 7.4 DATA

The **DATA** command can be used to modify the MOLPRO binary files.

- **UNIT**
  - Alias for NPL (should never be used)
- **RENAME**
  - `rec1,rec2`
  - Used to rename `rec1` to `rec2`. `rec1` and `rec2` must be given in the form `name.ifil`, where `ifil` is the number of a MOLPRO binary file (alias for NAME).
- **TRUNCATE**
  - `nen`
  - Used to truncate files after `nen-1` records (alias for NEN).
- **TRUNCATE**
  - `rec`
  - Used to truncate before record `rec`. `rec` must be given in the form `name.ifil`, where `ifil` is the number of a MOLPRO binary file.
- **COUNT**
  - Alias for NRE (presently not used)
- **COPY**
  - `rec1,rec2`
  - Copies record `rec1` to `rec2`. `rec1` and `rec2` must be given in the form `name1.ifil1,name2.ifil2`. If `nam2=0`, `nam2=nam1`. If `nam1=0`, all records are copied from file `ifil1` to file `ifil2`.

### 7.5 Assigning punch files (**PUNCH**)

**PUNCH,** `filename`, [REWIND]

Opens punch file named `filename`. If this file already exists, it is appended, unless the REWIND or NEW option is specified; in that case, any previous information on the punch file is overwritten. See **FILE** for machine dependent interpretation of filename. The punch file contains all important results (geometries, energies, dipole, transition moments etc). It can be read by a separate program **READPUN**, which can produce tables in user supplied format.

Example:

```
PUNCH, H2O.PUN [REWIND]
```

Allocates punch file `H2O.PUN`

Note that the file name is converted to lower case on unix machines.

### 7.6 MOLPRO system parameters (**GPARAM**)

The **GPARAM** card allows to change MOLPRO system parameters. This should only be used by experts!

**GPARAM,** `option=value,...`

The following options can be given in any order.

- **NOBUFF**
  - If present, disable system buffering
- **LSEG**
  - Disk sector length
- **INTREL**
  - Number of integer words per real word (should never be modified!)
- **IBANK**
  - Number of memory banks. Default is 2, which should always be o.k.
- **IVECT**
  - 0=scalar, 1=vector machine
- **MINVEC**
  - Minimum vector length for call to mxmb
- **LTRACK**
  - Page size in buffer routines (must be multiple of `lseg`)
8 VARIABLES

LENBUF  
length of integral buffer (file 1)

NTR  
length of integral records (must be multiple of 3·ltrack)

LTR  
disk sector length assumed in CI (default 1 is reasonable)

NCACHE  
machine cache size in bytes

IASYN  
if nonzero, use asynchronous I/O on CONVEX

MXMBLK  
column/row block size for mxma

MXMBLN  
link block size for mxma

NCPUS  
maximum number of cpus to be used in multitasking

MINBR1  
min number of floating point ops per processor

MXDMP  
highest file number to be treated as dump file with full functionality (1 ≤ . MXDMP ≤ .3).

The MXDMP option is for experts only! This prevents basis and geometry information from being written to dump files with higher file number than the given value, and can sometimes be useful for counterpoise corrected geometry optimizations. Note that some functionality is lost by giving this option, and errors will result unless all input is correct!

8 VARIABLES

Data may be stored in variables. A variable can be of type string, real or logical, depending on the type of the expression in its definition. Any sequence of characters which is not recognized as expression or variable is treated as string. In this section, we will discuss only real and logical variables. String variables will be discussed in more detail in section 8.3. Variables can be used anywhere in the input, but they can be set only outside the input blocks for specific programs. For example, if a variable is used within the input block for HF, it must have been set before the HF{...} input block.

MOLPRO automatically stores various results and data in system variables (see section 8.8.1), which can be used for further processing. A new feature of MOLPRO2002 is that most system variables are write protected and cannot be overwritten by the user. The input is automatically checked before the job starts, and should a system variable be set in the input the job will stop immediately with an error message. Only in some exceptions (see section 8.4), system variables can be modified using the SET command (but not with the simple NAME=value syntax). Note that due to the changed usage and syntax of the SET command, compatibility with MOLPRO92 input syntax is no longer maintained.

8.1 Setting variables

A variable can be defined using

variable1=value1, variable2=value2, ...

A variable definition is recognized by the equals sign in the first field of the input card. For example,

THRESH, ENERGY=1.d-8, GRADIENT=1.d-5

does not define variables; here ENERGY and GRADIENT are options for the THRESH directive.

Variables can have different types:
Numbers: The value is a number or an expression. The general form of value is
\( \text{expression} \ [\text{unit}] \)
unit is an optional string which can be used to associate a unit to the value. ANGSTROM, DEGREE, HARTREE are examples. Undefined variables in expressions are assumed to be zero (and defined to be zero at the same time).

Logicals: The value can be .TRUE. or .FALSE. (.T. and .F. also work), or a logical expression. Internally, .TRUE. is stored as 1 and .FALSE. as zero.

Strings: The value can either be a string enclosed in quotes or a string variable. See section 8.3 for more details.

8.2 Indexed variables

Variables can be indexed, but only one-dimensional indexing is available. Indexed variables can be defined either individually, e.g.

\[
\begin{align*}
R(1) &= 1.0 \text{ ANG} \\
R(2) &= 1.2 \text{ ANG} \\
R(3) &= 1.3 \text{ ANG}
\end{align*}
\]

or as a vector of values enclosed by square brackets:

\[
R=\begin{bmatrix} 1.0, 1.1, 1.2 \end{bmatrix} \text{ ANG}
\]

Subranges can also be defined, e.g.

\[
\begin{align*}
R(1) &= 1.0 \text{ ANG} \\
R(2:3) &= \begin{bmatrix} 1.1, 1.2 \end{bmatrix} \text{ ANG}
\end{align*}
\]

leads to the same result as the above two forms.

The type of each element depends on the type of the assigned value, and it is possible to mix types in one variable. Example:

\[
\begin{align*}
\text{geometry} &= \{\text{he}\} \\
\text{hf} \\
\text{result} &= \{\text{program, energy, status.gt.0}\}
\end{align*}
\]

yields:

\[
\begin{align*}
\text{RESULT(1)} &= \text{HF-SCF} \\
\text{RESULT(2)} &= -2.85516048 \text{ AU} \\
\text{RESULT(3)} &= \text{TRUE}
\end{align*}
\]

In this example the variables PROGRAM, ENERGY, and STATUS are system variables, which are set by the program (see section 8.4).
8.3 String variables

As explained already in section 8.1, string variables can be set as other variables in the form

\[ variable = 'string' \]
\[ variable = string_{variable} \]

Strings must be enclosed by quotes. Otherwise the string is assumed to be a variable, and if this is undefined it is assumed to be zero.

Alternatively, if the name of the variable is preceded by a dollar ($), all values are assumed to be a string. This can be a string variable, a quoted string, or an unquoted string. Note that unquoted strings are converted to upper case. Also note that quotes are compulsory if the string contains blanks.

Example:

\[ $str=[a,b+4,'This is an example for strings'] \]

yields

\[
\begin{align*}
\text{STR(1)} &= \text{A} \\
\text{STR(2)} &= \text{B+4} \\
\text{STR(3)} &= \text{This is an example for strings}
\end{align*}
\]

As a general rule, string variables are replaced by their value only if they are preceded by a dollar ($) (exceptions: in variable definitions, on \texttt{SHOW} cards, and in logical expressions on \texttt{IF} cards, the dollar is optional). This is a precaution to avoid commands which have the same name as a variable being interpreted as variables. Variables may also appear on \texttt{TEXT} or \texttt{TITLE} cards or in strings, but must be preceded by $ in these cases. Example:

\[ $METHOD=\textit{MCSCF} \]
\[ R=1.5 \]
\[ \texttt{TEXT},$\textit{method} \texttt{results \ for \ R=$R \ Bohr} \]

prints

\textit{MCSCF} \texttt{ results \ for \ R=1.5 \ Bohr}

String variables can be concatenated with strings or other string variables in the following way. Assume that variable \texttt{PROGRAM} has the value \textit{MRCI}. Setting

\[ \texttt{METHOD='$PROGRAM+Q'} \]

sets \texttt{METHOD} to \textit{MRCI+Q}. Alternatively, if we would also have a variable \texttt{VERSION} with value \textit{Q}, we could write

\[ \texttt{METHOD='$PROGRAM+$VERSION'} \]

Again, the value of \texttt{METHOD} would be \textit{MRCI+Q}. Note that the quotes are necessary in these cases.

Substring operations are not implemented.
8.4 System variables

As mentioned above, most system variables cannot be written by the user. In some exceptions, it is possible to redefine them using the `SET` command:

```
SET, variable = expression [,] [unit]
```

This holds for the following variables:

- **CHARGE**: Total charge of the molecule
- **NELEC**: Number of electrons
- **SPIN**: Spin quantum number, given as $2 \cdot M_S$ (integer)
- **SCFSPIN**: Same as **SPIN**, but only for HF
- **MCSPIN**: Same as **SPIN**, but only for MCSCF
- **CISPIN**: Same as **SPIN**, but only for MRCI
- **STATE**: State to be optimized
- **MCSTATE**: Same as **STATE** but only for MCSCF
- **CISTATE**: Same as **STATE** but only for MRCI
- **SYMMETRY**: State symmetry
- **SCFSYM**: Same as **SYMMETRY** but only for HF
- **MCSYM**: Same as **SYMMETRY** but only for MCSCF
- **CISYM**: Same as **SYMMETRY** but only for MRCI
- **ZSYMEL**: Symmetry elements
- **LQUANT**: Lambda quantum number for linear molecules
- **OPTCONV**: Geometry optimization convergence criterion
- **PROGRAM**: Last program name
- **CPUSTEP**: CPU-time of last program step
- **SYSTEPS**: System-time of last program step
- **WALLSTEP**: Elapsed-time of last program step
- **FOCKDONE**: Indicates if closed-shell fock operator is available.
- **MAXBASIS**: Max number of basis sets stored on dump files. If the maximum is reached, the last one is overwritten when a new one is made, and all information (including dump records etc) of the previous basis is lost. The default is the maximum possible number of basis sets (30), which cannot be exceeded.

8.5 Macro definitions using string variables

String variables for which the stored string has the form of an algebraic expression are evaluated to a number if they are preceded by two dollars ($$$). Example:

```
string='a+b'
a=3
b=4
text,This is string $string which evaluates to $$string
```
prints

** This is string a+b which evaluates to 7

This can be used to define simple macros, which can be used at various places in the subsequent input. For instance,

```
ECORR='ENERGY-ESCF' !define a macro
HF !do SCF calculation
ESCF=ENERGY !store SCF energy in variable ESCF
MULTI !do CASSCF
DEMC=ECORR !store CASSCF correlation energy in variable DEMC
MRCI !do MRCI
DECI=ECORR !store MRCI correlation energy in variable DECI
```

Here is an example of advanced use of macros and string variables:

```
***,test for parser
text,This fancy input demonstrates how string variables and macros can be used
text
basis=vdz !define basis set
gallery={O;H,O,r} !define geometry (z-matrix)
text
methods
$method=[rhf,2[casscf,2[mrci]]]
text,active spaces
$spaces=['[3,1,1]',3['[4,2,2]',3['[5,2,2]'])
text,symmetries
$symset=['1',2['[1,2,3]',1,'2'])
text,weight factors for state averaged casscf
$weights=['1','[1,1,1]',2[' ',1,'0.5,0.5]',2[' ']
text,scf occupation
set,scfocc=[3,2[1]]
text,bond distance
r=1.85

hf
do i=1,#method !loop over methods
mcocc=$spaces(i) !set active space for this run
set,symmetry=$symset(i) !set symmetries for this run
set,weight=$weights(i) !set weights for this run
$method(i) !now run method
e(i)='$energy' !save energies in strings
dipol(i)='$dmz' !save dipole moments in strings
enddo
```

```
table,method,spaces,symmetries,weights,e,dipol
head,method,spaces,symmetries,weights,energies,'dipole moments'
exit
```

```
http://www.molpro.net/info/current/examples/oh_macros.com
```

### 8.6 Indexed Variables (Vectors)

Variables may be indexed, but only one-dimensional arrays (vectors) are supported. The index may itself be a variable. For instance

```
METHOD(I)=PROGRAM
E(I)=ENERGY
```
are valid variable definitions, provided \texttt{I}, \texttt{PROGRAM}, and \texttt{ENERGY} are also defined variables. Indices may be nested to any depth.

Different elements of an array can be of different type (either \textit{real} or \textit{logical}). However, only one \textit{unit} can be assigned to an array. String variables have no associated value and cannot be mixed with the other variable types. Therefore, a given variable name can only be used either for a \textit{string} variable or a \textit{real} (\textit{logical}) variable.

Vectors (arrays) can be conveniently defined using square brackets:

\begin{verbatim}
R=[1.0,1.2,1.3] ANG
\end{verbatim}

This defines an array with three elements, which can be accessed using indices; for instance, \texttt{R(2)} has the value \texttt{1.2 ANG}. A repeat specifier can be given in front of the left bracket: \texttt{5[0]} is equivalent to \texttt{[0,0,0,0,0]}. Brackets can even be nested: for instance, \texttt{2[1,2,2[2.1,3.1]]} is equivalent to \texttt{[1,2,2.1,3.1,2.1,3.1,1,2,2.1,3.1,2.1,3.1]}.

Arrays can be appended from a given position just by entering additional elements; for instance,

\begin{verbatim}
R(4)=[1.4,1.5] ANG
\end{verbatim}

or

\begin{verbatim}
R(4:)=[1.4,1.5] ANG
\end{verbatim}

extends the above array to length 5. Previously defined values can be overwritten. For instance

\begin{verbatim}
R(2)=[1.25,1.35,1.45]
\end{verbatim}

modifies the above vector to \texttt{(1.0, 1.25, 1.35, 1.45, 1.5)}.

If no index is given on the left hand side of the equal sign, an existing variable of the same name is replaced by the new values, and all old values are lost. For instance

\begin{verbatim}
THETA=[100,110,120,130] set four values
...
THETA(1)=104 replace THETA(1) by a new value; THETA(2:4) are unchanged
...
THETA=[140,150] old variable THETA is replaced; THETA(3:4) are deleted
\end{verbatim}

Square brackets can also be used to define an array of strings, e.g.,

\begin{verbatim}
METHOD=[INT, HF, CASSCF, MRCI]
\end{verbatim}

These could be used as follows:

\begin{verbatim}
DO I=1,4
SMETHOD(I)
ENDDO
\end{verbatim}

The above input would be equivalent to

\begin{verbatim}
INT
HF
CASSCF
MRCI
\end{verbatim}
The current length of an array can be accessed by preceding \# to the variable name. For instance, in the above examples \#R and \#METHOD have the values 5 and 4, respectively. If a variable is not defined, zero is returned but no error occurs. This can be used to test for the existence of a variable, for example:

\[
\text{IF} \left( \#\text{SPIN.EQ.0.AND.}\#\text{NELEC.EQ.1} \right) \text{ SET, SPIN=MOD(NELEC,2)}
\]

This defines variable SPIN if it is unknown and if NELEC is a scalar (one dimensional) variable.

### 8.7 Vector operations

The following simple vector operations are possible:

- **Copying or appending a vector to another vector.** For instance \( S=R \) copies a vector \( R \) to a vector \( S \). \( S(3)=R \) copies \( R \) to \( S(3), S(4), \ldots, S(\#S+1)=R \) append to vector \( S \). It is also possible to access a range of subsequent elements in a vector: \( S=R(2:4) \) copies elements 2 to 4 of \( R \) to \( S(1), S(2), S(3) \). Note that \( R(2:) \) denotes elements \( R(2) \) to \( R(\#R) \), but \( R(2) \) denotes a single element of \( R \).

- **Vector-scalar operations:** \( R=R*2 \) multiplies each element of \( R \) by 2. Instead of the number 2, also scalar (one dimensional) variables or expressions can be used, e.g., \( R=R*\text{ANG} \) converts all elements of \( R \) from Ångström to bohr, or \( Z=R*\text{COS}(\text{THETA}) \) creates a vector \( Z \) with elements \( Z(i) = R(i)*\text{COS}(\text{THETA}) \). All other algebraic operators can be used instead of “*”. Note that the scalar must come last since the first variable in the expression determines the vector length.

- **Vector-vector operations:** If \( A \) and \( B \) are vectors of the same length, then \( A \times B \) is also a vector of this length. Here \( \times \) stands for any algebraic operator, and the operation is done for each pair of corresponding elements. For instance, \( A + B \) adds the vectors \( A \) and \( B \), and \( A \times B \) multiplies their elements. Note that the latter case is not a scalar product. If an attempt is made to connect two vectors of different lengths by an algebraic operator, an error occurs.

- **Intrinsic functions:** Assume \( \text{THETA}=[100,110,120,-130] \) to be a vector of angles (in degrees). In this case \( X=2*\text{COS}(\text{THETA}) \) is also a vector containing the cosines of each element of \( \text{THETA} \) multiplied by two, i.e., \( X(i) = 2*\text{COS}(\text{THETA}(i)) \). \( \text{MAX}(\text{THETA}) \) or \( \text{MIN}(\text{THETA}) \) return the maximum and minimum values, respectively, in array \( \text{THETA} \). Vector operations can also be nested, e.g., \( \text{MAX} \left( \text{ABS}(\text{THETA}) \right) \) returns the maximum value in array \( \text{ABS}(\text{THETA}) \).

At present, vector operations are not supported with string variables.

### 8.8 Special variables

#### 8.8.1 Variables set by the program

A number of variables are predefined by the program. The following variables can be used to convert between atomic units and other units:

\[
\begin{align*}
\text{EV}&=1.d0/27.2113839d0 \text{ HARTREE} \\
\text{KELVIN}&=1.d0/3.157747d5 \text{ HARTREE} \\
\text{KJOULE}&=1.d0/2625.500d0 \text{ HARTREE}
\end{align*}
\]
Further variables which are set during execution of the program:

- **INTYP**: defines integral program to be used. Either INTS (Seward) or INTP (Argos).
- **INTDONE**: has the value `.true.` if the integrals are done for the current geometry.
- **CARTESIAN**: Set to one if Cartesian basis functions are used.
- **SCFDONE**: has the value `.true.` if an SCF calculation has been done for the current geometry.
- **NUMVAR**: number of variables presently defined
- **STATUS**: status of last step (1=no error, -1=error or no convergence)
- **CHARGE**: Total charge of the molecule
- **NELEC**: number of electrons in last wavefunction
- **SPIN**: spin multiplicity minus one of last wavefunction
- **ORBITAL**: record of last optimized orbitals (set but never used in the program)
- **LASTORB**: Type of last optimized orbitals (RHF, UHF, UHFNAT, or MCSCF).
- **LASTSYM**: Symmetry of wavefunction for last optimized orbitals.
- **LASTSPIN**: $2 \times M_S$ for wavefunctions for last optimized orbitals.
- **LASTNELEC**: Number of electrons in wavefunction for last optimized orbitals.
- **ENERGR(istate)**: Reference energy for state `istate` in MRCI and CCSD.
- **ENERGY(istate)**: last computed total energy for state `istate` for the method specified in the input (e.g., HF, MULTI, CCSD(T), or CCSD[T]).
- **ENERGY_METHOD**: String variable holding name of the method used for calculating ENERGY
- **ENERGY_BASIS**: String variable holding name of the orbital basis-set used for calculating ENERGY
- **GEOMETRY_METHOD**: Equal to the value of `ENERGY_METHOD` for the most recent geometry optimisation
<table>
<thead>
<tr>
<th>Variable</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>GEOMETRY_BASIS</td>
<td>Equal to the value of ENERGY_BASIS for the most recent geometry optimisation</td>
</tr>
<tr>
<td>ENERGD(istate)</td>
<td>Total energy for state istate including Davidson correction (set only in CI)</td>
</tr>
<tr>
<td>ENERGP(istate)</td>
<td>Total energy for state istate including Pople correction (set only in CI)</td>
</tr>
<tr>
<td>ENERGT(1)</td>
<td>Total energy including perturbative triples (T) correction (set only in CCSD(T), QCI(T))</td>
</tr>
<tr>
<td>ENERGT(2)</td>
<td>Total energy including perturbative triples [T] correction (set only in CCSD(T), QCI(T))</td>
</tr>
<tr>
<td>ENERGT(3)</td>
<td>Total energy including perturbative triples –t correction (set only in CCSD(T), QCI(T))</td>
</tr>
<tr>
<td>EMP2</td>
<td>holds MP2 energy in MPn, CCSD, BCCD, or QCISD calculations, and RS2 energy in MRPT2 (CASPT2) calculations.</td>
</tr>
<tr>
<td>EMP3</td>
<td>holds MP3 energy in MP3 and MP4 calculations, and RS3 energy in MRPR3 (CASPT3) calculations.</td>
</tr>
<tr>
<td>EMP4</td>
<td>holds MP4(SDQ) energy in MP4 calculations. The MP4(SDTQ) energy is stored in variable ENERGY.</td>
</tr>
<tr>
<td>METHODC</td>
<td>String variable holding name of the methods used for ENERGC, e.g., CCSD, BCCD, QCI.</td>
</tr>
<tr>
<td>METHODT(1)</td>
<td>String variable holding name of the methods used for ENERGT(1), e.g., CCSD(T), BCCD(T), QCI(T).</td>
</tr>
<tr>
<td>METHODT(2)</td>
<td>String variable holding name of the methods used for ENERGT(2), e.g., CCSD[T], BCCD[T], QCI[T].</td>
</tr>
<tr>
<td>METHODT(3)</td>
<td>String variable holding name of the methods used for ENERGT(3), e.g., CCSD-T, BCCD-T, QCI-T.</td>
</tr>
<tr>
<td>ENERGC</td>
<td>Total energy excluding perturbative triples correction (set only in QCI or CCSD with triples correction enabled).</td>
</tr>
<tr>
<td>DFTFUN</td>
<td>total value of density functional in DFT or KS.</td>
</tr>
<tr>
<td>DFTFUNS(ifun)</td>
<td>value of ifun'th component of density functional in DFT or KS.</td>
</tr>
<tr>
<td>DFTNAME(ifun)</td>
<td>name of ifun'th component of density functional in DFT or KS.</td>
</tr>
<tr>
<td>DFTFAC(ifun)</td>
<td>factor multiplying ifun'th component of density functional in DFT or KS.</td>
</tr>
<tr>
<td>DFTEXFAC</td>
<td>factor multiplying exact exchange in KS.</td>
</tr>
<tr>
<td>PROP(istate)</td>
<td>computed property for state istate. See below for the names PROP of various properties.</td>
</tr>
<tr>
<td>PROGRAM</td>
<td>last program called, as specified in the input (e.g., HF, CCSD(T), etc.)</td>
</tr>
<tr>
<td>ITERATIONS</td>
<td>Number of iterations used. Set negative if no convergence or max number of iterations reached.</td>
</tr>
<tr>
<td>CPUSTEP</td>
<td>User-CPU time in seconds for last program called.</td>
</tr>
<tr>
<td>SYSSTEPS</td>
<td>System-CPU time in seconds for last program called.</td>
</tr>
<tr>
<td>WALLSTEP</td>
<td>Elapsed time in seconds for last program called.</td>
</tr>
</tbody>
</table>

The variable names for properties are the same as used on the EXPEC input cards.
By default, only the dipole moments are computed and defined. The values of other properties are only stored in variables if they are requested by EXPEC cards. If more than one state is computed (e.g., in state-averaged MCSCF, corresponding arrays \texttt{PROP(istate)} are returned. If properties are computed for more than one center, the center number is appended to the name, e.g. \texttt{EFX1}, \texttt{EFX2} etc.

If transition properties are computed, their values are stored in corresponding variables with prefix \texttt{TR}, e.g., \texttt{TRDMX}, \texttt{TRDZY}, \texttt{TRDZM} for transition dipole moments. If more than two states are computed, the index is \((i-1)(i-2)/2 + j\), where \(i > j \geq 1\) are state numbers. In a state-averaged calculation, states are counted sequentially for all state symmetries.

For instance, in the following state-averaged MCSCF

\texttt{MULTI;WF,14,1,0;STATE,3;WF,14,2,0;STATE,2;WF,14,3,0}

the states are counted as

\[
i \\
1 & 2 & 3 & 4 & 5 & 6
\]

\[
\text{Symmetry} \\
1 & 1 & 1 & 2 & 2 & 3
\]

\[
\text{Root in Sym.} \\
1 & 2 & 3 & 1 & 2 & 1
\]

### 8.8.2 Variables recognized by the program

All variables described below are checked by the program, but not set (except \texttt{NELEC} and \texttt{SPIN}). If these are not defined by the user, the program uses its internal defaults. The variables are only recognized and used if defined using the \texttt{SET} command, e.g.

\[
\text{SET, MCOCC}=[6,3,2]
\]

\[
\text{SET, STATE}=2
\]
Variables recognized by the SCF program:

- **CHARGE**: Total charge of the molecule (can be given instead of nelec)
- **NELEC**: number of electrons
- **SPIN**: spin multiplicity minus one
- **SCFSYM[METRY]**: wavefunction symmetry
- **SYMMETRY**: as SCFSYM; only used if SCFSYM is not present.
- **SCFOC[C]**: number of occupied orbitals in each symmetry for SCF
- **SCFCL[OSED]**: number of closed-shell orbitals in each symmetry for SCF
- **SCFORB**: record of saved orbitals in SCF
- **SCFSTART**: record of starting orbitals used in SCF

Variables recognized by the MCSCF program:

- **CHARGE**: Total charge of the molecule (can be given instead of nelec)
- **NELEC**: number of electrons
- **MCSYM[METRY]**: wavefunction symmetry. This can be an array for state-averaged calculations.
- **SYM**M**ETRY**: as MCSYM; only used if MCSYM is not present.
- **MCSPIN**: spin multiplicity minus one. This can be an array for state-averaged calculations, but different spin multiplicities can only be used in determinant CASSCF. If only one value is specified, this is used for all states
- **SPIN**: as MCSPIN; only used if MCSPIN is not present.
- **MCSTATE**: number of states for each symmetry in MCSCF
- **STATE**: as MCSTATE; only used if MCSTATE is not present.
- **WEIGHT**: weight factors for all states defined by SYMMETRY and STATE
- **LQUANT**: Eigenvalues of $L_z$ for linear molecules for each state defined by SYMMETRY and STATE.
- **MCSELECT**: records from which configurations can be selected and selection threshold
- **SELECT**: as MCSELECT; only used if MCSELECT is not present.
- **MCRESTRICT**: can be used to define occupancy restrictions
- **RESTRICT**: as MCRESTRCT; only used if MCRESTRCT is not present:
- **CONFIG**: if set to .true. or to one triggers use of CSFs
- **MCOC[C]**: number of occupied orbitals in each symmetry
- **OCC**: as MCOCC; only used if MCOCC is not present.
- **MCCL[OSED]**: number of optimized closed-shell orbitals in each symmetry
- **CLOSED**: as MCCCLOSED; only used if MCCCLOSED is not present.
- **MCFROZEN**: number of frozen core orbitals in each symmetry
- **FROZEN**: as MCFROZEN; only used if MCFROZEN is not present.
MCSTART record of starting orbitals
COREORB record of frozen core orbitals
MCORB record for saving optimized orbitals
MCSAVE records for saving CI wavefunction (like SAVE card in MCSCF)

Variables recognized by the CI/CCSD program:

CHARGE Total charge of the molecule (can be given instead of nelec)
NELEC number of electrons
SPIN spin multiplicity minus one
CISYM[METRY] wavefunction symmetry. If this is an array, only SYMMETRY(1) is used.
SYMMETRY as CISYM; only used if CISYM is not present.
CISTATE number of states in CI
STATE as CISTATE, only used if CISTATE is not present.
CISELECT records from which configurations can be selected
SELECT as CISELECT; only used if CISELECT is not present.
CISELECT records from which configurations can be selected
RESTRICT defines occupancy restrictions
as RESTRICT; only used if CISELECT is not present.
CI[C] number of occupied orbitals in each symmetry
OCC as OCC; only used if OCC is not present.
CICLOSED number of closed-shell orbitals in each symmetry
CLOSED as CICLOSED; only used if CICLOSED is not present.
CICORE number of core orbitals in each symmetry
CORE as CICORE; only used if CICORE is not present.
CIORB record of orbitals used in CI
CISAVE records for saving CI wavefunction (like SAVE card in CI)
CISTART records for restarting with previous CI wavefunction (like START card in CI)

Variables recognized by the DFT/KS program:

DF(ifun) or DFTNAME(ifun) name of ifun’th component of density functional.
DFTFAC(ifun) factor multiplying ifun’th component of density functional.
DFTEXFAC factor multiplying exact exchange in KS.

Example for the use of these variables for a state-averaged MCSCF (note that system variables can only be modified using the SET command, see section 8.4):

SET, NELEC=9 defines number of electrons
SET, SPIN=1 defines wavefunction to be a doublet
SET, SYMMETRY=[1, 2, 3] defines wavefunction symmetries for state averaged calculation
8 VARIABLES

\[ \text{SET, STATE} = [2, 1, 1] \] defines number of states to be averaged in each symmetry
\[ \text{WEIGHT} = [2, 2, 1, 1] \] defines weights for the above four states
\[ \text{OCC} = [5, 2, 2] \] number of occupied orbitals in each symmetry
\[ \text{CLOSED} = 2 \] number of closed-shell orbitals in symmetry 1
\[ \text{MCORB} = 3100.2 \] record for optimized orbitals
\[ \text{MULTI} \] do mcscf with above parameters

Note: Setting the variables \text{NELEC}, \text{SPIN}, or \text{SYMMETRY}, has the same effect giving these on a global \text{WF} directive. If the global \text{WF} directive is given after the variable definition, the values of the variables are replaced by the values given on the \text{WF} directive. Vice versa, if a variable definition follows a global \text{WF} directive, the new value of the variable is used in the following. Note that \text{WF} input cards in command blocks have preference over global \text{WF} directives or input variables.

8.9 Displaying variables

Variables or the results of expressions can be displayed in the output using \text{SHOW} and \text{TABLE}.

8.9.1 The \text{SHOW} command

The general form of the \text{SHOW} command is as follows:

\[ \text{SHOW} [ \text{ncol}, \text{format} ], \text{expression} \]

where \text{expression} can be an expression or variable, \text{ncol} is the number of values printed per line (default 6), and \text{format} is a format (default 6F15.8). This can be used to print vectors in matrix form. The specification of \text{ncol} and \text{format} is optional. Assume that \text{E} is a vector:

\[ \text{SHOW}, \text{E} \] prints \text{E} using defaults.
\[ \text{SHOW}[n], \text{E} \] prints \text{E} with \text{n} elements per line; (if \text{n} > 6, more than one line is needed, but in any case a new line is started after \text{n} elements).
\[ \text{SHOW}[n, 10f10.4], \text{E} \] prints \text{E} in the format given, with newline forced after \text{n} elements.

Note that the total length of the format should not exceed 100 characters (a left margin of 30 characters is always needed).

A \text{wild card} format can be used to show several variables more easily:
\[ \text{SHOW}, \text{qm*}, \text{dm*} \]
shows all variables whose names begin with \text{QM} and \text{DM}. Note that no letters must appear after the \text{*}, i.e., the wild card format is less general than in \text{UNIX} commands.

See the \text{TABLE} command for another possibility to tabulate results.
8.10 Clearing variables

Variables can be deleted using

\texttt{CLEAR, name1, name2, \ldots}

Wild cards can be used as in \texttt{SHOW}, e.g.,

\texttt{CLEAR, ENERG*}

clears all variables whose names begin with \texttt{ENERG}. All variables can be cleared using

\texttt{CLEARALL}

The length of vectors can be truncated simply by redefining the length specifier: \texttt{#R=2} truncates the array \texttt{R} to length 2. Higher elements are no longer available (but could be redefined). Setting \texttt{#R=0} is equivalent to the command \texttt{CLEAR, R}.

8.11 Reading variables from an external file

Variables can be read from an external file using

\texttt{READVAR, filename, [option]}

Such files can be saved, for instance by the geometry optimization program, and reused later to recover a certain optimized geometry. The format of the input in \texttt{filename} is the same as for ordinary input.

If \texttt{option=NOINDEX|IGNOREINDEX} is given then variable indices are ignored and only the last value saved is read (without index). This can be useful if for example a file saved with \texttt{SAVEACT} in a geometry optimization is read, and it is intended to continue with the variables that were saved last.

9 TABLES AND PLOTTING

9.1 Tables

Variables can be printed in Table form using the command

\texttt{TABLE, var1, var2, \ldots}

The values of each variable are printed in one column, so all variables used must be defined for the same range, and corresponding elements should belong together. For example, if in a calculation one has stored \texttt{R(i)}, \texttt{THETA(i)}, \texttt{ECI(i)} for each geometry \texttt{i}, one can print these data simply using

\texttt{TABLE, R, THETA, ECI}

By default, the number of rows equals the number of elements of the first variable. This can be changed, however, using the \texttt{RANGE} subcommand.

The first ten columns of a table may contain string variables. For instance,

\begin{verbatim}
hf;etot(1)=energy;method(1)=program;cpu(1)=cpustep
csd;etot(2)=energy;method(2)=program;cpu(2)=cpustep
qci;etot(3)=energy;method(3)=program;cpu(3)=cpustep
table,method,etot,cpu
\end{verbatim}
prints a table with the SCF, CCSD, and QCI results in the first, second, and third row, respectively. For other use of string variables and tables see, e.g. the examples h2o_tab.com and oh_macros.com

The appearance of the table may be modified using the following commands, which may be given (in any order) directly after the the TABLE card:

- **HEADING**, head1, head2,... Specify a heading for each column. By default, the names of the variables are used as headings.

- **FORMAT**, format Specify a format for each row in fortran style. format must be enclosed by quotes. Normally, the program determines automatically an appropriate format, which depends on the type and size of the printed data.

- **FTYP**, typ1, typ2, typ3,... Simplified form to modify the format. This gives the type (A, F, or D) for each column (sensible defaults are normally used).

- **DIGITS**, dig1, dig2, dig3,... Give the number of digits after the decimal points to be printed for each column (sensible defaults are normally used).

- **TYPE** Specify a data format for the table. The default is TEXT which gives a plain text file. Other possibilities are CSV (comma-separated fields suitable for a spreadsheet), LATEX (a LATEX table environment), MATHEMATICA (Mathematica code that assigns the table to an array), MATLAB (Matlab code that assigns the table to an array), MAPLE (Maple code that assigns the table to an array), HTML (an HTML TABLE construction), and XML (an XML document containing a tree representing the table. The actual format is XHTML).

- **SAVE**, file,status Specify a file on which the table will be written. If status is NEW, the file is rewound, otherwise it is appended. If file has a suffix that is one of txt, csv, tex, m, mpl, html, xml, and a TYPE command is not specified, then the type will be set to that which is conventionally appropriate for the suffix. If file is omitted, then a file name is automatically generated, with the form input.tablename: input is the basename of the input file (or molpro if running from standard input); n is a sequence number that is incremented by one each time a table is produced; ext is a suffix appropriate to the file format, e.g. txt, html, etc.

- **TITLE**, title Specify one line of a title (several TITLE cards may follow each other). Note that titles are only displayed in the SAVE file, if the SAVE command is given before the TITLE card.

- **SORT**, col1, col2,... Sort rows according to increasing values of the given columns. The columns are sorted in the order they are specified.

- **PRINT**, key1, key2,... Specify print options (TABLE, HEADING, TITLE, WARNING, FORMAT, SORT). The default is print for the first three, and noprint for the last three.

- **NOPRINT**, key1, key2,... Disable print for given keys.

- **NOPUNCH** Don’t write data to the punch file (data are written by default).

- **RANGE**, start,end Specify start and end indices of the variables to be printed.
Print also linear regression, upper and lower bounding lines, and quadratic fits of the data columns. The slopes and intercepts of these lines are saved in the Molpro variables REGRESSION_SLOPE, REGRESSION_INTERCEPT, LOWERBOUNDMIN_SLOPE, LOWERBOUNDMIN_INTERCEPT, UPPERBOUNDMIN_SLOPE, UPPERBOUNDMIN_INTERCEPT, LOWERBOUNDMAX_SLOPE, LOWERBOUNDMAX_INTERCEPT, UPPERBOUNDMAX_SLOPE, UPPERBOUNDMAX_INTERCEPT.

9.2 Plotting

[PLOT[,col1,col2,...]][,options]

Construct input for a plotting program using the table as data. PLOT is a subcommand of TABLE and must follow TABLE or any of its valid subcommands given in the previous section. More than one PLOT command can be included within a single TABLE, and each invocation generates a new plot. However, PLOT must appear after all other TABLE subcommands.

coll, col2,... are the names of the table columns to be plotted. These must be an exact subset of those given on the TABLE command. The first column is taken as abscissa, and the values of the remainder will be plotted against it. If no columns are specified, then the entire table is plotted; if a single column is specified, it will be used as abscissa, and all other columns in the table will be plotted as ordinate. options can be chosen from the following.

CMD=unix_plot_command unix_plot_command consists of the system command needed to start the plotting program, followed by any required options. The whole thing should normally be enclosed in quotation marks to preserve lower-case letters. The default is ‘xmgrace’. At present, the Grace program (also known as xmgrace, grace, gracebat), with only numerical data, is supported. The output is also compatible with the portable drop-in replacement for Grace, AptPlot, and if Grace is not found on the system, Molpro will attempt to use AptPlot as default instead.

FILE=plotfile By default the input file for the plotting program is saved in input.tablen.plotm.agr, where m is an automatically generated sequence number. The name of the plotfile can be modified using the FILE option.

INTERACTIVE By default, the plot is not shown on the screen but all plot data are saved in the given file. The plotting program can be started interactively by giving the INTERACTIVE option.

TYPE=type If TYPE is specified, type should be set to one of pdf, svg, png, jpeg or eps. The result is that the gracebat program is executed on the plot input file to generate the graph output file in the desired format. This feature depends on the availability of gracebat, and on it supporting the requested output format (for example, at present pdf is supported under Mac OS X, but not in some Linux systems).

BACKGROUND=rgb rgb should be a string of six hexadecimal digits specifying the red-green-blue colour to use for the background of the plot.

BACKGROUND=TRANSPARENT The background of the plot is made transparent (currently implemented only for TYPE=svg).
NOSPLINE

Prevents spline interpolation of data points.

CURVE=

type

Specifies type of curve to be drawn with points. Possibilities are SPLINE (default; spline interpolation); NONE (equivalent to NOSPLINE); REGRESSION (linear regression line); UPPERBOUNDMAX (maximum gradient line that bounds points from above); UPPERBOUNDMIN (minimum gradient line that bounds points from above); LOWERBOUNDMAX (maximum gradient line that bounds points from below); LOWERBOUNDMIN (minimum gradient line that bounds points from below).

NSPLINE=

Number of interpolation points (default 20).

LEGEND=’x, y’

Position legend at (x,y) on plot.

LEGEND=OFF

Do not draw legend; this behaviour is chosen automatically when there is only a single ordinate dataset.

PCOMMAND=’command’

Insert arbitrary Grace command into the plot file; for details, consult http://plasma-gate.weizmann.ac.il/Grace/doc/UsersGuide.html#s5.

The following additional directives can be given before the PLOT directive:

COLOUR,icolour1, icolour2,...

Colour map to be used for columns 1,2,...; zero means to use default values (colours black, blue, red, green cycle).

COLOUR,rgb1, rgb2,...

Absolute colours (6-hex-digit rgb values) to be used for columns 1,2,...;

SYMBOL,isymb1, isymb2,...

Symbol types to be used for columns 1,2,...; -1 means no symbols; zero means to use default values.

LINEWIDTH,width1, width2,...

Line widths to be used for columns 1,2,...; omit to use default values.

LINESTYLE,style1, style2,...

Line styles to be used for columns 1,2,...; omit to use default values.

9.3 Diatomic potential curve analysis

For the case that a table contains one or more potential energy functions for a diatomic molecule, with the first column containing bond lengths in Bohr or Ångstrom, it is possible to calculate spectroscopic constants using

DIATOMIC[, DEGREE=n][, MASS=m][, PRINT=p]

The data are fitted to a polynomial of degree n (default is number of points minus 1, ie interpolation), and spectroscopic constants calculated using reduced mass m expressed in u. Note that it is possible to constrain which bond lengths are used through the use of the RANGE subcommand.

10 MOLECULAR GEOMETRY

10.1 Geometry specifications

The geometry may be given in standard Z-matrix form, or XYZ form. The geometry specifications are given in the form
10 MOLECULAR GEOMETRY

[SYMmetry, options ]

[ORient, options ]

[ANGstrom]

GEOMETRY={
  atom specifications
}

GEOMETRY must come after the other commands that modify the way the geometry is constructed. The following are permitted as SYMMETRY options:

Any valid combination of symmetry generators, as described in section 10.2 below.

NOSYM Disable use of symmetry. Instead of SYMMETRY,NOSYM also just NOSYM can be used.

The following are permitted as ORIENT options:

CHARGE Orient molecule such that origin is centre of charge, and axes are eigenvectors of quadrupole moment.

MASS Orient molecule such that origin is centre of mass, and axes are eigenvectors of inertia tensor (default for Z-matrix input). Alternatively, the symmetry centre can be specified as CENTRE=MASS|CHARGE.

NOORIENT Disable re-orientation of molecule (default for XYZ-input).

SIGNX=±1 Force first non-zero x-coordinate to be positive or negative, respectively. Similarly, SIGNY, SIGNZ can be set for the y- and z-coordinates, respectively. This can be useful to fix the orientation of the molecule across different calculations and geometries. Alternatively, the system variables ZSIGNX, ZSIGNY, ZSIGNZ can be set to positive or negative values to achieve the same effect.

PLANEXZ For the C<sub>2v</sub> and D<sub>2h</sub> point groups, force the primary plane to be xz instead of the default yz. The geometry builder attempts by swapping coordinate axes to place as many atoms as possible in the primary plane, so for the particular case of a planar molecule, this means that all the atoms will lie in the primary plane. The default implements recommendation 5a and the first part of recommendation 5b specified in J. Chem. Phys. 55, 1997 (1955). PLANEXY and PLANEXY may also be specified, but note that the latter presently generates an error for C<sub>2v</sub>.

ANGstrom Forces bond lengths that are specified by numbers, or variables without associated units, to use the values as a number of Ångstrom, rather than Bohr.

10.1.1 Z-matrix input

The general form of an atom specification line is

[group [ , ] atom, p<sub>1</sub>, r, p<sub>2</sub>, α, p<sub>3</sub>, β, J]
or, alternatively,

\[ \text{group} \] \text{atom, } p_1, x, y, z

where

- **group**: atomic group number (optional). Can be used if different basis sets are used for different atoms of the same kind. The basis set is then referred to by this group number and not by the atomic symbol.

- **atom**: chemical symbol of the new atom placed at position \( p_0 \). This may optionally be appended (without blank) by an integer, which can act as sequence number, e.g., C1, H2, etc. Dummy centres with no charge and basis functions are denoted either Q or X, optionally appended by a number, e.g., Q1; note that the first atom in the Z-matrix must not be called X, since this may be confused with a symmetry specification (use Q instead).

- **\( p_1 \)**: atom to which the present atom is connected. This may be either a number \( n \), where \( n \) refers to the \( n \)'th line of the Z-matrix, or an alphanumeric string as specified in the atom field of a previous card, e.g., C1, H2 etc. The latter form works only if the atoms are numbered in a unique way.

- **\( r \)**: Distance of new atom from \( p_1 \). This value is given in bohr, unless ANG has been specified directly before or after the symmetry specification.

- **\( p_2 \)**: A second atom needed to define the angle \( \alpha(p_0, p_1, p_2) \). The same rules hold for the specification as for \( p_1 \).

- **\( \alpha \)**: Internuclear angle \( \alpha(p_0, p_1, p_2) \). This angle is given in degrees and must be in the range \( 0 < \alpha < 180^\circ \).

- **\( p_3 \)**: A third atom needed to define the dihedral angle \( \beta(p_0, p_1, p_2, p_3) \). Only applies if \( J = 0 \), see below.

- **\( \beta \)**: Dihedral angle \( \beta(p_0, p_1, p_2, p_3) \) in degree. This angle is defined as the angle between the planes defined by \( (p_0, p_1, p_2) \) and \( (p_1, p_2, p_3) \) \((-180^\circ \leq \beta \leq 180^\circ\)). Only applies if \( J = 0 \), see below.

- **\( J \)**: If this is specified and nonzero, the new position is specified by two bond angles rather than a bond angle and a dihedral angle. If \( J = \pm 1 \), \( \beta \) is the angle \( \beta(p_0, p_1, p_3) \). If \( J = 1 \), the triple vector product \( (p_1 - p_0) \cdot [(p_1 - p_2) \times (p_1 - p_3)] \) is positive, while this quantity is negative if \( J = -1 \).

- **\( x, y, z \)**: Cartesian coordinates of the new atom. This form is assumed if \( p_1 \leq 0 \); if \( p_1 < 0 \), the coordinates are frozen in geometry optimizations.

All atoms, including those related by symmetry transformations, should be specified in the Z-matrix. Note that for the first atom, no coordinates need be given, for the second atom only \( p_1, r \) are needed, whilst for the third atom \( p_3, \beta, J \) may be omitted. The 6 missing coordinates are obtained automatically by the program, which translates and re-orient the molecule such that the origin is at the centre of mass, and the axes correspond to the eigenvectors of the inertia tensor (see also CHARGE option above).
Variable names, and in general expressions that are linear in all dependent variables, may be used as well as fixed numerical values for the parameters \( r, \alpha \) and \( \beta \). These expressions are evaluated as late as possible, so that it is possible, for example, to set up loops in which these parameters are changed; the geometry optimizer also understands this construction, and will optimize the energy with respect to the value of the variables. Non-linear expressions should not be used, because the geometry optimization module is unable to differentiate them.

Once the reorientation has been done, the program then looks for symmetry \( D_{2h} \) and subgroups), unless the NOSYM option has been given. It is possible to request that reduced symmetry be used by using appropriate combinations of the options \( X, Y, Z, XY, XZ, YZ, XYZ \). These specify symmetry operations, the symbol defining which coordinate axes change sign under the operation. The point group is constructed by taking all combinations of specified elements. If symmetry is explicitly specified in this way, the program checks to see that the group requested can be used, swapping the coordinate axes if necessary. This provides a mechanism for ensuring that the same point group is used, for example, at all points in the complete generation of a potential energy surface, allowing the safe re-utilization of neighbouring geometry molecular orbitals as starting guesses, etc..

Note that symmetry is not implemented in density fitting methods, and in these cases the NOSYM option is implied automatically.

Also note that by default the automatic orientation of the molecule only takes place if the geometry is defined by internal (Z-matrix) coordinates. In case of XYZ Input the orientation is unchanged, unless the MASS option is specified in the geometry block.

### 10.1.2 XYZ input

Simple cartesian coordinates in Ångstrom units can be read as an alternative to a Z matrix. This facility is triggered by setting the MOLPRO variable GEOMTYP to the value XYZ before the geometry specification is given, but usually this does not need to be done, as a geometry specification where the first line is a single integer will be recognized as XYZ format, as will the case of the first line consisting of a chemical symbol followed by three cartesian coordinates. The geometry block should then contain the cartesian coordinates in Minnesota Computer Centre, Inc. XYZ format. Variable names, and in general expressions that are linear in all dependent variables, may be used as well as fixed numerical values. Non-linear expressions should not be used, because the geometry optimization module is unable to differentiate them.

The XYZ file format consists of two header lines, the first of which contains the number of atoms, and the second of which is a title. The remaining lines each specify the coordinates of one atom, with the chemical symbol in the first field, and the \( x, y, z \) coordinates following. A sequence number may be appended to the chemical symbol; it is then interpreted as the atomic group number, which can be used when different basis sets are wanted for different atoms of the same kind. The basis set is then specified for this group number rather than the atomic symbol. As a further extension, the first two header lines can be omitted.

Note that for XYZ input the default is not to reorient the molecule. Orientation can be forced, however, by the MASS or CHARGE options on the ORIENT directive.
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```
    geomtyp=xyz
    geometry={
      3               ! number of atoms
      This is an example of geometry input for water with an XYZ file
      O , 0.0000000000, 0.0000000000, -0.1302052882
      H, 1.4891244004, 0.0000000000, 1.0332262019
      H, -1.4891244004, 0.0000000000, 1.0332262019
    }
```

http://www.molpro.net/info/current/examples/h2o_xyzinput.com

The XYZ format had been specified within the documentation distributed with the Minnesota Supercomputer Center’s XMol package. Note that MOLPRO has the facility to write XYZ files with the PUT command (see section 10.3).

10.2 Symmetry specification

If standard Z-matrix input is used, MOLPRO determines the symmetry automatically by default. However, sometimes it is necessary to use a lower symmetry or a different orientation than obtained by the default, and this can be achieved by explicit specification of the symmetry elements to be used, as described below.

Generating symmetry elements, which uniquely specify the point group, can be specified on the SYMMETRY directive. This must be given before the geometry block. Each symmetry directive only affects the subsequent geometry block; after a geometry block has been processed, the defaults are restored. Note that the specification of symmetry elements inside the geometry block is no longer allowed.

The dimension of the point group is \(2^n\) (number of fields given). Each field consists of one or more of X, Y, or Z (with no intervening spaces) which specify which coordinate axes change sign under the corresponding generating symmetry operation. It is usually wise to choose z to be the unique axis where appropriate (essential for \(C_2\) and \(C_{2h}\)). In that case, the possibilities are:

- (null card) \(C_1\) (i.e., no point group symmetry)
- Z \(C_s\)
- XY \(C_2\)
- XYZ \(C_i\)
- X, Y \(C_{2v}\)
- XY, Z \(C_{2h}\)
- XZ, YZ \(D_2\)
- X, Y, Z \(D_{2h}\)

Note that Abelian point group symmetry only is available, so for molecules with degenerate symmetry, an Abelian subgroup must be used — e.g., \(C_{2v}\) or \(D_{2h}\) for linear molecules.

See section 4.8 for more details of symmetry groups and ordering of the irreducible representations. Also see section 10.1.1 for more information about automatic generation of symmetry planes.

Note that by default the automatic orientation of the molecule only takes place if the geometry is defined by internal (Z-matrix) coordinates. In case of XYZ Input the orientation is unchanged, unless the MASS option is specified in the geometry block.
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10.3 Writing files for postprocessing (PUT)

The PUT command may be used at any point in the input to print, or write to a file, the current geometry. The syntax is

```
PUT,style,file,status,info
```

If `style` is GAUSSIAN, a complete Gaussian input file will be written; in that case, `info` will be used for the first (route) data line, and defaults to '# SP'.

If `style` is XYZ, an XYZ file will be written (see also section 10.1.2). If `style` is XYZGRAD, an XYZ file including energy gradients will be written (columns are: x,y,z,charge,gx,gy,gz; gradient is given in -1*eV/A) If `style` is CRD, the coordinates will be written in CHARMM CRD format.

If `style` is MOLDEN, an interface file for the MOLDEN visualization program is created; further details and examples are given below.

If `style` is IRSPEC, a gnuplot input file will be written, which can be used to plot an IR spectrum. The gnuplot file contains Lorentz functions with the results of the previous vibrational calculation (VSCF \[54.1\], VCI \[55.1\]). Input examples can be found in these chapters.

If `style` is XML, a dump of the current state is written, including variables, geometry, basis set, latest orbitals. The file format is well-formed XML, according to the [https://www.molpro.net/info/2015.1/lib/schema/molpro-output.html](https://www.molpro.net/info/2015.1/lib/schema/molpro-output.html) schema. In this case, additional options can be given:

```
INDEX,n
```
Insert an index='n' attribute into the `<molecule>` node that is produced.

```
NOFREQUENCIES
```
Skip output of normal modes

```
NOORBITALS
```
Skip output of molecular orbitals

```
SKIPVIRT
```
Skip output of virtual molecular orbitals

```
NOBASIS
```
Skip output of basis set specification

```
NOVARIABLES
```
Skip output of Molpro variables

```
KEEPSPH
```
Express orbitals in terms of spherical-harmonic functions rather than converting to cartesian

If `style` is of the form BABEL/format, then, where possible, the external shell command obabel will be used to convert the geometry to any format supported by the OpenBabel package. For the possible values of format, see OpenBabel’s documentation. If obabel is not installed on the system, then nothing happens.

If `style` is omitted, the Z-matrix, current geometry, and, where applicable, gradient are written.

`file` specifies a file name to which the data is written; if blank, the data is written to the output stream. If `status` is omitted or set to NEW, any old contents of the file are destroyed; otherwise the file is appended.

10.3.1 Visualization of results using Molden

Geometry, molecular orbital, and normal mode information, when available, is dumped by PUT, MOLDEN in the format that is usable by MOLDEN.
The interface to the OpenMol program offers an alternative visualization possibility, and is described in section 3.8.

The example below generates all the information required to plot the molecular orbitals of water, and to visualize the normal modes of vibration:

```plaintext
***,H2O
geometry={(angstrom;o,h,o,roh,h,o,roh,h,theta)};
roh=1.0
theta=104.0
rhf;
optg;
{frequencies;
print,low,img;}
put,molden,h2o.molden;
```

http://www.molpro.net/info/current/examples/h2o_put_molden.com

The example below does a difference density by presenting its natural orbitals to MOLDEN. Note that although MOLDEN has internal features for difference density plots, the approach shown here is more general in that it bypasses the restriction to STO-3G, 3-21G, 4-31G and 6-31G basis sets.

```plaintext
gprint,orbitals
symmetry,y,planexz
geometry={O;H1,O,r;h2,O,r,h1,alpha}
r=1.8
alpha=104
int;
{hf;wf,10,1;orbital,2100.2}
{multi;wf,10,1;orbital,2140.2}
{matrop
load,dscf,density,2100.2 !load scf density
load,mdmcsdf,density,2140.2 !load mcscf density
add,ddiff,mdmcsdf,-1,dscf !compute dmcsdf-dscf
natorb,neworb1,dscf
natorb,neworb2,mdmcsdf
natorb,neworbs,ddiff
save,neworbs,2110.2
save,ddiff,2110.2}
put,molden,h2o_ddens.molden;orb,2110.2
```

http://www.molpro.net/info/current/examples/h2o_diffden_molden.com

### 10.4 Geometry Files

Using the format

```
GEOMETRY=file
```

the geometry definitions are read from `file`, instead of inline.

### 10.5 Lattice of point charges

```
LATTICE,[INFILE=input_file,][OUTFILE=output_file,][VARGRAD,][NUONLY,][REMOVE]
```
Includes a lattice of point charges, for use in QM/MM calculations for example (see section 59).

An external file (input file) should be given as input, with the following format:

Comment line
number of point charges N
x1,y1,z1,q1,flag1
;
xN,yN,zN,qN,flagN

The x, y and z fields stand for the point charge coordinates (in Å), q for its charge and flag=1 indicates that gradients should be computed for this lattice point (0 means no gradient).

outfile specifies a file name to which the lattice gradient is written; if blank, it will be written to the output stream.

VARGRAD (logical) Stores the lattice gradient in variable VARGRAD.
NUCONLY (logical) Disables gradient evaluation with respect to the lattice, independent of flag in the lattice file.
REMOVE (logical) Removes the lattice.

Symmetry is not supported for lattice gradients.

### 10.6 Redefining and printing atomic masses

The current masses of all atoms can be printed using

```mass,print```

The atomic masses can be redefined using

```mass,[type.][symbol=mass, ...]```

The optional keyword type can take either the value AVERAGE for using average isotope masses, or ISO[TOPE] for using the masses of the most abundant isotopes. This affects only the rotational constants and vibrational frequencies. As in most quantum chemistry packages, the default for type is AVERAGE. If INIT is given, all previous mass definitions are deleted and the defaults are reset.

Individual masses can be changed by the following entries, where symbol is the chemical symbol of the atom and mass is the associated mass. Several entries can be given on one MASS card, and/or several MASS cards can follow each other. The last given mass is used.

Note that specifying different isotope masses for symmetry related atoms lowers the symmetry of the system if the molecular centre of mass is taken as the origin. This effect can be avoided by using the charge centre as origin, i.e., specifying CHARGE as the option to an ORIENT directive before the GEOMETRY input:

```orient,charge; geometry={ ... }```

### 10.7 Dummy centres

```dummy,atom1,atom2,...```
Sets nuclear charges on atoms 1, 2 etc. to zero, for doing counterpoise calculations, for example. *atom1, atom2,…* can be Z-matrix row numbers or tag names. Note that the current setting of dummies is remembered by the program across restarts via the MOLPRO variable **DUMMYATOMS**. Dummies can be reset to their original charges using a **DUMMY** card with no entries. Dummy centres are also reset to their original charges if (i) an **INT** command is encountered, or (ii) a new geometry input is encountered.

The program does not recognize automatically if the symmetry is reduced by defining dummy atoms. Therefore, for a given dummy atom, either all symmetry equivalent atoms must also be dummies, or the symmetry must be reduced manually as required. An error will result if the symmetry is not consistent with the dummy centre definitions.

### 10.7.1 Counterpoise calculations

Counterpoise corrections are easily performed using dummy cards. One first computes the energy of the total system, and then for the subsystems using dummy cards. The process can, however, be automated using the command

**COUNTERPOISE**, \[key1=value, key2=value, \ldots\]

Without any options, this will calculate the ghost-orbital corrections to dimer interaction energies using the last energy calculation to define the dimer and the methods to be used. First of all, the molecule is automatically partitioned into two optimally separated fragments. This is done by finding the partitioning that has the largest minimum distance between any pair of atoms in different fragments. Optionally, one may give the option **SEPARATION**=distance; if the optimum fragment separation is smaller than distance, then it will be assumed that the system is not a non-bonded complex, and the counterpoise calculation will not be done at all. This gives support for running the same Molpro input for both dimers and monomers.

The counterpoise procedure performs four calculations. For each of the identified monomers, it calculates the energy at the dimer geometry using first the dimer basis set, and secondly just the basis functions tied to the monomer atoms. The difference between these, the counterpoise correction, is reported, and added to the previously-calculated dimer energy.

Further options that specify the calculation to be run can be specified exactly as for geometry optimisations; see section 46.1.1 for further details.
10.7.2 Example: interaction energy of OH-Ar

\*\*\*,OH(2Sig+)-Ar linear
memory,2,m
geometry={q1; !dummy center in center of mass
o,q1,ro;h,q1,ro,180; !geometry of OH
ar,q1,rar,o,theta,h,0} !geometry of Ar
roh=1.8 !OH bond-length
rar=7.5 !distance of Ar from center of mass
theta=0 !angle OH-Ar
ro=roh*16/17 !distance of O from center of mass
rh=roh*1/17 !distance of H from center of mass
basis=avdz !basis set
text,calculation for complex
{rhf;occ,8,3,3;wf,27,1,1} !RHF for total system
rccsd(t) !CCSD(T) for total system
e_ohar=energy !save energy in variable e_ohar
text,cp calculation for OH
dummy,ar
{rhf;occ,3,1,1;wf,9,1,1} !RHF for OH
rccsd(t) !CCSD(T) for OH
e_oh=energy !save energy in variable e_oh
text,cp calculation for Ar
dummy,o,h
hf !scf for Ar
ccsd(t) !CCSD(T) for Ar
e_ar=energy !save energy in variable e_ar
text,separate calculation for OH
geometry={(O;H,O,roh)} !geometry for OH alone
{rhf;occ,3,1,1;wf,9,1,1} !RHF for OH
rccsd(t) !CCSD(T) for OH
e_oh_inf=energy !save energy in variable e_oh_inf
text,separate calculation for Ar
geometry={(AR)} !geometry for OH alone
hf !scf for Ar
ccsd(t) !CCSD(T) for Ar
e_ar_inf=energy !save energy in variable e_ar_inf
de=(e_ohar-e_oh_inf-e_ar_inf)*tocm !compute uncorrected interaction energy
de_cp=(e_ohar-e_oh-e_ar)*tocm !compute counter-poise corrected interaction energy
bsse_oh=(e_oh-e_oh_inf)*tocm !BSSE for OH
bsse_ar=(e_ar-e_ar_inf)*tocm !BSSE for Ar
bsse_tot=bsse_oh+bsse_ar !total BSSE

http://www.molpro.net/info/current/examples/ohar_bsse.com

For performing counterpoise corrected geometry optimizations see section 46.4.7.

11 BASIS INPUT

11.1 Overview: sets and the basis library

Basis functions are used in Molpro not just for representing orbitals, but also for providing auxiliary sets for density fitting (see [13]) and for simplifying integrals through approximate identity
resolution in explicitly-correlated methods (see [35]). In order to accommodate this, the program maintains internally a number of different sets. The first of these always has the name ORBITAL and is the primary basis set for representing orbitals, and others can be defined as necessary as described below, or else are constructed automatically by the program when required. In the latter case, the density-fitting and other modules attempt to guess a reasonable library fitting basis that should be appropriate for the orbital basis set; it is advisable to check the choice when using anything other than a standard orbital basis set.

The basis sets may either be taken from the library, or may be specified explicitly, or any combination. Optionally, the basis function type can be chosen using the CARTESIAN or SPHERICAL commands.

### 11.2 Cartesian and spherical harmonic basis functions

MOLPRO uses spherical harmonics ($5d$, $7f$, etc) by default, even for Pople basis sets like 6-31G**. This behaviour may be different to that of other programs; However, cartesian functions can be requested using the CARTESIAN command.

**CARTESIAN**

If this command is encountered, the logical MOLPRO variable CARTESIAN is set to true (1.0), and all subsequent calculations use cartesian basis functions. This is remembered across restarts. One can switch back to spherical harmonics using the command

**SPHERICAL**

### 11.3 The basis set library

The basis set library consists of a set of plain text files, together with an associated index, that constitute a database of commonly-used basis sets (primitive gaussians and associated contractions) and effective core potentials. These files can be found in the source tree as `lib/*.libmol` and `lib/libmol.index`, but it is usually more convenient to query the database using one of the provided tools.

Many of the basis sets are taken directly from the Pacific Northwest National Laboratory basis set database, but there are others, notably the Stuttgart effective core potentials and bases.

A simple command-line interface to the database is provided through the `libmol` program. It requires the environment variable LIBMOL to point to the `lib/` directory, but this will default to the location of the source tree at compile time, so it is often not necessary to specify it. The command-line syntax is

```
libmol [-p print] [-e element] [-k key] [-t type] [-f format]
```

where the parameters are

- **print**: Output level; 0 means list matching keys, 1 means print also the entry.
- **element**: Specify chemical element. If omitted, all elements are searched.
- **key**: Specify record key. If omitted, all keys are searched.
- **type**: Specify entry type, i.e. $s, p, ...$. If omitted, all types are searched.
- **format**: One of text (default), molpro (MOLPRO input format), table (tabular) or html (html table) to govern the output format.
A more convenient way of browsing the basis library is through the web interface at http://www.molpro.net/info/basis.php.

11.4 Default basis sets

If a basis is not specified at all for any unique atom group, then the program assumes a global default. Presently, this default is VDZ, but may be overridden using

BASIS, basis

or

BASIS=basis

basis is looked up in the file lib/defbas, which generates an appropriate request for a complete contracted set, together in some cases with an ECP, from the library. This mapping includes the following commonly-used basis sets:

- All of the Dunning correlation consistent basis sets, through the use of either the standard name of the basis set (cc-pVXZ, aug-cc-pVXZ) or an abbreviation (VXZ, AVXZ). For Al-Ar the tight-d augmented sets are obtained through the standard name cc-pV(X+d)Z, aug-cc-pV(X+d)Z or VXZ+d, AVXZ+d. Sets X=D,T,Q,5 are available for H-Kr with X=6 available for B-Ne and Al-Ar.
- The correlation consistent basis sets for core correlation, cc-pCVXZ, aug-cc-pCVXZ or CVXZ, ACVXZ (X=D,T,Q,5), and the newer "weighted sets" cc-pwCVXZ, aug-cc-pwCVXZ or WCVXZ, AWCVXZ (X=D,T,Q,5). These are available for Li-Kr (CVXZ do not include Sc-Zn).
- Douglas-Kroll-Hess relativistic versions of the correlation consistent basis sets are available through use of the standard or abbreviated names with extension -DK, e.g., cc-pVXZ-DK or VXZ-DK. X=D-5 are available for H-Kr, while X=T are available for Y-Cd and Hf-Hg. Sets contracted for 3rd-order DKH are available for Hf-Hg with extension -DK3.
- The F12 basis sets of Peterson et al. for explicitly correlated calculations, cc-pVXZ-F12, cc-pCVXZ-F12 or VXZ-F12, CVXZ-F12 with X=D,T,Q. These are available for H-Ar.
- The Turbomole def2 family of basis sets, SV(P), SVP, TZVP, TZVPP, QZVP, and QZVPP. These are available for the entire periodic table except for the f-block elements.
- The older segmented Dunning/Hay double-zeta sets for the first row (DZ and D2P).
- The Roos ANO basis sets for H-Ar (ROOS).
- The Stuttgart ECPs and associated basis sets (e.g., ECP10MDF), as well as the ECP-based correlation consistent basis sets of Peterson and co-workers, cc-pVXZ-PP, aug-cc-pVXZ-PP, cc-pwCVXZ-PP, aug-cc-pwCVXZ-PP or VXZ-PP, AVXZ-PP, WCVXZ-PP, AWCVXZ-PP. The latter are available for Cu-Kr, Y-Xe, and Hf-Rn (core correlation sets currently only for transition metals).
- The Hay ECPs and corresponding basis sets (ECP1 and ECP2).
- Other members of the Karslruhe basis sets (SV, TZV, and, for some elements, TZVPP).
- The Binning/Curtiss sets for Ga–Kr (BINNING-SV, BINNING-SVP, BINNING-VTZ and BINNING-VTZP).
Most of the Pople basis sets, using their standard names (e.g., 6–31G*, 6–311++G(D,P), etc.). Note that specially in this case, the mechanism described below using parenthesized modifiers to restrict the basis set is disabled to allow the full range of standard basis sets to be specified.

In addition, many density fitting and resolution of the identity (RI) basis sets are available. For the correlation consistent basis sets of Dunning, the appropriate VXZ/JKFIT, VXZ/MP2FIT, AVXZ/MP2FIT sets of Weigend are chosen automatically in density fitted calculations (augmented versions AVXZ/JKFIT for Fock-matrix fitting are also available, but not used by default). For the def2 family of orbital basis sets, the appropriate auxiliary sets (e.g., TZVPP/JFIT, TZVPP/MP2FIT, TZVPP/MP2FIT) are used. In principle these JKFIT sets are universal and also applicable in combination with the AVXZ basis sets. Initial results indicate that they also work well with the cc-pVXZ-PP and aug-cc-pVXZ-PP series of basis sets.

For explicitly correlated F12 calculations that use the cc-pVXZ-F12 orbital basis sets, the corresponding VXZ-F12/OPTRI basis sets are used by default to construct the complementary auxiliary orbital basis (CABS). For other orbital basis sets, appropriate JKFIT sets are utilized by default.

Example:

```
BASIS=VTZ
```

generates valence triple zeta basis set for all atoms. Thus, the input

```
****,h2o cc-pVTZ basis  !A title
r=1.85,theta=104        !set geometry parameters
geometry={O;           !z-matrix geometry input
               H1,O,r;
               H2,O,r,H1,theta}
basis=VTZ               !use VTZ basis
hf                     !closed-shell scf
```

http://www.molpro.net/info/current/examples/h2o_scf_vtz.com

performs a Hartree-Fock calculation for H2O using the cc-pVTZ basis set.

Default basis sets can be defined anywhere in the input before the energy calculation to which it should apply using a single BASIS card as shown above. The default basis set applies to all types of atoms but can be superceded by different basis sets for specific atoms as explained in the next section. Some restrictions concerning the maximum angular momentum functions to be used, or the number of contracted functions are possible as follows:

The maximum angular momentum in the basis set can be reduced using syntax such as

```
BASIS,VQZ(D)
```

which would omit the f and g functions that would normally be present in the VQZ basis set.

```
BASIS,VQZ(D/P)
```

would specify additionally a maximum angular momentum of 1 on hydrogen, i.e. would omit d orbitals on hydrogen.

For generally contracted basis sets, an extended syntax can be used to explicitly give the number of contracted functions of each angular momentum. For example,

```
BASIS,ROOS(3s2p1d/2s)
```

generates a 6–31G*–sized basis set from the Roos ANO compilation.
Notes: *basis* must not be variable called BASIS. Furthermore, input like

\$BASIS=[AVDZ, AVTZ, AVQZ]

is not allowed, i.e. the keyword BASIS must not be preceded with $. One can loop over several basis sets using, for example, using

\$aobases=[AVDZ, AVTZ, AVQZ]
do ibas=1,#aobases
  basis=aobases(ibas)
  ...
enddo

### 11.5 Default basis sets for individual atoms

Different default basis sets for individual atoms can be specified with one-line BASIS commands by adding after the default basis \(atom1=name1, atom2=name2,\ldots\), where \(atomi\) are the chemical symbols, and \(namei\) are the associated basis set names. The name conventions for the atom specific basis sets work exactly as described above for default basis sets. Examples:

\texttt{basis=vtz,h=vdz}

uses cc-pVTZ as a general default, but for hydrogen atoms cc-pVDZ is used.

\texttt{basis,vtz,h=vdz}

or

\texttt{basis,default=vtz,h=vdz}

are equivalent to the above. Note that the default basis has to be specified before any atom specific sets.

### 11.6 Basis blocks

More specific basis set definitions for individual atoms can be given in BASIS input blocks, which have the following general form:

\begin{verbatim}
BASIS
  SET,setname1,[options]
  DEFAULT=name
  atom1=name1
  atom2=name2
  primitive basis set specifications
  SET,setname2,[options]
  ...
END
\end{verbatim}

Instead of the BASIS ...END block one can also use the structure \texttt{BASIS={...}}

Any number of basis sets can be be given in a basis block. The definition of each basis set is started by a \texttt{SET} directive, on which the name of the basis and further options can be specified.

By default, the first set in a basis block is the orbital basis, and in this case the directive \texttt{SET,ORBITAL} can be omitted.
DEFAULT specifies the default basis set, exactly as on one line basis input. It can be followed by specifications for individual atoms, e.g. O=AVTZ. The default and atom specifications can also be merged to one line, separated by commas, e.g.

\texttt{DEFAULT=VTZ, O=AVTZ, H=VDZ}

Here the basis sets AVTZ, VDZ overwrite the default basis set VTZ for the atoms O and H, respectively. This is exactly as described in section 11.5 for one-line basis inputs.

The specifications SET, DEFAULT, atom=name are all optional. If DEFAULT is not given, the previous default, as specified on the last previous BASIS card, is used.

Several BASIS cards and/or blocks can immediately follow each other. Always the last specification for a given atom and setname is used (the default setname is ORBITAL).

If a basis is not specified at all for any unique atom group, then the program assumes VDZ.

### 11.7 Auxiliary basis sets for density fitting or resolution of the identity

As described in the previous section, several basis sets can be defined in a basis block. The definition of each basis starts with a line

\texttt{SET.name[CONTEXT=context]}

where name is an arbitrary name that can be used later to choose the basis set using options like \texttt{df\_basis=\textit{name}}, \texttt{ri\_basis=\textit{name}} etc. CONTEXT can optionally be specified to select the basis types JFIT, JKFIT, MP2FIT, CCSDFIT, or OPTRI. This affects the choice of default basis sets. For example

```plaintext
basis={
default=avtz !default orbital basis set
set,df,context=mp2fit
default,avtz !use avtz/mp2fit
set,jk,context=jkfit
default,avtz !use avtz/jkfit
}
```

is equivalent to

```plaintext
basis={
default=avtz !default orbital basis set
set,df
default,avtz/mp2fit !use avtz/mp2fit
set,jk
default,avtz/jkfit !use vtz/jkfit
}
```

If the setname begins with JFIT, JKFIT, MP2FIT, CCSDFIT, or OPTRI, these strings define the default context.

Specific basis sets for individual atoms or explicit input of exponents and contraction coefficients can be given exactly in the same way as for orbital basis sets.
11.8 Primitive set definition

Default basis sets given using one-line BASIS commands or DEFAULT directives in a basis block can be overwritten by explicit specifications of basis functions (type, exponents, contraction coefficients).

A group of basis functions is defined by a data card specifying a set of primitive gaussians, optionally followed by one or more cards specifying particular contractions of primitives to be included in the final basis (see section 11.9 for specification of contractions).

If an individual basis function type (s, p, d, etc.) is specified for an atom, it is required that all other types are also defined, i.e., as soon as an explicit definition of a basis function for an atom is given, all defaults are erased for this atom.

There are four different input forms for basis functions, as explained below under a) to d). In case that options (e.g. SCALE, NPRIM) are specified, they can be given in any order, but no value without option key must be given after an option.

In all four cases type defines the angular symmetry (S, P, D, F, G, H, or I). type can include several types, e.g., SPD or DF (this usually makes sense only with default library contractions or no contractions). The basis is loaded for all atoms with tag name atom in the geometry input. If atom is an integer, it refers to a z-matrix row.

a) Library basis sets:

```
type,atom,name[SCALE=scale]SCALE2=scale2][NPRIM=nprim][DELETE=ndel];
```

Load basis named name from the library

If scale or scale2 is present, all exponents are scaled by scale or scale**2, respectively. If nprim is specified, the first nprim exponents only are taken from the library. If nprim is negative or ndel is given, the last |nprim| (ndel) basis functions from the library set are deleted. Associated with the library basis may be a set of default contraction coefficients which may be accessed in subsequent contraction cards. type can include several types, e.g., SPD or DF. This usually makes sense only with default contractions, i.e., such cards should be followed only by “C” without any other specifications for contractions.

b) Explicit basis input:

```
type,atom,exp1,exp2,...expn;expn+1,...;
```

General specification of exponents; continuation onto subsequent cards (separated by semicolon) is permitted as shown (the first card can hold up to 19 exponents, each following card 20 exponents).

The exponents (and other numerical parameters described below such as numbers of functions, and contraction coefficients) can be given as general input expressions, possibly involving variables. It is important to note, however, that these expressions are evaluated typically just once, at the same time as the complete basis set is parsed. This generally happens the first time that the basis set is required, perhaps before the first SCF calculation can be done. If the variables on which the basis depends are altered, this will not be noticed by the program, and the new basis set will not be used for subsequent stages of the computation. If, however, a new basis block is presented in the input, then the program marks as outdated any quantities such as integrals that have been calculated with the old basis set; subsequent job steps will then use the new basis.

c) Even tempered basis sets:
type,atom,EVEN,nprim,ratio,centre,dratio

or

type,atom,EVEN,NPRIM=nprim,[RATIO=ratio],[CENTRE=centre],[DRATIO=dratio]

Generates a generalized even tempered set of functions. The number of functions $n$ is specified by $nprim$, their geometric mean $c$ by $centre$, the mean ratio of successive exponents $r$ by $ratio$, and the variation of this ratio, $d$, by $dratio$. If $centre$ is not given, the previous basis of the same type is extended by diffuse functions. If in this case $ratio$ is not given, $r$ is determined from the exponents of the last two function of the previous basis. If this is not possible, the default $r = 2.5$ is adopted. $d = 1$ (the default) specifies a true even-tempered set, but otherwise the ratio between successive exponents changes linearly; the exponents are given explicitly by

$$\log e_i = \log c + ((n+1)/2-i) \log r + \frac{1}{2} ((n+1)/2-i)^2 \log d \quad i = 1,2, \ldots, n$$

Example 1

\[ SP,1,VTZ;C;SP,1,EVEN,1; \]
genetrates the generally contracted $s$ and $p$ triple-zeta basis sets for atom 1 and extends these by one diffuse function.

Example 2

\[ SPD,1,VTZ,DELETE=1;C;SP,1,EVEN,NPRIM=2,RATIO=2.5; \]
genetrates the generally contracted $s$, $p$ triple-zeta basis sets for atom 1. Two energy optimized $d$-functions of Dunning are included. The last $s$ and $p$ functions are deleted and replaced by two even tempered functions with ratio 2.5.

d) 3-term tempered basis sets:

type,atom,EVEN3,nprim,\alpha, \beta, \gamma

Generates a 3-parameter set of $nprim$ functions with exponents given by

$$e_0 = \alpha; \quad e_i = e_{i-1} \beta \left(1 + \frac{\gamma^2}{(nprim+1)^2}\right), \quad i = 1, \ldots, nprim - 1$$

e) Regular even tempered basis sets:

type,atom,EVENR,nprim,aa,ap,bb,bp

Generates an even tempered set of $nprim$ functions according to the “regular” prescription described in M W Schmidt and K Ruedenberg, J. Chem. Phys. 71 (1970) 3951. If any of the parameters $aa$, $ap$, $bb$, $bp$ is zero or omitted, the values are taken from table III of the above.

f) Even tempered basis set with confined progression:

type,atom,EVENP,nprim,\alpha, \beta, \gamma

Generates an even tempered basis set with $nprim$ functions and a maximal exponent given by $\alpha$. The progression (ratio) between the first and second exponent is adjusted using parameter $\beta$ and the progression between the last but one and the last exponent is adjusted with parameter $\gamma$. In between the progression is linearly interpolated. The explicit values of the progression factors are given by:

$$p(\beta) = \frac{\text{exponent}_{\text{next}}}{\text{exponent}_{\text{prev}}} = \frac{\pi}{2} (\arctan(\beta - 2.5) + \frac{\pi}{2}) + \sqrt{2}$$
so that for $\beta \ll 0 : p \to \sqrt{2}$ and for $\beta \gg 0 : p \to 5 + \sqrt{2}$ which limits the progression factors in between these two values and enables unconstrained basis set optimisations. For $\beta \approx 0$ the progression has a factor of about 2.

Generalises confined progression tempered basis sets by a third parameter (now $\gamma$) which defines the progression as above in the centre. The ratio factors are then determined by interpolating between $p(\beta) \to p(\gamma)$ and $p(\gamma) \to p(\delta)$.

### 11.9 Contracted set definitions

**a)** $C, \text{first.last}, c1, c2, \ldots; cn; cn+1, \ldots$

General specification of a contracted function. $\text{first.last}$ defines the range of primitives to be contracted. The order corresponds to the primitives as specified on the previous input card. $c1, c2 \ldots$ are the last – first + 1 contraction coefficients. Continuation onto a subsequent card is permitted as shown.

**b)** C;

Use default contractions from the library. This applies to both the number of contracted primitives and also to the number of different contraction sets.

**c)** $nC, \text{first.last}$;

$n$ contracted functions taken from the library. $\text{first.last}$ defines the range of primitives to be contracted. If $n$ is omitted and $\text{first.last}$ is specified, $n = 1$. If $\text{first.last}$ is omitted, the library default values are used. If both $n$ and $\text{first.last}$ are omitted, default values for both are used.

**d)** $nC, \text{first.last}, \text{record.file}, \text{orb.sym}$;

$n$ contracted functions taken from orbitals $\text{orb}, \text{orb} + 1, \ldots; \text{orb} + n - 1$ of symmetry $\text{sym}$ on molpro file $\text{record.file}$. The first nonzero coefficient in the specified orbital corresponds to the first associated basis function. $\text{first.last}$ specifies the range of primitives to be contracted. If $\text{first.last}$ is omitted, all coefficients from the specified orbitals are used.

Example

2C, 1.12, 2100.2, 1.1

generates two contractions, using the first 12 coefficients from orbitals 1.1 and 2.1. The orbitals are read from record 2100.2.

### 11.10 Examples

This shows the use of default basis sets for H$_2$O:

```plaintext
***, H2O
basis=VQZ(f/p)
R=0.95 ANG, THETA=104 DEGREE
geometry={(O;H1,O,R;H2,O,R,H1,THETA)
hf !do closed-shell SCF
```

[http://www.molpro.net/info/current/examples/h2o_vqz_fp.com](http://www.molpro.net/info/current/examples/h2o_vqz_fp.com)

This is equivalent to the explicit input form
This is an example for using multiple basis sets for density fitting and resolution of the identity:
12 EFFECTIVE CORE POTENTIALS

Pseudopotentials (effective core potentials, ECPs) may be defined at the beginning of BASIS blocks.

The general form of the input cards is

\[
\text{ECP,atom,[ECP specification]}
\]

which defines a pseudopotential for an atom specified either by a chemical symbol or a group number. The \textit{ECP specification} may consist either of a single keyword, which references a pseudopotential stored in the [library] or else of an explicit definition (extending over several input cards), cf. below.

12.1 Input from ECP library

The [basis set library] presently contains the pseudopotentials and associated valence basis sets by a) the Los Alamos group (P. J. Hay and W. R. Wadt, J. Chem. Phys. 82, 270 (1985) and following two papers), and b) the Stuttgart/Köln group (e.g., A. Nicklass, M. Dolg, H. Stoll and H. Preuß, J. Chem. Phys. 102, 8942 (1995); for more details and proper references, see the web page \url{http://www.tc.uni-koeln.de/PP/index.en.html}). Pseudopotentials a) are adjusted to orbital energies and densities of a suitable atomic reference state, while pseudopotentials b) are generated using total valence energies of a multitude of atomic states.

Library keywords in case a) are \textit{ECP1} and \textit{ECP2}; \textit{ECP2} is used when more than one pseudopotential is available for a given atom and then denotes the ECP with the smaller core definition. (For Cu, e.g., \textit{ECP1} refers to an Ar-like 18\textit{e}−-core, while \textit{ECP2} simulates a Ne-like 10\textit{e}− one with the 3\textit{s} and 3\textit{p} electrons promoted to the valence shell). For accurate calculations including electron correlation, promotion of all core orbitals with main quantum number equal to any of the valence orbitals is recommended.

Library keywords in case b) are of the form \textit{ECPnXY}; \textit{n} is the number of core electrons which are replaced by the pseudopotential, \textit{X} denotes the reference system used for generating the pseudopotential (\(X = S\): states of the single-valence-electron ion; \(X = \text{neutral}\): states of the neutral atom and of ions with low charge), and \(Y\) stands for the theoretical level of the reference data (\(Y = \text{HF}\): Hartree-Fock, \(Y = \text{WB}\): quasi-relativistic; \(Y = \text{DF}\): relativistic). For one- or two-valence electron atoms \(X = S\), \(Y = \text{DF}\) is a good choice, while otherwise \(X = M\), \(Y = \text{WB}\) (or \(Y = \text{DF}\)) is recommended. (For light atoms, or for the discussion of relativistic effects, the

\*

http://www.molpro.net/info/current/examples/h2o_basissets3.com

In the latter example, the speciations \textit{mp2fit} and \textit{jkfit}, respectively, can be omitted since these contexts are defaults for \textit{df\_basis} and \textit{df\_basis\_exch}, respectively.
corresponding $Y = HF$ pseudopotentials may be useful.) Additionally, spin-orbit (SO) potentials and core-polarization potentials (CPP) are available, to be used in connection with case b) ECPs, but these are not currently contained in the library, so explicit input is necessary here (cf. below).

In both cases, a) and b), the same keywords refer to the pseudopotential and the corresponding basis set, with a prefix MBS-... in case a).

### 12.2 Explicit input for ECPs

For each of the pseudopotentials the following information has to be provided:

- a card of the form
  \[
  \text{ECP,atom,n\_core},l_{\text{max}},l'_{\text{max}};
  \]
  where $n_{\text{core}}$ is the number of core electrons replaced by the pseudopotential $V_{ps}$, $l_{\text{max}}$ is the number of semi-local terms in the scalar-relativistic part of $V_{ps}$, while $l'_{\text{max}}$ is the corresponding number of terms in the SO part:
  \[
  V_{ps} = -\frac{Z - n_{\text{core}}}{r} + V_{l_{\text{max}}} + \sum_{l=0}^{l_{\text{max}}-1} (V_l - V_{l_{\text{max}}}) \mathcal{P}_l + \sum_{l=1}^{l'_{\text{max}}} \Delta V_l \mathcal{P}_l \cdot \mathbf{s} \mathcal{P}_l;
  \]
  the semi-local terms (with angular-momentum projectors $\mathcal{P}_l$) are supplemented by a local term for $l = l_{\text{max}}$.

- a number of cards specifying $V_{l_{\text{max}}}$, the first giving the expansion length $n_{l_{\text{max}}}$ in
  \[
  V_{l_{\text{max}}} = \sum_{j=1}^{n_{l_{\text{max}}}} c_j r^{m_j - 2} e^{-\gamma_j r^2}
  \]
  and the following $n_{l_{\text{max}}}$ ones giving the parameters in the form
  \[
  m_1, \gamma_1, c_1; m_2, \gamma_2, c_2; \ldots
  \]

- a number of cards specifying the scalar-relativistic semi-local terms in the order $l = 0, 1, \ldots, l_{\text{max}} - 1$. For each of these terms a card with the expansion length $n_l$ in
  \[
  V_l - V_{l_{\text{max}}} = \sum_{j=1}^{n_l} c'_j r^{m'_j - 2} e^{-\gamma'_j r^2}
  \]
  has to be given, and immediately following $n_l$ cards with the corresponding parameters in the form $m'_1, \gamma'_1, c'_1; m'_2, \gamma'_2, c'_2; \ldots$

- analogously, a number of cards specifying the coefficients of the radial potentials $\Delta V_l$ of the SO part of $V_{ps}$.
12

12.3 Example for explicit ECP input

***,CU
! SCF d10s1 -> d9s2 excitation energy of the Cu atom
! using the relativistic Ne-core pseudopotential
! and basis of the Stuttgart/Koeln group.
gprint,basis,orbitals
geometry={(cu)
basis
ECP,1,10,3;  ! ECP input
1;  ! NO LOCAL POTENTIAL
2;  ! S POTENTIAL
 2,30.22,355.770158;2,13.19,70.865357;
2;  ! P POTENTIAL
 2,33.13,233.891976;2,13.22,53.947299;
2;  ! D POTENTIAL
 2,38.42,-31.272165;2,13.26,-2.741104;
! (8s7p6d)/[6s5p3d] BASIS SET
s,1,33.538352,13.50535,2.815535,2.380405,.903243,.112662,.040486,.01;
c,1,33.538352,13.50535,2.815535,2.380405,.903243,.112662,.040486,.01;
p,1,93.454327,16.285464,5.994236,2.536875,.897934,.131729,.053087;
c,1,33.538352,13.50535,2.815535,2.380405,.903243,.112662,.040486,.01;
d,1,41.225006,12.34325,4.20192,1.379825,.383453,.1;
c,1,1.444694,.212105,.453423,.533465;
end
rhf;
e1=energy
{rhf;occ,4,1,1,1,1,1,1;closed,4,1,1,1,1,1;wf,19,7,1;}
e2=energy
de=(e2-e1)*toev  ! Delta E = -0.075 eV

http://www.molpro.net/info/current/examples/cu_ecp_explicit.com
12.4 Example for ECP input from library

***, AuH
! CCSD(T) binding energy of the AuH molecule at r(exp)
! using the scalar-relativistic 19-valence-electron
! pseudopotential of the Stuttgart/Koeln group

```plaintext
gprint, basis, orbitals;
gpc, geometry={au}
basis={
  ecp, au, ECP60MWB; ! ECP input
  spd, au, ECP60MWB; c, 1.2; ! basis set
  f, au, 1.41, 0.47, 0.15;
  g, au, 1.2, 0.4;
  spd, h, avtz; c;
}
rhf;
{rccsd(t); core, 1, 1, 1, 1;}
e1=energy
geometry={h}
rhf
e2=energy;
rAuH=1.524 ang ! molecular calculation
geometry={au; h, au, rAuH}
hf;
{ccsd(t); core, 2, 1, 1;}
e3=energy
d= (e3-e2-e1) * toev ! binding energy = 3.11 eV
```

http://www.molpro.net/info/current/examples/auh_ecp_lib.com

13 CORE POLARIZATION POTENTIALS

13.1 Input options

The calculation of core-polarization matrix elements is invoked by the CPP card, which can be called at an arbitrary position in the MOLPRO input, provided the usual AO integrals have been calculated before. The CPP card can have the following formats:

- CPP.INIT, ncentres;
- CPP.ADD,[factor];
- CPP.AE,[record.file];
- CPP.SET,[fcpp];

CPP.INIT,<ncentres>;

abs(<ncentres>) further cards will be read in the following format:

<atomtype>, <ntype>, <α_d>, <α_q>, <β_d>, <cutoff>, <q_eff>

<atomtype> specifies an atomic centre with polarizable core,
<ntype> fixes the form of the cutoff-function (choose 1 for Fuentealba/Stoll and 2 for Mueller/Meyer);
<α_d> is the static dipole polarizability,
<α_q> is the static quadrupole polarizability,
<β_d> is the first non-adiabatic correction to the dipole polarizability,
13 CORE POLARIZATION POTENTIALS

\(<\text{cutoff}\rangle\) is the exponential parameter of the cutoff-function, and
\(<q_{\text{eff}}\rangle\) is the effective charge of the core with which it polarizes its surroundings (only needed if it contributes orbitals to the CPP core (see below)).

When \(<\text{ncentres}\rangle\) is lower than zero, only CPP integrals are calculated and saved in record 1490.1. Otherwise, the \(h_0\) matrix (records 1200.1 and 1210.1) and the two-electron-integrals (record 1300.1) will be modified.

CPP,ADD,\(<\text{factor}\rangle\);

With this variant, previously calculated matrix elements of the polarization matrix can be added with the variable factor \(<\text{factor}\rangle\) (default: \(<\text{factor}\rangle = 1\)) to the \(h_0\)-matrix as well as to the two-electron integrals. In particular, CPP,ADD,-1.; can be used to retrieve the integrals without the polarization contribution.

CPP,AE,\(<\text{record.file}\rangle\);

This is equivalent to the CPP,ADD command (with factor 1), but additionally sets a flag that CPP integrals projected with respect to core orbitals should be used. The projection is necessary whenever explicitly treated polarizable cores are present. The core orbitals are taken from \textit{record.file}, and the CPP,AE command should be followed by a \textit{core} card specifying the numbers of these orbitals in the various irreducible representations. Currently, the code assumes that the polarizable cores are spherically symmetric.

CPP,SET,\(<\text{fcpp}\rangle\);

normally not necessary but may be used to tell MOLPRO after a restart, with what factor the polarization integrals are effective at the moment. Currently the CPP integrals are restricted to basis functions up to and including angular momentum 4, i.e. g functions.

13.2 Example for ECP/CPP

***,Na2
! Potential curve of the Na2 molecule
! using 1-ve ECP + CPP
gprint,basis,orbitals;
rvec=[2.9,3.0,3.1,3.2,3.3] ang
do i=1,#rvec
 rNa2=rvec(i)
geometry={na;na,na,rNa2}
basis={
 ecp,na,ecp10sdf; ! ecp input
 s,na,even,8,3,.5; ! basis input
 p,na,even,6,3,.2;
d,na,.12,.03;
}
cpp,init,1; ! CPP input
na,1,.9947,\ldots,62;
hf;
ehf(i)=energy
{cisd;core;}
eci(i)=energy
enddo
table,rvec,ehf,eci
---

\url{http://www.molpro.net/info/current/examples/na2_ecp_cpp.com}
13.3 Example for use of CPP in all-electron calculations

***, P_2: All-electron calculation with polarizable P(+5) cores; calculation of the potential print,basis,orbital;

basis=vtz

dist = [2000.,1.84,1.86,1.88,1.90,1.92,1.94,1.96] ang
do ii=1,#dist

geometry={P1;P2,P1,dist(ii)}

if (ii.eq.1) then!
!calculation of free atoms at large distance
!the resulting cores are kept frozen in subsequent calculations
{rhf;closed,4,1,1,,4,1,1;wf,spin=6;save,2101.2}!
e_scf(1)=energy
else

!symmetric orthogonalization of the cores for current distance
(merge,2102.2;orbital,2101.2;move;orth,3,1,1,,3,1,1;)

!calculation without CPP
{multi;occ,5,2,2,,4,1,1;frozen,3,1,1,,3,1,1,2102.2;start,2102.2;wf,30,1,0;canorb,2140.2;}!
e_scf(ii)=energy

!calculating CPP integrals
cpp,init,-1;P,1,0.1057,,,1.6132,5;

!projecting CPP integrals onto valence space
{cpp,ae,2102.2;core,3,1,1,,3,1,1;}

!following calculations are done with CPP; core must be frozen
{multi;occ,5,2,2,,4,1,1;frozen,3,1,1,,3,1,1,2102.2;start,2140.2;wf,30,1,0;canorb,2141.2;}!
e_scf_cpp(ii)=energy

(ccsd(t);occ,5,2,2,,4,1,1;core,3,1,1,,3,1,1;orbital,2141.2;)
e_ccsdt_cpp(ii)=energy
endif

table,dist,e_scf,e_scf_cpp,e_ccsdt_cpp
enddo

---

http://www.molpro.net/info/current/examples/p2_cpp.com

14 INTEGRATION

Before starting any energy calculations, the geometry and basis set must be defined in GEOMETRY and BASIS blocks, respectively. By default, two electron integrals are evaluated once and stored on disk. This behaviour may be overridden by using the input command gdirect (see section [14.3]) to force evaluation of integrals on the fly. MOLPRO checks if the one-and two-electron integrals are available for the current basis set and geometry, automatically computing them if necessary. The program also recognizes automatically if only the nuclear charges have been changed, as is the case in counterpoise calculations. In this case, the two-electron integrals are not recomputed.
14 INTEGRATION

14.1 Sorted integrals

If the integrals are stored on disk, immediately after evaluation they are sorted into complete symmetry-packed matrices, so that later program modules that use them can do so as efficiently as possible. As discussed above, it is normally not necessary to call the integral and sorting programs explicitly, but sometimes additional options are desired, and can be specified using the INT command, which should appear after geometry and basis specifications, and before any commands to evaluate an energy.

```
INT,[[NO]SORT,][SPRI=value]

SORT,[SPRI=value]
```

INT,NOSORT;SORT can be used to explicitly separate the integral evaluation and sorting steps, for example to collect separate timing data. With value set to more than 1 in the SPRI option, all the two-electron integrals are printed.

The detailed options for the integral sort can be specified using the AOINT parameter set, using the input form

```
AOINT, key1=value1, key2=value2, ...
```

AOINT can be used with or without an explicit INT command.

The following summarizes the possible keys, together with their meaning, and default values.

<table>
<thead>
<tr>
<th>Key</th>
<th>Description</th>
<th>Default</th>
</tr>
</thead>
<tbody>
<tr>
<td>c_final</td>
<td>Integer specifying the compression algorithm to be used for the final sorted integrals. Possible values are 0 (no compression), 1 (compression using 1, 2, 4 or 8-byte values), 2 (2, 4 or 8 bytes), 4 (4, 8 bytes) and 8. Default: 0</td>
<td>0</td>
</tr>
<tr>
<td>c_sort1</td>
<td>Integer specifying the compression algorithm for the intermediate file during the sort. Default: 0</td>
<td>0</td>
</tr>
<tr>
<td>c_seward</td>
<td>Integer specifying the format of label tagging and compression written by the integral program and read by the sort program. Default: 0</td>
<td>0</td>
</tr>
<tr>
<td>compress</td>
<td>Overall compression; c_final, c_seward and c_sort1 are forced internally to be not less than this parameter. Default: 1</td>
<td>1</td>
</tr>
<tr>
<td>thresh</td>
<td>Real giving the truncation threshold for compression. Default: 0.0, which means use the integral evaluation threshold (GTHRESH, TWOINT)</td>
<td>0.0</td>
</tr>
<tr>
<td>io</td>
<td>String specifying how the sorted integrals are written. Possible values are molpro (standard MOLPRO record on file 1) and eaf (Exclusive-access file). eaf is permissible only if the program has been configured for MPP usage, and at present molpro is implemented only for serial execution. molpro is required if the integrals are to be used in a restart job. For maximum efficiency on a parallel machine, eaf should be used, since in that case the integrals are distributed on separate processor-local files.</td>
<td>molpro</td>
</tr>
</tbody>
</table>

For backward-compatibility purposes, two convenience commands are also defined: COMPRESS is equivalent to AOINT, COMPRESS=1, and UNCOMPRESS is equivalent to AOINT, COMPRESS=0.
14 INTEGRATION

14.2 Imported hamiltonian

It is possible to import the second-quantised hamiltonian completely from outside MOLPRO. In order to do so, it is necessary to set up a job that simulates the desired calculation by having a basis set of exactly the same dimensions as the one to be imported. One can then import the hamiltonian using the command

\texttt{HAMILTONIAN, filename}

\textit{filename} is the name of a file that contains the hamiltonian in \texttt{FCIDUMP} format, which can be produced using Molpro’s \texttt{[FCI;DUMP]} facility, or by another method.

Note that this facility is fragile, and is limited to energy-only calculations. Attempts to calculate gradients or other properties will inevitably fail. At present, the implementation does not support the use of point-group symmetry.

14.3 INTEGRAL-DIRECT CALCULATIONS (\texttt{GDIRECT})

References:


Most methods implemented in \texttt{MOLPRO} can be performed integral-direct, i.e., the methods are integral driven with the two-electron integrals in the AO basis being recomputed whenever needed, avoiding the bottleneck of storing these quantities on disk. Exceptions are currently full CI (FC1), perturbative triple excitations (T), UMP2, RMP2, CPP, MRCI-F12, and RS2-F12. For small molecules, this requires significantly more CPU time, but reduces the disk space requirements when using large basis sets. However, due to efficient prescreening techniques, the scaling of the computational cost with molecular size is lower in integral-direct mode than in conventional mode, and therefore integral-direct calculations for extended molecules may even be less expensive than conventional ones. The break-even point depends strongly on the size of the molecule, the hardware, and the basis set. Depending on the available disk space, calculations with more than 150–200 basis functions in one symmetry should normally be done in integral-direct mode.

Integral-direct calculations are requested by the \texttt{DIRECT} or \texttt{GDIRECT} directives. If one of these cards is given outside the input of specific programs it acts globally, i.e. all subsequent calculations are performed in integral-direct mode. On the other hand, if the \texttt{DIRECT} card is part of the input of specific programs (e.g. HF, CCSD), it affects only this program. The \texttt{GDIRECT} directive is not recognized by individual programs and always acts globally. Normally, all calculations in one job will be done integral-direct, and then a \texttt{DIRECT} or \texttt{GDIRECT} card is required before the first energy calculation. However, further \texttt{DIRECT} or \texttt{GDIRECT} directives can be given in order to modify specific options or thresholds for particular programs.

The integral-direct implementation in \texttt{MOLPRO} involves three different procedures: (i) Fock matrix evaluation (\texttt{DFOCK}), (ii) integral transformation (\texttt{DTRAF}), and (iii) external exchange operators (\texttt{DKEXT}). Specific options and thresholds exist for all three programs, but it is also possible to specify the most important thresholds by general parameters, which are used as defaults for all programs.

Normally, appropriate default values are automatically used by the program, and in most cases no parameters need to be specified on the \texttt{DIRECT} directive. However, in order to guarantee sufficient accuracy, the default thresholds are quite strict, and in calculations for extended systems larger values might be useful to reduce the CPU time.
The format of the `DIRECT` directive is

```
DIRECT, key1=value1, key2=value2...
```

The following table summarizes the possible keys and their meaning. The default values are given in the subsequent table. In various cases there is a hierarchy of default values. For instance, if `THREST_D2EXT` is not given, one of the following is used: `[THREST_D2EXT, THR_D2EXT, THR_D3EXT, THR, default]`. The list in brackets is checked from left to right, and the first one found in the input is used. `default` is a default value which depends on the energy threshold and the basis set (the threshold is reduced if the overlap matrix contains very small eigenvalues).

**General Options (apply to all programs):**

**THREST** Integral prescreening threshold. The calculation of an integral shell block is skipped if the product of the largest estimated integral value (based on the Cauchy-Schwarz inequality) and the largest density matrix element contributing to the shell block is smaller than this value. In `DTRAF` and `DKEXT` effective density matrices are constructed from the MO coefficients and amplitudes, respectively.

**THRINT** Integral prescreening threshold. This applies to the product of the exact (i.e. computed) integral value and a density matrix. This threshold is only used in `DTRAF` and `DKEXT`. A shell block of integrals is skipped if the product of the largest integral and the largest element of the effective density matrix contributing to the shell block is smaller than this threshold. If it is set negative, no computed integrals will be neglected.

**THRPROD** Prescreening threshold for products of integrals and MO-coefficients (`DTRAF`) or amplitudes (`DKEXT`). Shell blocks of MO coefficients or amplitudes are neglected if the product of the largest integral in the shell block and the largest coefficient is smaller than this value. If this is set negative, no product screening is performed.

**THRMAX** Initial value of the prescreening threshold `THREST` for `DFOCK` and `DKEXT` in iterative methods (SCF, CI, CCSD). If nonzero, it will also be used for `DKEXT` in MP3 and MP4 (SDQ) calculations. The threshold will be reduced to `THREST` once a certain accuracy has been reached (see `VARRED`), or latest after `MAXRED` iterations. In CI and CCSD calculations, also the initial thresholds `THRINT_DKEXT` and `THRPROD_DKEXT` are influenced by this value. For a description, see `THRMAX_DKEXT`. If `THRMAX=0`, the final thresholds will be used from the beginning in all methods.

**SCREEN** Enables or disables prescreening.

- `SCREEN ≥ 0`: full screening enabled.
- `SCREEN < 0`: `THRPROD` is unused. No density screening in direct SCF.
- `SCREEN < -1`: `THRINT` is unused.
- `SCREEN < -2`: `THREST` is unused.

**MAXRED** Maximum number of iterations after which thresholds are reduced to their final values in CI and CCSD calculations. If `MAXRED=0`, the final thresholds will be used in CI and CCSD
from the beginning (same as THRMAX=0, but MAXRED has no effect on DSCF. In the latter case a fixed value of 10 is used.

VARRED
Thresholds are reduced to their final values if the sum of squared amplitude changes is smaller than this value.

SWAP
Enables or disables label swapping in SEWARD. Test purpose only.

Specific options for direct SCF (DFOCK):

THREST_DSCF
Final prescreening threshold in direct SCF. If given, it replaces the value of THREST.

THRMAX_DSCF
Initial prescreening threshold in direct SCF. This is used for the first 7-10 iterations. Once a certain accuracy is reached, the threshold is reduced to THREST_DSCF.

SWAP_DFOCK
Enables or disables label swapping in fock matrix calculation (test purpose only).

General options for direct integral transformation (DTRAF):

PAGE_DTRAF
Selects the transformation method.
PAGE_DTRAF=0: use minimum memory algorithm, requiring four integral evaluations.
PAGE_DTRAF=1: use paging algorithm, leading to the minimum CPU time (one integral evaluation for DMP2/LMP2 and two otherwise).

SCREEN_DTRAF
If given, replaces value of SCREEN for DTRAF.

MAXSHLQ1_DTRAF
Maximum size of merged shells in the first quarter transformation step (0: not used).

MINSHLQ1_DTRAF
Shells are only merged if their size is smaller than this value (0: not used).

MAXSHLQ2_DTRAF
Maximum size of merged shells in the second quarter transformation step (0: not used).

MINSHLQ2_DTRAF
Shells are only merged if their size is smaller than this value (0: not used).

MAXCEN_DTRAF
Maximum number of centres in merged shells (0: no limit).

PRINT_DTRAF
Print parameter for DTRAF.

General thresholds for all direct integral transformations:

THR_DTRAF
General threshold for DTRAF. If given, this is taken as default value for all thresholds described below.

THREST_DTRAF
AO prescreening threshold for DTRAF.
Defaults: [THR_DTRAF, THREST, default].

THRINT_DTRAF
Integral threshold for DTRAF.
Defaults: [THR_DTRAF, THRINT, default].

THRPROD_DTRAF
Product threshold for DTRAF.
Defaults: [THR_DTRAF, THRPROD, default].
Thresholds specific to direct integral transformations:

**THR.D2EXT**  
General threshold for generation of 2-external integrals. If given, this is used as a default for all D2EXT thresholds described below.

**THREST.D2EXT**  
Prescreening threshold for generation of 2-external integrals.  
Defaults: [THR.D2EXT, THREST.DTRAF, THR.DTRAF, THREST, default].

**THRINT.D2EXT**  
Integral threshold for generation of 2-external integrals.  
Defaults: [THR.D2EXT, THRINT.DTRAF, THR.DTRAF, THRINT, default].

**THRPROD.D2EXT**  
Product threshold for generation of 2-external integrals.  
Defaults: [THR.D2EXT, THRPROD.DTRAF, THR.DTRAF, THRPROD, default].

**THR.D3EXT**  
General threshold for generation of 3-external integrals. If given, this is used as a default for all D3EXT thresholds described below.

**THREST.D3EXT**  
Prescreening threshold for generation of 3-external integrals.  
Defaults: [THR.D3EXT, THREST.DTRAF, THR.DTRAF, THREST, default].

**THRINT.D3EXT**  
Integral threshold for generation of 3-external integrals.  
Defaults: [THR.D3EXT, THRINT.DTRAF, THR.DTRAF, THRINT, default].

**THRPROD.D3EXT**  
Product threshold for generation of 3-external integrals.  
Defaults: [THR.D3EXT, THRPROD.DTRAF, THR.DTRAF, THRPROD, default].

**THR.D4EXT**  
General threshold for generation of 4-external integrals. If given, this is used as a default for all D4EXT thresholds described below.

**THREST.D4EXT**  
Prescreening threshold for generation of 4-external integrals.  
Defaults: [THR.D4EXT, THREST.DTRAF, THR.DTRAF, THREST, default].

**THRINT.D4EXT**  
Integral threshold for generation of 4-external integrals.  
Defaults: [THR.D4EXT, THRINT.DTRAF, THR.DTRAF, THRINT, default].

**THRPROD.D4EXT**  
Product threshold for generation of 4-external integrals.  
Defaults: [THR.D4EXT, THRPROD.DTRAF, THR.DTRAF, THRPROD, default].

**THR.DCCSD**  
General threshold for generalized transformation needed in each CCSD iteration. If given, this is used as a default for THREST.DCCSD, THRINT.DCCSD, and THRPROD.DCCSD described below.

**THREST.DCCSD**  
Prescreening threshold for DCCSD transformation.  
Defaults: [THR.DCCSD, THREST.DTRAF, THR.DTRAF, THREST, default].
Integral threshold for DCCSD transformation.
Defaults: [THR_DCCSD, THRINT_DTRAF, THR_DTRAF, THRINT, default].

Product threshold for DCCSD transformation.
Defaults: [THR_DCCSD, THRPROD_DTRAF, THR_DTRAF, THRPROD, default].

Initial value for THREST_DCCSD in CCSD calculations. The threshold will be reduced to THREST_DCCSD once a certain accuracy has been reached (see VARRED), or latest after MAXRED iterations. The initial thresholds THRINT_DCCSD and THRPROD_DCCSD are obtained by multiplying their input (or default) values by THRMAX_DCCSD/THREST_DCCSD, with the restriction that the initial values cannot be smaller than the final ones.

Specific options for direct MP2 (DMP2):

**DMP2**
Selects the transformation method for direct MP2:

- DMP2=-1: automatic selection, depending on the available memory.
- DMP2=0: use fully direct method for DMP2 (min. two integral evaluations, possibly multipassing, no disk space).
- DMP2=1: use semi-direct method for DMP2 (one to four integral evaluations, depending on PAGE_DTRAF).
- DMP2=2: use DKEXT to compute exchange operators in DMP2 (one integral evaluation). This is only useful in local DMP2 calculations with many distant pairs.

**THR_DMP2**
General threshold for generation of 2-external integrals in DMP2. If given, this is used as a default for all DMP2 thresholds described below.

**THREST_DMP2**
Prescreening threshold for generation of 2-external integrals.
Defaults: [THR_DMP2, THREST_DTRAF, THR_DTRAF, THREST, default].

**THRINT_DMP2**
Integral threshold for generation of 2-external integrals.
Defaults: [THR_DMP2, THRINT_DTRAF, THR_DTRAF, THRINT, default].

**THRPROD_DMP2**
Product threshold for generation of 2-external integrals
Defaults: [THR_DMP2, THRPROD_DTRAF, THR_DTRAF, THRPROD, default].

Specific options for direct local MP2 (LMP2):

**DTRAF**
Selects the transformation method for direct LMP2:

- DTRAF $\geq$ 0: generates the 2-external integrals (exchange operators) first in AO basis and transforms these thereafter in a second step to the projected, local basis. The disk storage requirements hence scale cubically with molecular size.
- DTRAF = -1: generates the 2-external integrals (exchange operators) directly in projected basis. The disk storage requirements hence scale linearly with molecular size. This (together with PAGE_DTRAF = 0) is the recommended algorithm for very...
large molecules (cf. linear scaling LMP2, chapter [32]).

\[ D_{\text{TRAF}} = -2: \] alternative algorithm to generate the exchange operators directly in projected basis. Usually, this algorithm turns out to be computationally more expensive than the one selected with \( D_{\text{TRAF}} = -1 \). Note, that neither \( D_{\text{TRAF}} = -1 \) nor \( D_{\text{TRAF}} = -2 \) work in the context of LMP2 gradients.

**THR\_LMP2**
General threshold for generation of 2-external integrals in linear scaling LMP2. If given, this is used as a default for all LMP2 thresholds described below.

**THR\_LMP2**
Prescreening threshold for generation of 2-external integrals.
Defaults: \([\text{THR}\_\text{LMP2}, \text{THREST}_{\text{DTRAF}}, \text{THR}_{\text{DTRAF}}, \text{THREST}, \text{default}]\).

**THR\_Q1\_LMP2**
Threshold used in the first quarter transformation.
Defaults: \([\text{THR}\_\text{LMP2}, \text{THR}\_\text{PROD}_{\text{DTRAF}}, \text{THR}_{\text{DTRAF}}, \text{THR}\_\text{PROD}, \text{default}]\).

**THR\_Q2\_LMP2**
Threshold used in the second and subsequent quarter transformations.
Defaults: \([\text{THR}\_\text{LMP2}, \text{THR}\_\text{INT}_{\text{DTRAF}}, \text{THR}_{\text{DTRAF}}, \text{THR}\_\text{INT}, \text{default}]\).

**THR\_AO\_ATTEN**
Special threshold for prescreening of attenuated integrals \((\mu\mu|\nu\nu)\)
Default: \text{THREST\_LMP2}

**Options for integral-direct computation of external exchange operators (DKEXT):**

**DKEXT**
Selects driver for DKEXT.
\[ \text{DKEXT} = -1: \] use paging algorithm (minimum memory). This is automatically used if in-core algorithm would need more than one integral pass.
\[ \text{DKEXT} = 0: \] use in-core algorithm, no integral triples.
\[ \text{DKEXT} = 1: \] use in-core algorithm and integral triples.
\[ \text{DKEXT} = 2: \] use in-core algorithm and integral triples if at least two integrals of a triple differ.
\[ \text{DKEXT} = 3: \] use in-core algorithm and integral triples if all integrals of a triple differ.

**SCREEN\_DKEXT**
if given, replaces value of SCREEN for DKEXT.

**MAXSIZE\_DKEXT**
Largest size of merged shells in DKEXT \((0: \text{not used})\).

**MINSIZE\_DKEXT**
Shells are only merged if their size is smaller than this value. \((0: \text{not used})\).

**MAXCEN\_DKEXT**
Maximum number of centres in merged shells \((0: \text{no limit})\).

**SCREEN\_DKEXT**
Enables of disables screening in DKEXT.

**PRINT\_DKEXT**
Print parameter for DKEXT.

**SWAP\_DKEXT**
Enables of disables label swapping in DKEXT (test purpose only).

**MXMBLK\_DKEXT**
Largest matrix block size in DKEXT (only used with \text{DKEXT} \geq 1).
Thresholds for integral-direct computation of external exchange operators (DKEXT):

**THR\_DKEXT**  
General threshold for DKEXT. If given, this is used as a default for all DKEXT thresholds described below.

**THREST\_DKEXT**  
Prescreening threshold for DKEXT.  
Defaults: [THR\_DKEXT, THREST, default].

**THRINT\_DKEXT**  
Integral threshold for DKEXT.  
Defaults: [THR\_DKEXT, THRINT, default].

**THRPROD\_DKEXT**  
Product threshold for DKEXT.  
Defaults: [THR\_DKEXT, THRPROD, default].

**THRMAX\_DKEXT**  
Initial value for THREST\_DKEXT in CI, and CCSD calculations. If nonzero, it will also be used for DKEXT in MP3 and MP4 (SDQ) calculations. The threshold will be reduced to THREST\_DKEXT once a certain accuracy has been reached (see VARRED), or latest after MAXRED iterations. The initial thresholds THRINT\_DKEXT and THRPROD\_DKEXT are obtained by multiplying their input (or default) values by THRMAX\_DKEXT/THREST\_DKEXT, with the restriction that the initial values cannot be smaller than the final ones.

For historical reasons, many options have alias names. The following tables summarize the default values for all options and thresholds and also gives possible alias names.
Table 6: Default values and alias names for direct options.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Alias</th>
<th>Default value</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCREEN</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MAXRED</td>
<td>7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>VARRED</td>
<td>1.d-7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SWAP</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SWAP_DFOCK</td>
<td>SWAP</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DMP2</td>
<td>DTRAF</td>
<td>-1</td>
<td></td>
</tr>
<tr>
<td>PAGE_DTRAF</td>
<td>PAGE</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>SCREEN_DTRAF</td>
<td>SCREEN</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MAXSHLQ1_DTRAF</td>
<td>NSHLQ1</td>
<td>32</td>
<td></td>
</tr>
<tr>
<td>MINSHELQ1_DTRAF</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>MAXSHLQ2_DTRAF</td>
<td>NSHLQ2</td>
<td>16</td>
<td></td>
</tr>
<tr>
<td>MINSHELQ2_DTRAF</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MAXCEN_DTRAF</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PRINT_DTRAF</td>
<td>-1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SWAP_DTRAF</td>
<td>SWAP</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DKEKT</td>
<td>DREVKEXT</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>SCREEN_DKEXT</td>
<td>SCREEN</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>MAXCEN_DKEXT</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PRINT_DKEXT</td>
<td>-1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SWAP_DKEXT</td>
<td>SWAP</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MXMBLK_DKEXT</td>
<td>depends on hardware (-B parameter on molpro command)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 7: Default thresholds and alias names for direct calculations

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Alias</th>
<th>Default value</th>
</tr>
</thead>
<tbody>
<tr>
<td>THREST</td>
<td>THRAO</td>
<td>min($\Delta E \cdot 1.d - 2, 1.d - 9$)$^{a,b}$</td>
</tr>
<tr>
<td>THRINT</td>
<td>THRSO</td>
<td>min($\Delta E \cdot 1.d - 2, 1.d - 9$)$^{a,b}$</td>
</tr>
<tr>
<td>THRPROD</td>
<td>TRP</td>
<td>min($\Delta E \cdot 1.d - 3, 1.d - 10$)$^{a,b}$</td>
</tr>
<tr>
<td>THRMAX</td>
<td></td>
<td>1.d-8$^b$</td>
</tr>
<tr>
<td>THREST_DSCF</td>
<td>THRDSCF</td>
<td>$\leq$ 1.d-10 (depending on accuracy and basis set)</td>
</tr>
<tr>
<td>THRMAX_DSCF</td>
<td>THRDSCF_MAX</td>
<td>THRMAX</td>
</tr>
<tr>
<td>THR_DTRAF</td>
<td>THRDTRAF</td>
<td></td>
</tr>
<tr>
<td>THR_D2EXT</td>
<td>THR2EXT</td>
<td>THR_DTRAF</td>
</tr>
<tr>
<td>THR_D3EXT</td>
<td>THR3EXT</td>
<td>THR_DTRAF</td>
</tr>
<tr>
<td>THR_D4EXT</td>
<td>THR4EXT</td>
<td>THR_DTRAF</td>
</tr>
<tr>
<td>THR_DCCSD</td>
<td>THRCCSD</td>
<td>THR_DTRAF</td>
</tr>
<tr>
<td>THR_D2EXT_DCCSD</td>
<td>THRAO_D2EXT_DCCSD</td>
<td>[THR_D2EXT, THR_DTRAF]</td>
</tr>
<tr>
<td>THR_D3EXT_DCCSD</td>
<td>THRAO_D3EXT_DCCSD</td>
<td>[THR_D3EXT, THR_DTRAF]</td>
</tr>
<tr>
<td>THR_D4EXT_DCCSD</td>
<td>THRAO_D4EXT_DCCSD</td>
<td>[THR_D4EXT, THR_DTRAF]</td>
</tr>
<tr>
<td>THR_DCCSD_DCCSD</td>
<td>THRAO_DCCSD_DCCSD</td>
<td>[THR_DCCSD, THR_DTRAF]</td>
</tr>
<tr>
<td>THR_D2EXT_DCCSD</td>
<td>THRAO_D2EXT_DCCSD</td>
<td>[THR_D2EXT, THR_DTRAF]</td>
</tr>
<tr>
<td>THR_D3EXT_DCCSD</td>
<td>THRAO_D3EXT_DCCSD</td>
<td>[THR_D3EXT, THR_DTRAF]</td>
</tr>
<tr>
<td>THR_D4EXT_DCCSD</td>
<td>THRAO_D4EXT_DCCSD</td>
<td>[THR_D4EXT, THR_DTRAF]</td>
</tr>
<tr>
<td>THR_DCCSD_DCCSD</td>
<td>THRAO_DCCSD_DCCSD</td>
<td>[THR_DCCSD, THR_DTRAF]</td>
</tr>
<tr>
<td>THR_D2EXT_DCCSD</td>
<td>THRAO_D2EXT_DCCSD</td>
<td>[THR_D2EXT, THR_DTRAF]</td>
</tr>
<tr>
<td>THR_D3EXT_DCCSD</td>
<td>THRAO_D3EXT_DCCSD</td>
<td>[THR_D3EXT, THR_DTRAF]</td>
</tr>
<tr>
<td>THR_D4EXT_DCCSD</td>
<td>THRAO_D4EXT_DCCSD</td>
<td>[THR_D4EXT, THR_DTRAF]</td>
</tr>
<tr>
<td>THR_DCCSD_DCCSD</td>
<td>THRAO_DCCSD_DCCSD</td>
<td>[THR_DCCSD, THR_DTRAF]</td>
</tr>
<tr>
<td>THR_D2EXT_DCCSD</td>
<td>THRAO_D2EXT_DCCSD</td>
<td>[THR_D2EXT, THR_DTRAF]</td>
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<td>[THR_DCCSD, THR_DTRAF]</td>
</tr>
<tr>
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<td>[THR_D4EXT, THR_DTRAF]</td>
</tr>
<tr>
<td>THR_DCCSD_DCCSD</td>
<td>THRAO_DCCSD_DCCSD</td>
<td>[THR_DCCSD, THR_DTRAF]</td>
</tr>
</tbody>
</table>

a) $\Delta E$ is the requested accuracy in the energy (default 1.d-6).
b) The thresholds are reduced if the overlap matrix has small eigenvalues.
c) The default thresholds for DMP2 and LMP2 are 0.1 · $\Delta E$. 
15 DENSITY FITTING

14.3.1 Example for integral-direct calculations

```plaintext
memory,2,m
method=[hf,mp2,ccsd,qci,bcccd,multi,mrci,acpf,rs3] !some methods
basis=vdz !basis
gometry={o;h1,o,h2,o,r,h1,theta} !geometry
gdirect !direct option
r=1 ang,theta=104 !bond length and angle
do i=1,#method !loop over methods
method(i) !run method(i)
e(i)=energy !save results in variables
dip(i)=dmz
enddo
table,method,e,dip !print table of results
```

http://www.molpro.net/info/current/examples/h2o_direct.com

This job produces the following table:

<table>
<thead>
<tr>
<th>METHOD</th>
<th>E</th>
<th>DIP</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>-76.02145798</td>
<td>0.82747348</td>
</tr>
<tr>
<td>MP2</td>
<td>-76.22620591</td>
<td>0.00000000</td>
</tr>
<tr>
<td>CCSD</td>
<td>-76.23580191</td>
<td>0.00000000</td>
</tr>
<tr>
<td>QCI</td>
<td>-76.23596211</td>
<td>0.00000000</td>
</tr>
<tr>
<td>BCCD</td>
<td>-76.23565813</td>
<td>0.00000000</td>
</tr>
<tr>
<td>MULTI</td>
<td>-76.07843443</td>
<td>0.76283026</td>
</tr>
<tr>
<td>MRCI</td>
<td>-76.23369819</td>
<td>0.76875001</td>
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<tr>
<td>ACPF</td>
<td>-76.23820180</td>
<td>0.76283026</td>
</tr>
<tr>
<td>RS3</td>
<td>-76.23549448</td>
<td>0.75869972</td>
</tr>
</tbody>
</table>

15 DENSITY FITTING

Density fitting can be used to approximate the integrals in spin restricted Hartree-Fock (HF), density functional theory (KS), second-order Møller-Plesset perturbation theory (MP2 and RMP2), explicitly correlated MP2 (MP2-F12), all levels of closed-shell local correlation methods (LCC2, LMP2-LMP4, LQCISD(T), LCCSD(T)), as well as for CASSCF and CASPT2 methods. Density fitting is invoked by adding the prefix DF- to the command name, e.g. DF-HF, DF-KS, DF-MP2 and so on. Gradients are available for DF-HF, DF-KS, DF-MP2, DF-LMP2, DF-CASSCF, and DF-CASPT2. Symmetry is not implemented for density fitting programs. Therefore, symmetry is turned off automatically if DF- is found in the input.

By default, a fitting basis set will be chosen automatically that corresponds to the current orbital basis set and is appropriate for the method. For instance, if the orbital basis set is VTZ, the default fitting basis is VTZ/JKFIT for DF-HF or DF-KS, and VTZ/MP2FIT for DF-MP2. Other fitting basis sets from the library can be chosen using the DF_BASIS option, e.g.

```
BASIS=VTZ !use VTZ orbital basis
DF-HF,DF_BASIS=VQZ !use VQZ/JKFIT fitting basis
DF-MP2,DF_BASIS=VQZ !use VQZ/MP2FIT fitting basis
```

The program then chooses automatically the set which is appropriate for the method. Optionally, the basis type can appended to the basis name and then this supercedes the default, e.g.

```
DF-HF,DF_BASIS=VQZ/JKFIT !use VQZ/JKFIT fitting basis
```
Orbital basis sets can be chosen using type \texttt{ORBITAL} (but this is not recommended normally!). Contraction/uncontraction can be forced appending \texttt{(CONTRACT)} or \texttt{(UNCONTRACT)} to the basis name, e.g. 
\begin{verbatim}
DF\_BASIS=AVQZ\,(UNCONTRACT)/ORBITAL.
\end{verbatim}
If other options are given in parenthesis, these can be separated by commas, e.g. 
\begin{verbatim}
DF\_BASIS=AVQZ\,(f/d,\,UNCONTRACT)/ORBITAL.
\end{verbatim}
Alternative forms, which should work as well, are 
\begin{verbatim}
DF\_BASIS=AVQZ\,(f/d)\,(UNCONTRACT)/ORBITAL
or
DF\_BASIS=AVQZ\,(f/d)\,/ORBITAL\,(UNCONTRACT).
\end{verbatim}
Note that the \texttt{CONTRACT/UNCONTRACT} option cannot be used with basis set names previously defined in a basis block (see below).

Alternatively, fitting basis sets can be defined in a preceding basis block (see \cite{11}, and then be referred to with their set names, e.g.,
\begin{verbatim}
DF-HF, \ DF\_BASIS=MYJKBASIS
DF-MP2, \ DF\_BASIS=MYMP2BASIS
\end{verbatim}
where \texttt{MYJKBASIS} and \texttt{MYMP2BASIS} are sets defined in a basis block. In this case it is the responsibility of the user to ensure that the basis set is appropriate for the method.

Further options, as fully described in section \cite{15.1} can be added on the command line. In this case they are valid only for the current command. Alternatively, the options can be specified on a separate \texttt{DFIT} directive. If this is given within a command block, the options are used only for the current program; this is entirely equivalent to the case that the options are specified on the command line. However, if a \texttt{DFIT} (or \texttt{GDFIT}) directive is given outside of a command block, the specified options are used globally in all subsequent density fitting calculations in the same run.

The options specified on a global \texttt{DFIT} directive are also passed down to procedures. However, if a \texttt{DFIT} is given within a procedure, the corresponding options are used only in the same procedure and procedures called from it. When the procedure terminates, the options from the previous level are recovered.

\section{15.1 Options for density fitting}

The options described in this section have sensible default values and usually do not have to be given. Many options described below have alias names. These can be obtained using 
\begin{verbatim}
HELP,CFIT,ALIASES.
\end{verbatim}

\subsection{15.1.1 Options to select the fitting basis sets}

\begin{tabular}{ll}
\texttt{BASIS} & Basis set for fitting (Default: set corresponding to the orbital basis) \\
\texttt{BASIS\_COUL} & Basis set for Coulomb fitting (default \texttt{BASIS}) \\
\texttt{BASIS\_EXCH} & Basis set for exchange fitting (default \texttt{BASIS}) \\
\texttt{BASIS\_MP2} & Fitting basis set for DF-MP2 (default \texttt{BASIS}) \\
\texttt{BASIS\_CCSD} & Fitting basis set for DF-LCCSD (default \texttt{BASIS})
\end{tabular}
15.1.2 Screening thresholds

THRAO  
Threshold for neglecting contracted 3-index integrals in the AO basis (default 1.d-8).

THRMO  
Threshold for neglecting half-transformed 3-index integrals (default 1.d-8).

THRSW  
Threshold for Schwarz screening (default 1.d-5).

THROV  
Threshold for neglecting 2-index integrals in the AO (default 1.d-10).

THRPROD  
Product screening threshold for first half transformation (default 1.d-8).

Analogous thresholds for specific programs can be set by appending the above keywords by the following specifications

_SCFCoulomb and exchange fitting in DF-HF/DF-KS
_COULCoulomb fitting in DF-HF/DF-KS
_EXCHExchange fitting in DF-HF/DF-KS
_CPHFCoulomb and exchange fitting in CPHF
_SCFCGRDCoulomb and exchange fitting in DF-HF/DF-KS gradients

The default values are the same as for the general thresholds.

Further thresholds:

THR2HLF  
Threshold for second-half transformation in exchange fitting (default THRAO_SCF)

THRAO_SCF  
Threshold for local assembly of exchange matrix (default THRAO_SCF)

THRAO_FOCK  
Threshold for Coulomb fitting in DF-KS
(default MIN(THRAO_SCF*1.d-2,1.d-12))

15.1.3 Parameters to enable local fitting

Local fitting as described in H.-J. Werner, F. R. Manby, and P. J. Knowles, J. Chem. Phys. 118, 8149 (2003), Polly, H.-J. Werner, F. R. Manby, and Peter J. Knowles, Mol. Phys. 102, 2311 (2004), and M. Schütz, H.-J. Werner, R. Lindh and F. R. Manby, J. Chem. Phys. 121, 737 (2004) can be activated by setting LOCFIT=1. By default, local fitting is disabled, because under certain circumstances it can lead to unacceptable errors. For instance, local fitting must not be used in counter-poise calculations, since the lack of fitting functions at the dummy atoms can lead to wrong results.

Local fitting can be restricted to certain programs, using the following options:

LOCFIT  
If positive, use local fitting in all programs in which it is available (default 0).

LOCFIT_SCF  
If positive, use local fitting in SCF (default LOCFIT)

LOCFIT_MP2  
If positive, use local fitting in DF-LMP2; 1: use orbital domains; 2: use pair domains (default LOCFIT)
### 15.1.4 Parameters for fitting domains

The following options can be used to modify the domains used in local fitting. These parameters only have an effect if `LOCFIT=1`. The local fitting domains are determined in two steps: first primary orbital domains are determined. In the LMP2 and LCCSD programs, the primary orbital domains are the same as used for excitation domains and determined by the Boughton-Pulay procedure, as described in Sect. 32. Depending on the value of `FITDOM_MP2` or `FITDOM_CCSD` for LMP2 and LCCSD, respectively, either the orbital domains are used directly or united pair domains are generated. In DF-HF the primary orbital domains include all basis functions at atoms which have Löwdin charges greater or equal to `THRCHG_SCF`. In the second step the primary fitting domains are extended using either distance criteria (`RDOMAUX`, in bohr) or bond connectivity criteria (`IDOMAUX`). `IDOMAUX=1` means to include all functions at atoms which are at most one bond distant from the primary domains. By default, distance criteria are used. However, if `IDOMAUX.ge.0`, the distance criteria are ignored and connectivity is used.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td><code>LOCFIT_F12</code></td>
<td>If positive, use local fitting in DF-LMP2-F12 (default <code>LOCFIT</code>)</td>
</tr>
<tr>
<td><code>LOCFIT_CCSD</code></td>
<td>If positive, use local fitting in DF-LCCSD (default <code>LOCFIT</code>)</td>
</tr>
<tr>
<td><code>LOCFIT_2EXT</code></td>
<td>If positive, use local fitting in LCCSD 2ext transformation (default <code>LOCFIT_CCSD</code>)</td>
</tr>
<tr>
<td><code>LOCFIT_3EXT</code></td>
<td>If positive, use local fitting in LCCSD 3ext transformation (default <code>LOCFIT_CCSD</code>)</td>
</tr>
<tr>
<td><code>LOCFIT_4EXT</code></td>
<td>If positive, use local fitting in LCCSD 4ext transformation (default <code>LOCFIT_CCSD</code>)</td>
</tr>
<tr>
<td><code>LOCFIT_CPHF</code></td>
<td>If positive, use local fitting in CPHF (default <code>LOCFIT</code>)</td>
</tr>
<tr>
<td><code>LOCFIT_SCFGRD</code></td>
<td>If positive, use local fitting in gradient calculations (default <code>LOCFIT</code>)</td>
</tr>
<tr>
<td><code>LOCORB</code></td>
<td>If positive, use localized orbitals in DF-HF (default 1)</td>
</tr>
<tr>
<td><code>LOCTRA</code></td>
<td>If positive, use local screening in first half transformation (default <code>LOCFIT</code>)</td>
</tr>
<tr>
<td><code>DSCREEN</code></td>
<td>If positive, enable density screening in LMP2 (default 0)</td>
</tr>
<tr>
<td><code>KSCREEN</code></td>
<td>If positive, enable fit-basis Schwarz screening in LMP2 (default depends on <code>LOCTRA</code>)</td>
</tr>
<tr>
<td><code>THRCHG_SCF</code></td>
<td>Parameter to select the primary orbital domains in local exchange fitting (default 0.1). All atoms are included which have Löwdin charges greater than this value. The primary domains are extended according to <code>RDOMAUX_SCF</code> or <code>IDOMAUX_SCF</code>.</td>
</tr>
<tr>
<td><code>FITDOM_MP2</code></td>
<td>Parameter to select primary fitting domains in LMP2 transformation (default 3). 1: use orbital domains; 2: use united orbital domains of strong pairs; 3: use united orbital domains of strong and weak pairs (default 3). The primary domains are extended according to <code>RDOMAUX_MP2</code> or <code>IDOMAUX_MP2</code>.</td>
</tr>
<tr>
<td><code>FITDOM_CCSD</code></td>
<td>Similar to <code>FITDOM_MP2</code> but used for LCCSD 2-ext transformation.</td>
</tr>
<tr>
<td><code>RDOMAUX_SCF</code></td>
<td>Distance criterion for fitting domain extension in SCF (default 5.0)</td>
</tr>
</tbody>
</table>
Connectivity criterion for fitting domain extension in SCF (default 0).

Distance criterion for core orbital fitting domain extension in SCF (default RDOMAUX_SCF).

Connectivity criterion for core orbital fitting domain extension in SCF (default IDOMAUX_SCF).

Distance criterion for fitting domain extension in the initial SCF iterations (default 3.0).

Connectivity criterion for fitting domain extension in the initial SCF iterations (default 1).

Distance criterion for fitting domain extension in the final SCF iterations (default RDOMAUX_SCF).

Connectivity criterion for fitting domain extension in the final SCF iterations (default IDOMAUX_SCF).

Distance criterion for fitting domain extension in LMP2. The default value depends on FITDOM_MP2.

Connectivity criterion for fitting domain extension in LMP2. The default value depends on FITDOM_MP2.

Distance criterion for fitting domain extension in LCCSD. The default value depends on FITDOM_CCSD.

Connectivity criterion for fitting domain extension in LCCSD. The default value depends on FITDOM_CCSD.

Distance criterion for fitting domain extension in CPHF (default 3.0).

Distance criterion for fitting domain extension in gradients (default 5.0).

Switches the DF-LMP2 analytic gradient to Grimmes SCS scaled MP2 energy functional (default 0).

15.1.5 Miscellaneous control options

There is a rather large number of parameters. Many of these should normally not be changed, and therefore only a subset is described here. A full list can be obtained using

HELP, CFIT
16  THE SCF PROGRAM

The Hartree-Fock self-consistent field program is invoked by one of the following commands:

\texttt{HF} or \texttt{RHF} \hspace{1cm} \text{calls the spin-restricted Hartree-Fock program}

\texttt{UHF} or \texttt{UHF-SCF, options} \hspace{1cm} \text{calls the spin-unrestricted Hartree-Fock program}

In contrast to older versions of \texttt{MOLPRO}, the \texttt{HF} and \texttt{RHF} directives have identical functionality and can both be used for closed-shell or open-shell calculations. Other aliases are \texttt{HF-SCF} or \texttt{RHF-SCF}.

Often, no further input is necessary. By default, the number of electrons is equal to the nuclear charge, the spin multiplicity is 1 (singlet) for an even number of electrons and 2 (doublet) otherwise, and the wavefunction is assumed to be totally symmetric (symmetry 1) for singlet calculations. The Aufbau principle is used to determine the occupation numbers in each symmetry. Normally, this works well in closed-shell and many open-shell cases, but sometimes wrong occupations are obtained. In such cases, the \texttt{OCC} and/or \texttt{CLOSED} directives can be used to force convergence to the desired state. The default behaviour can be modified either by options on the command line, or by directives.

In open-shell cases, we recommend to use the \texttt{WF}, \texttt{OCC}, \texttt{CLOSED}, or \texttt{OPEN} cards to define the wavefunction uniquely. Other commands frequently used are \texttt{START} and \texttt{ORBITAL} (or \texttt{SAVE}) to modify the default records for starting and optimized orbitals, respectively. The \texttt{SHIFT} option or directive allows to modify the level shift in the \texttt{RHF} program, and \texttt{EXPEC} to calculate expectation values of one-electron operators (see section 6.13). Section 16.10 discusses strategies for dealing difficult molecules and convergence problems.

Density fitting can be used for closed and open-shell spin-restricted HF and is invoked by a prefix \texttt{DF-} (\texttt{DF-HF} or \texttt{DF-RHF}, see section 15). For UHF, only Coulomb fitting is possible (\texttt{CF-UHF}). Density fitting very much speeds up calculations for large molecules. The greatest savings are seen for large basis sets with high angular momentum functions. For details see R. Polly, H.-J. Werner, F. R. Manby, and Peter J. Knowles, \textit{Fast Hartree-Fock theory using local density fitting approximations}, Mol. Phys. 102, 2311 (2004). \textbf{All publications resulting from DF-HF or DF-KS calculations should cite this work.}

16.1  Options

In this section the options for \texttt{HF} | \texttt{RHF} | \texttt{UHF} are described. For further options affecting Kohn-Sham calculations see section 17. For compatibility with previous \texttt{MOLPRO} versions, options can also be given on subsequent directives, as described in later sections.

16.1.1  Options to control HF convergence

\texttt{ACCU\{RACY\}=\texttt{accu}} \hspace{1cm} \text{Convergence threshold for the density matrix (square sum of the density matrix element changes). If } \texttt{accu}>1, \text{ a threshold of } 10^{-\texttt{accu}} \text{ is used. The default depends on the global ENERGY threshold, and the threshold is automatically tightened in geometry optimizations or frequency calculations (unless a tight threshold is given).}

\texttt{ENERGY=\texttt{thrden}} \hspace{1cm} \text{The convergence threshold for the energy. The default depends on the global ENERGY threshold.}
START=record  Record holding start orbitals.
SAVE|ORBITAL=record  Dump record for orbitals.
MAXIT=maxit  Maximum number of iterations (default 60)
SHIFTA|SHIFTC=shifta  Level shift for closed-shell orbitals in RHF (default −0.3) and α-spins orbitals in UHF (default 0).
SHIFTB|SHIFTO=shiftb  Level shift for open-shell orbitals in RHF and β-spin orbitals in UHF (default 0)
NITORD|NITORDER=nitord  Starting with iteration nitocc, the orbital occupation pattern is kept fixed: The orbitals are reordered after each iteration to obtain maximum overlap with the closed-shell/open-shell/virtual spaces from the previous iteration. This takes only effect after nitord iterations. The default depends on the quality of the starting guess.
NITSH|NITSHIFT=nitsh  If the iteration count is smaller than nitsh, the shifts are set to zero. The default depends on the quality of the starting guess.
NITCL|NITCLOSED=nitcl  If the iteration count is smaller than nitcl, only the closed-shell part of the Fock matrix is used (default nitcl=0). This option is left for compatibility purposes, it almost never helps.
NITOCC=nitocc  Starting with iteration nitocc the occupation pattern is kept fixed. The default depends on the quality of the starting guess.
NITORT|NITORTH=nitort  The orbitals are reorthonormalized after every nitort iterations. The default is nitort=10.

Note that in case of a restart the iteration count starts with 3.

16.1.2 Options for the diagonalization method

In calculations with very large basis sets, the diagonalization time becomes a significant fraction of the total CPU time. This can be reduced using the orbital rotation method as described in R. Polly, H.-J. Werner, F. R. Manby, and Peter J. Knowles, Mol. Phys. 102, 2311 (2004))

MINROT=minrot  If minrot≥0, the orbital rotation method is employed. Explicit diagonalization of the full Fock matrix is performed in the first minrot iterations and in the last iteration. If minrot=0, a default is used which depends on the starting guess.
NEXPR=nexpr  Number of terms used in the exponential expansion of the unitary orbital transformation matrix (default 4).
DEROT=nexpr  Energy gap used in the orbital rotation method. For orbitals within ±derot hartree of the HOMO orbital energy the Fock matrix is constructed and diagonalized (default 1.0)
JACOBI=jacobi  If nonzero, use Jacobi diagonalization.

16.1.3 Options for convergence acceleration methods (DIIS)

For more details, see IPOL directive.

IPTYP=iptyp  Interpolation type (default DIIS, see IPOL directive).
IPNIT|DIIS\_START=ipnit \hspace{1em} First iteration for DIIS interpolation.
IPSTEP|DIIS\_STEP=ipstep \hspace{1em} Iteration increment for DIIS interpolation.
MAXDIS|MAXDIIS=maxdis \hspace{1em} Max number of Fock matrices used in DIIS interpolation (default 10).

### 16.1.4 Options for integral direct calculations

DIRECT \hspace{1em} (logical). If given, do integral-direct HF.
THRMIN|THR\_DSCF\_MIN=value \hspace{1em} Final integral screening threshold for DSCF.
THRMAX|THR\_DSCF\_MAX=value \hspace{1em} Initial integral screening threshold for DSCF.
THRINT|THR\_DSCF=value \hspace{1em} Same as THR\_DSCF\_MIN.
PRESCREEN=value \hspace{1em} If nonzero, use density screening (default).
DISKSIZE=value \hspace{1em} Max disk size in Byte for semi-direct calculations (currently disabled).
BUFSIZE=value \hspace{1em} Max memory buffer size for semi-direct calculations (currently disabled).
THRDISK=value \hspace{1em} Threshold for writing integrals to disk (currently disabled).
PRINT\_DFOCK=value \hspace{1em} Print option for direct Fock matrix calculation.

### 16.1.5 Special options for UHF calculations

NATORB=record \hspace{1em} Save natural charge orbitals in given record.
UNOMIN=unomin \hspace{1em} Minimum occupation number for UNO-CAS (default 0.02)
UNOMAX=unomax \hspace{1em} Maximum occupation number for UNO-CAS (default 1.98)

### 16.1.6 Options for local density-fitting calculations


LOCFIT=locfit \hspace{1em} If nonzero, use local fitting for exchange. If > 1, also use local fitting for Coulomb (not recommended).
RDOM=locfit \hspace{1em} Radius for fitting domain selection in local fitting (default 5 bohr).
RDOMC=locfit \hspace{1em} Radius for fitting domain selection for core orbitas in local fitting (default RDOM).
DOMSEL=domesel \hspace{1em} Criterion for selecting orbital domains in local fitting (default 0.1).
16.1.7 Options for polarizabilities

POLARI=value
If nonzero, compute analytical dipole polarizabilities. See also the POLARI directive (section 16.8), which allows to specify various one-electron operators (by default, the dipole operator is used).

THRCPHF=thresh
Threshold for CPHF if polarizabilities are computed (default 1.d-6).

16.1.8 Printing options

PRINT|ORBPRINT=value
Number of virtual orbitals to be printed. If value=0, the occupied orbitals are printed.

DEBUG=value
Option for debug print.

16.2 Defining the wavefunction

The number of electrons and the total symmetry of the wavefunction are specified on the WF card:

WF.elec,sym,spin

where

elec is the number of electrons
sym is the number of the irreducible representation
spin defines the spin symmetry, \( spin = 2 \times S \) (singlet=0, doublet=1, triplet=2 etc.)

Note that these values take sensible defaults if any or all are not specified (see section 16.8). For example, \{rhf; wf,sym=N,spin=M\} gives the explicit values N for the symmetry and M for the spin of the wave function, but uses the default number of electrons.

16.2.1 Defining the number of occupied orbitals in each symmetry

OCC,n₁,n₂,...,n₈

To avoid convergence problems in cases with high symmetry, this card should be included whenever the occupation pattern is known in advance. \( n_i \) is the number of occupied orbitals in the irreducible representation \( i \). The total number of orbitals must be equal to \((\text{elec}+\text{spin})/2\) (see WF card).

16.2.2 Specifying closed-shell orbitals

CLOSED,n₁,n₂,...,n₈

This optional card can be used in open-shell calculations to specify the number of closed-shell orbitals in each symmetry. This makes possible to force specific states in the absence of an OPEN card.
16.2.3 Specifying open-shell orbitals

OPEN, orb₁.sym₁, orb₂.sym₂, ..., orbₙ.symₙ

This optional card can be used to specify the singly occupied orbitals. The number of singly occupied orbitals must be equal to spin, and their symmetry product must be equal to sym (see WF card). If the OPEN card is not present, the open shell orbitals are selected automatically. The algorithm tries to find the ground state, but it might happen that a wrong state is obtained if there are several possibilities for distributing the open shell electrons among the available orbitals. This can also be avoided using the CLOSED card. If orbᵢ.sym is negative, this orbital will be occupied with negative spin (only allowed in UHF).

16.3 Saving the final orbitals

ORBITAL, record.file
SAVE, record.file

The optimized orbitals, and the corresponding density matrix, fock matrix, and orbital energies are saved on record.file. SAVE is an alias for ORBITAL. If this card is not present, the defaults for record are:

- RHF: 2100
- UHF: 2200 (holds both α and β-spin orbitals and related quantities)

These numbers are incremented by one for each subsequent calculation of the same type in the same input. Note that this holds for the sequence number in the input, independently in which order they are executed (see section 4.3).

The default for file is 2.

16.4 Starting orbitals

The START directive can be used to specify the initial orbitals used in the SCF iteration. It is either possible to generate an initial orbital guess, or to start with previously optimized orbitals. Alternatively, one can also use a previous density matrix to construct the first fock operator.

If the START card is absent, the program tries to find suitable starting orbitals as follows:

First: Try to read orbitals from record specified on the ORBITAL or SAVE card or the corresponding default (see ORBITAL). All files are searched.

Second: Try to find orbitals from a previous SCF or MCSCF calculation. All files are searched.

Third: If no orbitals are found, the starting orbitals are generated using approximate atomic densities or eigenvectors of h (see below).

Since these defaults are usually appropriate, the START card is not required in most cases.
16.4.1 Initial orbital guess

An initial orbital guess can be requested as follows:

```
START,[TYPE=]option
```

The `option` keyword can be:

- **H0**
  - Use eigenvectors of $h$ (core Hamiltonian) as starting guess.

- **ATDEN**
  - Use natural orbitals of a diagonal density matrix constructed using atomic orbitals and atomic occupation numbers (default).

Note that it is also possible to use orbitals from previous (e.g., smaller basis set) calculations as starting orbitals (see section 16.4.2 below).

Example:

```
r=1.85,theta=104 !set geometry parameters
geometry={O; !z-matrix geometry input
  H1,O,r;
  H2,O,r,H1,theta}
basis=STO-3G !first basis set
hf !scf using STO-3G basis
basis=6-311G !second basis set
hf !scf using 6-311G basis set
```

The second calculation uses the optimized orbitals of the STO-3G calculation as starting guess. This is done by default and no `START` card is necessary. The explicit use of `START` and `SAVE` cards is demonstrated in the example in the next section.

The following input is entirely equivalent to the one in the previous section:

```
r=1.85,theta=104 !set geometry parameters
geometry={O; !z-matrix geometry input
  H1,O,r;
  H2,O,r,H1,theta}
basis=STO-3G !first basis set
hf !scf using STO-3G basis
start,atdens !use atomic density guess
save,2100.2 !save orbitals to record 2100.2
basis=6-311G !second basis set
hf !scf using 6-311G basis set
start,2100.2 !start with orbitals from the previous STO-3G calculation.
save,2101.2 !save optimized orbitals to record 2101.2
```

Beware, however, that STO-3G is a very poor basis set and usually gives very bad starting vectors. This technique is best used in combination with reasonable small basis sets (e.g., cc-pVDZ or def2-SVP) or minimal basis sets with a proper representation of the occupied atomic orbitals (e.g, 6-31G or MINAO/MINAO-PP):
memory, 50, m

! CuO2(NH3)4
geometry={
N -2.244097 0.000000 -0.017684
N 1.111652 -1.671116 -0.178974
N 1.111652 1.671116 -0.178974
N -0.306059 0.000000 -2.311080
Cu -0.179579 0.000000 -0.290548
O -0.184327 0.000000 1.594789
O 1.053213 0.000000 2.103145
H -2.331519 0.000000 1.002818
H 0.614110 0.000000 -2.753879
H -0.793743 0.815054 -2.687415
H -0.793743 -0.815054 -2.687415
H -2.764729 0.814552 -0.345484
H -2.764729 -0.814552 -0.345484
H 0.635193 2.543632 0.052739
H 0.635193 -2.543632 0.052739
H 1.616225 1.397092 0.672915
H 1.616225 -1.397092 0.672915
H 1.809254 1.910324 -0.883324
H 1.809254 -1.910324 -0.883324
H 1.616225 1.397092 0.672915
H 1.616225 -1.397092 0.672915
H 1.809254 1.910324 -0.883324
H 1.809254 -1.910324 -0.883324
}

wf, charge=1, spin=2

! select all-electron minimal basis sets for H, N, O and ECP10 based basis
! set for Cu; using MINAO-PP here instead of MINAO allows us to project
! the obtained wave function on the cc-pVTZ-PP basis later on.
basis=MINAO, Cu=MINAO-PP

! Run HF to get an initial guess for the valence electronic
! structure. The level shifts damp and stabilize the convergence.
{rhf; shift,-1.0,-0.5; save,2100.2}

! select the actual basis set and start RHF with projected wave function
! from MINAO basis. nitord=1 asks RHF to reorder orbitals in each
! iteration to maximize overlap with the closed and active space
! from the last iteration.
basis=AVTZ, Cu=VTZ-PP, H=VDZ(p)
{df-rhf, nitord=1; start,2100.2}

http://www.molpro.net/info/current/examples/minao_startorb.com

16.4.2 Starting with previous orbitals

START, [RECORD=] record_file, [specifications]

reads previously optimized orbitals from record record on file file. Optionally, a specific orbital
set can be specified as described in section 4.11.

The specified dump record may correspond to a different geometry, basis set, and/or symmetry
than used in the present calculation. Using starting orbitals from a different basis set can be
useful if no previous orbitals are available and the ATDENS option cannot be used (see above).

The following example shows how to change the symmetry between scf calculations. Of course,
this example is quite useless, but sometimes it might be easier first to obtain a solution in higher
symmetry and then convert this to lower symmetry for further calculations.
16.4.3 Starting with a previous density matrix

START,DENSITY=record.file.[specifications]

A density matrix is read from the given dump record and used for constructing the first fock matrix. A specific density matrix can be specified as described in section 4.11. It is normally not recommended to use the DENSITY option.

16.5 Rotating pairs of orbitals

ROTATE,orb1.sym,orb2.sym,angle

Performs a $2 \times 2$ rotation of the initial orbitals $orb_1$ and $orb_2$ in symmetry $sym$ by $angle$ degrees. With $angle=0$ the orbitals are exchanged. See MERGE for other possibilities to manipulate orbitals. In UHF, by default only the $\beta$-spin orbitals are rotated. The initial $\alpha$-spin orbitals can be rotated using

ROTATEA,orb1.sym,orb2.sym,angle

In this case ROTATEB is an alias for ROTATE.
16.6 Using additional point-group symmetry

Since MOLPRO can handle only Abelian point-groups, there may be more symmetry than explicitly used. For instance, if linear molecules are treated in \( C_{2v} \) instead of \( C_{\infty v} \), the \( \delta_{[x^2-y^2]} \) orbitals appear in symmetry 1 \( (A_1) \). In other cases, a linear geometry may occur as a special case of calculations in \( C_3 \) symmetry, and then one component of the \( \pi \)-orbitals occurs in symmetry 1 \( (A') \). The program is able to detect such hidden “extra” symmetries by blockings in the one-electron Hamiltonian \( h \) and the overlap matrix \( S \). Within each irreducible representation, an “extra” symmetry number is then assigned to each basis function. These numbers are printed at the end of the integral output. Usually, the extra symmetries are ordered with increasing \( l \)-quantum number of the basis functions. This information can be used to determine and fix the extra symmetries of the molecular orbitals by means of the \texttt{SYM} command.

\texttt{SYM,irrep,sym(1),sym(2),\ldots,sym(n)}

\( \text{sym}(i) \) are the extra symmetries for the first \( n \) orbitals in the irreducible representation \( \text{irrep} \). For instance, if you want that in a linear molecule the orbitals 1.1 to 3.1 are \( \sigma \) and 4.1, 5.1 \( \delta \), the \texttt{SYM} card would read (calculation done with X,Y as symmetry generators):

\texttt{SYM, 1, 1, 1, 1, 2, 2}

If necessary, the program will reorder the orbitals in each iteration to force this occupation. The symmetries of occupied and virtual orbitals may be specified. By default, symmetry contaminations are not removed. If \( \text{irrep} \) is set negative, however, symmetry contaminations are removed. Note that this may prevent convergence if degenerate orbitals are present.

16.7 Expectation values

\texttt{EXPEC,oper_1,oper_2,\ldots,oper_n}

Calculates expectation values for one-electron operators \( \text{oper}_1, \text{oper}_2, \ldots, \text{oper}_n \). See section [6.13] for the available operators. By default, the dipole moments are computed. Normally, it is recommended to use the \texttt{GEXPEC} directive if expectation values for other operators are of interest. See section [6.13] for details.

16.8 Polarizabilities

\texttt{POLARIZABILITY[,oper_1,oper_2,\ldots,oper_n]}

Calculates polarizabilities for the given operators \( \text{oper}_1, \text{oper}_2, \ldots, \text{oper}_n \). See section [6.13] for the available operators. If no operators are specified, the dipole polarizabilities are computed.

Presently, this is working only for closed-shell without direct option.

The polarizabilities are stored in the variables \texttt{POLXX}, \texttt{POLXY}, \texttt{POLXZ}, \texttt{POLYY}, \texttt{POLYZ}, \texttt{POLZZ}.

16.9 Miscellaneous directives

All commands described in this section are optional. Appropriate default values are normally used.
16.9.1 Level shifts

SHIFT,shifta,shiftb

A level shift of shifta and shiftb hartree for $\alpha$- and $\beta$-spin orbitals, respectively, is applied. This can improve convergence, but has no effect on the solution. shifta = $-0.2$ to $-0.3$ are typical values. The defaults are shifta = 0 and shiftb = $-0.3$ in closed and open-shell calculations, respectively, and shiftb = 0.

Applying large negative level shifts like \{rhf; shift, $-1.0, -0.5$\} will often stabilize convergence at the expense of making it somewhat slower. See section 16.10.

16.9.2 Maximum number of iterations

MAXIT,maxit

sets the maximum number of iterations to maxit. The default is maxit = 60.

16.9.3 Convergence threshold

ACCU,accu

This threshold applies to the square sum of the density matrix element changes (same as option ACCU). If accu $> 1$, a threshold of $10^{-accu}$ is used. The default depends on the global ENERGY threshold, and the threshold is automatically tightened in geometry optimizations or frequency calculations (unless a tight threshold is given).

16.9.4 Sanity check on the energy

NOENEST

This disables the sanity check on the energy even if the energy value is unreasonable. Otherwise, the energy will be automatically checked by default.

16.9.5 Print options

ORBPRINT,print,test

This determines the number of virtual orbitals printed at the end of the calculation. By default, print = 0, i.e., only the occupied orbitals are printed. print = $-1$ suppresses printing of orbitals entirely. test = 1 has the additional effect of printing the orbitals after each iteration.

16.9.6 Interpolation

IPOL,iptyp,ipnit,ipstep,maxdis

This command controls iterative subspace interpolation. iptyp can be:

DIIS  direct inversion of the iterative subspace. This is the default and usually yields fast and stable convergence.

KAIN  Krylov-subspace accelerated inexact newton. A method similar to DIIS.
NONE

No interpolation.

\textit{ipnit} is the number of the iteration in which the interpolation starts (default: as soon as possible). \textit{ipstep} is the iteration increment between interpolations (default: 1, i.e., every iteration). \textit{maxdis} is the maximum dimension of the DIIS matrix (default 10). \textit{iptyp} and \textit{maxdis} can also be set as options. E.g.,

\{\texttt{rhf,maxdis=20,iptyp='DIIS'; shift,-1.0,-0.5}\}

16.9.7 Reorthonormalization of the orbitals

\texttt{ORTH,nitort}

The orbitals are reorthonormalized after every \texttt{nitort} iterations. The default is \texttt{nitort}= 10.

16.9.8 Direct SCF

\texttt{DIRECT,\_\_\_\_options}

If this card is present, the calculation is done in direct mode. See section \ref{sec:gdirect} for options. Normally, it is recommended to use the global \texttt{GDIRECT} command to request the direct mode. See section \ref{sec:gdirect} for details.

16.10 Handling difficult cases: When SCF does not converge

General suggestions:

\begin{itemize}
  \item Carry out convergence experiments with a small but reasonable basis set (e.g., cc-pVDZ, def2-SVP, aug-cc-pVDZ, ASVP). STO-3G is \textit{not} a reasonable basis set.
\end{itemize}

Before you start you should check:

\begin{itemize}
  \item Whether your geometry is sensible (e.g., look for Angstrom/Bohr conversion issues). Note that Molpro prints bond distances in both Angstroms and atomic units at the top of an output.
  \item Whether you have selected the correct electronic state (spin and symmetry). Molpro tries to guess spatial symmetries of open-shell compounds automatically if none are provided. However, the guess is not always right. In such a case you need to give the symmetry manually (in the simplest case as \texttt{wf,sym=N,spin=M}. See section \ref{sec:spin}). Molpro does \textit{not} attempt to guess the spin state of the input compound automatically; it defaults to spin=0 for systems with even numbers of electrons and spin=1 for odd-numbered species.
\end{itemize}

If convergence problems persist, the following techniques can be attempted:

Hartree-Fock options & Small-basis initial guess:

\begin{itemize}
  \item \textbf{Level shifts}: Adding a level shift like \{\texttt{rhf; shift,-1.0,-0.5}\} stabilizes the current RHF solution against changes and leads to smoother (but slower) convergence. That should be your first try; it is often sufficient.
\end{itemize}
• **Occupation freezing:** The option \{rhf,nitord=N\} can be used to freeze orbital occupations at iteration N. When the programs emits warnings about reassigned orbital occupations, you could try to freeze the occupations only later (give a higher N) or earlier (give a smaller N).

By freezing the occupation pattern you tell the RHF program to try to lock on whatever solution it currently is pursuing. This often helps if multiple RHF solutions with similar energies are present and otherwise the program would oscillate between some of them.

Note that \{rhf,nitord=1\} will tell RHF to lock onto the initial occupation; if combined with orbital rotation or advanced initial guesses this can often be used to converge to specific solutions (e.g., some excited states).

• **Minimal-basis SCF guess:** Try to obtain a Hartree-Fock solution with a minimal-basis AO set first and to use this as initial guess for the actual Hartree-Fock calculation. For this purpose we provided the basis set definition "MINAO" (to complement cc-pVnZ basis sets) and "MINAO-PP" (to complement cc-pVnZ-PP sets with ECPs). See section [16.4.1] for an example. These sets simply consist of the AO part of the cc-pVTZ or cc-pVTZ-PP basis sets, stripped of all their polarization functions. Since a minimal basis has fewer degrees of freedom than a real basis set, convergence is often easier, and it can still provide reasonable guess for the valence electronic structure.

Note: The MINAO basis sets are very small, so conventional Hartree-Fock (in integral-direct mode if necessary) is typically much faster than density-fitting Hartree-Fock.

• **Increasing the DIIS dimension:** In rare cases \{rhf,maxdis=30,iptyp='DIIS',nitord=20; shift,-1.0,-0.5\} can find solutions which are not found in the standard settings. Usually increasing the DIIS dimension beyond 10 (the default) just slows down convergence. It is also worthwhile to try a variation of DIIS known as KAIN (Krylov-subspace accelerated inexact Newton): \{rhf,maxdis=10,iptyp='KAIN',nitord=10; shift,-1.0,-0.5\} which sometimes shows different convergence behavior than straight DIIS.

Cationic or Anionic initial guess:

• If molecule X does not converge, it might still be possible to converge X^+ (X^{2+}, ..) and use this as initial guess for the actual computation. Particularly if X^+ is a closed-shell compound this will often work. If using this technique, you need to be careful about the final state you arrive in. Because your initial guess is biased, the X calculation might converge to an excited state.

Density-functional initial guess:

• For transition metals and transition states sometimes DFT methods show better convergence behavior than RHF. You might perform a DFT calculation (possibly with a smaller basis set) and use it as initial guess for the SCF. E.g.,

{df-rks,b-lyp; coarsegrid; save,2100.2}
{df-rhf,nitord=1; orbital,2100.2}

If all else fails: Use the MCSCF program. The MCSCF program uses an advanced orbital optimization algorithm which is much more robust than the SCF method, and which can converge almost everything you give to it (but it is often slower and sometimes locks on an excited state if started from an atomic density guess). MCSCF can also calculate Hartree-Fock solutions if used with suitable input cards.
16.11 Advanced use: Core-excited states

Some kinds of excited or higher ionized states can be calculated using a so-called delta-SCF procedure. Here the excitation/ionization energy is obtained as difference of the SCF solutions for the ground state and the excited/ionized state. If the excited state is reasonably well described by a single determinant, this procedure is normally quite accurate.

The example
This example calculates the N 1s core-hole binding energy of pyridine using a delta-SCF procedure. It calculates a SCF solution in the ground state, then in the core-excited state, and reports the difference. The example shows how to obtain the core-excited state of a core of your choice.

memory,20,m;
geometry=pyridine.xyz

we use default basis sets for all atoms except the one we wish to calculate the core hole of, in this case N is. For this atom, we uncontract the s and p functions of the basis to give the core hole more opportunities for relaxation.

Notes:
- Uncontracting the complete basis would of course also work, but might be more expensive
- For correlated calculations, you would need additional tight correlation functions for the hole (e.g., use a cc-pwCVnZ basis on the affected atom and cc-pVTZ on the rest)

basis=
  default,def2-TZVPP
  sp,N,def2-TZVPP ! no "c;" following -- uncontracted.
  df,N,def2-TZVPP;c; ! use d and f functions with contractions.
}

reference calculation, normal DFT. We also uncontract the fitting basis to fit the core region more accurately.
(df-rks,pbe,df_basis=def2-tzvpp(u))
ENORMAL = ENERGY ! remember energy of ground state calculation.

localize orbitals. This isolates the cores of the individual atoms also in the case of degeneracy. And, in particular, it shows us which orbital is the N 1s we are looking for. It comes out as orbital 1.1.

{df-rks,pbe,df_basis=def2-tzvpp(u),nitord=1;
   ! in the program, closed-shell orbitals always have lower numbers
   ! than open-shell orbitals. In order to get the core hole state, we need to exchange the localized N1s orbital (1.1) with whatever came out at the highest orbital number (21.1) before. (Because the latter one will be considered as singly-occupied. If we would not use localized orbitals, 21.1 would be the HOMO).
   rotate,1.1,21.1; ! exchange orbitals 1.1 and 21.1
   orbital,2101.2; ! use the localized orbitals as input
   wf,spin=1,charge=1 ! one open-shell orbital (implicitly 21.1)
}
EWITH_HOLE = ENERGY

run population analysis again to see if we arrived at the right state. This should be indicated by an active orbital occupation of about 1.0 on the N 1s orbital.

{ibba}

show the result, converted to electron volts.
(table,(EWITH_HOLE-ENORMAL)*toev

http://www.molpro.net/info/current/examples/pyridine-N1s-core-hole.com
shows how to use the delta-SCF procedure to calculate the N 1s core binding energy in pyridine, by employing localized orbitals and moving them to the HOMO position using a ROTATE card (Sec. 16.5). In the core-excited state calculation, SCF is prevented from collapsing to the ground state by using the option NITORD=1 (Sec. 16.1), which asks SCF to lock onto the input solution.
Density-functional theory calculations may be performed using one of the following commands:

- **DFT**
  - to calculate functional of a previously computed density.
- **RKS** or **RKS-SCF**
  - calls the spin-restricted Kohn-Sham program. **KS** and **KS-SCF** are aliases for **RKS**.
- **UKS** or **UKS-SCF**
  - calls the spin-unrestricted Kohn-Sham program

Each of these commands may be qualified with the key-names of the functional(s) which are to be used, and further options:

```
command, key1, key2, key3, ..., options
```

If no functional keyname is given, the default is **LDA** (see below). Following this command may appear directives specifying options for the density-functional modules (see section 17.2) or the Hartree-Fock program (see section 16.1).

On completion of the functional evaluation, or self-consistent Kohn-Sham calculation, the values of the individual functionals are stored in the MOLPRO vector variable **DFTFUNS**; the total is in **DFTFUN**, and the corresponding individual functional names in **DFTNAME**.

Energy gradients are available for self-consistent Kohn-Sham calculations.

Density fitting can be used for closed and open-shell spin-restricted KF and is invoked by a prefix **DF-** (**DF-KS** or **DF-RKS**, see section 15). For UKS, only Coulomb fitting is possible (**CF-UKS**). Density fitting is highly recommended (unless explicit symmetry handling is required), as the induced errors are negligible and it offers **massive** speed increases, particularly for pure functionals. For details see R. Polly, H.-J. Werner, F. R. Manby, and Peter J. Knowles, *Fast Hartree-Fock theory using local density fitting approximations*, Mol. Phys. **102**, 2311 (2004). *All publications resulting from DF-HF or DF-KS calculations should cite this work.*

Normally, sensible defaults are used to define the integration grid. The accuracy can be controlled using options as described in section 17.1 or directives as described in section 17.2. More control is provided by the **GRID** command, as described in section 17.3.

### 17.1 Options

The following options may be specified on the **KS** or **UKS** command lines:

- **GRID=target**
  - Specifies the grid target accuracy (per atom). The default is 1.d-6 unless this has been modified using a global **THRESH, GRID** option.
- **COARSE** (logical)
  - If **true**, perform initial iterations with a coarser grid. Default is **false**.
- **GRIDMAX=gridmax**
  - In the initial iterations, the grid accuracy is \( \min(\text{gridmax}, \text{target} \times \text{coarsefac}) \) (only if **COARSE** is set).
- **COARSEFAC=coarsefac**
  - Factor for initial grid accuracy (see above). The default is 1000.
- **GRIDGRAD=0 or 1**
  - Defines whether grid weight derivatives are included in analytical gradient calculations (default: 1). Disabling these can improve convergence in geometry optimizations.
DFTFAC = \{fac1,fac2,\ldots\}  Factors for each functional. The number of given values must agree with the number of functionals.

EXFAC = factor  Fraction of exact exchange added to the functional. The default depends on the functional.

TOLORB = value  Threshold for orbital screening (default depends on energy threshold).

In addition, all options valid for HF (see section [16.1] can be given.

17.2 Directives

The following options may be used to control the operation of the DFT modules. In the Kohn-Sham case, these may come in any order before or after directives for the SCF program as described in Section [16]

17.2.1 Density source (DENSITY, ODENSITY)

DENSITY.orbc.filec, \ldots ODENSITY.orbo.fileo, \ldots

For non-self-consistent DFT calculations, specifies the source of the density matrix. The total density is read from orbc.filec, with further options specifying density sets in the standard way as described in Section [4.1]. ODENSITY can be used to specify the spin density. The defaults are the densities last written by an SCF or MCSCF program.

17.2.2 Thresholds (DFTTHRESH)

DFTTHRESH, key1=value1, key2=value2 \ldots

Sets various truncation thresholds. key can be one of the following.

TOTAL  Overall target accuracy (per atom) of density functional. Defaults to the value of the global threshold GRID or the value specified by option GRID. For proper use of this threshold, other thresholds should be left at their default value of zero.

ORBITAL  Orbital truncation threshold.

DENSITY  Density truncation threshold.

FOCK  Fock matrix truncation threshold.

17.2.3 Exact exchange computation (EXCHANGE)

EXCHANGE, factor

For Kohn-Sham calculations, compute exchange energy according to Hartree-Fock formalism and add the contribution scaled by factor to the fock matrix and the energy functional. Otherwise, the default is factor = 0, i.e., the exchange is assumed to be contained in the functional, and only the Coulomb interaction is calculated explicitly.

DFTFACTOR, fac1, fac2, \ldots

Provide a factor for each functional specified. The functionals will be combined accordingly. By default, all factors are one.
17.2.4 Double-hybrid functionals \((\text{DH, DSDH})\)

\DH, \ax, \ac

initiates a double-hybrid calculation (Ref. [1]) where \(\ax\) is the fraction of HF exchange and \(\ac\) is the fraction of MP2 correlation. A self-consistent KS calculation is performed with functional
\[
E^{\text{HF}}_x + (1 - \ax)E^{\text{DFT}}_x[\rho] + (1 - \ac)E^{\text{DFT}}_c[\rho].
\]
One then needs to call the MP2 program to add the MP2 contribution \(\ac E^{\text{MP2}}_c\). If \(\ac\) is not given, \(\ac = \ax^2\) is assumed, according to Ref. [2].

\DSDH, \ax, \ac

initiates a density-scaled double-hybrid calculation (Ref. [2]) where \(\ax\) is the fraction of HF exchange and \(\ac\) is the fraction of MP2 correlation. A self-consistent KS calculation is performed with functional
\[
E^{\text{HF}}_x + (1 - \ax)E^{\text{DFT}}_x[\rho] + E^{\text{DFT}}_c[\rho] - \ac E^{\text{DFT}}_c[\rho_{\text{scaled}}],
\]
where \(\rho_{\text{scaled}}\) is the scaled density. In the case of meta-GGA functionals, the kinetic energy density \(\tau\) is also scaled, according to Ref. [3]. One then needs to call the MP2 program to add the MP2 contribution \(\ac E^{\text{MP2}}_c\). If \(\ac\) is not given, \(\ac = \ax^2\) is assumed, according to Ref. [2].

Example of input for B2-PLYP calculation (Ref. [1]):
\[
\{\text{ks}, \text{b}, \text{lyp}; \text{dh}, 0.53, 0.27;\}
\]
mp2;

Example of input for 1DH-BLYP calculation (Ref. [2]):
\[
\{\text{ks}, \text{b}, \text{lyp}; \text{dh}, 0.65;\}
\]
mp2;

Example of input for DS1DH-TPSS calculation (Ref. [3]):
\[
\{\text{ks}, \text{tpss}; \text{dsdh}, 0.725;\}
\]
mp2;

Unrestricted calculations \((\text{uks, ump2})\) can also be done.

References:

17.2.5 Rangehybrid methods \((\text{RANGEHYBRID})\)

For coupling of short-range (sr-)DFT with long-range (lr-)ab-initio methods, one first has to specify the coupling parameter \(\mu\) in the sr interelectronic interaction \(\sum_{i<j} \text{erf}(\mu r_{ij})/r_{ij}\); this can be done by setting a variable (e.g. \mu = 0.5). As a next step, long-range ERIs have to be calculated by calling the integral program (e.g. \text{int}; \text{erf}, \mu;).

Then sr-DFT/lr-HF calculations can be performed by calling the RKS program with the additional subcommand rangehybrid. Available short-range functionals are \text{exerf} and \text{ecerf} for sr-LDA, and \text{exerfpbe} and \text{ecerfpbe} for sr-PBE; as usual, the functionals have to be specified after the \text{rks} command (e.g. \text{rks}, \text{exerf}, \text{ecerf};). The underlying short-range LDA correlation functional is that of S. Paziani, S. Moroni, P. Gori-Giorgi, G.B. Bachelet, Phys. Rev. B 73, 155111 (2006).

Finally, sr-DFT/lr-post-HF calculations can be done by adding, within a call of the chosen post-HF program, two subcommands: \text{srxcdft} followed by the desired short-range functionals (e.g. \text{srxcdft}, \text{exerf}, \text{ecerf};), and \text{dftden} followed by the record number from which the density for the sr functionals is taken. Implementations are available for \text{ci}, \text{mp2}, \text{ccsd}, \text{ccsd(t)}, and the corresponding local MP2 and CC methods w/wo density-fitting.
17.2.6 Exchange-correlation potential (POTENTIAL)

POTENTIAL, rec.fil

For stand-alone DFT calculations, compute exchange-correlation potential pseudo-matrix elements, defined formally as the differential of the sum of all specified functionals with respect to elements of the atomic orbital density matrix. The matrix is written to record rec on file fil.

17.2.7 Grid blocking factor (DFTBLOCK)

DFTBLOCK, nblock

Respecify the number of spatial integration points treated together as a block in the DFT integration routines (default 128). Increasing nblock may enhance efficiency on, e.g., vector architectures, but leads to increased memory usage.

17.2.8 Dump integrand values (DFTDUMP)

DFTDUMP, file, status

Write out values of the integrand at grid points to the file file. The first line of file contains the number of functional components; there then follows a line for each functional giving the input key of the functional. Subsequent lines give the functional number, cartesian coordinates, integrand value and integration weight with Fortran format (I2,3F15.10,F23.15).

17.2.9 Asymptotic correction for xc-potentials (ASYMP)

ASYMP, shift, α, β, b

Activates the gradient-regulated asymptotic correction (GRAC) approach for exchange-correlation potentials of Grüning et al. (J. Chem. Phys. 114, 652 (2001)). The user has to supply a shift parameter (Δxc) for the bulk potential which should approximate the difference between the HOMO energy (εHOMO) obtained from the respective standard Kohn-Sham calculation and the (negative) ionisation potential of the monomer (IP):

$$\Delta_{xc} = \varepsilon_{HOMO} - (-IP)$$

(1)

This method accounts for the derivative discontinuity of the exact xc-potential and that is missing in approximate ones. The parameters α and β determine the interpolation function (see Eq. (2.3) in the above reference) and are set to α = 0.5 and β = 40 by default, respectively. The parameter b is the parameter of the asymptotic xc-potential from van Leeuwen and Baerends (Phys. Rev. A 49, 2421 (1994), Eqns. (54,55)) and is set to b=0.05 by default.

In case of gradient or laplacian functionals the modified GRAC scheme of Bast et al. (Chem. Phys. Chem. 9, 445 (2008)) is used.

If shift is set to zero in the input the program will estimate the ionisation energy from the HOMO energy during the SCF (as soon as the HOMO energy is converged to a given threshold) and then sets the bulk shift automatically. This is done by using a linear fit of DFT HOMO energies to ionisation energies calculated with the ΔSCF method for a range of molecules (see also S. Hirata et al., J. Phys. Chem. A, 107, 10154 (2003)).
17.3 Numerical integration grid control (GRID)

Density functionals are evaluated through numerical quadrature on a grid in three-dimensional space. Although the sensible defaults will usually suffice, the parameters that define the grid can be specified by using the GRID top-level command, which should be presented before the DFT or KS commands that will use the grid. Alternatively, GRID and its subcommands can be presented as directives within the KS program.

GRID, orb.file, status

The integration grid is stored on record orb.file (default 1800.2). The information on disk consists of two parts: the parameters necessary to define the grid, and a cache of the evaluated grid points and weights. The latter is flagged as ‘dirty’ whenever any parameters are changed, and whenever the geometry changes; if the cache is dirty, then when an attempt is made to use the grid, it will be recalculated, otherwise the cached values are used.

If status is OLD, an attempt to restore the grid from a previous calculation is performed; effectively, the old grid provides a template of parameters which can be adjusted using the parameter commands described below. If status is NEW, the grid is always created with default parameters. If status is UNKNOWN (the default), a new grid is created either if record orb.file does not exist; otherwise the old grid is used.

The GRID command may be followed by a number of parameter-modifying subcommands. The currently implemented default parameters are equivalent to the following input commands.

```
GRIDTHRESH, 1e-5, 0, 0
RADIAL, LOG, 3, 1.0, 20, 25, 25, 30
ANGULAR, LEBEDEV, 0.0, 0.0
LMIN, 0, 0, 0, 0
LMAX, 53, 53, 53, 53
VORONOI, 10
GRIDSAVE
GRIDSYM
```

17.3.1 Target quadrature accuracy (GRIDTHRESH)

GRIDTHRESH, acc, accr, acca

Specify the target accuracy of integration. Radial and angular grids are generated adaptively, with the aim of integrating the Slater-Dirac functional to the specified accuracy. acc is an overall target accuracy, and is the one that should normally be used; radial and angular grid target accuracies are generated algorithmically from it. However, they can be adjusted individually by specifying accr and acca respectively.

17.3.2 Radial integration grid (RADIAL)

RADIAL, method, m_r, scale, n_0, n_1, n_2, n_3

Specify the details of the radial quadrature scheme. Four different radial schemes are available, specified by method = EM, BECKE, AHLRICHS or LOG, with the latter being the default.

EM is the Euler-Maclaurin scheme defined by C. W. Murray, N. C. Handy and G. J. Laming, Mol. Phys. 78 (1993) 997. m_r, for which the default value is 2, is defined in equation (6) of the above as

\[ r = \alpha \frac{x^{m_r}}{(1-x)^{m_r}} \]  

(2)
whilst \( \text{scale} \) (default value 1) multiplied by the Bragg-Slater radius of the atom gives the scaling parameter \( \alpha \).

LOG is the scheme described by M. E. Mura and P. J. Knowles, J. Chem. Phys. 104 (1996) 9848. It is based on the transformation

\[
r = -\alpha \log_e (1 - x^{m_r}) ,
\]

with \( 0 \leq x \leq 1 \) and simple Gauss quadrature in \( x \)-space. The recommended value of \( m_r \) is 3 for molecular systems, giving rise to the Log3 grid; \( m_r=4 \) is more efficient for atoms. \( \alpha \) is taken to be \( \text{scale} \) times the recommended value for \( \alpha \) given by Mura and Knowles, and \( \text{scale} \) defaults to 1.

BECKE is as defined by A. D. Becke, J. Chem. Phys. 88 (1988) 2547. It is based on the transformation

\[
r = \alpha \frac{(1+x)}{(1-x)} ,
\]

using points in \( -1 \leq x \leq +1 \) and standard Gauss-Chebyshev quadrature of the second kind for the \( x \)-space quadrature. Becke chose his scaling parameters to be half the Bragg-Slater radius except for hydrogen, for which the whole Bragg-Slater radius was used, and setting \( \text{scale} \) to a value other than 1 allows a different \( \alpha \) to be used. \( m_r \) is not necessary for this radial scheme.

AHLRICHS is the radial scheme defined by O. Treutler and R. Ahlrichs, J. Chem. Phys. 102 (1995) 346. It is based on the transformation their M4 mapping

\[
r = \frac{\alpha}{\log_2 2} \left( \frac{2}{1-x} \right) ,
\]

with using standard Gauss-Chebyshev quadrature of the second kind for the \( x \)-space integration. \( m_r \) is not necessary for this radial scheme.

\( n_0, n_1, n_2, n_3 \) are the degrees of quadrature \( n_r \) (see equation (3) of Murray et al.), for hydrogen/helium, first row, second row, and other elements respectively.

accr as given by the THR command specifies a target accuracy; the number of radial points is chosen according to a model, instead of using an explicit \( n_i \). The stricter of \( n_i \), accr is used, unless either is zero, in which case it is ignored.

**17.3.3 Angular integration grid (ANGULAR)**

\text{ANGULAR, method, accr, crowd}

\text{LMIN, } l_{\text{min}}^0, l_{\text{min}}^1, l_{\text{min}}^2, l_{\text{min}}^3

\text{LMAX, } l_{\text{max}}^0, l_{\text{max}}^1, l_{\text{max}}^2, l_{\text{max}}^3

Specify the details of the angular quadrature scheme. The default choice for \text{method} is LEBEDEV (ie. as in A. D. Becke, J. Chem. Phys. 88 (1988) 2547) which provides angular grids of octahedral symmetry. The alternative choice for \text{method} is LEGENDRE which gives Gauss-Legendre quadrature in \( \theta \) and simple quadrature in \( \phi \), as defined by C. W. Murray, N. C. Handy and G. J. Laming, Mol. Phys. 78 (1993) 997.

Each type of grid specifies a family of which the various members are characterized by a single quantum number \( l \); spherical harmonics up to degree \( l \) are integrated exactly. \( l_{\text{min}}^i \) and \( l_{\text{max}}^i \), \( i = 0, 1, 2, 3 \) specify allowed ranges of \( l \) for H–Be, B–Ca, Sc–Ba, and La– respectively. The \( l_{\text{min}}^i \) are
further moderated at run time so that for any given atom they are not less than \(2i+4\) or twice the maximum angular momentum of the basis set on the atom; this constraint can be overridden by giving a negative value in \(\text{LMIN}\), and in this case just its absolute value will be used as the lower bound. For the Lebedev grids, if the value of \(l\) is not one of the set implemented in \text{MOLPRO} (3, 5, 7, 9, 11, 13, 15, 17, 19, 23, 29, 41, 47, 53), then \(l\) is increased to give the next largest angular grid available. In general, different radial points will have different \(l\), and in the absence of any moderation described below, will be taken from \(l_{i}^{\text{max}}\).

crowd is a parameter to control the reduction of the degree of quadrature close to the nucleus, where points would otherwise be unnecessarily close together; larger values of crowd mean less reduction thus larger grids. A very large value of this parameter, or, conventionally, setting it to zero, will switch off this feature.

acca is a target energy accuracy. It is used to reduce \(l\) for a given radial point as far as possible below \(l_{i}^{\text{max}}\) but not lower than \(l_{i}^{\text{max}}\). The implementation uses the error in the angular integral of the kernel of the Slater-Dirac exchange functional using a sum of approximate atomic densities. If acca is zero, the global threshold is used instead, or else it is ignored.

### 17.3.4 Atom partitioning of integration grid (VORONOI)

\text{VORONOI} \(m_{\mu}\)

Controls Becke-V oronoi partitioning of space. The algorithm of C. W. Murray, N. C. Handy and G. J. Laming, Mol. Phys. 78 (1993) 997 is used, with \(m_{\mu}\) defined by equation (24). The default value is 10.

### 17.3.5 Grid caching (GRIDSAVE, NOGRIDSAVE)

\text{NOGRIDSAVE}

disables the disk caching of the grid, i.e., forces the recalculation of the grid each time it is needed.

\text{GRIDSAVE}

forces the use of a grid cache where possible.

### 17.3.6 Grid symmetry (GRIDSYM, NOGRIDSYM)

\text{NOGRIDSYM}

switches off the use of symmetry in generating the integration grid, whereas

\text{GRIDSYM}

forces the use of any point-group symmetry.

### 17.3.7 Grid printing (GRIDPRINT)

\text{GRIDPRINT},key=value, ...

controls printing of the grid, which by default is not done. At present, the only possible value for key is \text{GRID}, and value should be specified as an integer. \text{GRID}=0 causes the total number of integration points to be evaluated and reported; \text{GRID}=1 additionally shows the number of points on each atom; \text{GRID}=2 causes the complete set of grid points and weights to be printed.
17.4 Density Functionals

Widely used functional combinations can be specified via convenient keywords. These can be entered, for example via \{df-rks,pbe\} (do a single KS calculation with PBE) or \{dfunc,pbe\} (which will instruct all following KS calculations to use PBE by default). The following table lists the defined alias density functional combinations:
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<th>alias</th>
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<th>Ref</th>
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<td>DIRAC LYP VWN5</td>
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</table>
17.4.1 Technical definitions of density functional inputs

In the following, $\rho_\alpha$ and $\rho_\beta$ are the $\alpha$ and $\beta$ spin densities; the total spin density is $\rho$;

The gradients of the density enter through

$$\sigma_{\alpha\alpha} = \nabla\rho_\alpha \cdot \nabla\rho_\alpha, \quad \sigma_{\beta\beta} = \nabla\rho_\beta \cdot \nabla\rho_\beta, \quad \sigma_{\alpha\beta} = \nabla\rho_\alpha \cdot \nabla\rho_\beta,$$

$$\sigma = \sigma_{\alpha\alpha} + \sigma_{\beta\beta} + 2\sigma_{\alpha\beta}.$$

(6)

$$\chi_\alpha = \sqrt{\sigma_{\alpha\alpha}/\rho_\alpha^{4/3}}, \quad \chi_\beta = \sqrt{\sigma_{\beta\beta}/\rho_\beta^{4/3}}.$$  

(7)

$$\upsilon_\alpha = \nabla^2 \rho_\alpha, \quad \upsilon_\beta = \nabla^2 \rho_\beta, \quad \upsilon = \upsilon_\alpha + \upsilon_\beta.$$

(8)

Additionally, the kinetic energy density for a set of (Kohn-Sham) orbitals generating the density can be introduced through

$$\tau_\alpha = \sum_i |\nabla \phi_i|^2, \quad \tau_\beta = \sum_i |\nabla \phi_i|^2, \quad \tau = \tau_\alpha + \tau_\beta.$$  

(9)

All of the available functionals are of the general form

$$F[\rho_\alpha, \rho_\beta, \sigma_{ss}, \sigma_{\bar{s}s}, \tau_s, \tau_\bar{s}, \upsilon_s, \upsilon_{\bar{s}}] = \int d^3 r K(\rho_\alpha, \rho_\beta, \sigma_{ss}, \sigma_{\bar{s}s}, \tau_s, \tau_\bar{s}, \upsilon_s, \upsilon_{\bar{s}}).$$

(10)

where $\bar{s}$ is the conjugate spin to $s$.

17.4.2 Lists of component density functionals

Below is a list of the primary correlation and exchange functionals supported by MOLPRO. These can be combined into total density functionals. For example, the following input will produce a B3LYP calculation:

$$\{\text{dfunc,B88,DIRAC,LYP,VWN5,dftfac=[0.72,0.08,0.81,0.19]},\text{exfac=0.2}\}$$

$$\{\text{df-rks}\}$$

Note that many commonly used combinations of primary functionals are predefined as alias keywords (e.g., $\{\text{df-rks,b3lyp}\}$ is an equivalent input. See above).
M12C


doi:10.1063/1.4768228

EXACT

Exact Exchange Functional. Hartree-Fock exact exchange functional can be used to construct hybrid exchange-correlation functional.

XC-M06


doi:10.1007/s00214-007-0310-x

M062XC

M06-2X Meta-GGA Correlation Functional

doi:10.1007/s00214-007-0310-x

ECERPBE


doi:10.1063/1.1824896

BRUEG


As for BR but with $\gamma = 0.8$.

G96

Gill’s 1996 Gradient Corrected Exchange Functional

doi:G96

B86R

$\alpha \beta \gamma$ Re-optimised. Re-optimised $\beta$ of B86 used in part 3 of Becke’s 1997 paper.

doi:10.1063/1.475007

XC-M06-HF


doi:10.1021/jp066479k

DIRAC

Slater-Dirac Exchange Energy. Automatically generated Slater-Dirac exchange.

doi:10.1103/PhysRev.81.385

B88

Becke 1988 Exchange Functional

doi:10.1103/PhysRevA.38.3098

XC-M06-2X


doi:10.1007/s00214-007-0310-x

VWN5

Vosko-Wilk-Nusair (1980) V local correlation energy. VWN 1980(V) functional. The fitting parameters for $\Delta \varepsilon_c(r_s, \zeta)_V$ appear in the caption of table 7 in the reference.

doi:VWN80
**THGFCO** .. Density and gradient dependent first row exchange-correlation functional.
doi:10.1016/S0009-2614(97)00586-1

doi:10.1021/jz201525m

**B86MGC** $X\alpha\beta\gamma$ with Modified Gradient Correction. B86 with modified gradient correction for large density gradients.
doi:10.1063/1.451353

doi:10.1063/1.2912068

**THGFCFO** .. Density and gradient dependent first row exchange-correlation functional. FCFO = FC + open shell fitting.
doi:10.1016/S0009-2614(97)00586-1

**M06LC** M06-L Meta-GGA Correlation Functional
doi:10.1063/1.2370993

**VWN3** Vosko-Wilk-Nusair (1980) III local correlation energy. VWN 1980(III) functional
doi:VWN80

doi:10.1021/jz200616w

**PBESOLX** PBEsol Exchange Functional
doi:10.1103/PhysRevLett.100.136406

doi:10.1063/1.2921797

doi:10.1063/1.2126975

doi:10.1021/ct0502763

**TH4** .. Density and gradient dependent first and second row exchange-correlation functional.
doi:TH3/4

M06LX  
M06-L Meta-GGA Exchange Functional

TH1  

PBESOLC  
PBEsol Correlation Functional

PBEX  
PBE Exchange Functional

THGFL  
Density dependent first row exchange-correlation functional for closed shell systems.

M06HFC  
M06-HF Meta-GGA Correlation Functional

B97RDF  
Density functional part of B97 re-parameterized by Hamprecht et al. Re-parameterization of the B97 functional in a self-consistent procedure by Hamprecht et al. This functional needs to be mixed with 0.21*exact exchange.

TFKE  

TPSSX  

XC–M08–SO  

PW92C  

PW91X  
Perdew-Wang 1991 GGA Exchange Functional

VSXC  

LTA  
Local τ Approximation. LSDA exchange functional with density represented as a function of τ.

MK00  
Exchange Functional for Accurate Virtual Orbital Energies

CS2  
CS2 is defined through

\[ K = -a \left( \rho + 2b\rho^{-5/3} \left[ \rho t_\alpha + \rho t_\beta - \rho t_W \right] e^{-c\rho^{-1/3}} \right) \]

where

\[ t_\alpha = \frac{\tau_\alpha - \frac{\upsilon_\alpha}{8}}{2} \]
\[ t_\beta = \frac{\tau_\beta - \frac{\upsilon_\beta}{8}}{2} \]
\[ t_W = \frac{1}{8} \frac{\sigma}{\rho} - \frac{1}{2} \frac{\upsilon}{b} \]

and the constants are \( a = 0.04918, b = 0.132, c = 0.2533, d = 0.349 \).

**M06HFX**

M06-HF Meta-GGA Exchange Functional
doi:10.1021/jp066479k

**PBEXREV**

Revised PBE Exchange Functional. Changes the value of the constant \( R \) from the original PBEX functional
doi:10.1103/PhysRevLett.80.890

**TH2**

.. Density and gradient dependent first row exchange-correlation functional.
doi:10.1021/jp980259s

**HCTH147**

Handy least squares fitted functional
doi:10.1063/1.480732

**STEST**

Test for number of electrons

**EXERFPBE**

doi:10.1063/1.1824896

**LYP**


**M06X**

M06 Meta-GGA Exchange Functional
doi:10.1007/s00214-007-0310-x

**B88C**

Becke 1988 Correlation Functional. Correlation functional depending on B86MGC exchange functional with empirical atomic parameters, \( t \) and \( u \). The exchange functional that is used in conjunction with B88C should replace B88MGC here.
doi:10.1063/1.454274

**TH3**

.. Density and gradient dependent first and second row exchange-correlation functional.
doi:TH3/4

**THGFC**

.. Density and gradient dependent first row exchange-correlation functional for closed shell systems. Total energies are improved by adding \( DN \), where \( N \) is the number of electrons and \( D = 0.1863 \).
doi:10.1016/S0009-2614(97)00586-1
M05-2X Meta-GGA Correlation Functional

\[ \varepsilon^c_{\text{SR}}(r_s, \zeta, \mu) = \frac{3}{4\pi} \frac{\phi_4(\zeta)}{\alpha r_s} - \frac{1}{2} (1 + \zeta)^{4/3} f_x(r_s, \mu (1 + \zeta)^{-1/3}) + \frac{1}{2} (1 - \zeta)^{4/3} f_x(r_s, \mu (1 - \zeta)^{-1/3}) \]

with

\[ \phi_n(\zeta) = \frac{1}{2} [(1 + \zeta)^{n/3} + (1 - \zeta)^{n/3}], \]

\[ f_x(r_s, \mu) = -\frac{\mu}{\pi} \left[ (2y - 4y^3) e^{-1/4y^2} - 3y + 4y^3 + \sqrt{\pi} \text{erf} \left( \frac{1}{2y} \right) \right], \quad y = \frac{\mu \alpha r_s}{2} \]

and \( \alpha = (4/9\pi)^{1/3} \).

HCTH93 Handy least squares fitted functional

\[ \varepsilon^c_{\text{PW92}}(r_s, \zeta) - \left[ \phi_2(\zeta) \frac{3}{4\pi} \frac{Q(\frac{r_s}{\alpha(\zeta)})}{\phi_2(\zeta)} + a_1 \mu^3 + a_2 \mu^4 + a_3 \mu^5 + a_4 \mu^6 \right] (1 + b_0^2 \mu^2)^4, \]

ECERF Short-range LDA correlation functional. Local-density approximation of correlation energy for short-range interelectronic interaction \( \text{erf}(\mu r_{12})/r_{12} \).

where

\[ Q(x) = \frac{2\ln(2) - 2}{\pi^2} \ln \left( \frac{1 + ax + bx^2 + cx^3}{1 + ax + dx^2} \right), \quad (19) \]

with \( a = 5.84605 \), \( c = 3.91744 \), \( d = 3.44851 \), and \( b = d - 3\pi\alpha^2/(4\ln(2) - 4) \). The parameters \( a_i(r_s, \zeta) \) are given by

\[
\begin{align*}
  a_1 & = 4b_0^6 C_3 + b_0^8 C_5, \\
  a_2 & = 4b_0^6 C_2 + b_0^8 C_4 + 6b_0^4 e_c \text{PW92}, \\
  a_3 & = b_0^8 C_3, \\
  a_4 & = b_0^8 C_2 + 4b_0^4 e_c \text{PW92}, \\
  a_5 & = b_0^8 e_c \text{PW92},
\end{align*}
\]

with

\[
\begin{align*}
  C_2 & = -\frac{3(1 - \zeta^2) g_c(0, r_s, \zeta = 0)}{8r_s^3} \\
  C_3 & = -(1 - \zeta^2) \frac{g(0, r_s, \zeta = 0)}{\sqrt{2\pi} r_s^3} \\
  C_4 & = -\frac{9c_4(r_s, \zeta)}{64r_s^3} \\
  C_5 & = -\frac{9c_5(r_s, \zeta)}{40\sqrt{2\pi} r_s^3},
\end{align*}
\]

\[
\begin{align*}
  c_4(r_s, \zeta) & = \left( \frac{1 + \zeta}{2} \right)^2 g'' \left( 0, r_s \left( \frac{2}{1 + \zeta}, \zeta = 1 \right) \right) \left( \frac{1 - \zeta}{2} \right)^2 \times \\
  & \left( \frac{1 + \zeta}{2} \right)^2 g'' \left( 0, r_s \left( \frac{2}{1 - \zeta}, \zeta = 1 \right) \right) + (1 - \zeta^2) D_2(r_s) - \frac{\Phi_8(\zeta)}{5\alpha^2 r_s^2} \\
  c_5(r_s, \zeta) & = \left( \frac{1 + \zeta}{2} \right)^2 g'' \left( 0, r_s \left( \frac{2}{1 + \zeta}, \zeta = 1 \right) \right) \left( \frac{1 - \zeta}{2} \right)^2 \times \\
  & \left( \frac{1 + \zeta}{2} \right)^2 g'' \left( 0, r_s \left( \frac{2}{1 - \zeta}, \zeta = 1 \right) \right) + (1 - \zeta^2) D_3(r_s), \quad (20)
\end{align*}
\]

and

\[
\begin{align*}
  b_0(r_s) & = 0.784949 r_s \quad (21) \\
  g''(0, r_s, \zeta = 1) & = \frac{2^{5/3}}{5\alpha^2 r_s^2} \frac{1 - 0.02267r_s}{(1 + 0.4319r_s + 0.04r_s^2)} \quad (22) \\
  D_2(r_s) & = \frac{e^{-0.547r_s}}{r_s^3} \left( -0.388r_s + 0.676r_s^2 \right) \quad (23) \\
  D_3(r_s) & = \frac{e^{-0.31r_s}}{r_s^3} \left( -4.95r_s + r_s^2 \right) \quad (24)
\end{align*}
\]

Finally, \( e_c \text{PW92}(r_s, \zeta) \) is the Perdew-Wang parametrization of the correlation energy of the standard uniform electron gas [J.P. Perdew and Y. Wang, Phys. Rev. B 45, 13244 (1992)], and

\[
\begin{align*}
  g(0, r_s, \zeta = 0) & = \frac{1}{2} \left( 1 - Br_s + Dr_s^2 + Er_s^3 + Fr_s^4 \right) e^{-dr_s}, \quad (25)
\end{align*}
\]
is the on-top pair-distribution function of the standard jellium model [P. Gori-Giorgi and J.P. Perdew, Phys. Rev. B 64, 155102 (2001)], where \( B = -0.0207, C = 0.08193, D = -0.01277, E = 0.001859, d = 0.7524 \). The correlation part of the on-top pair-distribution function is \( g_c(0, r_s, \zeta = 0) = g(0, r_s, \zeta = 0) - \frac{1}{2} \).

**M05X**

M05 Meta-GGA Exchange Functional  

**MK00B**

Exchange Functional for Accurate Virtual Orbital Energies. MK00 with gradient correction of the form of B88X but with different empirical parameter.  

**TPSSC**

[doi:10.1103/PhysRevLett.91.146401](https://doi.org/10.1103/PhysRevLett.91.146401)

**PBEC**

PBE Correlation Functional  
[doi:10.1103/PhysRevLett.77.3865](https://doi.org/10.1103/PhysRevLett.77.3865)

**XC-M06-L**


**BW**


**XC-M08-HX**

[doi:10.1021/ct800246v](https://doi.org/10.1021/ct800246v)

**BR**


\[
K = \frac{1}{2} \sum_s \rho_s U_s, \tag{26}
\]

where

\[
U_s = -(1 - e^{-x} - xe^{-x/2})/b, \tag{27}
\]

\[
b = \frac{x^3 e^{-x}}{8 \pi \rho_s}, \tag{28}
\]

and \( x \) is defined by the nonlinear equation

\[
\frac{xe^{-2x/3}}{x-2} = \frac{2 \pi^{2/3} \rho_s^{5/3}}{3 Q_s}, \tag{29}
\]

where

\[
Q_s = (\nu_s - 2 \gamma D_s)/6, \tag{30}
\]
\[ D_s = \tau_s - \frac{\sigma_{ss}}{4\rho_s} \]  

and

\[ \gamma = 1. \]  


CS1 is formally identical to CS2, except for a reformulation in which the terms involving \( \nu \) are eliminated by integration by parts. This makes the functional more economical to evaluate. In the limit of exact quadrature, CS1 and CS2 are identical, but small numerical differences appear with finite integration grids.

### 17.4.3 Implementing new functionals

New functionals are implemented based upon the automatic code generation (ACG) program (doi:10.1016/S0010-4655(01)00148-5). In order to work the program requires the maple mathematics program and an XSLT parser, defined by the variable XSLT in CONFIG.

The format of the input file is an XML file containing all of the information about the new functional. All density functional XML files are placed in the directory lib/df and are automatically activated on the next instance of the make command in the MOLPRO base directory.

The root element of the XML document is \texttt{content}. At the next level the element, \texttt{functional} is expected, 1 per file.

The \texttt{functional} element has an \texttt{id} attribute which is used as the keyword for the functional in MOLPRO, and optional \texttt{doi} attribute for specifying a reference. The allowed elements are defined in table 8. The final element is \texttt{maple} for which multiple cases are allowed. A typical maple expression such as

\[ A := 1.2; \]

is written as

\[ \text{<maple lhs}="A">1.2</maple>. \]

To input a Maple procedure such as

\[ \text{add_together} := \text{proc}(a, b) \ a + b \ \text{end;} \]

one should write

\[ \text{<maple lhs}="\text{add_together}" \ proc="a,b">a+b</maple>. \]

As an example the Perdew-Wang 1991 GGA exchange functional is given below:
17.4.4 Implementing new hybrid-functionals

Hybrid functionals are defined in the file lib/dalias.registry. Entries can be added to this file as required, and then run make to update the other registry files.

17.5 Empirical damped dispersion correction

Empirical damped dispersion corrections can be calculated in addition to Kohn-Sham calculations. This is particularly important in cases where long-range correlation effects become dominant.

The dispersion correction can be added to the DFT energy by using

```
ks, <func>; disp
```

The total energy will then be calculated as

\[ E_{\text{DFT-D}} = E_{\text{DFT}} + E_{\text{disp}} \] (33)

Currently the default dispersion correction added to the DFT energy is the D3 dispersion correction developed by Grimme et al., see Ref. [1]. The disp keyword can have the following additional options:

- **FUNC** Functional name (default: FUNC=’pbe’).
- **VERSION** Can have values 2 and 3 according to parametrisations from Refs. [2] and [3] (default: VERSION=3)
- **ANAL** Performs a detailed analysis of pair contributions.
- **GRAD** Cartesian gradients are computed. (note that geometry optimisations with DFT+dispcorr3 are currently not yet possible).
- **TZ** Use special parameters for calculations with triple-zeta basis sets. Preliminary results in the SI of Ref. [3] indicate that results are slightly worse than with the default parameters and QZVP type basis sets. This option should be carefully tested for future use in very large computations.
Alternatively, the D3 dispersion correction can also be calculated separately from the DFT calculation using the following template:

\[
\begin{align*}
ks, & <\text{func}> \\
eks &= \text{energy} \\
dispcorr3 &= \\
eks_{\text{plus disp}} &= eks + edisp
\end{align*}
\]

The older DFT-D1 [2] or DFT-D2 [3] methods by Grimme can still be used invoking

\[
\begin{align*}
ks, & <\text{func}> \\
eks &= \text{energy} \\
dispcorr &= \\
eks_{\text{plus disp}} &= eks + edisp
\end{align*}
\]

with the following options to dispcorr:

- **MODE**: Adjusts the parametrisation used: MODE=1 uses parameters from Ref. [1] and MODE=2 uses parameters from Ref. [2] (default: MODE=1)
- **SCALE**: Overall scaling parameter \(s_6\) (see Eq. (34) and Refs. [2,3] for optimised values).
- **ALPHA**: Damping function parameter (see Eq. (37)). Smaller values lead to larger corrections for intermediate distances.

In the DFT-D1 and DFT-D2 method the dispersion energy is calculated as

\[
E_{\text{disp}} = -s_6 \sum_{i,j<i} N_{\text{atoms}} f_{\text{damp}}(R_{ij}) \frac{C_{i\rightarrow j}^6}{R_{ij}^6},
\]

where \(N_{\text{atoms}}\) is the total number of atoms, \(R_{ij}\) is the interatomic distance of atoms \(i\) and \(j\), \(s_6\) is a global scaling parameter depending on the choice of the functional used and the \(C_{i\rightarrow j}^6\) values are calculated from atomic dispersion coefficients \(C_i^6\) and \(C_j^6\) in the following way:

\[
\begin{align*}
C_{i\rightarrow j}^6 &= 2 \frac{C_i^6 C_j^6}{C_i^6 + C_j^6} \quad (\text{Ref. [1]}) \\
C_i^6 &= \sqrt{C_i^6 C_j^6} \quad (\text{Ref. [2]})
\end{align*}
\]

The function \(f_{\text{damp}}\) damps the dispersion correction for shorter interatomic distances and is given by:

\[
f_{\text{damp}}(R_{ij}) = \frac{1}{1 + \exp[-\alpha (R_{ij}/(R_{i\text{vdW}}^i + R_{j\text{vdW}}^j) - 1)]}
\]

where \(R_{i\text{vdW}}^i\) being the van-der-Waals radius for atom \(i\) and \(\alpha\) is a parameter that is usually set to 23 (Ref. [1]) or 20 (Ref. [2]).

References:


(see also [http://toc.uni-muenster.de/DFTD3/index.html](http://toc.uni-muenster.de/DFTD3/index.html) for further documentation).
17.6 Time-dependent density functional theory

The time-dependent density functional linear response theory program can be used to calculate excitation energies or response properties for molecules. The program currently has the following restrictions:

- No point-group symmetry can be used in TDDFT.
- The program only works in conjunction with density-fitting of electron repulsion integrals, i.e., the user must supply an auxiliary basis set, see section 15 for details.
- Currently the exchange-correlation kernel is approximated by the adiabatic local density approximation (ALDA).
- In case of the calculation of excitation energies using hybrid-DFT functionals the reduced hessian matrix is approximated by the hermitian matrix $A^2 - B^2$, i.e., it is assumed that $A$ and $B$ commute. This works well for small systems/basis sets, but the excitation energies may deviate more strongly from the eigenvalues of the full hessian in case of larger systems/basis sets.

A typical input for calculating the ten lowest excitation energies is given by:

```plaintext
ks,<func>; save,2100.2
df-tddft,orb=2100.2,nexcit=10
```

yielding, e.g., the following output:

```
n  eig    oscill.stren.    eig (eV)
1     0.15429481     0.00000361   4.19857508
12-> 13             0.999706     0.14361479
11-> 14             0.000034     0.35333048
10-> 20             0.000027     0.58330205
10-> 16             0.000016     0.43005338
```

As shown by the above snippet, the output will contain the excitation energies, oscillator strengths and the four most important orbital contributions to the respective transition. The latter is characterised by the orbital index pairs (\(\text{<occ>} \rightarrow \text{<virt>}\)), the coefficient of this index pair in the eigenvector, and the orbital energy differences contained in the last column showing the uncoupled excitation energy for comparison.

For the calculation of frequency-dependent dipole-dipole polarisabilities use, e.g.:

```plaintext
ks,<func>; save,2100.2
df-tddft,orb=2100.2,pert='DMX',pert='DMY',pert='DMZ',om=[0.0,1.0]
```

which calculates $\alpha(\omega)$ and its cartesian components at the frequencies $\omega = 0$ (static response) and $\omega = 1$. Response property calculations are possible for all properties described in section 6.13.

The following list summarises the possible options to TDDFT:

ORB Record for input orbitals (required).
AUXBAS  Auxiliary basis set (default: 'MP2FIT')
FEXX  Factor for nonlocal exchange.
FXC  Factor for local exchange-correlation.
FU  Factor for Coulomb kernel contribution (default: 1).
MAXIT  Maximum number of iterations in Davidson and conjugate-gradient solver.
NEXCIT  Number of excitation energies requested (default: 0).
DAV  Switches (1,2) between two different Davidson eigensolvers (default: 2).
OM  Real frequencies for which the linear response is calculated, example: \(\Omega = [0.0, 1.0, 2.0]\) calculates the response at \(\omega = 0.0, 1.0\) and \(2.0\).
OMI  Imaginary frequencies for which the linear response is calculated.
PERT  Perturbations for which the linear response is calculated, example: \(\text{PERT} = \{'\text{DMX}', \text{PERT} = \{'\text{DMY}', \text{PERT} = \{'\text{DMZ}'\}\) calculates the dipole-dipole polarisabilities for the three cartesian components (see section[6.13] for available properties).
TOLDAV  Convergence tolerance used in the Davidson eigensolver.
THRCG  Convergence tolerance used in the conjugate-gradient solver.
NSUBMAX  Maximum subspace used in Davidson eigensolver (default: \(10 \times \text{NEXCIT}\))
TRIP  Set to '1' for triplet excitation energies (default: 0).
C6  Set to '1' for calculating \(C_6\) dispersion coefficients (default: 0).
NQUAD  Number of quadrature points used in the calculation of dispersion coefficients.
FXCFIT  Set to '1' for approximating the exchange-correlation kernel matrix with density-fitting (default: 0).
DENTHR  Threshold for density in the calculation of the exchange-correlation kernel matrix on the auxiliary basis set (default: 1d-7).
FULL  Set to '1' for a full diagonalisation of the hessian matrix (experimental).
CRITC  Convergence threshold for the coefficients of the last added basis vector in the 2nd Davidson eigensolver (default: 1d-7).
CRITR  Convergence threshold for residual vector norms in the 2nd Davidson eigensolver (default: 1d-7).
ORTHO  The threshold over which loss of orthogonality is assumed in the 2nd Davidson eigensolver (default: 1d-8).
NDUMP  Number of excitation vectors (transformed to AO basis) written to file (default: 0).
DUMP  Record for dump of excitation vectors (default: 5000.2).
17.7 Random-phase approximation

The random-phase approximation program (rpatddft) can be used to calculate RPA correlation energies after a SCF calculation. Additionally, it can be used to calculate dynamic dipole polarizabilities, $C_6$ dispersion coefficients, and excitation energies. The program currently works without point-group symmetry.

List of the main keywords:

ECORR, <list of methods>
Calculation of RPA correlation energies [1] (see options below)

PROPERTIES, <list of methods>
Calculation of dynamic dipole polarizabilities and $C_6$ dispersion coefficients [10] (see options below)

EXCIT, <list of methods>
Calculation of excitation energies [11] (see options below)

as well as:

ORB,<orbrec>
Record for input orbitals (required).

STAB
Check matrices stability conditions in RPA calculations. When used without an ECORR, EXCIT or PROPERTIES keyword, check the Hessian and RPA matrices eigenvalues and do nothing more.

INTAC,NLAMBDAn,LAMBDA=<lambda>,WEIGHT=<weight>
Number of quadrature points for the Gauss-Legendre numerical integration along the adiabatic connection for RPA calculations (default is 7). If LAMBDA and WEIGHT are given, assumes a one-point quadrature with given abscissa and weight.

INTFREQ,METHFREQ=<methfrq>,NFREQ=<nfreq>
Options for the numerical integration over the frequency variable of RPA calculations. METHFREQ governs the type of quadrature used (0=default is Gauss-Chebyshev, 1 and 2 are Gauss-Legendre, 3 is Clenshaw-Curtis) and NFREQ governs the number of quadrature points (default is 16).

INTEGRAL,<nbr>
Specify the two-electron integral transformation routine: 0 (still the default for spin-unrestricted and gradient calculations) is the ‘old’ one, 1 is the ‘old’ one that has been cleaned up, and 2 (default otherwise) is a much more efficient transformation using Molpro’s “transform” routine.

DFTKERNEL,<funcx>[,<funcc>]
Specify the exchange and correlation kernel for EXCIT (if only one argument is given, it is understood to be the exchange-correlation kernel).

NOMP2
The MP2 energy is calculated in certain situations where it is available almost for free, provided that some matrices are allocated. This behavior can be switched off by this NOMP2 keyword.
DIELSOLID

Use the solid-state variant when performing DIEL calculations.

NOSPINBLOCK

For spin-unrestricted calculations, use a formalism where matrices are of $\alpha\alpha + \alpha\beta + \beta\alpha + \beta\beta$ dimensions (the default is to use a formalism with a nospinflip/splinflip block structure).

NOSPINFLIP

Exclude spin-flip dimensions of unrestricted RPA calculations that use the NOSPINBLOCK formalism (not suitable for all RPA variants).

C6

Computes C6 coefficients from last two saved polarizabilities.

TDA

Tamm-Dancoff approximation for EXCIT and PROPERTIES.

OCC,<nocc>

Explicitly specify the number of occupied orbitals (useful for fake pseudopotential calculations).

CORE,<core>

Specify core orbitals (default: last specified core orbitals or, if none, atomic inner shells).

PRINT,<nbr>

Level of print expected from the output (from 0 (default) to 3).

Calculation of RPA correlation energies

ECORR, <list of methods>

If no method is given, a SO2–RCCD calculation will be done (see below).

There are two main RPA variants [1]: dRPA (direct RPA, without the inclusion of an Hartree-Fock exchange kernel in the response function) and RPax (with the Hartree-Fock exchange kernel included in the response function).

There are four main formulations in which the RPA equations can be derived. The adiabatic-connection fluctuation-dissipation theorem (ACFDT) equation involves integrations both over frequency and coupling constant: an analytical integration along the frequency variable followed by a quadrature on the coupling constant yields the adiabatic connection formulation (AC) [1], while an analytic integration on the coupling constant followed by a numerical integration over the frequency yields the dielectric formulation (DIEL) [2]. Two other formulations are obtained when the two integrations are carried out analytically: the plasmon formula (PLASMON) [1] and the ring coupled cluster doubles formulation (RCCD) [3]. These four formulations are not in general equivalent.

Most variants+formulations can readily be used in a spin-unrestricted context [6]. This is implemented in the code and does not need any further input from the user: the RPA program recognizes the spin-unrestricted character of a SCF calculation that was done beforehand and acts accordingly.

Gradients of most of the RCCD-formulation RPA energies are available, both without range-separation with RHF orbitals and with range-separation with RSH orbitals [9]. The calculations are triggered by the presence of the keyword FORCE or OPTG after the energy-related section (see examples at the end of the section).

The user can test the RPA program using make rpatddfttest, which proposes a variety of tests for RPA correlation energy calculations.

The keywords for the methods are constructed on the model:

<variant>-<formulation>-<alternative>

For the AC formulation, the available methods are:
<table>
<thead>
<tr>
<th>Keyword</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>DRPAI-AC</td>
<td>dRPA calculation (see Refs. [1] and [4]).</td>
</tr>
<tr>
<td>DRPAII-AC</td>
<td>dRPA calculation, using antisymmetrized two-electron integrals (see Refs. [1] and [4]).</td>
</tr>
<tr>
<td>RPAXI-AC</td>
<td>RPAX calculation (see Refs. [1] and [5]).</td>
</tr>
<tr>
<td>RPAXII-AC</td>
<td>RPAX calculation, using antisymmetrized two-electron integrals (see Refs. [1] and [5]).</td>
</tr>
<tr>
<td>DRPAI-AC-ALT</td>
<td>dRPA calculation using an alternative derivation (see Ref. [7]).</td>
</tr>
<tr>
<td>RPAXI-AC-ALT</td>
<td>RPAX calculation using an alternative derivation (see Ref. [7]).</td>
</tr>
<tr>
<td>DRPAI-AC-NOINT</td>
<td>dRPA calculation without integration along the adiabatic connection (using the “kinetic” and “potential” contributions, sometimes called the “alternative plasmon formula”, see Ref. [1]).</td>
</tr>
<tr>
<td>RPAXII-AC-NOINT</td>
<td>RPAX calculation without integration along the adiabatic connection (using the “kinetic” and “potential” contributions, sometimes called the “alternative plasmon formula”, see Ref. [1]).</td>
</tr>
<tr>
<td>DRPAI-DIEL</td>
<td>dRPA calculation (see Ref. [2]).</td>
</tr>
<tr>
<td>DRPAIIA-DIEL</td>
<td>dRPA-Ila approximation (see Ref. [2]).</td>
</tr>
<tr>
<td>RPAXIA-DIEL</td>
<td>RPAX-Ia approximation (see Ref. [2]).</td>
</tr>
<tr>
<td>DRPAI-RCCD</td>
<td>dRPA-I calculation (see Ref. [3]).</td>
</tr>
<tr>
<td>RPAXII-RCCD</td>
<td>RPAX-II calculation (Szabo-Ostlund variant 1 is calculated too, see Ref. [3]).</td>
</tr>
<tr>
<td>SO2-RCCD</td>
<td>Szabo-Ostlund variant 2 (see Ref. [3]).</td>
</tr>
<tr>
<td>SOSEX-RCCD</td>
<td>dRPA-I+SOSEX correction (see Ref. [3]).</td>
</tr>
<tr>
<td>RPAX2-RCCD</td>
<td>RPAX2 approximation (see Ref. [8]).</td>
</tr>
<tr>
<td>DRPAI-PLASMON</td>
<td>dRPA-I calculation (see Ref. [1]).</td>
</tr>
<tr>
<td>RPAXII-PLASMON</td>
<td>RPAX-II calculation (see Ref. [1]).</td>
</tr>
</tbody>
</table>

Note that to all these keywords are associated energy variables defined as:

ECORR_VARIANT_FORMULATION_ALTERNATIVE

(see the examples below).

Example of a dRPA-I calculation using the PBE functional:
Example of a range-separated RPax-I calculation using the short-range PBE exchange-correlation functional and the range-separated parameter \( \mu = 0.5 \):

\[
\{ \text{int;erf,0.5} \} \\
\{ \text{rks,exerfpbe,ecerfpbe;rangehybrid;orbital,2101.2} \} \\
\{ \text{rpatddft;} \\
\quad \text{orb,2101.2;} \\
\quad \text{ecorr,RPAXI-AC} \\
\} \\
e=\text{ECORR\_RPAXI\_AC}
\]

Example of several RPA calculations in the same run:

\[
\{ \text{rhf,orbital,2101.2} \} \\
\{ \text{rpatddft;} \\
\quad \text{orb,2101.2;} \\
\quad \text{ecorr,DRPAI-AC,RPAXII-RCCD,DRPAI-DIEL} \\
\} \\
e1=\text{ECORR\_DRPAI\_AC} \\
e2=\text{ECORR\_RPAXII\_RCCD} \\
e3=\text{ECORR\_DRPAI\_DIEL}
\]

(the calculations are done with the same transformed integrals, i.e. without redoing the integral transformation).

Example of a dRPA-I gradient calculation:

\[
\{ \text{rks,pbe,orbital,2101.2} \} \\
\{ \text{rpatddft;} \\
\quad \text{orb,2101.2;} \\
\quad \text{ecorr,DRPAI-RCCD} \\
\} \\
\text{force}
\]

Example of a geometry optimization at the LDA+dRPA-I level:

\[
\{ \text{int;erf,0.5} \} \\
\{ \text{rks,exerf,ecerf;rangehybrid;orbital,2101.2} \} \\
\{ \text{rpatddft;} \\
\quad \text{orb,2101.2;} \\
\quad \text{ecorr,DRPAI-RCCD} \\
\} \\
\text{optg}
\]

Calculation of properties, excitation energies and oscillator strengths

\text{PROPERTIES, METHOD=<method>}
\text{EXCIT, METHOD=<method>}

The \text{EXCIT} calculations output shows the excitation energies in ua, eV and nm, the oscillator strengths in length and velocity gauge, as well as the major excitations involved in each mode.

The methods available are:
DRPA

Direct random-phase approximation (or time-dependent Hartree).

TDHF

Time-dependent Hartree-Fock.

TDDFT

Time-dependent density-functional theory.

RS-TDDFT


The exchange density functionals (FUNCX) available are:

LDAXERF

(short-range LDA exchange density functional for the erf interaction [12]).

The correlation density functionals (FUNCC) available are:

LDAC

(Perdew-Wang-92 LDA correlation density functional)

LDACERF

(short-range LDA correlation density functional for the erf interaction [13]).

Example of a range-separated time-dependent density-functional theory calculation using the short-range LDA exchange-correlation functional and the range-separated parameter mu=0.5:

```plaintext
mu=0.5
{int;erf,mu;save}
{rks,exerf,ecerf;rangehybrid;orbital,2101.2}
{int}
{setmu,mu}
{rpatddft;orb,2101.2;excit,method=rs-tddft;
 dftkernel,funcx=ldaxerf,funcc=ldacerf
}
```

References

17.8 Examples

The following shows the use of both non-self-consistent and self-consistent DFT.

g = \{c;n,c,r\}
r = 1.1 \text{ angstrom}
dfunc,b-lyp
rhf;method(1)=program
dft;edf(1)=dftfun
uhf;method(2)=program
dft;edf(2)=dftfun
uks;method(3)=program,edf(3)=dftfun
dft;method(4)=program,edf(4)=dftfun
table,dftname,dftfuns

http://www.molpro.net/info/current/examples/cndft.com

18 ORBITAL LOCALIZATION

Localized orbitals are calculated according to the Boys, Pipek-Mezey or NLMO criteria. Localization takes place within each symmetry species separately. If complete localization is desired, no symmetry should be used. All subcommands can be abbreviated by three characters.

The localization program is invoked by the \texttt{LOCALI} command

\texttt{LOCALI [],\textit{method},[\textit{LOCMETHOD}=\textit{locmethod}],[\textit{REFORB}=\textit{record}]} \n
The keyword \textit{method} can be either \texttt{BOYS}, \texttt{PIPEK} or \texttt{NATURAL}. By default, the valence orbitals from the last energy calculation are localized using the Boys criterion. Only orbital subsets which leave the energy invariant are transformed. These defaults can be modified using the optional commands described in the following sections.

The option \textit{LOCMETHOD} only applies to Pipek-Mezey localization. The value \textit{locmethod} can take the following values:

- \textit{locmethod}=1: Standard iterative localization method
- \textit{locmethod}=2: Use second-order localization method. Redundant rotations will be eliminated.
- \textit{locmethod}=3: First do a first iterations using the standard method, then invoke locmethod=2. This option is recommended in cases with redundant rotations, e.g., benzene.

The option \textit{REFORB} has the same effect as the directive \texttt{REFORB} described further below.

18.1 Defining the input orbitals (\texttt{ORBITAL})

\texttt{ORBITAL,record.file.specifications}

The orbitals to be localized are read from dump record \textit{record.file}. A state specific orbital set can be selected using \textit{specifications}, as explained in section \texttt{4.11}. Default are the orbitals calculated last.
18.2 Saving the localized orbitals (SAVE)

SAVE,record.file

This specifies the dump record where the localized orbitals are stored. If the dump record already exists, the localized orbitals are added to it. Default is the input record (cf. ORBITAL).

18.3 Choosing the localization method (METHOD)

METHOD,method

The localization method method can be either BOYS, PIPEK or NATURAL. This can also be specified as argument on the LOCALI card (see above).

18.4 Delocalization of orbitals (DELOCAL)

DELOCAL

If this card is present, the orbitals are delocalized.

18.5 Localizing AOs (LOCAO)

LOCAO

If this card is present, the number of AOs contributing to each MO is minimized. This can be useful to rotate degenerate orbitals (e.g., px, py, pz in an atom) so that pure orbitals (in this case px, py, pz) result.

This implies Pipek-Mezey localization.

18.6 Selecting the orbital space

By default, only the valence orbitals are localized, in order to ensure invariance of subsequent electron correlation treatments. This behaviour can be modified using the OCC and CORE directives.

18.6.1 Defining the occupied space (OCC)

OCC, \( o_1, o_2 \ldots \)

defines the highest orbital \( o_i \) in each symmetry \( i \) to be localized.

18.6.2 Defining the core orbitals (CORE)

CORE, \( c_1, c_2 \ldots \)

The first \( c_i \) orbitals in each symmetry are treated as core orbitals and not localized. Thus, orbitals \( c_i + 1 \) to \( o_i \) are localized in symmetry \( i \).
18.6.3 Defining groups of orbitals (GROUP, OFFDIAG)

GROUP, orb1, orb2, orb3, ...

This card defines groups of orbitals to be localized as follows:

GROUP, 1.1, 2.1, 3.1  a group of orbitals 1-3 in symmetry 1
GROUP, 1.1, -3.1    equivalent to previous example
GROUP, 3.1, 5.1, -8.1  this group includes orbitals 3, 5, 6, 7, 8 in symmetry 1

Orbitals in different groups are localized independently. Orbitals not included in any group are unchanged.

18.6.4 Localization between groups (OFFDIAG)

OFFDIAG

If this card is present, localize between groups instead of within groups.

18.7 Ordering of localized orbitals

ORDER, type

If type=CHARGE, the orbitals are ordered according to their charge centroids (default).

If type=FOCK, the orbitals are ordered according to increasing diagonal elements of the fock operator (PIPEK) or increasing Coulson-additive orbital energies (BOYS). This requires a Fock operator from the preceding energy calculation. For localization of Hartree-Fock orbitals, this operator is stored in the dump record and automatically found. For localization of MCSCF orbitals, an effective fock operator is computed from the MCSCF density matrix (see DENSITY option). Alternatively, a dump record of a previous SCF calculation can be specified on the FOCK card, and then the fock operator is read from this record. For degenerate orbitals, further ordering according to the the coordinates of charge centres is attempted (first according to largest z-coordinates, then according to x, then y).

This card does not apply to NLMO localization.

18.7.1 No reordering (NOORDER)

NOORDER

If this card is present, the localized orbitals are not reordered. This is useful if localized orbitals are used as starting guess, and it is intended that their order remains unchanged.

18.7.2 Ordering using domains (SORT)

SORT, [THRCHCHG=charge][THREIG=eps].GROUP=igrp][REVERT], centrelist

This directive only works for Pipek-Mezy localization. The orbitals are ordered according to domains and the given centrelist. The contributions of the centres to domains are determined by Löwdin charges. Only centres with charges greater than THRCHCHG (default 0.4) are included in these domains. The orbitals are reordered according to the following criteria:
1.) The primary centre in a domain is the one with largest charge, the secondary centre the one with the next largest charge. Orbitals are reordered separately within each localization group. First all orbitals are sorted so that the primary centres are in the order of the given `centrelist`. Orbitals with primary centres which are not in `centrelist` come last.

2.) Within each group of orbitals found for a given primary centre, those containing only one centre (lone pairs) are included first. The remaining ones are ordered so that the secondary atoms are in the order of `centrelist`. Orbitals with secondary centres which are not in `centrelist` come last.

3.) If `REVERT` is given, the order in each localization group is reverted.

4.) If `GROUP` is given, only the orbitals in the given group are reordered. `igrp` is 2 for closed shells and inactive orbitals, 1 for open-shells in single reference methods, and 3 for active orbitals in CASSCF calculations.

5.) If `THREIG` is given, only orbitals with energies larger than the given value are reordered. `eps` must be negative. The remaining orbitals come last (first if `REVERT` is given).

Note that core orbitals are neither localized nor reordered.

18.7.3 Defining reference orbitals (REFORB)

`REFORB,record.file.specifications`

The localized orbitals are reordered such that the overlap with the reference orbitals read from `record.file` is maximized. This is useful for local correlation treatments for keeping the order of the localized constant for different geometries. A state specific orbital set can be selected using `specifications`, as explained in section 4.11.

18.7.4 Selecting the fock matrix (FOCK)

`FOCK,record.file`

This specifies a record holding a Fock operator to be used for ordering the orbitals. Note that only SCF dump records hold fock operators. Default is the Fock operator from the energy calculation which produced the input orbitals.

18.7.5 Selecting a density matrix (DENSITY)

`DENSITY,record.file.specifications`

This specifies a record holding a density matrix for construction of a fock operator used for ordering the orbitals. This can be used if no fock operator is available, and has only an effect for MCSCF localizations. By default, the (state averaged) MCSCF density is used. A state specific density matrix can be selected using `specifications` as described in section 4.11.

18.8 Localization thresholds (THRESH)

`THRESH,thresh,eorder`

`thresh` is a threshold for localization (default 1.d-12). If `eorder` is nonzero (default 1.d-4), the orbitals whose energy difference is smaller then `eorder` are considered to be degenerate and reordered according to the position of their charge centres (see section 18.7).
18 ORBITAL LOCALIZATION

18.9 Options for PM localization (PIPEK)

Some special options exist for Pipek-Mezey localization (all optional):

PIPEK, METHOD=method, DELETE=ndel, MAXDL=maxdl, THRESH=thresh, ORDER=iorder, STEP=step

METHOD:  
- method=1: use 2x2 rotation method (default);
- method=2: use Newton-Raphson method;
- method=3: Initial iterations using 2x2 rotation method, final convergence using NR method.

DELETE:  
Delete the last ndel basis functions of each angular momentum type for each atom in PM localization. This can be useful to achieve proper localization with diffuse (augmented) basis sets.

MAXDL:  
If ndel>0 delete functions only up to angular momentum maxdl.

ORDER:  
- If iorder=1, order final orbitals according to increasing diagonal fock matrix elements;
- If iorder=2, order final orbitals according charge centres (default).

THRESH:  
Localization threshold (same as on THRESH directive).

STEP:  
Max step size in NR method (default 0.1d0).

18.10 Printing options (PRINT)

PRINT,[ORBITAL=]pri [,CHARGE] [,CENTRES] [,TEST] [,TRAN];

If ORBITAL is given, the localized orbitals are printed.
If CHARGE or CENTRES is given, the charge centres of the localized orbitals are printed.
If TRAN is given, the transformation matrix is printed (Boys only).
If TEST is given, intermediate information is printed.
MULTI is a general MCSCF/CASSCF program written by P. J. Knowles and H.-J. Werner (1984).

Bibliography:


All publications resulting from use of this program must acknowledge the above. See also:


This program allows one to perform CASSCF as well as general MCSCF calculations. For CASSCF calculations, one can optionally use Slater determinants or CSFs as a $N$-electron basis. In most cases, the use of Slater determinants is more efficient. General MCSCF calculations must use CSFs as a basis.

A quite sophisticated optimization method is used. The algorithm is second-order in the orbital and CI coefficient changes and is therefore quadratically convergent. Since important higher order terms in the independent orbital parameters are included, almost cubic convergence is often observed. For simple cases, convergence is usually achieved in 2-3 iterations. However, convergence problems can still occur in certain applications, and usually indicate that the active space is not adequately chosen. For instance, if two weakly occupied orbitals are of similar importance to the energy, but only one of them is included in the active set, the program might alternate between them. In such cases either reduction or enlargement of the active orbital space can solve the problem. In other cases difficulties can occur if two electronic states in the same symmetry are almost or exactly degenerate, since then the program can switch from one state to the other. This might happen near avoided crossings or near an asymptote. Problems of this sort can be avoided by optimizing the energy average of the particular states. It is also possible to force convergence to specific states by choosing a subset of configurations as primary space (PSPACE). The hamiltonian is constructed and diagonalized explicitly in this space; the coefficients of the remaining configurations are optimized iteratively using the P-space wavefunction as zeroth order approximation. For linear molecules, another possibility is to use the LQUANT option, which makes it possible to force convergence to states with definite $\Lambda$ quantum number, i.e., $\Sigma, \Pi, \Delta$, etc. states.

19.1 Structure of the input

All sub-commands known to MULTI may be abbreviated by four letters. The input commands fall into several logical groups; within each group commands may appear in any order, but the groups must come in correct order.

a) The program is invoked by the command MULTI or MCSCF

b) cards defining partitioning of orbitals spaces – OCC, FROZEN, CLOSED

c) general options (most commands not otherwise specified here)

d) a WF card defining a state symmetry
e) options pertaining to that state symmetry – WEIGHT, STATE, LQUANT (must be given after WF)
f) configuration specification for that state symmetry – SELECT, CON, RESTRICT
g) definition of the primary configurations for that state symmetry - PSPACE
h) further general options

Stages d) through to h) may be repeated several times; this is the way in which you specify an average energy of several states of different symmetry.

Some options can be specified on the MULTI command line:

MULTI, options

Selected options:

MAXIT
Max. number of iterations (default 10)
ENERGY
Convergence threshold for energy
GRADIENT
Convergence threshold for gradient
STEP
Convergence threshold for steplength
FAILSAFE
(logical) Use options for more robust convergence
FORCEINP
(logical) If true, process all input in geometry optimizations and frequency calculations (Default is false). By default, most input is ignored in these cases and taken from the initial calculation; also, the orbitals are taken from the previous geometry (OPTG or the reference point (FREQUENCIES). Disabling this behaviour by setting FORCEINP is normally not recommended. See also the FORCEINP directive for OPTG.

Many further options and thresholds, which can also be given on the command line, are described in section 19.8.5

19.2 Defining the orbital subspaces

19.2.1 Occupied orbitals

OCC, n1, n2, ..., n8;

ni specifies numbers of occupied orbitals (including FROZEN and CLOSED) in irreducible representation number i. In the absence of an OCC card, the information from the most recent MCSCF calculation is used, or, if there is none, those orbitals corresponding to a minimal valence set, i.e., full valence space, are used.

19.2.2 Frozen-core orbitals

FROZEN, n1, n2, ..., record.file.type;

ni is the number of frozen-core orbitals in irrep number i. These orbitals are doubly occupied in all configurations and not optimized. Note that in earlier MOLPRO versions this directive was
called \texttt{CORE} and has now been renamed to avoid confusion with \texttt{CORE} orbitals in the MRCI and CCSD programs.

\textit{record.file} is the record name for frozen core orbitals; if not supplied, taken from \texttt{orb} on \texttt{START} card. \textit{record.file} can be specified in any field after the last nonzero $n_i$. It should always be given if the orbital guess is from a neighbouring geometry and should then specify the SCF orbitals calculated at the present geometry. If a subsequent gradient calculation is performed with this wavefunction, \textit{record.file} is mandatory and must specify closed-shell SCF orbitals at the present geometry. Note that \textit{record} must be larger than 2000.

\textit{type} optionally specified the orbital type, e.g., ALPHA, BETA, or NATURAL if UHF/UKS orbitals are used.

If the \texttt{FROZEN} card is omitted, then the numbers of core orbitals are taken from the most recent MCSCF calculation, or otherwise no orbitals are frozen. If the \texttt{FROZEN},\textit{record.file}, then the orbitals corresponding to atomic inner shells are taken, i.e., $1s$ for Li–Ne, $1s^22s^2p$ for Na–Ar, etc. A \texttt{FROZEN} card without any specification resets the number of frozen core orbitals to zero.

\subsection*{19.2.3 Closed-shell orbitals}

\texttt{CLOSED,$n_1,n_2,\ldots,n_8$}

$n_i$ is the number of closed-shell orbitals in irrep number $i$, inclusive of any \texttt{FROZEN} orbitals. These orbitals do not form part of the active space, i.e., they are doubly occupied in all CSFs. In contrast to the core orbitals (see \texttt{FROZEN}), these orbitals are fully optimized.

If the \texttt{CLOSED} card is omitted, then the data defaults to that of the most recent MCSCF calculation, or else the atomic inner shells as described above for \texttt{FROZEN}.

\subsection*{19.2.4 Freezing orbitals}

\texttt{FREEZE,\textit{orb.sym};}

The specified orbital will not be optimized and will remain identical to the starting guess. \textit{orb.sym} should be an active or closed-shell orbital. If \textit{orb.sym} is a frozen core orbital, this card has no effect.

\subsection*{19.3 Defining the optimized states}

Each state symmetry to be optimized is specified by one WF card, which may optionally be followed by \texttt{STATE}, \texttt{WEIGHT}, \texttt{RESTRICT}, \texttt{SELECT}, \texttt{CON}, and/or \texttt{PSPACE} cards. All cards belonging to a particular state symmetry as defined on the \texttt{WF} card must form a block which comes directly after the \texttt{WF} card. The cards can be in any order, however.

\subsection*{19.3.1 Defining the state symmetry}

The number of electrons and the total symmetry of the wavefunction are specified on the WF card:

\texttt{WF,elec,sym,spin}

where
elec is the number of electrons
sym is the number of the irreducible representation
spin defines the spin symmetry, \( spin = 2S \) (singlet=0, doublet=1, triplet=2, etc.)

Note that these values take sensible defaults if any or all are not specified (see section 4.8).

The input directives STATE, WEIGHT, LQUANT, SELECT, PUNCSF always refer to the state symmetry as defined on the previous WF card. If such a directive is found before a WF card has been given, an error occurs. If any of these cards and a WF card is given, the variables STATE, WEIGHT, LQUANT, SELECT are not used, and the number of state symmetries defaults to one, regardless of how many symmetries are specified in variable [MC]SYMMETRY.

### 19.3.2 Defining the number of states in the present symmetry

\[ \text{STATE}, \text{nstate}; \]

\( \text{nstate} \) is the number of states in the present symmetry. By default, all states are optimized with weight 1 (see WEIGHT card). The STATE directive must follow a WF card.

### 19.3.3 Specifying weights in state-averaged calculations

\[ \text{WEIGHT}, w(1), w(2), \ldots, w(\text{nstate}); \]

\( w(i) \) is the weight for the state \( i \) in the present symmetry. By default, all weights are 1.0. See also STATE card. If you want to optimize the second state of a particular state symmetry alone, specify

\[ \text{STATE}, 2; \text{WEIGHT}, 0, 1; \]

Note, however, that this might lead to root-flipping problems. WEIGHT should follow a STATE directive.

### 19.3.4 Dynamical weighting

Dynamical weighting, as described in J. Chem. Phys. 120, 7281 (2004), can be activated using DYNW, dynfac

The weights for each state are then computed as

\[ w = \frac{1}{\cosh(\text{dynfac} \times \Delta E)^2} \]  

where \( \Delta E \) is the energy difference (in Hartree) between the state under consideration and the ground state. This is dynamically adjusted during the optimization process.

### 19.4 Defining the configuration space

By default, the program generates a complete configuration set (CAS) in the active space. The full space may be restricted to a certain occupation pattern using the RESTRICT option. Alternatively, configurations may be selected from the wavefunction of a previous calculation using SELECT, or explicitly specified on CON cards. Note that this program only allows to select or
specify orbital configurations. For each orbital configuration, all spin couplings are always included. Possible \texttt{RESTRICT}, \texttt{SELECT} and \texttt{CON} cards must immediately follow the \texttt{WF} card which defines the corresponding state symmetry.

### 19.4.1 Occupation restrictions

\texttt{RESTRICT,nmin,nmax,orb1,orb2,...,orb_n;}

This card can be used to restrict the occupation patterns. Only configurations containing between \texttt{nmin} and \texttt{nmax} electrons in the specified orbitals \texttt{orb1}, \texttt{orb2},...\texttt{orb_n} are included in the wavefunction. If \texttt{nmin} and \texttt{nmax} are negative, configurations with exactly \texttt{abs(nmin)} and \texttt{abs(nmax)} electrons in the specified orbitals are deleted. This can be used, for instance, to omit singly excited configurations. The orbitals are specified in the form \texttt{number.sym}, where \texttt{number} is the number of the orbital in irrep \texttt{sym}. Several \texttt{RESTRICT} cards may follow each other. \texttt{RESTRICT} only works if a \texttt{CONFIG} card is specified before the first \texttt{WF} card.

\texttt{RESTRICT} cards given before the first \texttt{WF} cards are global, i.e., are active for all state symmetries. If such a global restrict card is given, variable \texttt{[MC]}\texttt{RESTRICT} is not used.

Additional state-specific \texttt{RESTRICT} cards may be given after a \texttt{WF} card. These are used in addition to the global orbital restrictions.

If neither state-specific nor global \texttt{RESTRICT} cards are found, the values from the variable \texttt{[MC]}\texttt{RESTRICT} are used.

### 19.4.2 Selecting configurations

\texttt{SELECT,ref1,ref2,refthr,refstat,mxshrf;}

This card is used to specify a configuration set other than a CAS, which is the default. This option automatically triggers the \texttt{CONFIG} option, which selects CSFs rather than determinants. Configurations can be defined using \texttt{CON} cards, which must follow immediately the \texttt{SELECT} card. Alternatively, if \texttt{ref1} is an existing \texttt{MOLPRO} record name, the configurations are read in from that record and may be selected according to a given threshold.

\texttt{ref1=rec1.file} \hspace{1cm} (\texttt{rec1> 2000}) The configurations are read in from the specified record. If \texttt{ref1} is not specified, the program assumes that the configurations are read from subsequent \texttt{CON} cards (see \texttt{CON}).

\texttt{ref2=rec2.file} \hspace{1cm} (\texttt{rec2> 2000}) Additional configurations are read from the specified record. If \texttt{rec2} is negative, all records between \texttt{rec1} and \texttt{abs(rec2)} are read. All configurations found in this way are merged.

\texttt{refthr} Selection threshold for configurations read from disc (records \texttt{rec1}--\texttt{rec2}). This applies to the norm of all CSFs for each orbital configuration.

\texttt{refstat} Specifies from which state vector the configurations are selected. This only applies to the case that the configurations were saved in a state-averaged calculation. If \texttt{refstat} is not specified, the configurations are selected from all states.

\texttt{mxshrf} max. number of open shells in the selected or generated configurations.
19.4.3 Specifying orbital configurations

CON, n₁, n₂, n₃, n₄, ...

Specifies an orbital configuration to be included in the present symmetry. The first CON card must be preceded by a SELECT card. n₁, n₂ etc. are the occupation numbers of the active orbitals (0, 1, or 2). For example, for

OCC, 5, 2, 2; CLOSED, 2, 1, 1;

n₁ is the occupation of orbital 3.1 (number.sym), n₂ is the occupation of orbital 4.1, n₃ of 5.1, n₄ of 2.2, and n₅ of 2.3. Any number of CON cards may follow each other.

Example for the BH molecule:

OCC, 4, 1, 1;  ! four sigma, one pi orbitals are occupied
FROZEN, 1;  ! first sigma orbital is doubly occupied and frozen
WF, 6, 1;  ! 6 electrons, singlet Sigma+ state
SELECT  ! triggers configuration input
CON, 2, 2  ! 2sigma**2, 3sigma**2
CON, 2, 1, 1 ! 2sigma**2, 3sigma, 4sigma
CON, 2, 0, 2 ! 2sigma**2, 4sigma**2
CON, 2, 0, 0, 2 ! 2sigma**2, 1pi_x**2
CON, 2, 0, 0, 0, 2 ! 2sigma**2, 1pi_y**2

19.4.4 Selecting the primary configuration set

PSPACE, thresh

The Hamiltonian is constructed and diagonalized explicitly in the primary configuration space, which can be selected with the PSPACE card. The coefficients of the remaining configurations (Q-space) are optimized iteratively using the P-space wavefunction as zeroth order approximation.

If thresh is nonzero, it is a threshold for automatically selecting all configurations as P-space configurations which have energies less than emin + thresh, where emin is the lowest energy of all configurations. Further P-space configurations can be specified using CON cards, which must follow immediately after the PSPACE card. These are merged with the ones selected according to the threshold. Automatic selection can be avoided by specifying a very small threshold. There is a sensible default value for thresh (0.4), so you usually don’t need a pspace card in your input. Furthermore, if the number of configurations in the MCSCF is less than 20, all configurations go into the P-space unless you give a PSPACE card in the input.

A P-space threshold defined on a PSPACE card before the first WF (or STATE, WEIGHT, SELECT, PUNCSF if WF is not given) card is global, i.e., valid for all state symmetries. State-specific thresholds can be defined by placing a PSPACE card after the corresponding WF card. In the latter case the PSPACE card can be followed by CON cards, which define state-specific P-space configurations.

19.4.5 Projection to specific Λ states in linear molecules

Since MOLPRO can only use Abelian point groups (e.g. C₂ᵥ instead of Cᵥ for linear molecules), Δₓ²−y² states as well as Σ⁺ states occur in the irreducible representation number 1, for example. Sometimes it is not possible to predict in advance to which state(s) the program will converge. In such cases the LQUANT option can be used to specify which states are desired.

LQUANT, lam(1), lam(2), ..., lam(nstate);
\( \lambda(i) \) is the \( \Lambda \) quantum number of state \( i \), i.e., 0 for \( \Sigma \) states, 1 for \( \Pi \) states, 2 for \( \Delta \) states, etc. The matrix over \( \Lambda^2 \) will be constructed and diagonalized in the P-space configuration basis. The eigenvectors are used to transform the P-space hamiltonian into a symmetry adapted basis, and the program then selects the eigenvectors of the correct symmetry. The states will be ordered by symmetry as specified on the \texttt{LQUANT} card; within each symmetry, the states will be ordered according to increasing energy.

### 19.5 Restoring and saving the orbitals and CI vectors

\textsc{MULTI} normally requires a starting orbital guess. In this section we describe how to define these orbitals, and how to save the optimized orbitals. In a CASSCF calculation, one has the choice of transforming the final orbitals to natural orbitals (the first order density matrix is diagonalized), to pseudo-canonical orbitals (an effective Fock-operator is diagonalized), or of localizing the orbitals.

#### 19.5.1 Defining the starting orbitals

\textsc{START,record,[options];}

\begin{itemize}
  \item \texttt{record}: dump record containing starting orbitals. As usual, \texttt{record} has the form \texttt{irec.ifil}, where \texttt{irec} is the record number (e.g., 2140), and \texttt{ofil} the file number (usually 2). The \texttt{options} can be used to select orbitals of a specific type; for details, see section \texttt{4.11}.
  
  If this card is missing, the program tries to find suitable starting orbitals as follows:
  
  First: Try to read orbitals from the record specified on the \texttt{ORBITAL} card (or the corresponding default, see \texttt{ORBITAL}). All files are searched.
  
  Second: Try to find orbitals from the most recent MCSCF calculation. All files are searched.
  
  Third: Try to find orbitals from the most recent SCF calculation. All files are searched.
\end{itemize}

If no orbitals are found, a starting orbital guess is generated.

It is often useful to employ MCSCF orbitals from a neighbouring geometry as starting guess (this will happen automatically if orbitals are found, see the above defaults). Note, however, that frozen-core orbitals should always be taken from an SCF or MCSCF calculation at the present geometry and must be specified separately on the \texttt{FROZEN} card. Otherwise the program is likely to stop with error “non-orthogonal core orbitals”. The program remembers where to take the core orbitals from if these have been specified on a \texttt{FROZEN} card in a previous MCSCF calculation.

#### 19.5.2 Defining the starting CI coefficients

\textsc{MULTI} normally obtains configuration mixing coefficients by a robust eigenvector solver that converges on the lowest eigenvalues, and applies a phase convention such that the largest coefficient is forced to be positive. For most purposes, this approach is satisfactory.

Sometimes one wants a guarantee that the CI vector is phase matched to that of a previous geometry. This can be achieved by using \texttt{SAVE,CI=record.file} (see section \texttt{19.5.5}) in the first job, and in the restart.
The phase convention applied for the rest of the calculation is then that, for each optimised state, the largest coefficient in the original CI vector defines the sign of the corresponding coefficient in the optimised vector.

### 19.5.3 Rotating pairs of initial orbitals

**ROTATE, orb1.sym, orb2.sym, angle**

Performs a $2 \times 2$ rotation of the initial orbitals $orb1$ and $orb2$ in symmetry $sym$ by $angle$ degrees. With $angle=0$ the orbitals are exchanged. **ROTATE** is meaningful only after the **START** card. See **MERGE** for other possibilities to manipulate orbitals.

### 19.5.4 Saving the final orbitals

**ORBITAL, record.file**

The orbitals are dumped to record $record.file$. Default for $record$ is 2140 and $file=2$. This default record number is incremented by one for each subsequent MCSCF calculation in the same job (see section [4.11]). Therefore, if several different MCSCF calculations at several geometries are performed in one job, each MCSCF will normally start with appropriate orbitals even if no **ORBITAL** or **START** card is present.

The **ORBITAL** card can be omitted if a **NATORB**, **CANORB** or **LOCORB** card is present, since $orb$ can also be specified on these cards (the same defaults for $orb$ as above apply in these cases).

### 19.5.5 Saving the CI vectors and information for a gradient calculation

**Old form (obsolete):**

`SAVE,cidump,refsav,grdsav;`

**New form:**

`SAVE,[CI=cidump,][REF=refsav,][GRD=grdsav];`

This directive must be placed before any **WF** or **STATE** cards. The options can be given in any order.

- $cidump$: record name for saving the CI vectors. By default, the vectors are only written to a scratch file. If **NATORB**, **CANORB** or **LOCORB** cards are present, $cidump$ should be specified on these cards. At present, there is hardly any use of saved CI vectors, and therefore this option is rarely needed.

- $refsav$: record name for saving the orbital configurations and their weights for use in subsequent MULTI or CI calculations using the **SELECT** directive. If wavefunctions for more than one state symmetry are optimized in a state-averaged calculation, the weights for each state symmetry are saved separately on records $refsav+(istsym−1)\times100$, where $istsym$ is the sequence number of the **WF** card in the input. If several **NATORB**, **CANORB**, or **LOCORB** cards are present, the record number is increased by 1000 for each subsequent orbital set. Note that this option implies the use of CSFs, even of no **CONFIG** card (see section [19.6.1]) is present.

- $grdsav$: record name for saving the information which is needed in a subsequent gradient calculation. This save is done automatically to record 5000.1 if the input contains a **FORCE** or **OPTG** card, and therefore the **GRD** option is normally not required.
19.5.6 Natural orbitals

NATORB,[record.][options]

Request to calculate final natural orbitals and write them to record record. The default for record is 2140.2, or what else has been specified on an ORBITAL card, if present. By default, the orbitals are not printed and the hamiltonian is not diagonalized for the new orbitals The following options can be specified (in any order):

CI
Diagonalize the hamiltonian in the basis of the computed natural orbitals and print the configurations and their associated coefficients. This has the same effect as the GPRINT,CIVECTOR directive (see section 6.12) By default, only configurations with coefficients larger than 0.05 are printed. This threshold can be modified using the THRESH (see section 19.8.2) or GTHRESH (see section 6.11) options.

STATE=state
Compute natural orbitals for the specified state. state has the form istate.isym, e.g., 3.2 for the third state in symmetry 2. In contrast to earlier versions, isym refers to the number of the irreducible representation, and not the sequence number of the state symmetry. It is therefore independent of the order in which WF cards are given. The specified state must have been optimized. If STATE is not given and two or more states are averaged, the natural orbitals are calculated with the state-averaged density matrix (default).

SPIN=ms2
Compute natural orbitals for states with the specified spin. ms2 equals 2*S, i.e., 0 for singlet, 1 for doublet etc. This can be used to together with STATE to select a specific state in case that states of different spin are averaged. If STATE is not specified, the state-averaged density for all states of the given spin is used.

SAVE=record
Request to save the civector(s) to the specified record.

ORBITAL=record
Request to save the orbitals to the specified record (same effect as specifying record as first argument (see above).

PRINT=nvirt
Request to print nvirt virtual orbitals in each symmetry. By default, the orbitals are not printed unless the ORBPRINT option (see section 19.8.1) is present or the global GPRINT,ORBITALS (see section 6.12) directive has been given before. The PRINT option on this card applies only to the current orbitals.

Several NATORB, CANORB, and LOCORB cards (for different states) may follow each other. In contrast to earlier versions of MOLPRO the different orbital sets can all be stored in one dump record (but different records still work). See section 4.11 for information about dump records and how specific orbital sets can be requested in a later calculation.

19.5.7 Pseudo-canonical orbitals

CANORB,[record.][options]

or
CANONICAL,[record.][options]

Request to canonicalize the final orbitals, and writing them to record record. All options have the same effect as described for NATORB.

19.5.8 Localized orbitals

LOCORB,[record.][options]

or

LOCAL,[record.][options]

Request to localize the final orbitals, and writing them to record record. All options have the same effect as described for NATORB.

Note: LOCAL is interpreted by MULTI, but LOCALI is a separate command which calls the localization program and not recognized by MULTI. In order to avoid confusion, it is recommended to use LOCORB rather than LOCAL as subcommand within MULTI.

19.5.9 Diabatic orbitals

In order to construct diabatic states, it is necessary to determine the mixing of the diabatic states in the adiabatic wavefunctions. In principle, this mixing can be obtained by integration of the non-adiabatic coupling matrix elements. Often, it is much easier to use an approximate method, in which the mixing is determined by inspection of the CI coefficients of the MCSCF or CI wavefunctions. This method is applicable only if the orbital mixing is negligible. For CASSCF wavefunctions this can be achieved by maximizing the overlap of the active orbitals with those of a reference geometry, at which the wavefunctions are assumed to be diabatic (e.g. for symmetry reasons). The orbital overlap is maximized using using the new DIAB command in the MCSCF program. Only the active orbitals are transformed.

This procedure works as follows: first, the orbitals are determined at the reference geometry. Then, the calculations are performed at displaced geometries, and the "diabatic" active orbitals, which have maximum overlap with the active orbitals at the reference geometry, are obtained by adding a DIAB directive to the input:

Old form (Molpro96, obsolete):

DIAB,orbref, orbsav, orb1,orb2,pri

New form:

DIAB,orbref,TYPE=orbtype[,STATE=state][,SPIN=spin][,MS2=ms2][,SAVE=orbsav][,ORB1=orb1,ORB2=orb2][,PRINT=pri][,METHOD=method]

Here orbref is the record holding the orbitals of the reference geometry, and orbsav is the record on which the new orbitals are stored. If orbsav is not given (recommended!) the new orbitals are stored in the default dump record (2140.2) or the one given on the ORBITAL directive (see section §19.5.4). In contrast to earlier versions of MOLPRO it is possible that orbref and orbsav are the same. The specifications TYPE, STATE, SPIN can be used to select specific sets of reference orbitals, as described in section §4.11. orb1, orb2 is a pair of orbitals for which the overlap is to be maximized. These orbitals are specified in the form number:sym, e.g. 3.1 means the third orbital in symmetry 1. If orb1, orb2 are not given, the overlap of all active orbitals is maximized. pri is a print parameter. If this is set to 1, the transformation angles for each orbital are printed for each Jacobi iteration. method determines the diabatization method.
method=1 (default): use Jacobi rotations; method=2: use block diagonalization. Both methods yield very similar results. method=2 must only be used for CASSCF wavefunctions. method=-1 and method=-2: as the positive values, but AO overlap matrix of the current geometry is used. This minimizes the change of the MO coefficients, rather than maximizing the overlap to the neighbouring orbitals.

Using the defaults described above, the following input is sufficient in most cases:

```
DIAB,orbref
```

Using Molpro98 is not necessary any more to give any GEOM and DISPL cards. The displacements and overlap matrices are computed automatically (the geometries are stored in the dump records, along with the orbitals).

The diabatic orbitals have the property that the sum of orbital and overlap contributions in the non-adiabatic coupling matrix elements become approximately zero, such that the adiabatic mixing occurs only through changes of the CI coefficients. This allows to determine the mixing angle directly from the CI coefficients, either in a simple way as described for instance in J. Chem. Phys. 89, 3139 (1988), or in a more advanced manner as described by Pacher, Cederbaum, and Köppel in J. Chem. Phys. 89, 7367 (1988). Recently, an automatic procedure, as described in J. Chem. Phys. 102, 0000, (1999) has been implemented into MOLPRO. This is available in Version 99.1 and later and is described in section 42.

Below we present an example for the first two excited states of H$_2$S, which have $B_1$ and $A_2$ symmetry in $C_{2v}$, and $A'\prime\prime$ symmetry in $C_S$. We first perform a reference calculation in $C_{2v}$ symmetry, and then determine the diabatic orbitals for displaced geometries in $C_S$ symmetry. Each subsequent calculation uses the previous orbitals as reference. One could also use the orbitals of the $C_{2v}$ calculation as reference for all other calculations. In this case one would have to take out the second-last input card, which sets reforb=2141.2.
***, H2S diabatic $\Delta^\prime$ states

basis=VDZ
symmetry=x, planeyz
orient=nonorient
geometry={s; h1, s, r1; h2, s, r2, h1, theta}
gprint, orbitals, civec

text, reference calculation for C2V
theta=92.12, r1=2.3, r2=2.3
{hf; occ, 7, 2; wf, 18, 1}
{multi; occ, 9, 2; closed, 4, 1; wf, 18, 2; state, 2; orbital, 2140.2}
reforb=2140.2

text, calculations at displaced geometries
rd=[2.4, 2.5, 2.6]
do i=1, #rd
r2=rd(i)
{multi; occ, 9, 2; closed, 4, 1; wf, 18, 2; state, 2; orbital, 2141.2}
diab, reforb)
reforb=2141.2
enddo

http://www.molpro.net/info/current/examples/h2s_diab.com

See section 42 for the automatic generation of diabatic energies.

### 19.6 Selecting the optimization methods

By default, MULTI uses the non-linear optimization method developed by Werner, Meyer, and Knowles. Other methods, such as the Newton-Raphson procedure or the Augmented Hessian procedure, are also implemented and can be selected using the ITERATIONS directive (for state-averaged calculations, only the non-linear optimization method can be used). For CASSCF calculations, the CI problem is solved in a basis of Slater determinants, unless a CONFIG card is given. Some procedures may be disabled using the DONT directive.

#### 19.6.1 Selecting the CI method

CONFIG, key;

key may be DET or CSF, and defaults to CSF. If no CONFIG or SELECT card is given, the default is determinants (CASSCF).
19.6.2 Selecting the orbital optimization method

The **ITERATIONS** directive can be used to modify the defaults for the optimization method. It consists of a sequence of several cards, which should be enclosed in a pair of curly brackets.

```plaintext
{ ITERATIONS:
   DO, method1, iter1[, TO, iter2];
   DONT, method2, iter3[, TO, iter4];
   ... 
}
```

*method* can be one of the following:

- **DIAGCI**: Diagonalize Hamiltonian in the beginning of the specified iterations. This is the default for iteration 1.
- **INTERNAL**: Optimize internal orbitals at the beginning of the specified iterations. This is default for second and subsequent iterations.
- **WERNER**: Use Werner-Meyer-Knowles non-linear optimization method for the specified iterations. This is the default for all iterations.
- **AUGMENT**: Use step-restricted Augmented Hessian method for the specified iterations.
- **NEWTON**: Use Newton-Raphson method for specified iterations.
- **UNCouple**: Do not optimize orbitals and CI coefficients simultaneously in the specified iterations. This option will set DIAGCI for these iterations.
- **NULL**: No orbital optimization.

19.6.3 Disabling the optimization

In addition to the **ITERATIONS** directive described above, some procedures can be disabled more simply using the **DONT** directive. **DONT,code**

*code* may be

- **ORBITAL**: Do initial CI but don’t optimize orbitals.
- **WAVEFUNC**: Do not optimize the orbitals and CI coefficients (i.e. do only wavefunction analysis, provided the orbitals and CI coefficients are supplied (see START card)).
- **WVFN**: Alias for WAVEFUNC.
- **ANAL**: Do no wavefunction analysis.

19.6.4 Disabling the extra symmetry mechanism

**NOEXTRA**

This card disables the search for extra symmetries. By default, if extra symmetries are present, each orbital is assigned to such an extra symmetry and rotations between orbitals of different extra symmetry are not performed.
19.7 Calculating expectation values

By default, the program calculates the dipole expectation and transition moments. Further expectation values or transition properties can be computed using the \texttt{TRAN}, \texttt{TRAN2} and \texttt{EXPEC}, \texttt{EXPEC2} directives.

19.7.1 Matrix elements over one-electron operators

\texttt{EXPEC,oper}_1,\texttt{oper}_2,\ldots,\texttt{oper}_n
\texttt{TRAN,oper}_1,\texttt{oper}_2,\ldots,\texttt{oper}_n

Calculate expectation values and transition matrix elements for the given one-electron operators. With \texttt{EXPEC} only expectation values are calculated. \texttt{oper}_i is a codeword for the operator. The available operators and their associated keywords are given in section 6.13.

19.7.2 Matrix elements over two-electron operators

\texttt{EXPEC2,oper}_1,\texttt{oper}_2,\ldots,\texttt{oper}_n
\texttt{TRAN2,oper}_1,\texttt{oper}_2,\ldots,\texttt{oper}_n

Calculate transition matrix elements for two-electron operators. This is presently only useful for angular momentum operators. With \texttt{EXPEC2} only diagonal matrix elements will be computed. For instance

\texttt{TRAN2, LXX} calculates matrix elements for $L_x^2$
\texttt{TRAN2, LYY} calculates matrix elements for $L_y^2$
\texttt{TRAN2, LXZ} calculates matrix elements for $\frac{1}{2}(L_xL_z+L_zL_x)$
\texttt{TRAN2, LXX, LYY, LZZ} calculates matrix elements for $L_x^2$, $L_y^2$, and $L_z^2$. The matrix elements for the sum $L^2$ are also printed.

19.7.3 Saving the density matrix

\texttt{DM,[spindens]}

If the \texttt{DM} directive is given, the first order density matrix in AO basis is written to the dump record specified on the \texttt{ORBITAL} card (default 2140.2). If no \texttt{ORBITAL} card is present, but a record is specified on a \texttt{NATORB}, \texttt{CANORB}, or \texttt{LOCORB} card, the densities are saved to the first record occurring in the input. In a state-averaged calculation the SA-density, as well the individual state densities, are saved. See section 4.11 for information about how to recover any of these densities for use in later programs.

If \texttt{spindens} is a number greater than zero, the spin density matrices are also saved. Note that a maximum of 50 density matrices can be saved in one dump record.

If no \texttt{DM} directive is given), the first order density matrix is saved in single-state calculations, and only the stage-averaged density matrix in state-averaged calculations.

19.8 Miscellaneous options

All commands described in this section are optional. Appropriate default values are normally used. Note that printing of the orbitals and civectors can also be requested using the global \texttt{GPRINT} command, or by giving \texttt{NATORB} or \texttt{CANORB} options.
19.8.1 Print options

ORBPRINT[$nvirt$]

requests the occupied and $nvirt$ virtual orbitals in each symmetry to be printed (default $nvirt=0$). By default, the program does not print the orbitals, unless the ORBPRINT directive or a global GPRINT, ORBITALS (see section 6.12) command is present. Specific orbital sets can be printed using the PRINT option on a NATORB, CANORB, or LOCORB card (see section 19.5.6). To print additional information at the end of the calculation, use

PRINT,key1,key2,...;

Printing is switched on for key1, key2,... To print information in each iteration, use

IPRINT,key1,key2,...;

Possible print keys are:

- MICRO: print details of “microiterations” — useful for finding out what’s going wrong if no convergence
- REF: print summary of configuration set (CSFs only)
- REF1: print list of configuration set (CSFs only)
- COR: print summary of intermediate spaces used in CSF calculation
- COR1: print list of intermediate configuration sets (CSFs only)
- PSPACE: print list of configurations making up the “primary” space
- ORBITALS: print orbitals (see also ORBPRINT)
- NATORB: print natural orbitals (see also ORBPRINT)
- VIRTUALS: print virtual orbitals (see also ORBPRINT)
- CIVECTOR: print CI vector (better use CANORB or NATORB)
- INTEGRAL: print transformed integrals (for testing only!)
- DENSITY: print density matrices
- HESSIAN: print hessian
- DIAGONAL: print diagonal elements of hessian
- GRADIENT: print gradient
- LAGRANGI: print Lagrangian
- STEP: print update vector
- ADDRESS: print addressing information (for testing only!)
- DEBUG: print debugging information
- CI2: print debugging information in routine ci2 (Warning: may be long!!)
- IO: print debugging information in I/O routines

19.8.2 Convergence thresholds

Convergence thresholds can be modified using

ACCURACY,[GRADIENT=conv],[STEP=sconv],[ENERGY=econv]

where
conv

Threshold for orbital gradient (default $10^{-2}$).

\[ econv \]

Threshold for change of total energy (default $10^{-6}$).

\[ sconv \]

Threshold for size of step (default $10^{-3}$).

The default values can be modified using the global `GTHRESH` command (see section 6.11). Normally, the above default values are appropriate.

### 19.8.3 Maximum number of iterations

\[ \text{MAXITER,} \text{maxit}; \]

\[ \text{maxit} \]

is maximum number of iterations (default 20). If the calculation does not converge in the default number of iterations, you should first think about the reason before increasing the limit. In most cases the choice of active orbitals or of the optimized states is not appropriate (see introduction of MULTI). The maximum allowed value of `maxit` is 40. If the calculation has not converged in this number of iterations, it is likely that the active space is not reasonable. Note: slow convergence can occur in RASSCF calculations if single excitations into weakly occupied orbitals are present. These should be eliminated using

\[ \text{RESTRICT, -1, -1, orbital list} \]

### 19.8.4 Test options

\[ \text{TEST,} i_1, i_2, i_3, \ldots; \]

Activate testing options numbered \( i_1, i_2, \ldots \). Please do not use unless you know what you are doing!

### 19.8.5 Special optimization parameters

The following parameters can also be given as options on the `MULTI` command line.

\[ \text{STEP,} \text{radius,} \text{trust1,} \text{tfac1,} \text{trust2,} \text{tfac2}; \]

Special parameters for augmented hessian method. For experts only!

\[ \text{GOPER,} \text{igop}; \]

Use G-operator technique in microiterations (Default). If `igop.lt.0` do not use G-operators.

\[ \text{COPT,} \text{ciacc,} \text{copvar,} \text{maxci,} \text{cishft,} \text{icimax,} \text{icimx1,} \text{icimx2,} \text{icstrt,} \text{icstep}; \]

Special parameters for the direct CI method. For experts only!

\[ \text{ciacc} \]

grad threshold for CI diagonalization

\[ \text{copvar} \]

start threshold for CI-optimization

\[ \text{maxci} \]

max. number of CI-optimizations per microiteration

\[ \text{cishft} \]

denominator shift for q-space

\[ \text{icimax} \]

max. number of CI-optimizations in first macroiteration

\[ \text{icimx1} \]

max. number of CI-optimizations in second and subsequent iterations

\[ \text{icimx2} \]

max. number of CI-optimizations in internal absorption step
icstrt first microiteration with CI-optimization
icstep microiteration increment between CI-optimizations

INTOPT,maxito,maxitc,maxrep,nitrep,iuprod;
Special parameters for internal optimization scheme. For experts only!
NONLINEAR,imax;r,ipri,dmax,drdamp,gfak1,gfak2,gfak3,irdamp,ntexp
Special parameters for non-linear optimization scheme. For experts only!
Old form (obsolete):
THRESH,thrpri,thrpun,varmin,varmax,thrdiv,thrdoub
New form:
THRESH[,THRPRIT=thrpri][,THRPUN=thrpun][,VARMIN=varmin]
[,VARMAX=varmax][,THRDIV=thrdiv][,THRDUB=thrdoub]

thrpri threshold for printing CI coefficients (default 0.04)
thrpun threshold for writing CI coefficients to the punch file. Default is no write to the punch file
varmin,varmax thresholds for non-linear optimization scheme. For experts only!
thrdoub threshold for detecting almost doubly occupied orbitals for inclusion into the pseudo canonical set (default 0, i.e. the feature is disabled).

DIIS,disvar,augvar,maxdis,maxaug,idsci,igwgt,igvec,idstrt,idstep;
Special parameters for DIIS convergence acceleration. For experts only!

19.8.6 Saving wavefunction information for CASVB

VBDUMP[,vbdump];
For users of the valence bond program CASVB, all wavefunction information that may subsequently be required is saved to the record vbdump. The default is not to write this information. If the keyword is specified without a value for vbdump, then record 4299.2 is used. This keyword is not needed prior to variational CASVB calculations.

19.8.7 Saving transformed integrals

TRNINT,tnint;

trnint specifies the record name for integrals in the basis of active CASSCF MOs. These are used for example by CASVB (see section 43.5). The default value for trnint is 1900.1.

19.9 Coupled-perturbed MCSCF

The coupled-perturbed MCSCF is required for computing gradients with state-averaged orbitals, non-adiabatic couplings, difference gradients or polarizabilities. We note that the present implementation is somewhat preliminary and not very efficient.
19.9.1 Gradients for SA-MCSCF

For computing state-averaged gradients, use

\texttt{CPMCSCF,GRAD,state,[SPIN=spin],[MS2=ms2],[ACCU=thresh],[RECORD=record]}

where \texttt{state} specifies the state (e.g., 2.1 for the second state in symmetry 1) for which the gradients will be computed. \texttt{spin} specifies the spin of the state: this is half the value used in the corresponding WF card (e.g., 0=Singlet, 0.5=Doublet, 1=Triplet). Alternatively, \texttt{MS2} can be used, where \texttt{ms2} = 2*spin, i.e., the same as specified on WF cards. The specification of \texttt{SPIN} or \texttt{MS2} is only necessary if states with different spin are state-averaged. \texttt{record} specifies a record on which the gradient information is stored (the default is 5101.1). \texttt{thresh} is a threshold for the accuracy of the CP-MCSCF solution. The default is 1.d-7.

The gradients are computed by a subsequent call to \texttt{FORCES} or \texttt{OPTG}.

Note: if for some reason the gradients are to be computed numerically from finite energy differences, it is in state-averaged calculations necessary to give, instead of the \texttt{CPMCSCF} input, the following:

\texttt{SAVE,GRAD=-1}

Otherwise the program will stop with an error message.

19.9.2 Difference gradients for SA-MCSCF

For computing difference gradients, use

\texttt{CPMCSCF,DGRAD,state1,state2,[ACCU=thresh],[RECORD=record]}

where \texttt{state1} and \texttt{state2} specify the two states considered. (e.g., 2.1,3.1 for the second and third states in symmetry 1) The gradient of the energy difference will be computed. Both states must have the same symmetry. \texttt{record} specifies a record on which the gradient information is stored (the default is 5101.1). \texttt{thresh} is a threshold for the accuracy of the CP-MCSCF solution. The default is 1.d-7.

The gradients are computed by a subsequent call to \texttt{FORCES} or \texttt{OPTG}.

19.9.3 Non-adiabatic coupling matrix elements for SA-MCSCF

For computing non-adiabatic coupling matrix elements analytically, use

\texttt{CPMCSCF,NACM,state1,state2,[ACCU=thresh],[RECORD=record]}

where \texttt{state1} and \texttt{state2} specify the two states considered. (e.g., 2.1,3.1 for the second and third states in symmetry 1) Both states must have the same symmetry. \texttt{record} specifies a record on which the gradient information is stored (the default is 5101.1). This will be read in the subsequent gradient calculation. \texttt{thresh} is a threshold for the accuracy of the CP-MCSCF solution. The default is 1.d-7.

\texttt{NADC} and \texttt{NADK} are an aliases for \texttt{NADC}, and \texttt{SAVE} is an alias for \texttt{RECORD}.

The matrix elements for each atom are computed by a subsequent call to \texttt{FORCES}.

Note: this program is not yet extensively tested and should be used with care!
19.9.4 MCSCF Hessians

The MCSCF/CASSCF hessian can be computed analytically (only without symmetry) using

\[ \text{CPMCSCF, HESS, [ACCU=\text{value}]} \]

where the \text{ACCU} option specifies the convergence threshold in the CPMCSCF calculation (default \(1.d^{-4}\)). The hessian is stored on record 5300.2 and can be used in a subsequent frequency calculation.

Example:

\{\text{multi;cpmcscf,hess,accu=1.d-5}\}
frequencies

Note that the \text{NOEXTRA} option is used when computing a hessian.

19.10 Optimizing valence bond wavefunctions

\text{VB=\{\ldots\}}

Using this keyword, the optimization of the CI coefficients is carried out by \text{CASVB}. The \text{VB} keyword can be followed by any of the directives described in section 43. Energy-based optimization of the VB parameters is the default, and the output level for the main \text{CASVB} iterations is reduced to \(-1\).

19.11 Total Position-Spread tensor (TPS)

Bibliography:


All publications resulting from use of this program must acknowledge the above. See also:


The total position-spread (TPS) tensor is a quantity originally introduced in the modern theory of electrical conductivity. In the case of molecular systems, this tensor measures the fluctuation of the electrons around their mean positions, which corresponds to the delocalization of the electronic charge within a molecular system. The TPS can discriminate between metals and insulators taking information from the ground state wave function. This quantity can be very useful as an indicator to characterize Intervalence charge transfer processes, the bond nature of molecules (covalent, ionic or weakly bonded), and Metalinsulator transition.

The program is invoked by \text{TRAN2} inside the \text{MULTI} input block:

\text{TRAN2,RXX,RYY,RZZ,RXY,RXZ,RYZ;}

The three different classes of contributions to the CASSCF wave function can be printed by using the keyword:
19.12 Hints and strategies

MCSCF is not a “black box” procedure like SCF! For simple cases, for example a simple CASSCF with no CLOSED orbitals, this program will converge in two or three iterations. For more complicated cases, you may have more trouble. In that case, consider the following:

- Always start from neighbouring geometry orbitals when available (this is the default).
- The convergence algorithm is more stable when there are no CLOSED orbitals, i.e., orbitals doubly occupied in all configurations, but fully optimized. Thus a reasonable approach is to make an initial calculation with CLOSED replaced by FROZEN (all doubly occ. frozen).
- If still no success, you can switch off the coupling between CI coefficients and orbital rotations for a few iterations, e.g.:
  ```
  { ITERATIONS; DO, UNCOUPLE, 1, TO, 2; }
  ```
  and/or disable the simultaneous optimization of internal orbitals & CI, e.g.:
  ```
  { ITERATIONS; DONT, INTERNAL, 1, TO, 2; }
  ```

You can often get a clue about where the program starts to diverge if you include:

```plaintext
IPRINT, MICRO;
```

in the data. Also consider the general remarks at the beginning of this chapter. For the details of the algorithms used, see J. Chem. Phys 82, 5053 (1985); Chem. Phys. Letters 115, 259 (1985); Advan. Chem. Phys. 59, 1 (1987);

19.13 Examples

The simplest input for a CASSCF calculation for H$_2$O, $C_2v$ symmetry, is simply:

```plaintext
gometry={o;h1,o,r;h2,o,r,h1,theta} !Z-matrix geometry input
r=1 ang !bond length
theta=104 !bond angle
hf !do scf calculation
multi !do full valence casscf
```

This could be extended, for instance, by the following input cards

```plaintext
OCC,4,1,2; ! specify occupied space
CLOSED,2 ! specify closed-shell (inactive) orbitals
FROZEN,1; ! specify frozen core orbitals
WF,10,1; ! define wavefunction symmetry
START,2100.2; ! read guess orbitals from record 2100, file 2
ORBITAL,2140.2; ! save final orbitals to record 2140, file 2
NATORB,PRINT,CI ! print natural orbitals and diagonalize the hamiltonian
! for the natural orbitals. The largest CI coefficients
! are printed.
```

http://www.molpro.net/info/current/examples/h2o_casscf.com
Example for a state-averaged calculation for CN, $X$ and $B$ $^2\Sigma^+$ states, and $A$ $^2\Pi_x$, $^2\Pi_y$ states averaged. A full valence CASSCF calculation is performed

```
***,cn
r=2.2 !define bond length
geometry=(c;n,c,r)
(rhf;occ,5,1,1;wf,13,1,1;
orbital,2100.2) !RHF calculation for sigma state

(multi;occ,6,2,2;closed,2)
start,2100.2; !Start with RHF orbitals from above
save,ref=4000.2 !Save configuration weights for CI in record 4000.2
wf,13,1,1;state,2;wf,13,2,1;wf,13,3,1; !Define the four states
natorb,ci,print; !Print natural orbitals and associated ci-coefficients
tran,lz !Compute matrix elements over LZ
expec2,lzz) !compute expectation values for LZZ
```

http://www.molpro.net/info/current/examples/cn_sa_casscf.com

Example for an RASSCF (restricted active space) calculation for N$_2$, including SCF determinant plus all double excitations into valence orbitals. The single excitations are excluded. $D_{2h}$ symmetry, CSF method used:

```
***,N2
geometry=(N1;N2,N1,r) !geometry input
r=2.2 !bond length
(hf;occ,3,1,1,,2;wf,14,1;save,2100.2) !scf calculation

(multi;occ,3,1,1,,3,1,1;
frozen,1,,,1,2100.2;
config; !Use CSF method
wf,14,1;
restrict,0,2,3.5,1.6,1.7;
restrict,-1,-1,3.5,1.6,1.7;
print,ref1 !Print configurations
natorb,ci,print) !Print natural orbitals and CI coeffs
```

http://www.molpro.net/info/current/examples/n2_rasscf.com

20 THE CI PROGRAM

Multiconfiguration reference internally contracted configuration interaction

Bibliography:

For excited state calculations:

For explicitly correlated MRCI (MRCI-F12):

All publications resulting from use of the corresponding methods must acknowledge the above.
The first internally correlated MRCI program was described in:

The command CI or CI-PRO or MRCI calls the MRCI program.
The command MRCI-F12 calls the explicitly correlated MRCI-F12 program.
The command CISD calls fast closed-shell CISD program.
The command QC1 calls closed-shell quadratic CI program.
The command CCSD calls closed-shell coupled-cluster program.

The following options may be specified on the command line:

- NOCHECK: Do not stop if no convergence.
- DIRECT: Do calculation integral direct.
- NOSING: Do not include singly external configurations.
- NOPAIR: Do not include doubly external configurations (not valid for single reference methods).
- MAXIT=value: Maximum number of iterations.
- MAXITI=value: Maximum number of microiterations (for internals).
- SHIFTI=value: Denominator shift for update of internal configurations.
- SHIFTS=value: Denominator shift for update of singles.
- SHIFTP=value: Denominator shift for update of doubles.
- THRDEN=value: Convergence threshold for the energy.
- THRVAR=value: Convergence threshold for the CI-vector. This applies to the square sum of the changes of the CI-coefficients.
- SWAP|NOSWAP: If SWAP is given, the MRCI wavefunctions are reordered according to maximum overlap with the reference functions (this only applies in multi-state calculations). The default is NOSWAP, i.e. the states are ordered according to increasing MRCI energy.
- ROTREF=value: If value=0 the cluster corrections are not printed for the rotated reference energies (cf. Section 20.7). If value=1 all corrections are printed. If value=-1 the 2009.1 behaviour is recovered.

20.1 Introduction

The internally contracted MRCI program is called by the CI command. This includes as special cases single reference CI, CEPA, ACPF, MR-ACPF and MR-AQCC. For closed-shell reference functions, a special faster code exists, which can be called using the CISD, QC1, or CCSD commands. This also allows to calculate Brueckner orbitals for all three cases (QC1 and CCSD are identical in this case).

The explicitly correlated variant is called by the command MRCI-F12, see section 20.8.

With no further input cards, the wavefunction definition (core, closed, and active orbital spaces, symmetry) corresponds to the one used in the most recently done SCF or MCSCF calculation. By default, a CASSCF reference space is generated. Other choices can be made using the OCC, CORE, CLOSED, WF, SELECT, CON, and RESTRICT cards. The orbitals are taken from the corresponding SCF or MCSCF calculation unless an ORBITAL directive is given. The
wavefunction may be saved using the SAVE directive, and restarted using START. The EXPEC directive allows to compute expectation values over one-electron operators, and the TRAN directive can be used to compute transition matrix elements for one-electron properties. Natural orbitals can be printed and saved using the NATORB directive.

For excited state calculations see STATE, REFSTATE, and PROJECT.

20.2 Specifying the wavefunction

Note: All occupations must be given before WF, PAIRSS, DOMAIN, REGION or other directives that need the occupations.

20.2.1 Occupied orbitals

OCC,$n_1,n_2,...,n_8$;

$n_i$ specifies numbers of occupied orbitals (including CORE and CLOSED) in irreducible representation number $i$. If not given, the information defaults to that from the most recent SCF, MCSCF or CI calculation.

20.2.2 Frozen-core orbitals

CORE,$n_1,n_2,...,n_8$;

$n_i$ is the number of frozen-core orbitals in irrep number $i$. These orbitals are doubly occupied in all configurations, i.e., not correlated. If no CORE card is given, the program uses the same core orbitals as the last CI calculation; if there was none, then the atomic inner shells are taken as core. To avoid this behaviour and correlate all electrons, specify

CORE

20.2.3 Closed-shell orbitals

CLOSED,$n_1,n_2,...,n_8$

$n_i$ is the number of closed-shell orbitals in irrep number $i$, inclusive of any core orbitals. These orbitals do not form part of the active space, i.e., they are doubly occupied in all reference CSFs; however, in contrast to the core orbitals (see CORE), these orbitals are correlated through single and double excitations. If not given, the information defaults to that from the most recent SCF, MCSCF or CI calculation. For calculations with closed-shell reference function (closed=occ), see CISD, QCI, and CCSD.

20.2.4 Defining the orbitals

ORBIT,name.file,[specifications];

name.file specifies the record from which orbitals are read. Optionally, various specifications can be given to select specific orbitals if name.file contains more than one orbital set. For details see section 4.11. Note that the IGNORE_ERROR option can be used to force MPn or triples calculations with non-canonical orbitals.

The default is the set of orbitals from the last SCF, MCSCF or CI calculation.
20.2.5 Defining the state symmetry

The number of electrons and the total symmetry of the wavefunction are specified on the WF card:

\texttt{WF, elec, sym, spin}

where

- \texttt{elec}: is the number of electrons
- \texttt{sym}: is the number of the irreducible representation
- \texttt{spin}: defines the spin symmetry, \texttt{spin} = 2S (singlet=0, doublet=1, triplet=2, etc.)

The WF card must be placed after any cards defining the orbital spaces \texttt{OCC, CORE, CLOSED}. The \texttt{REF} card can be used to define further reference symmetries used for generating the configuration space, see \texttt{REF}.

20.2.6 Additional reference symmetries

\texttt{REF, sym;}

This card, which must come after the \texttt{WF} directive, defines an additional reference symmetry used for generating the uncontracted internal and singly external configuration spaces. This is sometimes useful in order to obtain the same configuration spaces when different point group symmetries are used. For instance, if a calculation is done in \texttt{C\textsubscript{s}} symmetry, it may happen that the two components of a Π state, one of which appears in \texttt{A}\textsuperscript{′} and the other in \texttt{A}\textsuperscript{′′}, come out not exactly degenerate. This problem can be avoided as in the following example:

For a doublet \texttt{A}\textsuperscript{′} state:

\begin{verbatim}
WF,15,1,1; !define wavefunction symmetry (1)
REF,2; !define additional reference symmetry (2)
\end{verbatim}

and for the doublet \texttt{A}\textsuperscript{′′} state:

\begin{verbatim}
WF,15,2,1; !define wavefunction symmetry (2)
REF,1; !define additional reference symmetry (1)
\end{verbatim}

For linear geometries the same results can be obtained more cheaply using \texttt{C\textsubscript{2v}} symmetry,

\begin{verbatim}
WF,15,2,1; !define wavefunction symmetry (2)
REF,1; !define additional reference symmetry (1)
REF,3; !define additional reference symmetry (3)
\end{verbatim}

or

\begin{verbatim}
WF,15,3,1; !define wavefunction symmetry (2)
REF,1; !define additional reference symmetry (1)
REF,2; !define additional reference symmetry (2)
\end{verbatim}

Each \texttt{REF} card may be followed by \texttt{RESTRICT, SELECT, and CON} cards, in the given order.
20.2.7 Selecting configurations

SELECT, ref1, ref2, refthr, refstat, mxshrf;

This card is used to specify a reference configuration set other than a CAS, which is the default. Configurations can be defined using CON cards, which must appear after the SELECT card. Alternatively, if ref1 is an existing MOLPRO record name, the configurations are read in from that record and may be selected according to a given threshold.

The select card must be placed directly after the WF or REF card(s), or, if present, the RESTRICT cards. The general order of these cards is

WF (or REF)  
RESTRICT (optional)  
SELECT (optional)  
CON (optional)  

ref1=rec1.file:  
(rec1>2000) The configurations are read in from the specified record. See section 19.5.5 about how to save the configurations in the MCSCF calculation. If ref1 is not specified, the program assumes that the configurations are read from subsequent CON cards (see CON).

ref2=rec2.file:  
(rec2>2000) additional configurations are read from the specified record. If rec2 is negative, all records between rec1 and abs(rec2) are read. All configurations found in this way are merged.

refthr:  
Selection threshold for configurations read from disc (records rec1–rec2). This applies to the norm of all CSFs for each orbital configuration.

refstat:  
Specifies from which state vector the configurations are selected. This only applies to the case that the configurations were saved in a state-averaged calculation. If refstat is zero or not specified, the configurations are selected from all states. If refstat is greater than zero, then the specified reference state is used. If refstat is less than zero, then all appropriate reference states are used. Lastly, if refstat is of the form istat1.istat2, states istat1 through istat2 are used.

mxshrf:  
maximum number of open shells in the selected or generated configurations.

20.2.8 Occupation restrictions

RESTRICT, nmin, nmax, orb1, orb2, ..., orbN;

This card can be used to restrict the occupation patterns in the reference configurations. Only configurations containing between nmin and nmax electrons in the specified orbitals orb1, orb2, ..., orbN are included in the reference function. If nmin and nmax are negative, configurations with exactly abs(nmin) and abs(nmax) electrons in the specified orbitals are deleted. This can be used, for instance, to omit singly excited configurations. The orbitals are specified in the form number.sym, where number is the number of the orbital in irrep sym. Several RESTRICT cards may follow each other.
The \texttt{RESTRICT} cards must follow the \texttt{WF} or \texttt{REF} cards to which they apply. The general order of these cards is

\begin{verbatim}
WF (or REF)  
RESTRICT (optional)  
SELECT (optional)  
CON (optional)
\end{verbatim}

If a \texttt{RESTRICT} card precedes the \texttt{WF} card, it applies to all reference symmetries. Note that \texttt{RESTRICT} also affects the spaces generated by \texttt{SELECT} and/or \texttt{CON} cards.

\subsection*{20.2.9 Explicitly specifying reference configurations}

\texttt{CON}, n_1, n_2, n_3, n_4, \ldots

Specifies an orbital configuration to be included in the reference function. $n_1, n_2$ etc. are the occupation numbers of the active orbitals (0, 1, or 2). Any number of \texttt{CON} cards may follow each other, but they must all appear directly after a \texttt{SELECT} card.

\subsection*{20.2.10 Defining state numbers}

\texttt{STATE}, nstate, nroot(1), nroot(2), \ldots, nroot(nstate);

\texttt{nstate} is the number of states treated simultaneously; \texttt{nroot(i)} are the root numbers to be calculated. These apply to the order of the states in the initial internal CI. If not specified, \texttt{nroot(i)}=i. Note that it is possible to leave out states, i.e.,

\begin{verbatim}
STATE, 1, 2;  \! calculates second state  
STATE, 2, 1, 3;  \! calculates first and third state
\end{verbatim}

All states specified must be reasonably described by the internal configuration space. It is possible to have different convergence thresholds for each state (see \texttt{ACCU} card). It is also possible not to converge some lower roots which are included in the list \texttt{nroot(i)} (see \texttt{REFSTATE} card). For examples, see \texttt{REFSTATE} card.

\subsection*{20.2.11 Defining reference state numbers}

\texttt{REFSTATE}, nstatr, nrootr(1), nrootr(2), \ldots, nrootr(nstatr);

\texttt{nstatr} is the number of reference states for generating contracted pairs. This may be larger or smaller than \texttt{nstate}. If this card is not present, \texttt{nstatr}=\texttt{nstate} and \texttt{nrootr(i)}=\texttt{nroot(i)}. Roots for which no reference states are specified but which are specified on the \texttt{STATE} card (or included by default if the \texttt{nroot(i)} are not specified explicitly on the \texttt{STATE} card) will not be converged, since the result will be bad anyway. However, it is often useful to include these states in the list \texttt{nroot(i)}, since it helps to avoid root flipping problems. Examples:

\begin{verbatim}
state, 2;
\end{verbatim}

will calculate two states with two reference states.

\begin{verbatim}
state, 2; refstate, 1, 2;
\end{verbatim}
will optimize second state with one reference state. One external expansion vector will be generated for the ground state in order to avoid root flipping. The results printed for state 1 are bad and should not be used (unless the pair space is complete, which might happen in very small calculations).

\[\text{state,1,2;refstate,1,2;}\]

As the second example, but no external expansion vectors will be generated for the ground state. This should give exactly the same energy for state 2 as before if there is no root flipping (which, however, frequently occurs).

\[\text{state,2;accu,1,1,1;}\]

Will calculate second state with two reference states. The ground state will not be converged (only one iteration is done for state 1) This should give exactly the same energy for state 2 as the first example.

20.2.12 Specifying correlation of orbital pairs

\[\text{PAIR,iorb1.isy1,iorb2.isy2,np;}\]

is a request to correlate a given orbital pair.

\[\begin{align*}
np=1: & \quad \text{singlet pair} \\
np=-1: & \quad \text{triplet pair} \\
np=0: & \quad \text{singlet and triplet pair (if possible)}
\end{align*}\]

Default is to correlate all electron pairs in active and closed orbitals. See also \texttt{PAIRS} card.

\[\text{PAIRS,iorb1.isy,iorb2.isy,np;}\]

Correlate all pairs which can be formed from orbitals \(\text{iorb1.isy1 through iorb2.isy2}\). Core orbitals are excluded. Either \(\text{iorb2}\) must be larger than \(\text{iorb1}\) or \(\text{isy2}\) larger than \(\text{isy1}\). If \(\text{iorb1.isy1}=\text{iorb2.isy2}\) the \texttt{PAIRS} card has the same effect as a \texttt{PAIR} card. \texttt{PAIR} and \texttt{PAIRS} cards may be combined.

If no \texttt{PAIR} and no \texttt{PAIRS} card is specified, all valence orbitals are correlated. The created pair list restricts not only the doubly external configurations, but also the all internal and semi internals.

20.2.13 Restriction of classes of excitations

\[\text{NOPAIR;}\]

No doubly external configurations are included.

\[\text{NOSINGLE;}\]

No singly external configurations are included.

\[\text{NOEXC;}\]

Perform CI with the reference configurations only.
20.3 Options

20.3.1 Coupled Electron Pair Approximation

CEPA($ncepa$);

($0 \leq ncepa \leq 3$). Instead of diagonalizing the hamiltonian, perform CEPA calculation, CEPA type $ncepa$. This is currently available only for single configuration reference functions.

20.3.2 Coupled Pair Functional (ACPF, AQCC)

ACPF,$options$
AQCC,$options$

where options can be

GACPFI=$gacpfi$
GACPFE=$gacpfe$

Instead of diagonalizing the hamiltonian, perform ACPF calculation or AQCC calculation. Using the options GACPFI and GAPCPE. The internal and external normalization factors $gacpfi$, $gacpfe$ may be reset from their default values of 1, $2/nelec$ and $1, 1-(nelec-2)(nelec-3)/nelec(nelec-1)$, respectively.

The ACPF and related methods are currently not robustly working for excited states. Even though it sometimes works, we do not currently recommend and support these methods for excited state calculations.

20.3.3 Projected excited state calculations

PROJECT,$record,nprojc$;

Initiate or continue a projected excited state calculation, with information stored on $record$. If $nprojc > 0$, the internal CI vectors of $nprojc$ previous calculations are used to make a projection operator. If $nprojc = -1$, this calculation is forced to be the first, i.e. ground state, with no projection. If $nprojc = 0$, then if $record$ does not exist, the effect is the same as $nprojc = -1$; otherwise $nprojc$ is recovered from the dump in $record$. Thus for the start up calculation, it is best to use project.$record,-1$; for the following excited calculations, use project.$record$.

At the end of the calculation, the wavefunction is saved, and the information in the dump $record$ updated. The project card also sets the tranh option, so by default, transition hamiltonian matrices are calculated.

For example, to do successive calculations for three states, use

\[ci;...;project,3000.3,-1;\]
\[ci;...;project,3000.3;\]
\[ci;...;project,3000.3;\]

20.3.4 Transition matrix element options

TRANH,$option$;

If $option > -1$, this forces calculation of transition hamiltonian matrix elements in a TRANS or PROJECT calculation. If $option < 1$, this forces calculation of one electron transition properties.
20.3.5 Convergence thresholds

ACCU, istate, energy, coeff;

Convergence thresholds for state $istate$. The actual thresholds for the energy and the CI coefficients are $10^{-energy}$ and $10^{-coeff}$. If this card is not present, the thresholds for all states are the default values or those specified on the THRESH card.

20.3.6 Level shifts

SHIFT, shiftp, shifts, shifti;

Denominator shifts for pairs, singles, and internals, respectively.

20.3.7 Maximum number of iterations

MAXITER, maxit, maxiti;

$maxit$: maximum number of macroiterations;
$maxiti$: maximum number of microiterations (internal CI).

20.3.8 Restricting numbers of expansion vectors

MAXDAV, maxdav, maxvi;

$maxdav$: maximum number of external expansion vectors in macroiterations;
$maxvi$: maximum number of internal expansion vectors in internal CI.

20.3.9 Selecting the primary configuration set

PSPACE, select, npspac;

$select$: energy criterion for selecting p-space configurations. If negative, a test for p-space $H$ is performed.
$npspac$: minimum number of p-space configurations. Further configurations are added if either required by select or if configurations are found which are degenerate to the last p-space configuration. A minimum number of nspace is automatically determined from the state specifications.

20.3.10 Canonicalizing external orbitals

FOCK, $n_1, n_2, \ldots$;

External orbitals are obtained as eigenfunctions of a Fock operator with the specified occupation numbers $n_i$. Occupation numbers must be provided for all valence orbitals.
20.3.11  Saving the wavefunction

SAVE,savecp,saveco,idelcg;

or

SAVE,[CIVEC=savecp],[CONFIG=saveco],[DENSITY=dupprec],[NATORB=dupprec],[FILES]

savecp: record name for save of wavefunction. If negative the wavefunction is saved after each iteration, else at the end of the job. In case of coupled cluster methods (CCSD, QCISD, BCCD), the wavefunction is saved in each iteration in any case.

saveco: record name for save of internal configurations and their maximum weight over all states for subsequent use as reference input (see SELECT card). If the record already exists, the record name is incremented by one until a new record is created.

idelcg: if nonzero or FILES is specified, don’t erase icfil and igfil (holding CI and residual vectors) at the end of the calculation.

dupprec: Dump record for saving density matrix and natural orbitals. Only one dump record must be given. In any case the density matrix and the natural orbitals are saved. See also DM or NATORB cards.

20.3.12  Starting wavefunction

START,readc1,irest;

readc1: record name from which the wavefunction is restored for a restart. In the case of coupled cluster methods (CCSD, QCISD, BCCD), the amplitudes are read from record readc1 and used for restart.

irest: If nonzero, the CI coefficients are read and used for the restart; otherwise, only the wavefunction definition is read in.

20.3.13  One electron properties

EXPEC,oper1,oper2,oper3, . . . ;

After the wavefunction determination, calculate expectation values for one-electron operators operi. See section [6.13] for the available operators and their keywords. In multi-state calculations or in projected calculations, also the transition matrix elements are calculated.

20.3.14  Transition moment calculations

TRANS,readc1,readc2,[BIORTH],[oper1,oper2,oper3, . . . ];

Instead of performing an energy calculation, only calculate transition matrix elements between wavefunctions saved on records readc1 and readc2. See section [6.13] for a list of available operators and their corresponding keywords. If no operator names are specified, the dipole transition moments are calculated.
If option **BIORTH** is given, the two wavefunctions may use different orbitals. However, the number of active and inactive orbitals must be the same in each case. Note that **BIORTH** is not working for spin-orbit matrix elements. Under certain conditions it may happen that biorthogonalization is not possible, and then an error message will be printed.

### 20.3.15 Saving the density matrix

\[ \text{DM,record.ifil,[idip]}; \]

The first order density matrices for all computed states are stored in record \( \text{record} \) on file \( \text{ifil} \). If \( \text{idip} \) is not zero, the dipole moments are printed starting at iteration \( \text{idip} \). See also \( \text{NATORB} \).

In case of transition moment calculation, the transition densities are also stored, provided both states involved have the same symmetry.

### 20.3.16 Natural orbitals

\[ \text{NATORB,[RECORD=]record.ifil,[PRINT=nprint],[CORE=[natcor]]}; \]

Calculate natural orbitals. The number of printed external orbitals in any given symmetry is \( nprint \) (default 2). \( nprint=-1 \) suppressed the printing. If \( \text{record} \) is nonzero, the natural orbitals and density matrices for all states are saved in a dump record \( \text{record} \) on file \( \text{ifil} \). If \( \text{record.ifil} \) is specified on a \( \text{DM} \) card (see above), this record is used. If different records are specified on the \( \text{DM} \) and \( \text{NATORB} \) cards, an error will result. The record can also be given on the \( \text{SAVE} \) card. If \( \text{CORE} \) is specified, core orbitals are not printed.

Note: The dump record must not be the same as \( \text{savecp} \) or \( \text{saveco} \) on the \( \text{SAVE} \) card, or the record given on the \( \text{PROJECT} \).

### 20.3.17 Miscellaneous options

\[ \text{OPTION,code1=value,code2=value,...} \]

Can be used to specify program parameters and options. If no codes and values are specified, active values are displayed. The equal signs may be omitted. The following codes are allowed (max 7 per card):

- **NSTATE**: see state card
- **NSTATI**: number of states calculated in internal CI
- **NSTATR**: see refstat card
- **NCEPA**: see CEPA card
- **NOKOP**: if nonzero, skip integral transformation
- **ITRDM**: if \( \geq 0 \) transition moments are calculated
- **ITRANS**: if nonzero, perform full integral transformation (not yet implemented)
- **IDIP**: Print dipole moments from iteration number \( value \)
- **REFOPT**: if nonzero, optimize reference coefficients; otherwise extract reference coefficients from internal CI
- **IAVDEN**: average HII and HSS denominators over spin couplings if nonzero
IDELCG: if.ne.0 then destroy files icfil,igfil at end
IREST: if nonzero, restart
NATORB: if nonzero, natural orbitals are calculated and printed. The number of printed external orbitals per symmetry is min(natorb,2)
WFNAT: if nonzero, natural orbitals are saved to this record
IPUNRF: if nonzero, punch coefficients of reference configurations
NPUPD: if nonzero, update pairs in nonorthogonal basis, otherwise in orthogonal basis.
MAXIT: see maxiter card
MAXITI: see maxiter card
MAXDAV: see maxdav card
MAXVI: see maxdav card
NOSING: see nosing card
NOPAIR: see nopair card
MXSHRF: see select card
IKCPS=0: In CIKEXT, only K(CP) is calculated; this option taken when and only when no singles.
IKCPS=1: only K(CP') is calculated. Implies that modified coupling coefficients are used.
IKCPS=2: K(CP) and K(CP') are calculated. Default is IKCPS=2 except when single reference configuration, when IKCPS=1.
IOPTGM: Option for density matrix routines.
IOPTGM=0: all quantities in density matrix routines are recalculated for each intermediate symmetry (max. CPU, min. core).
IOPTGM=1: quantities precalculated and stored on disk (max. I/O, min. core).
IOPTGM=2: quantities precalculated and kept in core (min. CPU, max. core).
IOPTOR: If nonzero, calculate intermediate orbitals for each pair. Might improve convergence in some cases, in particular if localized orbitals are used.

20.3.18 Miscellaneous parameters

PARAM, code1=value, code2=value...

Redefine system parameters. If no codes are specified, the default values are displayed. The following codes are allowed:

LSEG: disc sector length
INTREL: number of integers per REAL*8 word
IVECT=0: scalar machine
IVECT=1: vector machine
MINVEC: call MXMB in coupling coefficient routines if vector length larger than this value.

IBANK: number of memory banks for vector machines. If IBANK>1, vector strides which are multiples of IBANK are avoided where appropriate.

LTRACK: number of REAL*8 words per track or block (for file allocation)

LTR: determines how matrices are stored on disc. If LTR=LSEG, all matrices start at sector boundaries (which optimizes I/O), but unused space is between matrices (both on disc and in core). With LTR=1 all matrices are stored dense. This might increase I/O if much paging is necessary, but reduce I/O if everything fits in core.

NCPUS: Maximum number of CPUs to be used in multitasking.

20.4 Miscellaneous thresholds

THRESH,code1=value,code2=value...

If value=0, the corresponding threshold is set to zero, otherwise 10^(-value). The equal signs may be omitted. If no codes are specified, the default values are printed. The following codes are allowed (max 7 per card):

ZERO: numerical zero

THRDLSP: delete pairs if eigenvalue of overlap matrix is smaller than this threshold.

PNORM: delete pair if its norm is smaller than this threshold (all pairs are normalized to one for a closed shell case).

PRINTCI: print CI coefficients which are larger than this value.

INTEG: omit two-electron integrals which are smaller than this value.

ENERGY: convergence threshold for energy; see also: ACCU card.

COEFF: convergence threshold for coefficients; see also: ACCU card.

SPARSE: omit coefficient changes which are smaller than this value.

EQUAL: set values in the internal vector and the diagonal elements equal if they differ by less than this value. Useful for keeping track of symmetry.

20.5 Print options

PRINT,code1=value,code2=value,...

Print options. Generally, the value determines how much intermediate information is printed. value=1 means no print (default for all codes). In some of the cases listed below the specification of higher values will generate even more output than described. The equal signs and zeros may be omitted. All codes may be truncated to three characters. The following codes are allowed (max 7 per card):

ORBITALS: print orbitals
JOP=0: print operator list
JOP=1: print coulomb operators in MO basis
JOP=2: print coulomb operators in AO and MO basis
KOP: as JOP for internal exchange operators
KCP=0: print paging information for CIKEXT
KCP=1: print external exchange operators in MO basis
KCP=2: print operators in AO and MO basis
DM=0: print paging information for CIDIMA
DM=1: print density matrix in MO basis
DM=2: print density matrix in AO and MO basis
FPP=0: print energy denominators for pairs
FPP=1: in addition, print diagonal coupling coefficients in orthogonal basis.
FPP=2: print operators FPP
CP=0: print update information for pairs in each iteration
CP=1: print pair matrix updates (MO basis)
CP=2: in addition print pair matrices (MO basis)
CP=3: print CP in AO basis (in CIKEXT)
CI=0: print convergence information for internal CI
CI=1: print internal CI coefficients and external expansion coefficients
CS: as CP for singles
CPS=0: print paging information for CICPS
CPS=1: print matrices CPS in MO basis
GPP=0: print paging information for CIGPQ
GPP=1: print matrices GP at exit of CIGPQ
GPS=0: print paging information for CIGPS
GPS=1: print vectors GS at exit CIGPS
GSP=1: print matrices GP at exit CIGPS
GPI=0: print paging information for CIGPI
GPI=1: print total GP in orthogonal basis
GPI=2: print matrices GP and TP
GIP=0: print paging information for CIGIP
GIP=1: print GI at exit CIGIP
GSS=0: print paging information for CIGSS
GSS=1: print vectors GS at exit CIGSS
GSI=0: print paging information for CIGSI
GSI=1: print GS at exit CIGSI
GIS=0: print paging information for CIGIS
GIS=1: print GI at exit CIGIS
GII: print intermediate information in internal CI
DPQ: print coupling coefficients $\alpha(P,Q)$
EPQ: print coupling coefficients $\beta(P,Q)$
HPQ: print coupling coefficients $\gamma(P,Q)$
DPI: print coupling coefficients for pair-internal interactions
DSS: not yet used
DSI: not yet used
LOG: At end of each iteration, write summary to log file. Delete at end of job if LOG=0
CC=0: print address lists for coupling coefficients
CC=1: print coupling coefficients
DEN=1: print internal first order density
DEN=2: print internal second order density
DEN=3: print internal third order density
DEN=4: print first, second and third order densities
GAM=1: print first order transition densities
GAM=2: print second order transition densities
GAM=3: print first and second order transition densities
PAIRS=0: print list of non redundant pairs
PAIRS=1: print list of all pairs
CORE=0: print summary of internal configurations ($N,N-1$ and $N-2$ electron)
CORE=1: print internal configurations ($N,N-1,N-2$)
REF=0: print summary of reference configurations
REF=1: print reference configurations and their coefficients
PSPACE: print p-space configurations
HII: print diagonal elements for internals
HSS: print diagonal elements for singles
SPQ: various levels of intermediate information in pair orthogonalization routine.
TEST=0: print information at each subroutine call
TEST=1: print in addition information about I/O in LESW, SREIBW
TEST=2: print also information about I/O in FREAD, FWRITE
CPU: print analysis of CPU and I/O times
ALL: print everything at given level (be careful!)
20.6 Examples

***, Single reference CISD and CEPA-1 for water
r=0.957, angstrom
\theta=104.6, degree;
geometry={O; !z-matrix geometry input
H,O,r;
H2,O,r,H1,\theta}
\{hf;wf,10,1;\} !TOTAL SCF ENERGY -76.02680642
\{ci;occ,3,1,1;core,1;wf,10,1;\} !TOTAL CI(SD) ENERGY -76.22994348
\{cepa(1);occ,3,1,1;core,1;wf,10,1;\} !TOTAL CEPA(1) ENERGY -76.23799334
http://www.molpro.net/info/current/examples/h2o_cepa1.com

***, Valence multireference CI for X and A states of H2O
\texttt{gthresh, energy=1.d-8}
r=0.957, angstrom, \theta=104.6, degree;
geometry={O; !z-matrix geometry input
H1,O,r;
H2,O,r,H1,\theta}
\{hf;wf,10,1;\} !TOTAL SCF ENERGY -76.02680642
\{multi;occ,4,1,2;closed,2;frozen,1;wf,9,2,1;wf,9,1,1;tran,ly\}
! MCSCF ENERGY -75.66755631
! MCSCF ENERGY -75.56605896
\{ci;occ,4,1,2;closed,2;core,1;wf,9,2,1;save,7300.1\}
! TOTAL MRCI ENERGY -75.79831209
\{ci;occ,4,1,2;closed,2;core,1;wf,9,1,1;save,7100.1\}
! TOTAL MRCI ENERGY -75.71309879
\{ci;trans,7300.1,7100.1,ly\}
! Transition moment <1.3|X|1.1> = -0.14659810 a.u.
! Transition moment <1.3|LY|1.1> = 0.96200488i a.u.
http://www.molpro.net/info/current/examples/h2op_mrci_trans.com

***, BH singlet Sigma and Delta states
r=2.1
gleometry={b;h,b,r}
\{hf;occ,3;wf,6,1;\}
\{multi;occ,3,1,1;frozen,1;wf,6,1;state,3;lquant,0,2,0;wf,6,4;lquant,2;
tran,lz;
expec2,lzlz;\}
\! Sigma states:- energies -25.20509620 -24.94085861
\{ci;occ,3,1,1;core,1;wf,6,1;state,2,1,3;\}
\! Delta states:- energies -24.98625171
\{ci;occ,3,1,1;core,1;wf,6,1;state,1,2;\}
\! Delta state:- xy component
\{ci;occ,3,1,1;core,1;wf,6,4;\}
http://www.molpro.net/info/current/examples/bh_mrci_sigma_delta.com

20.7 Cluster corrections for multi-state MRCI

In the following, we assume that

$$\Psi_{\text{ref}}^{(n)} = \sum_R C_{Rn}^{(0)} \Phi_R$$  \hspace{1cm} (39)
\( \Psi^{(n)}_{\text{mrci}} = \sum_R C_{Rn} \Phi_R + \Psi_c \) (40)

are the normalized reference and MRCI wave functions for state \( n \), respectively. \( C_R^{(0)} \) are the coefficients of the reference configurations in the initial reference functions and \( C_{Rn} \) are the relaxed coefficients of these configurations in the final MRCI wave function. \( \Psi_c \) is the remainder of the MRCI wave function, which is orthogonal to all reference configurations \( \Phi_R \).

The corresponding energies are defined as

\[
E_{\text{ref}}^{(n)} = \langle \Psi_{\text{ref}}^{(n)} | \hat{H} | \Psi_{\text{ref}}^{(n)} \rangle,
\]

(41)

\[
E_{\text{mrci}}^{(n)} = \langle \Psi_{\text{mrci}}^{(n)} | \hat{H} | \Psi_{\text{mrci}}^{(n)} \rangle.
\]

(42)

The standard Davidson corrected correlation energies are defined as

\[
E_{\text{D}}^{(n)} = E_{\text{corr}}^{(n)} \cdot \left( 1 - \frac{c_n^2}{c_n^2} \right)
\]

(43)

where \( c_n \) is the coefficient of the (fixed) reference function in the MRCI wave function:

\[
c_n = \langle \Psi_{\text{ref}}^{(n)} | \Psi_{\text{mrci}}^{(n)} \rangle = \sum_R C_{Rn} C_{Rn},
\]

(44)

and the correlation energies are

\[
E_{\text{corr}}^{(n)} = E_{\text{mrci}}^{(n)} - E_{\text{ref}}^{(n)}.
\]

(45)

In the vicinity of avoided crossings this correction may give unreasonable results since the reference function may get a small overlap with the MRCI wave function. One way to avoid this problem is to replace the reference wave function \( \Psi_{\text{ref}}^{(n)} \) by the the relaxed reference functions

\[
\Psi_{\text{rlx}}^{(n)} = \sum_R C_{Rn} \Phi_R \sqrt{\sum_R C_{Rn}^2},
\]

(46)

which simply leads to

\[
c_n^2 = \sum_R C_{Rn}^2.
\]

(47)

Alternatively, one can linearly combine the fixed reference functions to maximize the overlap with the MRCI wave functions. This yields projected functions

\[
\Psi_{\text{prj}}^{(n)} = \sum_m | \Psi_{\text{ref}}^{(m)} \rangle \langle \Psi_{\text{ref}}^{(m)} | \Psi_{\text{mrci}}^{(n)} \rangle = \sum_m | \Psi_{\text{ref}}^{(m)} \rangle d_{mn}
\]

(48)

with

\[
d_{mn} = \langle \Psi_{\text{ref}}^{(m)} | \Psi_{\text{mrci}}^{(n)} \rangle = \sum_R \overline{C}_{Rm} C_{Rn}.
\]

(49)

These projected functions are not orthonormal. The overlap is

\[
\langle \Psi_{\text{prj}}^{(m)} | \Psi_{\text{prj}}^{(n)} \rangle = (d^\dagger d)_{mn}.
\]

(50)
Symmetrical orthonormalization, which changes the functions as little as possible, yields

\[
\Psi^{(n)}_{\text{rot}} = \sum_m \langle \Psi^{(m)}_{\text{rot}} \rangle u_{mn},
\]

\[
u = d^\dagger d^{-1/2}.
\]

The overlap of these functions with the MRCI wave functions is

\[
\langle \Psi^{(m)}_{\text{rot}} | \Psi^{(n)}_{\text{mrci}} \rangle = [(d^\dagger d)(d^\dagger d)^{-1/2}]_{mn} = [(d^\dagger d)^{1/2}]_{mn}.
\]

Thus, in this case we use for the Davidson correction

\[
c_n = [(d^\dagger d)^{1/2}]_{nn}.
\]

The final question is which reference energy to use to compute the correlation energy used in eq. (43). In older MOLPRO version (to 2009.1) the reference wave function which has the largest overlap with the MRCI wave function was used to compute the reference energy for the corresponding state. But this can lead to steps of the Davidson corrected energies if the order of the states swaps along potential energy functions. In this version there are two options: the default is to use for state \( n \) the reference energy \( n \), cf. eq. (45) (assuming the states are ordered according to increasing energy). The second option is to recompute the correlation energies using the rotated reference functions

\[
E_{\text{corr}}^{(n)} = E_{\text{MRCI}}^{(n)} - \langle \Psi^{(n)}_{\text{rot}} | \hat{H} | \Psi^{(n)}_{\text{rot}} \rangle
\]

Both should give smooth potentials (unless at conical intersections or crossings of states with different symmetries), but there is no guarantee that the Davidson corrected energies of different states don’t cross. This problem is unavoidable for non-variational energies. The relaxed and rotated Davidson corrections give rather similar results; the rotated one yields somewhat larger cluster corrections and was found to give better results in the case of the \( F + H_2 \) potential [see J. Chem. Phys. 128, 034305 (2008)].

By default, the different cluster corrections listed in Table 9 are computed in multi-state MRCI calculations. By default, \( \text{ENERGD}(n) = \text{ENERGD0}(n) \). This can be

Table 9: Cluster corrections computed in multi-state MRCI calculations. By default, the energies are in increasing order of the MRCI total energy. In single-state calculations only the fixed and relaxed values are available.

<table>
<thead>
<tr>
<th>Name</th>
<th>( c_n ) (Eq.)</th>
<th>( E_{\text{corr}}^{(n)} ) (Eq.)</th>
<th>Variable</th>
</tr>
</thead>
<tbody>
<tr>
<td>Using standard reference energies:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fixed</td>
<td>(44)</td>
<td>(45)</td>
<td>\text{ENERGD1}(n)</td>
</tr>
<tr>
<td>Relaxed</td>
<td>(47)</td>
<td>(45)</td>
<td>\text{ENERGD0}(n)</td>
</tr>
<tr>
<td>Rotated</td>
<td>(54)</td>
<td>(45)</td>
<td>\text{ENERGD2}(n)</td>
</tr>
<tr>
<td>Using rotated reference energies:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Relaxed</td>
<td>(47)</td>
<td>(55)</td>
<td>\text{ENERGD3}(n)</td>
</tr>
<tr>
<td>Rotated</td>
<td>(54)</td>
<td>(55)</td>
<td>\text{ENERGD4}(n)</td>
</tr>
</tbody>
</table>

changed by setting \text{OPTION,CLUSTER}=x; then \( \text{ENERGD}(n) = \text{ENERGDx}(n) \) (default \( x = 0 \). The behaviour of Molpro 2009.1 and older can be retrieved using \text{MRCI,SWAP,ROTREF}=-1.
20.8 Explicitly correlated MRCI-F12

The only change needed for including explicitly correlated terms is to append -F12 to the MRCI command. All other options work as described before. It is recommended to use correlation consistent basis sets (aug-cc-pVnZ or VnZ-F12) since for these the appropriate fitting and RI auxiliary basis sets are chosen automatically. Otherwise it may be necessary to specify these basis sets as described for single-reference methods in section 35.

The following options (to be given on the MRCI-F12 command line) are specific to MRCI-F12:

\[ \text{SCALF12} = \text{scalf12} \]

If scalf12=1 (default) the explicitly correlated contributions are treated variationally (SFIX ansatz, see J. Chem. Phys. 134, 034113 (2011). If scalf12=0 intermediate normalization is used (FIX ansatz).

\[ \text{SINGLES} = \text{isingles} \]

isingles=1: use singles-CI CABS singles correction (default); isingles=2: use perturbational CABS singles correction; isingles=3: include couplings of CABS singles with MRCI terms.


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Bibliography:

Original RS2/RS3:

New internally contracted RS2C:

All publications resulting from use of this program must acknowledge the above.

The commands

\[ \text{RS2, options} \]
\[ \text{RS2C, options} \]
\[ \text{RS3, options} \]

are used to perform second or third-order perturbation calculations. RS3 always includes RS2 as a first step. For closed-shell single-reference cases, this is equivalent to MP2 or MP3 (but a different program is used). RS2C calls a new more efficient second-order program (see below), which should normally be used if third-order is not required (note that RS3C is not available).

for RS2 an explicitly correlated version as described in T. Shiozaki and H.-J. Werner, J. Chem. Phys. 133, 141103 (2010) is available. This is called using the command

\[ \text{RS2-F12, options} \]

Options can be the following:

\[ \text{Gn} \]
Use modified zeroth order Hamiltonian, see section 21.4
21.1 Introduction

Multireference perturbation calculations are performed by the MRCI program as a special case. For RS2 (CASPT2, RASPT2) only matrix elements over a one-electron operator need to be computed, and therefore the computational effort is much smaller than for a corresponding MRCI. For RS3 (CASPT3) the energy expectation value for the first-order wavefunction must be computed and the computational effort is about the same as for one MRCI iteration. The RS2 and RS3 programs use the same configuration spaces as the MRCI, i.e., only the doubly external configurations are internally contracted.

A new version of the program has been implemented in which also subspaces of the singly external and internal configuration spaces are internally contracted (see reference given above). This program, which is called using the keyword RS2C, is more efficient than RS2, in particular for large molecules with many closed-shell (inactive) orbitals. It is recommended to use this program for normal applications of second-order multireference perturbation theory (CASPT2, RASPT2). Note that it gives slightly different results than RS2 due to the different contraction scheme. It should also be noted that neither RS2 or RS2C are identical with the CASPT2 of Roos et al. [J. Chem. Phys. 96, 1218 (1992)], since certain configuration subspaces are left uncontracted. However, the differences are normally very small. The last point that should be mentioned is that the calculation of CASPT2/RASPT2 density matrices (and therefore molecular properties) is presently possible only with the RS2 command and not with RS2C.

The results of multireference perturbation theory may be sensitive to the choice of the zeroth-order Hamiltonian. This dependence is more pronounced in second-order than in third-order. Several options are available, which will be described in the following sections. It may also
happen that $(\hat{H}^{(0)} - E^{(0)})$ in the basis of the configuration state functions becomes (nearly) singular. This is known as "intruder state problem" and can cause convergence problems or lead to a blow-up of the wavefunction. Often, such problems can be eliminated by including more orbitals into the reference wavefunction, but of course this leads to an increase of the CPU time. The use of modified Fock operators (see below) or level shifts, as proposed by Roos and Andersson [Chem. Phys. Lett. 245, 215 (1995)] may also be helpful. Presently, only "real" level shifts have been implemented.

With no further input cards, the wavefunction definition (core, closed, and active orbital spaces, symmetry) corresponds to the one used in the most recently done SCF or MCSCF calculation. By default, a CASSCF reference space is generated. Other choices can be made using the OCC, CORE, CLOSED, WF, SELECT, CON, and RESTRICT cards, as described for the CI program. The orbitals are taken from the corresponding SCF or MCSCF calculation unless an ORBITAL directive is given.

For a CASPT2 calculation, the zeroth-order Hamiltonian can be brought to a block-diagonal form when (pseudo)canonical orbitals are used. This leads to fastest convergence. It is therefore recommended that in the preceding MULTI calculation the orbitals are saved using the CANONICAL directive (note that the default is NATORB).

Most options for MRCI calculations (like STATE, REFSTATE etc.) apply also for RS2(C) and RS3 and are not described here again. Some additional options which specific for CASPT2/3 and are described below.

### 21.2 Excited state calculations

There are two possibilities to perform excited state calculations:

1) One can calculate each state separately. This is done using the card

```
STATE,1,root
```

where `root` is the desired root (i.e., 2 for the first excited state). In this case the Fock operator used in the zeroth-order Hamiltonian is computed using the density for the given state.

2) Alternatively, two or more states can be computed simultaneously, using

```
STATE, n,[root1, root2, . . . , rootn]
```

where `n` is the number of states to be computed. The default is to compute the lowest `n` roots. Optionally, this default can be modified by specifying the desired roots `rooti` as shown. One should note that this does not correspond to the multi-state CASPT2 as described in section 21.3.

In the case that several states are computed simultaneously, the fock operator employed in the zeroth-order Hamiltonian is computed from a state-averaged density matrix, and the zeroth-order Hamiltonians for all states are constructed from the same fock operator. By default, equal weights for all states are used. This default can be modified using the WEIGHT directive

```
WEIGHT,w1, w2,. . . ,wn.
```

If a REFSTATE card is given (see section 20.2.11), the state-averaged fock operator is made for all reference states, and the WEIGHT card refers to the corresponding states.
21.3 Multi-State CASPT2

Multi-state CASPT2 is implemented as described by Finley et al. CPL 288, 299 (1998). Currently this can only be used with the RS2 program (i.e., not with RS2C). There are two different modes in which MS-CASPT2 calculations can be performed:

(i) Each of the states to be mixed is computed independently, and finally all states are mixed. In the following, such calculations will be denoted SS-SR-CASPT2 (single-state, single reference CASPT2). There is one contracted reference state for each CASPT2 calculation that is specific for the state under consideration. This is the cheapest method, but there are no gradients available in this case. It is the users responsibility to make sure that no state is computed twice.

(ii) All $n_{states}$ states are treated together, with $n_{states}$ contracted reference states. This is more expensive, but should give a more balanced description since the different reference states can mix in the CASPT2. It is required that $n_{states}$ equals the number of states specified on the STATE directive. For this case, denoted "MS-MR-CASPT2" (multi-state multi reference CASPT2), analytical energy gradients are available, see section 21.7. It is recommended to use the ”extended” (XMS) multi-state CASPT2 option, which guarantees invariance of the theory with respect to unitary rotations of the reference functions. The method yields improved potentials in the vicinity of avoided crossings and conical intersections [see T. Shiozaki and H.-J. Werner, J. Chem. Phys. 133, 141103 (2010) and T. Shiozaki, C. Woywod and H.-J. Werner, Phys. Chem. Chem. Phys. 15, 262 (2013)].

21.3.1 Performing SS-SR-CASPT2 calculations

If one wants to mix together $n_{states}$ CASPT2 wavefunctions, a $n_{states}$ single-state, single-reference CASPT2 calculations must be run.

The first calculation must use

\{RS2,MIX=$n_{states}$, INIT, options
STATE, 1, 1;\}

and the subsequent ones

\{RS2, MIX=$n_{states}$, options
STATE, 1, istate;\}

for $istate = 2, \ldots, n_{states}$. Further options can be given, for instance a level shift.

At the end of each calculation, the CASPT2 wavefunction is stored, and at the end of the last CASPT2 calculation the Bloch Hamiltonian and the corresponding overlap matrix are automatically assembled and printed. The Hamiltonian is diagonalized after symmetrization following Brandow IJQC 15, 207 (1979), as well as with simple half-sum (averaging). The MS-CASPT2 energy and mixing coefficients printed in each case.

The variable MSENERGY(i) (with i=1,...,$n_{states}$) is set to the multi-state energies obtained with half-sum diagonalization. If a Level Shift is present, MSEENERGY(i) contains the multi-state energies obtained with half-sum diagonalization of the Bloch Hamiltonian whose diagonal elements (CASPT2 energies) have been corrected with the level shift.

Example: SS-SR-CASPT2 calculation for LiF
r=[3,4,5,6,7,8,9,10] ang
i=1
geometry={Li
F,1,r(i)}
basis=vtz,F=avtz
hf !Hartree-Fock
do i=1, #r !loop over range of bond distances
multi
closed,3,0,0,0
occ, 5,2,2,0
wf;state,2 !SA-CASSCF for 2 states
canonical,ci)
{rs2,MIX=2, INIT
wf;state,1,1} !single state CASPT2 for reference state 1
el_caspt2(i)=energy !unmixed caspt2 energy for ground state
{rs2,MIX=2
wf;state,1,2} !single state CASPT2 for reference state 2
e2_caspt2(i)=energy !unmixed caspt2 energy for excited state
e1_mscaspt2(i)=msenergy(1) !ms-caspt2 energy for ground state
e2_mscaspt2(i)=msenergy(2) !ms-caspt2 energy for excited state
endo
{table,r,e1_caspt2,e2_caspt2,e1_mscaspt2,e2_mscaspt2
title,SS-SR-CASPT2 for LiF
plot,file='lif_sr_mscaspt2.plot' }

This produces the plot

SS-SR-CASPT2 for LiF
21.3.2 Performing MS-MR-CASPT2 calculations

In the case of multi-state multi-reference CASPT2 calculations, only a single run is needed:

```
{RS2,MIX=nstates,options
STATE,nstates}
```

For using the XMS-CASPT2 method option XMS=1 or XMS=2 has to be set. The two variants differ in the treatment of level shifts. XMS=1 is a fully invariant treatment (recommended), while with XMS=2 the level shift is only applied to the diagonal of H0.

Example: MS-MR-CASPT2 calculation for LiF

```
r={3,4,5,6,7,8,9,10} ang
i=1
geometry={LiF,1,r(i)}
basis=vtz,F=avtz
hf !Hartree-Fock
do i=1,#r !loop over range of bond distances
{multi closed,3,0,0,0
occ, 5,2,2,0
wf;state,2 !SA-CASSCF for 2 states
canonical,ci}
{rs2,MIX=2
wf;state,2} !2-state MS-CASPT2 with 2 reference states
e1_caspt2(i)=energu(1) !unmixed caspt2 energy for ground state
e2_caspt2(i)=energu(2) !unmixed caspt2 energy for ground state
e1_mscaspt2(i)=msenergy(1) !ms-caspt2 energy for ground state
e2_mscaspt2(i)=msenergy(2) !ms-caspt2 energy for excited state
{rs2,MIX=2,XMS=1
wf;state,2} !2-state XMS-CASPT2 with 2 reference states
e1_xmscaspt2(i)=msenergy(1) !ms-caspt2 energy for ground state
e2_xmscaspt2(i)=msenergy(2) !ms-caspt2 energy for excited state
enddo
{table,r,e1_caspt2,e2_caspt2,e1_mscaspt2,e2_mscaspt2,e1_xmscaspt2,e2_xmscaspt2
title,MS-MR-CASPT2 for LiF
plot,file='lif_mr_mscaspt2.plot'
}
```

This produces the plot

```
http://www.molpro.net/info/current/examples/lif_mr_mscaspt2.com
```
One can clearly see that this gives smoother potentials than the SS-SR-CASPT2 calculation in the previous section. Also, the avoided crossing is shifted to longer distances, which is due to the improvement of the electron affinity of F.

Example for xms-caspt2 for pyrrole B1 states
***,Pyrrole
memory,128,M;

geometry={
  10
  RS2/VTZ ENERGY=-209.73179172
  H 0.0000000000 -0.0000000001 2.1166896815
  H 0.0000000000 -2.1059182363 0.7619888215
  H 0.0000000000 2.1059182368 0.7619888221
  H 0.0000000000 1.3572481815 -1.8483571903
  N 0.0000000000 -0.0000000001 1.1133413258
  C 0.0000000000 1.1228834673 0.3278824921
  C 0.0000000000 -1.1228834675 0.3278824917
  C 0.0000000000 -0.7098361247 -1.8483571900
  C 0.0000000000 0.7098361249 -1.8483571900
}
gexpec,sm

basis=avtz

(hf;wf,symmetry=1,spin=0)

multi
occ,11,3,7,2;closed,9,0,6,0;
wf,symmetry=1,spin=0;state,1; !1A1 state
wf,symmetry=2,spin=0;state,2; !B1 states
wf,symmetry=4,spin=0;state,2; !A2 states
}
ecas=energy

shift=0.2

(rs2,shift=shift; !caspt2 for 1A1 state
 wf,symmetry=1,spin=0;state,1,1)
er2s(1)=energy

(rs2,shift=shift,mix=2,xms=1; !xms-caspt2 for B1 states
 wf,symmetry=2,spin=0;state,2)
er2s(2)=msenergy(1)
er2s(3)=msenergy(2)
der2s=(ecas-ecas(1))*toev !vertical excitation energies in eV
ders2=(ers2-ers2(1))*toev

$state=[1A1,1B1,2B1]
table,state,ecas,ers2,decas,ders2
digits,,7,7,7,3,3,3,3
---

http://www.molpro.net/info/current/examples/pyrrole_xms_caspt2.com

This produces:

<table>
<thead>
<tr>
<th>STATE</th>
<th>ECAS</th>
<th>ERS2</th>
<th>DECAS</th>
<th>DERS2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1A1</td>
<td>-208.9123879</td>
<td>-209.7458973</td>
<td>0.00000000</td>
<td>0.000</td>
</tr>
<tr>
<td>1B1</td>
<td>-208.7459999</td>
<td>-209.5298616</td>
<td>4.5276489</td>
<td>5.879</td>
</tr>
<tr>
<td>2B1</td>
<td>-208.7397557</td>
<td>-209.5261196</td>
<td>4.6975625</td>
<td>5.980</td>
</tr>
</tbody>
</table>
21.4 Modified Fock-operators in the zeroth-order Hamiltonian.

The \( g_1, g_2, \) and \( g_3 \) operators proposed by Andersson [Theor. Chim. Acta 91, 31 (1995)] as well as a further \( g_4 \) operator may be used. \( g_4 \) makes CASPT2 calculations size extensive for cases in which a molecule dissociates to high-spin open-shell (RHF) atoms.

The index \( n \) of the operator to be used is specified on the RS2, RS2C, or RS3 card:

\[
\text{RS2,option} \\
\text{RS2C,option} \\
\text{RS3,option}
\]

where \( \text{option} \) can be \( G1, G2, G3, \) or \( G4 \). This option can be followed or preceded by other valid options.

21.5 Level shifts

Level shifts are often useful to avoid intruder state problems in excited state calculations. MOLPRO allows the use of shifts as described by Roos and Andersson, [Chem. Phys. Lett. 245, 215 (1995)]. The shift can be specified on the RS2 or RS2C card

\[
\text{RS2} [,Gn][,SHIFT=\text{shift}],\text{IPEA=value} \\
\text{RS2C} [,Gn][,SHIFT=\text{shift}],\text{IPEA=value}
\]

Typical choices for the shift is are \( 0.1 - 0.3 \). Only two figures after the decimal point are considered. The shift affects the results, the printed energies as well as the \textsc{energy} variable include the energy correction for the shift as proposed by Roos and Andersson. At convergence, also the uncorrected energies are printed for comparison.

Alternatively (or in addition), the IPEA shift of G. Ghigo, B. O. Roos, and P.A. Malmqvist, Chem. Phys. Lett. 396, 142 (2004) can be used. The implementation is not exactly identical to the one in MOLCAS, since in our program the singly external configurations are not (RS2) or only partially (RS2C) contracted. In Molpro, the shift is implemented as follows:

\[
\frac{1}{2} D_{pp} \varepsilon \text{ is added to the occupied part of the Fock matrix; in addition, } 2\varepsilon \text{ is added as a general shift (not corrected). } \varepsilon \text{ is the value specified with the IPEA option (default 0). A value of } 0.20-0.25 \text{ is recommended. This removes intruder state problems to a large extent and usually improves the results. Note that the method is not exactly orbital invariant, and pseudo-canonical orbitals should be used (see CANONICAL option in MULTI).}
\]

It is possible to use \text{SHIFT} and \text{IPEA} simultaneously, but it does not make sense to use one of the \textit{G}-options together with \text{IPEA}.

21.6 Integral direct calculations

RS2, RS2C, and RS3 calculations with very large basis sets can be performed in integral-direct mode. The calculation will be direct if a global \textsc{direct} or \textsc{gdirect} card appears earlier in the input. Alternatively, (mainly for testing) \textsc{direct} can be specified as an option on the \textit{RSn[C]} card:

\[
\text{RS2} [,Gn][,SHIFT=\text{shift}][,\textsc{direct}] \\
\text{RS2C} [,Gn][,SHIFT=\text{shift}][,\textsc{direct}]
\]

Density fitting is also available, and as usual invoked by the prefix \textit{DF-}, i.e. \textit{DF-RS2, DF-RS2C}. 
21.7 CASPT2 gradients


CASPT2 analytic energy gradients are computed automatically if a FORCE or OPTG command follows (see sections [45] and [46]). Analytical gradients are presently only available for RS2 calculations (not RS2C), and only for the standard $\hat{H}^{(0)}$ (not G1, G2 etc). Gradients can be computed for single-state calculations, as well as multi-state MS-MR-CASPT2 (see section 21.3. However, only states with the same symmetry and spin and the same number of electrons as in the optimized state can be included in the preceding SA-CASSCF (CONFIG,DET must not be given in the CASSCF).

In single state calculations, the gradient is automatically computed for the state computed in CASPT2/RSPT2 (i.e., using STATE, 1, 2 the second state in the symmetry under consideration is computed, see section [21.2]. The program works with state-averaged MCSCF (CASSCF) orbitals, and no CPMCSCF directive is needed. It is necessary that the state under consideration is included in the preceding (state-averaged) MCSCF/CASSCF. The RS2 gradient program can also be used to compute state-averaged MCSCF/CASSCF gradients by using the NOEXC directive.

In a multi-state MS-MR-CASPT2 calculation, the state for which the gradient is computed must be specified using the ROOT option (default ROOT=1), i.e.,

\[ RS2, MIX=nstates, \text{ROOT}=i_{optroot} \]

where \( 1 \leq i_{optroot} \leq nstates \).

Level shifts can be used. By default, the exact gradient of the level-shift corrected energy is computed. For a non-zero shift, this requires to solve the CASPT2 Z-vector equations, which roughly doubles the computational effort. In single state calculations it is possible to ignore the effect of the level shift on the gradient and not to solve the Z-vector equation. This variant, which is described in the above paper, may be sufficiently accurate for many purposes. It is invoked using the IGNORE option, e.g.

\[ RS2, \text{SHIFT}=0.2, \text{IGNORE} \]

Any publications employing the CASPT2 gradients should cite the above paper. A citation for MS-CASPT2 gradient method is P. Celani and H.-J. Werner, to be published.

Example:

CASPT2 geometry optimizations for H2O:
memory,8,m
gthresh,energy=1.d-10
!basis=vdz
R=2.0
R0=R
Theta=100
geometry={
    H1,O,R;
    H2,O,R,H1,THETA}

hf;accu,12

{multi;closed,2}
rs2,shift=0.3,ignore
    !ignore shift in computing gradient, i.e., no cp-caspt2
optg,gradient=1.d-5
e_opt(1)=energy
r_opt(1)=r
theta_opt(1)=theta
method(1)='rs2,analytical,ignore'

rs2,shift=0.3
    !exact gradient with shift
optg,gradient=1.d-5
e_opt(2)=energy
r_opt(2)=r
theta_opt(2)=theta
method(2)='rs2,analytical,exact'

rs2,shift=0.3
    !numerical gradient with shift
optg,gradient=1.d-5,numerical,fourpoint
    !use four-point numerical gradient
e_opt(3)=energy
r_opt(3)=r
theta_opt(3)=theta
method(3)='rs2,analytical'

rs2c,shift=0.3
    !numerical gradient of rs2c with shift
optg,gradient=1.d-5,fourpoint
    !use four-point numerical gradient
e_opt(4)=energy
r_opt(4)=r
theta_opt(4)=theta
method(4)='rs2c,numerical'

table,method,r_opt,theta_opt,e_opt
digits,,4,4,8

http://www.molpro.net/info/current/examples/h2o_caspt2_opt.com

This produces the Table

<table>
<thead>
<tr>
<th>METHOD</th>
<th>R_OPT</th>
<th>THETA_OPT</th>
<th>E_OPT</th>
</tr>
</thead>
<tbody>
<tr>
<td>rs2,analytical,ignore</td>
<td>1.8250</td>
<td>102.1069</td>
<td>-76.22789382</td>
</tr>
<tr>
<td>rs2,analytical,exact</td>
<td>1.8261</td>
<td>102.1168</td>
<td>-76.22789441</td>
</tr>
<tr>
<td>rs2,numerical</td>
<td>1.8261</td>
<td>102.1168</td>
<td>-76.22789441</td>
</tr>
<tr>
<td>rs2c,numerical</td>
<td>1.8260</td>
<td>102.1187</td>
<td>-76.22787681</td>
</tr>
</tbody>
</table>

MS-CASPT2 geometry optimization for the second excited \( ^3B_2 \) state if H\(_2\)O:
memory,8,m
qthresh,energy=1.d-12
!
basis=vdz
R=2.0
R0=R
Theta=100
step=0.001
geometry={
    H1,O,R;
    H2,O,R,H1,THETA}

hf;accu,12
multi !state averaged casscf for various triplet states
closed,2
wf,10,1,2
state,3
wf,10,2,2
state,2
wf,10,3,2
state,3
canonical,2140.2
rs2,mix=3,root=2,shift=0.2 !optimized second 3B2 state
wf,10,3,2 !3B2 wavefunction symmetry
state,3 !include 3 states
optg,gradient=1.d-5 !geometry optimization using analytical gradients
e_opt(1)=msenergy(2) !optimized ms-caspt2 energy
r_opt(1)=r !optimized bond distance
theta_opt(1)=theta !optimized bond angle
method(1)='rs2,analytical'
rs2,mix=3,shift=0.2 !optimized second 3B2 state
wf,10,3,2 !3B2 wavefunction symmetry
state,3 !include 3 states
optg,variable=msenergy(2),gradient=1.d-5,fourpoint
    !geometry optimization using numerical gradients
e_opt(2)=msenergy(2) !optimized ms-caspt2 energy
r_opt(2)=r !optimized bond distance
theta_opt(2)=theta !optimized bond angle
method(2)='rs2,numerical'
table,method,r_opt,theta_opt,e_opt
digits,,4,4,8

http://www.molpro.net/info/current/examples/h2o_mscaspt2_opt.com

This produces the table

<table>
<thead>
<tr>
<th>METHOD</th>
<th>R_OPT</th>
<th>THETA_OPT</th>
<th>E_OPT</th>
</tr>
</thead>
<tbody>
<tr>
<td>rs2,analytical</td>
<td>2.4259</td>
<td>96.7213</td>
<td>-75.81630628</td>
</tr>
<tr>
<td>rs2,numerical</td>
<td>2.4259</td>
<td>96.7213</td>
<td>-75.81630628</td>
</tr>
</tbody>
</table>

21.8 Coupling MRCI and MRPT2: The CIPT2 method

For particularly difficult cases with strong intruder problems, or in which second-order perturbation theory fails to predict reliable results, a new method that couples MRCI and CASPT2 has been developed. This variant is invoked using the CIPT2 directive:

CIPT2

In this case all excitations solely from active orbitals are treated by MRCI, while the remaining excitations involving inactive (closed-shell) orbitals are treated by second-order perturbation theory. Both methods are coupled by minimizing an appropriate energy functional. Of course, this method is much more expensive than MRPT2. The cost is comparable to the cost for an MRCI without correlating the inactive orbitals.

21.9 Further options for CASPT2 and CASPT3

Other options can be set using the OPTION command. These options are mainly used for testing purposes and should be used with care. It should be noted that the only option that can be modified in the RS2C program is IFDIA: all others only work with RS2/RS3.

OPTION,code1=value,code2=value,...

Of relevance for the CASPT2/3 program are the following options:

<table>
<thead>
<tr>
<th>Code</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>IPROCS=0</td>
<td>(Default). Calculation uses uncontracted singles with RS2.</td>
</tr>
<tr>
<td>IPROCS=1</td>
<td>Non-interacting singles are projected out during update. This is an approximate procedure which should be used with care.</td>
</tr>
<tr>
<td>IPROCS=2</td>
<td>The singles are fully internally contracted in RS2. This is achieved via a projection operator during the coefficient update and may be inefficient.</td>
</tr>
<tr>
<td>IPROCS=3</td>
<td>Only singles with one or two holes in the closed-shells are internally contracted in RS2 using a projection operator.</td>
</tr>
<tr>
<td>IPROCI=0</td>
<td>(Default). Calculation uses uncontracted internals with RS2.</td>
</tr>
<tr>
<td>IPROCI=1</td>
<td>Internals with two holes in the inactive space are internally contracted in RS2 using a projection operator.</td>
</tr>
<tr>
<td>IPROCS=3,IPROCI=1</td>
<td>This combination of options reproduces with RS2 the RS2C result using projection operators. This requires lot of memory and disk space and it is feasible only for small molecules.</td>
</tr>
<tr>
<td>IFDIA=0</td>
<td>(Default). All off-diagonal elements of the effective Fock matrix are included.</td>
</tr>
<tr>
<td>IFDIA=1</td>
<td>The internal-external block of the Fock-matrix is neglected. This eliminates the single-pair coupling.</td>
</tr>
<tr>
<td>IFDIA=2</td>
<td>All off-diagonal elements of the Fock matrix are neglected. This corresponds to CASPT2D of Andersson et al. Note: in this case the result is not invariant to rotations among active orbitals!</td>
</tr>
<tr>
<td>IHINT=0</td>
<td>(Default). Only one-electron integrals are used in the zeroth-order Hamiltonian for all interactions.</td>
</tr>
<tr>
<td>IHINT=1</td>
<td>The all-internal two-electron integrals are used in the zeroth-order Hamiltonian for the internal-internal and single-single interactions.</td>
</tr>
</tbody>
</table>
22 NEVPT2 calculations

Reference literature:


All publications resulting from use of this program must acknowledge the above.

22.1 General considerations

NEVPT2 is a form of second-order multireference perturbation theory which can be applied to CAS–SCF wavefunctions or, more generally, to CAS–CI wavefunctions. The term NEVPT is an acronym for “n–electron valence state perturbation theory”. While we refer the reader to the pertinent literature (see above), we limit ourselves to recalling here that the most relevant feature of NEVPT2 consists in that the first order correction to the wave function is expanded over a set of properly chosen multireference functions which correctly take into consideration the two–electron interactions occurring among the active electrons. Among the properties ensured by NEVPT2 we quote:

• Strict separability (size consistence): the energy of a collection of non–interacting systems equals the sum of the energies of the isolated systems
• Absence of intruder states: the zero-order energies associated to the functions of the outer space are well separated from the zero-order energy of the state being studied, thus avoiding divergences in the perturbation summation

• The first order correction to the wavefunction is an eigenfunction of the spin operators $S^2$ and $S_z$

• Electronically excited states are dealt with at the same level of accuracy as the ground state

• NEVPT2 energies are invariant under a unitary transformation of the active orbitals. Furthermore, the choice of canonical orbitals for the core and virtual orbitals (the default choice) ensure that the results coincide with those of an enlarged version of the theory fully invariant under rotations in the core and virtual orbital spaces, respectively

• NEVPT2 coincides with MP2 in the case of a HF wave function

NEVPT2 has been implemented in two variants both of which are present in MOLPRO, these are the strongly contracted (SC) and the partially contracted (PC) variants. The two variants differ by the number of perturber functions employed in the perturbation summation. The PC–NEVPT2 uses a richer function space and is in general more accurate than the SC–NEVPT2. The results of SC–NEVPT2 and PC–NEVPT2 are anyway usually very close to one another.

22.2 Input description

NEVPT2 must follow a CAS–SCF or CAS–CI calculation. The command

```plaintext
NEVPT2, options
```

has to be specified to carry out a second–order perturbation calculation. NEVPT2 is part of the MRCI program and uses the options of the latter. Of particular relevance are the options CORE, CLOSED, OCC, WF and STATE of the MRCI program. There is, at the moment, only one option specific to NEVPT2 which can be provided by the user:

```plaintext
THRNEVPT2
```

The threshold to discard small coefficients in the CAS wavefunction (default = 0.0),

The present implementation of NEVPT2 is state–specific, i.e. the perturbation theory can only be applied to a single state. The multi–state (or quasi–degenerate) version of NEVPT2 will be implemented in MOLPRO in the near future.

An example is provided where the energies of the ground state and of the first $^1A_2$ ($n \rightarrow \pi^*$) excited state of formaldehyde are calculated.
***
memory,20,m
file,1,h2co.int,new
file,2,h2co.wf,new
gthresh,energy=1.d-9
gthresh,orbital=1.d-8
gthresh,civec=1.d-8

geomtyp=zmat
geometry
O,, 0.000000000, 0.000000000, 0.0196594609
C,, 0.000000000, 0.000000000, 2.3248507925
H1,, 0.000000000, 1.7597110083, 3.3972521023
H2,, 0.000000000, -1.7597110083, 3.3972521023
end

basis=6-31G*

{hf
wf,16,1,0}

{multi
closed,4,0,1,0
occ,6,2,4,0
wf,16,1,0
state,1
natorb,2140.2,state=1.1
}

{nevpt2,thrden=1.0d-10,thrvar=1.0d-10
core,2,0,0,0
closed,4,0,1,0
occ,6,2,4,0
orbit,2140.2,state=1.1
wf,16,1,0
state,1,1
}

{multi
closed,4,0,1,0
occ,6,2,4,0
wf,16,4,0
state,1
start,2140.2
natorb,2141.2,state=1.4
}
{nevpt2,thrden=1.0d-10,thrvar=1.0d-10
core,2,0,0,0
closed,4,0,1,0
occ,6,2,4,0
orbit,2141.2,state=1.4
wf,16,4,0
state,1,1
}

http://www.molpro.net/info/current/examples/form_nevpt2.com

23 MØLLER PLESSET PERTURBATION THEORY

Closed-shell Møller-Plesset perturbation theory up to full fourth order [MP4(SDTQ)] is part of the coupled-cluster program.
The commands **MP2**, **MP3**, **MP4** perform the MP calculations up to the specified order (lower orders are included).

**MP4; NOTRIPL**; performs MP4(SDQ) calculations.

Normally, no further input is needed if the **MPn** card directly follows the corresponding HF-SCF. Otherwise, occupancies and orbitals can be specified as in the CI program. The resulting energies are stored in variables as explained in section 8.8.

Dual basis set calculations are possible for the closed-shell methods, see section 24.14.

### 23.1 Expectation values for MP2

**EXPEC[,** **TYPE=** **type**][,**opname]**

One-electron properties can be computed if an **EXPEC** card follows the **MP2** card (the **GEXPEC** directive has no effect in this case). Properties are obtained as analytical energy derivatives with or without taking into account the orbital relaxation, which can be specified as

**TYPE**:  
- **type=RELAX**: Compute fully relaxed properties with taking into account the orbital relaxation (default). Nonrelaxed properties are also computed and printed. For MP2, this option is highly recommended.
- **type=NORELAX**: Compute properties without taking into account the orbital relaxation.

Note that, in MP2, calculation of fully relaxed properties may be much more expensive than computing only the energy or properties without the orbital relaxation effect. The syntax for operators **opname** is explained in section 6.13. See also **DM** in section 23.3 and **NATORB** in section 23.4.

### 23.2 Expectation values for MP3

**EXPEC[,**opname]**] Fully relaxed one-electron properties are available for MP3 (see section 25.6, Paper 2). Currently, this is only working without frozen core orbitals, i.e. **CORE, 0** must be specified. MP2 properties are also computed and printed.

### 23.3 Saving the density matrix

**DM,record.ifil**;

The first-order density matrix in AO basis is stored in record **record** on file **ifil**. Two types of density matrices are stored in the same record: the one without orbital relaxation contribution is stored as **set 1**, meanwhile with the orbital relaxation contribution, it is stored as **set 2**. If the **NORELAX** directive is given on the **EXPEC** card prior to the **DM** card, only the orbital unrelaxed density matrix is computed and stored. See also **NATORB** in section 23.4.

### 23.4 Natural orbitals

**NATORB,[** RECORD=** record.ifil,** PRINT=nprint,** CORE=[natcor]**];
Calculate natural orbitals. The number of printed external orbitals in any given symmetry is \( n_{\text{print}} \) (default 2). \( n_{\text{print}}=-1 \) suppressed the printing. The natural orbitals and the density matrix are saved in a dump record \( \text{record} \) on file \( \text{ifil} \). If \( \text{record}.\text{ifil} \) is specified on a \( \text{DM} \) card (see above), this record is used. If different records are specified on the \( \text{DM} \) and \( \text{NATORB} \) cards, an error will result. The record can also be given on the \( \text{SAVE} \) card. Natural orbitals are computed for both the nonrelaxed and relaxed density matrices if available, which are stored in the same record as \( \text{set 1} \) and \( \text{set 2} \), respectively.

Note that the effective (relaxed) density matrix of non-variational methods like MP2 or CCSD does not strictly behave as a density matrix. For instance, it has non-zero matrix elements between core and valence orbitals, and therefore core orbitals are affected by the natural orbital transformation. Also, occupation numbers can be greater than 2.0 or less than 0.0. If \( \text{CORE} \) is given (\( \text{natcor}=1 \)), the core orbitals are frozen by excluding them from the natural orbital transformation.

### 23.5 Polarizabilities and second-order properties for MP2

Analytical MP2 static dipole polarizabilities and other second order properties can be computed using the \( \text{POLARI} \). By default the dipole operator is used, but other one-electron operators can be specified on the \( \text{POLARI} \) directive. Currently, this is only working without frozen core orbitals, i.e., \( \text{CORE,0} \) must be given. This option is only available without using the density fitting approximation. The dipole polarizabilities are stored in the variables \( \text{POLXX, POLXY, POLXZ, POLYY, POLYZ, POLZZ} \).

Example:

```plaintext
{ mp2
  core,0
  polari,dm,qm}
```

Computes the full tensors for the dipole and quadrupole operators.

Nonsymmetrized first-order perturbed density matrix resulting from CP equations for MP2 can be stored for further use if \( \text{RECMP2}=\text{record}.\text{ifil} \) is given.

### 23.6 CPHF for gradients, expectation values and polarizabilities

The accuracy and other parameters of the CPHF calculations necessary to compute gradients and response properties can be modified using the \( \text{CPHF} \) directive:

\[
\text{CPHF, [THRMIN=thrmn], [THRMAX=thrmx], [MAXIT=maxit], [SHIFT=shift], [SAVE=record], [START=record], [DIIS=idiis], [DISM=disim]}
\]

- **THRMIN**: CPHF convergence threshold (default 1.d-6). \( \text{THRESH} \) and \( \text{ACCU} \) are aliases for this.
- **THRMAX**: initial CPHF convergence threshold in geometry optimizations. Once the geometry is converged to a certain accuracy (depending on \( \text{OPTCONV} \)), the threshold is stepwise reduced to \( \text{THRMIN} \). The default is \( \text{THRMAX}=\min(1.d-6, \text{THRMIN} \times 100) \); Values larger than 1.d-6 are ignored.
- **MAXIT**: Maximum number of iterations (default 50).
SHIFT  Level shift for CPHF (default 0.1).
DIIS  First macroiteration in which DIIS is used (default 1).
DISM  First microiteration in which DIIS is used (default 1; in microiterations the core contribution is frozen).
SAVE  Record on which the CPHF solution can be saved for later restarts. The solution is saved automatically in geometry optimizations and frequency calculations.
START  Record from which initial guess is read. A starting guess is read automatically in geometry optimizations and frequency calculations.

In density-fitting MP2, only THRMIN is active, the rest of the options are handled automatically.

23.7 Density-fitting MP2 (DF-MP2, RI-MP2)

DF-MP2.options

invokes the density fitted MP2 program. The present implementation works only without symmetry. RI-MP2 is an alias for the command DF-MP2.

The following options can be specified:

BASIS_MP2=basis:  Fitting basis set. basis can either refer to a basis set defined in a BASIS block, or to a default fitting basis set (only available for correlation consistent basis sets). If a correlation consistent orbital basis set is used, the corresponding MP2 fitting basis is generated by default. In all other cases, the fitting basis must be defined.

THRAO=value:  Screening threshold for 3-index integrals in the AO basis
THRMO=value:  Screening threshold for 3-index integrals in the MO basis
THROV=value:  Screening threshold for 2-index integrals of fitting basis.
THRPROD=value:  Screening product threshold for first half transformation.
SPARSE=value:  If Non-zero, use sparse algorithm in second-half transformation (default).

See section [13] for a more general description of density fitting. Expectation values and gradients can also be computed with DF-MP2.

23.8 Spin-component scaled MP2 (SCS-MP2)

The spin-component scaled MP2 energy as proposed by Grimme (J. Chem. Phys. 118, 9095 (2003)) is printed automatically using the default scaling factors (1.2 for antiparallel spin, 1/3 for parallel spin). These factors can be modified using the options SCSFACS and SCSFACT, respectively, i.e.

MP2, SCFSFACS=facs, SCSFACT=fact

The SCS-MP2 total energy is stored in the variable EMP2_SCS. Gradients and first-order properties can be computed for SCS-MP2 by setting the option SCSGRD=1. This only operational for density fitted MP2 and local MP2 methods, i.e. using
DF-MP2,[DF_BASIS=fitbasis],SCSGRD=1,[SCSFACS=facs],[SCSFAC=fact]

followed by FORCES or OPTG. In these cases, the SCS-MP2 total energy replaces the MP2 total energy in the variable EMP2. Expectation values can also be computed with DF-SCS-MP2, where the SCS-MP2 density matrix is used instead of the MP2 density matrix (see section 23.1). For DF-LMP2 see section 32.
24 THE CLOSED SHELL CCSD PROGRAM

Bibliography:

All publications resulting from use of this program must acknowledge the above.

The CCSD program is called by the CISD, CCSD, BCCD, or QCI directives. CID or CCD can be done as special cases using the NOSINGL directive. The code also allows to calculate Brueckner orbitals (QCI and CCSD are identical in this case). Normally, no further input is needed if the CCSD card follows the corresponding HF-SCF. Optional ORBITAL, OCC, CLOSED, CORE, SAVE, START, PRINT options work as described for the MRCI program in section 20. The only special input directives for this code are BRUECKNER and DIIS, as described below.

The following options may be specified on the command line:

- NOCHECK: Ignore convergence checks.
- DIRECT: Do calculation integral direct.
- NOSING: Do not include singly external configurations.
- MAXIT= value: Maximum number of iterations.
- SHIFTS= value: Denominator shift for update of singles.
- SHIFTP= value: Denominator shift for update of doubles.
- THRDAEN= value: Convergence threshold for the energy.
- THRVAR= value: Convergence threshold for CC amplitudes. This applies to the square sum of the changes of the amplitudes.
- SAVE= record: Save CCSD wavefunction to this record.
- START= record: Restart CCSD wavefunction from a previously written record.

The convergence thresholds can also be modified using

THRESH,ENERGY= thrden, COEFF= thrvar

Convergence is reached if the energy change is smaller than thrden (default 1.d-6) and the square sum of the amplitude changes is smaller than thrvar (default 1.d-10). The THRESH card must follow the command for the method (e.g., CCSD) and then overwrites the corresponding global options (see GTHRESH, sec. 6.11).

The computed energies are stored in variables as explained in section 8.8. As well as the energy, the $T_1$ diagnostic (T. J. Lee and P. R. Taylor, Int. J. Quant. Chem. S23 (1989) 199) and the $D_1$ diagnostic (C. L. Janssen and I. M. B. Nielsen, Chem. Phys. Lett. 290 (1998), 423, and T. J. Lee. Chem. Phys. Lett. 372 (2003), 362) are printed and stored for later analysis in the variables T1DIAG and D1DIAG, respectively.

For geometry optimization and computing first-order properties see section 24.11.

24.1 Coupled-cluster, CCSD

The command CCSD performs a closed-shell coupled-cluster calculation. Using the CCSD (T) command, the perturbative contributions of connected triple excitations are also computed.

If the CCSD is not converged, an error exit will occur if triples are requested. This can be avoided using the NOCHECK option.
In this case the (T) correction will be computed even if the CCSD did not converge. Note: NOCHECK has no effect in geometry optimizations or frequency calculations.

For further information on triples corrections see under RCCSD.

In cases that the Hartree-Fock reference determinant does not sufficiently dominate the wavefunction, the program will stop with a message UNREASONABLE NORM. CALCULATION STOPPED. This can be avoided by setting the option CC_NORM_MAX=value on the CCSD command line. The calculation is stopped if the square norm of the wavefunction (in intermediate normalization) exceeds 1+nval*CC_NORM_MAX, where nval is the number of correlated valence orbitals. The default value is CC_NORM_MAX=0.2.

### 24.2 Quadratic configuration interaction, QCI

QCI or QCISD performs quadratic configuration interaction, QCISD. Using the QCI(T) or QCISD(T) commands, the contributions of connected triples are also computed by perturbation theory. Normally, no further input is needed if the QCI card follows the corresponding HF-SCF. Otherwise, occupancies and orbitals can be specified as in the CI program. For modifying DIIS directives, see section 24.7.

For avoiding error exits in case of no convergence, see CCSD(T).

### 24.3 Brueckner coupled-cluster calculations, BCCD

BCCD,[SAVEORB=record],[PRINT],[TYPE=.type]

In addition, the same options as for CCSD can be used.

BCCD performs a Brueckner coupled-cluster calculation and computes Brueckner orbitals. With these orbitals, the amplitudes of the singles vanish at convergence. Using the BCCD(T) command, the contributions of connected triples are also computed by perturbation theory. Normally, no further input is needed if the BCCD card follows the corresponding HF-SCF. Otherwise, occupancies and orbitals can be specified as in the CI program. BRUECKNER parameters can be modified using the BRUECKNER directive.

The Brueckner orbitals and approximate density matrix can be saved on a MOLPRO dump record using the SAVEORB option. The orbitals are printed if the PRINT option is given. TYPE can be used to specify the type of the approximate density to be computed:

- **TYPE=REF**

- **TYPE=TOT**
  - Compute and store density with contribution of pair amplitudes (linear terms). Normally, this does not seem to lead to an improvement.

- **TYPE=ALL**
  - Compute and store both densities

Note: The expectation variables are stored in variables as usual. In the case that both densities are made, the variables contain two values, the first corresponding to REF and the second to TOT (e.g., DMZ(1) and DMZ(2)). If TYPE=REF or TYPE=TOT is give, only the corresponding values are stored.

For avoiding error exits in case of no convergence, see CCSD(T).
24.3.1 The BRUECKNER directive

```
BRUECKNER, orbbrk,ibrstr;ibrueck,brsfak;
```

This directive allows the modification of options for Brueckner calculations. Normally, none of the options has to be specified, and the BCCD command can be used to perform a Brueckner CCD calculation.

- `orbbrk`: if nonzero, the Brueckner orbitals are saved on this record.
- `ibrstr`: First iteration in which orbitals are modified (default=3).
- `ibrueck`: Iteration increment between orbital updates (default=1).
- `brsfak`: Scaling factor for singles in orbital updates (default=1).

24.4 Singles-doubles configuration interaction, CISD

Performs closed-shell configuration interaction, CISD. The same results as with the CI program are obtained, but this code is somewhat faster. Normally, no further input is needed. For specifying DIIS directives, see section 24.7.

24.5 Quasi-variational coupled cluster, QVCCD


24.6 Distinguishable cluster, DCD

DCSD, BDCD, or ODCD perform closed-shell distinguishable cluster calculations with singles, Brueckner orbitals, or optimized orbitals, respectively. All CCSD and BCCD options (24) can be also used for distinguishable cluster calculations. The analytical gradients (45.1), explicit correlation (35), open-shell versions (26), and a linear-scaling implementation (32) are all available for the DCSD method. All reported calculations using this feature should cite:


24.7 The DIIS directive

```
DIIS, itedis, incdis, maxdis, itydis;
```

This directive allows to modify the DIIS parameters for CCSD, QCISD, or BCCD calculations.

- `itedis`: First iteration in which DIIS extrapolation may be performed (default=2).
incdis: Increment between DIIS iterations (default=1).
maxdis: Maximum number of expansion vectors to be used (default=6).
itydis: DIIS extrapolation type. itydis=1 (default): residual is mini-
       mized. itydis=2: $\Delta T$ is minimized.

In addition, there is a threshold THRDIS which may be modified with the THRESH directive. DIIS extrapolation is only done if the variance is smaller than THRDIS.

### 24.8 Saving the wavefunction

**SAVE,**record;

**record:** record name for save of wavefunction. The wavefunction is saved in each iteration. This has the same effect as the SAVE option.

### 24.9 Starting wavefunction

**START,**record;

**record:** record name from which the wavefunction is restored for a restart. This has the same effect as the START option.

If the option MAXIT=1 is set on the CCSD command line, no further iterations will be performed. (Note: in this case there is no check whether the previous wavefunction was converged.) It is then for example possible to compute the triples correction using the restarted CCSD wavefunction.
24.10  Examples

24.10.1  Single-reference correlation treatments for H₂O

```plaintext
****, h2o test
memory, i, m
geometry={o;h1,o,r;h2,o,r,h1,theta}
basis=vtz
r=1 ang
theta=104
hf
text, examples for single-reference correlation treatments

CI
CISD using MRCI code
CEPA(1)
copa-1 using MRCI code
MP2
Second-order Moeller-Plesset
MP3
Second and third-order MP
MP4
Second, third, and fourth-order MP4(SDTQ)
MP4;notripl
MP4(SDQ)
CISD
CISD using special closed-shell code
CCSD(T)
coupled-cluster CCSD(T)
QCISD(T)
quadratic configuration interaction QCISD(T)
BCCD(T)
Brueckner CCD(T) calculation

http://www.molpro.net/info/current/examples/h2o_ccsd.com
```

24.10.2  Single-reference correlation treatments for N₂F₂

```plaintext
****, N2F2 CIS GEOMETRY (C2h)

rnn=1.223, ang
rnf=1.398, ang
alpha=114.5;
geometry={N1
      N2,N1,rnn
      F1,N1,rnf,N2, alpha
      F2,N2,rnf,N1, alpha,F1, 180}
basis=vtz
$method=[hf,cisd,ccsd(t),qcisd(t),bccd(t)]
do i=1, #method
$method(i)
e(i)=energy
enddo
table, method, e
title, Results for n2f2, basis=vtz
```

This calculation produces the following table:

```
Results for n2f2, basis=VTZ

<table>
<thead>
<tr>
<th>METHOD</th>
<th>E</th>
<th>E-ESCF</th>
</tr>
</thead>
<tbody>
<tr>
<td>CISD</td>
<td>-308.4634948</td>
<td>-0.78283137</td>
</tr>
<tr>
<td>BCCD(T)</td>
<td>-308.6251173</td>
<td>-0.94445391</td>
</tr>
<tr>
<td>CCSD(T)</td>
<td>-308.6257931</td>
<td>-0.94512967</td>
</tr>
<tr>
<td>QCISD(T)</td>
<td>-308.6274755</td>
<td>-0.94681207</td>
</tr>
</tbody>
</table>

http://www.molpro.net/info/current/examples/n2f2_ccsd.com
```
24.11 Expectation values

**EXPEC[^][METHOD=][method][,[TYPE=][type][,opname]]**

One-electron properties in closed-shell QCISD, QCISD(T), CCD, CCSD, and DCSD can be computed by using **EXPEC**. (the **GEXPEC** directive has no effect in this case). The following options can be specified:

**METHOD:**

- **method=E**DERIV: Default case. Properties are obtained as analytical energy derivatives.
- **method=XCCSD**: eXpectation-value CCSD method (with the exponential ansatz used also for bra) – see section 25.6.
- **method=XCCSD(3)**: A simplified version of XCCSD – see section 25.6. It is also available for the local CCSD method.

**TYPE:**

- **type=RELAX**: Compute fully relaxed properties with taking into account the orbital relaxation (default). Nonrelaxed properties are also computed and printed.
- **type=NORELAX**: Compute properties without taking into account the orbital relaxation. The **TYPE** option has only effect for the analytical energy derivatives.

Note that, in CCSD, the orbital relaxation effect on properties is less pronounced than, for example, in MP2. By default, only dipole moments are computed. The syntax for operators **opname** is explained in section 6.13. See also **DM** in section 24.12 and **NATORB** in section 24.13.

24.12 Saving the density matrix

**DM,record.ifil;**

The first-order density matrix in AO basis is stored in record **record** on file **ifil**. For details, see section 23.3. See also **NATORB** in section 24.13.

24.13 Natural orbitals

**NATORB,[RECORD=][record.ifil],[PRINT=nprint],[CORE=[natcor]];**

Calculate natural orbitals. The options are the same as for MP2. For details, see section 23.4.

24.14 Dual basis set calculations

Dual basis set calculations are possible with the closed-shell MP2 and CCSD codes (conventional and local, also with density fitting where available). Normally this means that the Hartree-Fock calculation is done with a smaller basis set than the correlation calculation. In MOLPRO, two possibilities exist: the recommended one is to perform the HF and MP2 or CCSD calculations using the same basis set, and only omit higher angular momentum functions in the HF. This means that the resulting HF orbitals can be used directly in the correlation calculation. Alternatively, one can use entirely different basis sets in HF and the correlation calculation; in this case the orbitals in the correlation calculation are determined by a least square fit to the HF orbitals. This is less efficient (in particular in fully direct calculations) and somewhat less
accurate. In any case, a new Fock matrix is computed in the MP2/CCSD program and block
diagonalized in the occupied and virtual orbital subspaces. A perturbative singles correction is
applied in the MP2 in order to reduce the HF basis set error.

Typically, the input is as follows:

```
basis=vtz(d/p) !triple zeta basis set without f on heavy atoms and without d on hydrogen
hf !Hartree-Fock in the small basis
basis=vtz !full cc-pVTZ basis set to be used in ccsd
ccsd(t),dual=1 !ccsd calculation
```

The option `dual=1` is required, otherwise the program will stop with an error message saying
that the basis set of the reference orbitals is inconsistent. This is a precaution in order to avoid
unexpected results.

Similarly, this works for other closed-shell single reference methods such as MP2, QCISD,
MP2-F12, CCSD-F12, and for the local variants LMP2, LQCISD, LCCSD in either con-
ventional or direct mode. Furthermore, dual basis set DF-LMP2, DF-LCCSD, DF-LMP2-F12
calculations are possible.
25 EXCITED STATES WITH EQUATION-OF-MOTION CCSD (EOM-CCSD)

Excitation energies for singlet states can be computed using equation-of-motion (EOM) approach. For the excitation energies the EOM-CCSD method gives the same results as linear response CCSD (LR-CCSD) theory. Accurate results can only be expected for excited states dominated by single excitations. The states to be computed are specified on an EOM input card, which is a subcommand of CCSD. The following input forms are possible

**EOM***, **state1**, **state2**, **state3**, . . .

Computes the given states. Each state is specified in the form **number.sym**, e.g., 5.3 means the fifth state in symmetry 3. Note that state 1.1 corresponds to the ground state CCSD wavefunction and is ignored if given.

**EOM**, **−n1.sym1**, **−n2.sym2**, . . .

computes the first **n1** states in symmetry **sym1**, **n2** in **sym2** etc.

**EOM**, **n1.sym1**, **−n2.sym1**, . . .

computes states **n1** through **n2** in symmetry **sym1**.

The different forms can be combined, e.g.,

**EOM**, **−3.1, 2.2, 2.3, −5.3**

computes states 1-3 in symmetry 1, the second excited state in symmetry 2, and the second through fifth excited states in symmetry 3. Note that state 1.1 is the ground-state CCSD wavefunction.

By default, an error exit will result if the CCSD did not converge and a subsequent EOM calculation is attempted. The error exit can be avoided using the **NOCHECK** option on the CCSD command (see also CCSD(T)).

### 25.1 Options for EOM

Normally, no further input is needed for the calculation of excitation energies.

EOM-CCSD amplitudes can be saved using **SAVE=record.ifil**. The vectors will be saved after every refreshing of the iteration space and at the end of the calculation. The calculation can be restarted from the saved vectors, if **START=record.ifil** is specified. The set of vectors to be computed can be different in old and restarted calculations. However, if both cards (**SAVE** and **START**) are specified and the records for saving and restarting are identical, the sets of vectors should be also identical, otherwise chaos. The identical **SAVE** and **START** records can be useful for potential energy surfaces calculations, see section 25.4.1.

By default, only excitation energies are calculated, since the calculation of properties is about two times as expensive, as the calculation of energies only. The one-electron properties and transition moments (expectation type, as defined in: J.F. Stanton and R.J. Bartlett, J. Chem. Phys., 98 7029 (1993)) can be calculated by adding **TRANS=1** to EOM card. The CCSD ground state is treated as a special case. If **RELAX** option is specified on the **EXPEC** card, also the relaxed one-electron density matrix is calculated for the ground state. (Currently, the relaxed CCSD density matrix through the EOM program is available for all-electron calculations only.) By default, dipole moments are calculated. Other required properties can be specified using **EXPEC** card. Properties are saved in MOLPRO variables, e.g. the x-component of the dipole moment is saved in **DMX**, its pure electron part in **DMXE**, transition moment – in **TRDMX** (left and
right transition moments are stored separately). If DENSAVE=record.ifil is specified, excited-state densities are saved to record.ifil, otherwise they are saved to the record given in DM card. If TRANS=2, transition density matrices from/to the ground state will be saved provided that DENSAVE=record.ifil or DM card are specified and nonzero. If TRANS=3, transition moments among excited states are also calculated, and finally if TRANS=4, all transition densities will be saved (note that the last option should be used with caution because the number of densities to be stored will quickly exceed the allowed maximum). For an example see section 25.4.2.

When properties are needed, the left EOM-CCSD wave functions are calculated first. It is possible to use them as starting guesses for the right EOM-CCSD wave functions. This option is controlled by STARTLE (default 0). If STARTLE=1, left vectors are just used as a start for right vectors; if STARTLE=2, starting vectors, obtained from the left vectors are additionally biorthogonalized to the left vectors; finally, if STARTLE=3, also the final right vectors are biorthogonalized to the left vectors. The last possibility is of particular importance for degenerate states.

It is possible to make the program to converge to a vector, which resembles a specified singles vector. This option is switched on by FOLLOW=n card (usually n=2 should be set). FOLLOW card should be always accompanied with EXFILE=record.ifil card, where record.ifil contains singles vectors from a previous calculation, see section 25.4.3.

### 25.2 Options for EOMPAR card

Normally, no further input is needed. However, some defaults can be changed using the EOMPAR directive:

EOMPAR, key1=value1, key2=value2,...

where the following keywords key are possible:

- **MAXDAV=**nv
  - Maximum value of expansion vectors per state in Davidson procedure (default 20).

- **INISINGL=**ns
  - Number of singly excited configurations to be included in initial Hamiltonian (default 20; the configurations are ordered according to their energy). Sometimes INISINGL should be put to zero in order to catch states dominated by double excitations.

- **INIDOUBL=**nd
  - Number of doubly excited configurations to be included in initial Hamiltonian (default 10).

- **INIMAX=**nmax
  - Maximum number of excited configurations to be included in initial Hamiltonian. By default, $n_{\text{max}} = n_{\text{s}} + n_{\text{d}}$.

- **MAXITER=**itmax
  - Maximum number of iterations in EOM-CCSD (default 50).

- **MAXEXTRA=**maxex
  - Maximum number of extra configurations allowed to be included in initial Hamiltonian (default 0). In the case of near degeneracy it is better to include a few extra configurations to avoid a slow convergence.

- **EOMLOCAL=**eoml
  - If set to 0, non-local calculation (default). EOMLOCAL=1 switches on the local module (experimental!).

- **INIMAX=**ini
  - Number of CSFs included in initial Hamiltonian, used only if INISINGL and INIDOUBL are both zero.

All keywords can be abbreviated by at least four characters.
25.3 Options for EOMPRINT card

The following print options are mostly for testing purposes and for looking for the convergence problems.

\texttt{EOMPRINT, key1=value1, key2=value2,...}

where the following keywords \texttt{key} are possible:

\textbf{DAVIDSON=}\texttt{ipr}

Information about Davidson procedure:
- \texttt{ipr=1} print results of each ”small diagonalization”
- \texttt{ipr=2} also print warning information about complex eigenvalues
- \texttt{ipr=3} also print hamiltonian and overlap matrix in trial space.

\textbf{DIAGONAL=}\texttt{ipr}

Information about configurations:
- \texttt{ipr=1} print the lowest approximate diagonal elements of the transformed hamiltonian
- \texttt{ipr=2} print orbital labels of important configurations
- \texttt{ipr=3} print all approximate diagonal elements
- \texttt{ipr=4} also print the long form of above.

\textbf{PSPACE=}\texttt{ipr}

Print information about the initial approximate hamiltonian:
- \texttt{ipr=2} print the approximate hamiltonian used to find the first approximation.

\textbf{HEFF=}\texttt{ipr}

Print information about effective Hamiltonian:
- \texttt{ipr=2} print columns of effective hamiltonian and overlap matrix in each iteration

\textbf{RESIDUUM=}\texttt{ipr}

Print information about residual vectors:
- \texttt{ipr=-1} no print in iteration
- \texttt{ipr=0} print energy values + residuum norm (squared) for each iteration (default)
- \texttt{ipr=1} also print warning about complex eigenvalue, and a warning when no new vectors is added to the trial space due to the too small norm of the residuum vector.
- \texttt{ipr=2} also print how many vectors are left

\textbf{LOCEOM=}\texttt{ipr}

\texttt{ipr=1} prints overlaps of sample and tested vectors in each iteration, if \texttt{FOLLOW} card is present. Increasing \texttt{ipr} switches on more and more printing, mostly related to the local EOM-CCSD method.

\textbf{POPUL=}\texttt{ipr}

if \texttt{ipr=1}, do a population analysis of the singles part of the rhs EOM-CCSD wave function. By default the L"owdin method is used. The Mulliken analysis can be forced by adding \texttt{MULLPRINT=1} to \texttt{EOM} card. Note that a more correct (but more expensive) approach is to calculate and analyse the EOM-CCSD density matrix, see section [25.1]

\textbf{INTERMED=}\texttt{ipr}

Print intermediates dependent on ground state CCSD amplitudes:
- \texttt{ipr=0} no print (default)
- \texttt{ipr=1} print newly created intermediates
- \texttt{ipr=2} also print more intermediates-related information
25.4 Examples

25.4.1 PES for lowest excited states for hydrogen fluoride

This example shows how to calculate potential energy surfaces for several excited states using restart from a previous calculation.

```plaintext
***, PES for several lowest states of hydrogen fluoride
memory,2,m
basis=avdz ! define basis set
gometry={h;f,h,r} ! z-matrix
r=0.8 Ang ! start from this distance
do n=1,100 ! loop over distances
  rr(n)=r ! save distance for table
  hf ! do SCF calculation
  ccsd ! do CCSD calculation, try to restart
  start,4000.2,save,4000.2 ! and save final T amplitudes
  eom,-2.1,-1.2,-1.4,start=6000.2,save=6000.2 ! do EOM-CCSD calculation, try to restart
  ! and save final excited states' amplitudes
  ebase(n)=energy(1) ! save ground state energy for this geometry
  e2(n)=energy(2)-energy(1) ! save excitation energies for this geometry
  e3(n)=energy(3)-energy(1)
  e4(n)=energy(4)-energy(1)
  r=r+0.01 ! increment distance
endo ! end of do loop
table,rr,ebase,e2,e3,e4 ! make table with results
digits,2,8,5,5,5,5,5,5,5,5 ! modify number of digits
head,R(Ang),EGRST,E_EXC(2.1),E_EXC(1.2),E_EXC(1.4)! modify headers of table
! title of table
title,EOM-CCSD excitation energies for hydrogen fluoride (in hartree), basis $basis
save,hf_eom_ccsd.tab ! save table in file
```

This calculation produces the following table:

<table>
<thead>
<tr>
<th>R(ANG)</th>
<th>EGRST</th>
<th>E_EXC(2.1)</th>
<th>E_EXC(1.2)</th>
<th>E_EXC(1.4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.80</td>
<td>-100.23687380</td>
<td>0.56664</td>
<td>0.41204</td>
<td>0.56934</td>
</tr>
<tr>
<td>0.81</td>
<td>-100.24094256</td>
<td>0.56543</td>
<td>0.40952</td>
<td>0.56812</td>
</tr>
<tr>
<td>0.82</td>
<td>-100.24451598</td>
<td>0.56422</td>
<td>0.40695</td>
<td>0.56690</td>
</tr>
</tbody>
</table>

etc.

25.4.2 EOM-CCSD transition moments for hydrogen fluoride

This example shows how to calculate and store CCSD and EOM-CCSD density matrices, calculate dipole and quadrupole moments (transition moments from the ground to excited states are calculated), and how to use the EOM-CCSD excited state density for Mulliken population analysis.
25 EXCITED STATES WITH EQUATION-OF-MOTION CCSD (EOM-CCSD)

***, Properties and transition moments for several lowest states of hydrogen fluoride
memory,2,m
basis=avdz ! define basis set
gamey=(h,f,h,r) ! z-matrix
r=0.92 Ang ! define distance

hf
(ccsd
dm,5600.2 ! density matrices will be stored here
expec,response,qm ! require quadrupole moments
eom,=3.1,-2.2,-2.3,-2.4,trans=1} ! do EOM-CCSD calculation + properties
pop;density,5600.2,state=2.4 ! make population analysis for state 2.4

http://www.molpro.net/info/current/examples/hf_eom_prop.com

This calculation produces the following table:

<table>
<thead>
<tr>
<th>State</th>
<th>Exc. Energy (eV)</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>14.436</td>
<td>0.000000000</td>
<td>0.000000000</td>
<td>0.65349466</td>
</tr>
</tbody>
</table>

Right transition moment

Left transition moment

Dipole strength 0.45007246

Oscillator strength 0.15917669

Dipole moment 0.00000000 0.00000000 0.88758090

e etc.

25.4.3 Calculate an EOM-CCSD state most similar to a given CIS state

This example shows how to force the convergence of the EOM-CCSD program to a state, which resembles at most a given CIS state.

***, EOM-CCSD, vector following procedure
memory,2,m
basis=avdz ! define basis set
gamey=(h,f,h,r) ! z-matrix
r=0.92 Ang ! define distance
hf;save,2100.2 ! do SCF calculation, save orbitals
cis,-4.4,exfile=6000.2 ! do CIS calculation, save amplitudes
ccsd;save,4000.2 ! do CCSD calculation, save amplitudes
eom,-4.4,checkovlp=1,exfile=6000.2 ! do EOM-CCSD calculation,
eompar,inisingl=200,inidoubl=0 ! for first approximation take 200 single CSF
ccsd;start,4000.2 ! of approximate hamiltonian
eom,2.4,follow=2,exfile=6000.2,checkovlp=1 ! do EOM-CCSD calculation for state closest
eompar,inisingl=200,inidoubl=0 ! to 2.4 CIS state, check overlap of singles
eomprint,loce=1 ! with CIS vectors stored in exfile

http://www.molpro.net/info/current/examples/hf_eom_conv.com
In this example the CIS state 2.4 corresponds to the EOM-CCSD state 1.4!

25.5 Excited states with CIS

Excitation energies can also be calculated using the Configuration-Interaction Singles (CIS) method. By default, singlet excited states are calculated. Triplet excited states can be obtained by setting $\text{triplet}=1$ in EOM card. This method cannot be expected to give accurate results, but can be used for quite large molecules. The states to be computed are specified as in EOM. Setting $\text{trans}=1$ switches on the calculation of dipole transition moments (length gauge), while $\text{trans}=2$ allows to obtain additionally one-electron properties of excited states. By default, dipole moments are calculated. Other required properties can be specified using EXPEC card. $\text{trans}=0$ and 1 work in direct mode.

```plaintext
hf cis,-3.1,1.2,trans=2
```

25.6 First- and second-order properties for CCSD from expectation-value CC theory (XCCSD)

First-order and frequency-dependent second-order properties, derived from the expressions based on the expectation value of a one-electron operator, can be obtained with the CPROP directive for the closed-shell CCSD method. For first-order properties obtained from the energy-derivative approach see section 24.11. The expectation-value methods utilized in the program are described in the following papers:


Note that properties obtained from the expectation-value expression with the coupled cluster wave function are not equivalent to these derived from gradient or linear-response methods, although the results obtained with both methods are quite similar. In XCC the exponential ansatz for the wave function is utilized for the bra side, too.

For the first-order properties the one-electron operators should be specified in the EXPEC card, while for the second-order properties – in the POLARI card. A density can be saved by specifying the DM card.

For the first-order properties the option $\text{XDEN}=1$ should be usually given. Other options specify a type of the one-electron density, which can be either the density directly derived from the expectation-value expression, see Eq. (8) of Paper 2, or the modified formula, rigorously correct through the $O(W^3)$ Möller-Plesser (MP) order, denoted as $\hat{X}(3)_{\text{resp}}$ in Papers 1 and 2. In the first case the option $\text{PROP\_ORDER}=n$ can be used to specify the approximation level for single and double excitation parts of the so-called $S$ operator (see [2], Eq. (9)); $n = \pm 2, \pm 3, \pm 4$, where for a positive $n$: all approximations to $S$ up to $n$ are used, and for a negative $n$ only a density with $S$ obtained on the $|n|$ level will be calculated. Another option related to the $S$ operator is $\text{HIGH\_W}=n$, where $n = 0, 1$; if $n=0$, some parts of $S_1$ and $S_2$ operators of a high MP order are neglected. Below an example of a standard use of this method is given:

```plaintext
CPROP,XDEN=1,PROP\_ORDER=-3,HIGH\_W=0
```
The combination above is also available by writing \texttt{EXPEC,XCCSD} after the CCSD card. A cheap method denoted as XCCSD(3), obtained by a simplification of the original XCCSD formula, is available by setting

\texttt{CPROP,XDEN=-21}

or by writing \texttt{EXPEC,XCCSD(3)} after the CCSD card.

In the second case the options \texttt{X3RESP=1} and the \texttt{CPHF,1} card (or alternatively the \texttt{EXPEC} card) should be specified,

\texttt{CPROP,XDEN=1,X3RESP=1;CPHF,1}

For the second-order properties always the following options should be given:

\texttt{CPROP,PROPAGATOR=1,EOMPROP=1}

The recommended CCSD(3) model from Paper 4 requires that additionally the \texttt{PROP_ORDER=3} and \texttt{HIGHW=0} options are specified. Frequencies for dynamic properties (in atomic units) should be given in variables \texttt{OMEGA_RE} (real parts) and \texttt{OMEGA_IM} (imaginary parts). If one of these arrays is not given, it is filled with zeros. Other options for the second-order properties involve

\texttt{OMEGAG} (default 0.3). There are two linear-equation solvers, \texttt{OMEGAG} is a minimum frequency, for which the second solver (working for large frequencies) is used.

\texttt{DISPCOEF=n} if \( n > 0 \), calculate dispersion integrals for the van der Waals coefficients with operators given in the \texttt{POLARI} card, using \( n \) as a number of frequencies for the numerical integration. In this case the frequency values given in \texttt{OMEGA_RE} and \texttt{OMEGA_IM} are ignored. If two molecules are calculated in the same script one after another, also the mixed dispersion integrals are calculated. The isotropic \( C_6 \) coefficient is stored in a variable \texttt{DISPC6}, the isotropic \( C_9 \) nonadditive coefficient – in a variable \texttt{DISPC9}. All necessary informations for the calculation of dispersion integrals are written to the ascii file \texttt{name.dispinfo}, where \texttt{name} is the name of the \texttt{MOLPRO} script.

\texttt{THRPROPAG} if given, use this threshold as a convergence criterion for the linear-equation solver for the first-order perturbed CCSD amplitudes.

\texttt{STARTT1=n} various start options for the iterative linear-equation solver for the first-order perturbed CCSD amplitudes, the most useful is \( n = 0 \) (zero start) and \( n = 7 \) (start from the negative of the r.h.s. vector rescaled by some energetic factors dependent on the diagonal of the Fock matrix and the specified frequency).

26 OPEN-SHELL COUPLED CLUSTER THEORIES

Spin unrestricted (\texttt{RHF-UCCSD}) and partially spin restricted (\texttt{RHF-RCCSD}) open-shell coupled cluster theories as described in J. Chem. Phys. 99 (1993) 5219 (see also erratum, J. Chem. Phys., 112 (2000) 3106) are available in \texttt{MOLPRO}. In both cases a high-spin \texttt{RHF} reference wavefunction is used. No coupled cluster methods based on UHF orbitals are implemented in \texttt{MOLPRO} (the only correlation method in \texttt{MOLPRO} which uses UHF orbitals is \texttt{UMP2}). In the
description that follows, the acronyms RCCSD and UCCSD are used, but the theories should normally be referred to as RHF–RCCSD, RHF–UCCSD, in order to distinguish them from alternative ansätze based on spin-unrestricted orbitals. The program will accept either the full or abbreviated acronyms as input commands.

In the RCCSD theory certain restrictions among the amplitudes are introduced, such that the linear part of the wavefunction becomes a spin eigenfunction (this is not the case in the UCCSD method, even if an RHF reference function is used). At present, the implementation of RCCSD is only preliminary, and no CPU time is saved by as compared to UCCSD. However, improved algorithms, as described in the above publication, are currently being implemented, and will be available in the near future.

The input and the options are exactly the same as for closed-shell CCSD, except that RCCSD or UCCSD are used as keywords. By default, the open-shell orbitals are the same as used in the RHF reference function, but this can be modified using OCC, CLOSED, and WF cards.

Distinguishable cluster calculations can be performed using RDCSD or UDCSD commands.

Perturbative triples corrections are computed as follows:

\[
\begin{align*}
\text{RCCSD} (T), & \quad \text{UCCSD} (T) \quad \text{triples corrections are computed as defined by J. D. Watts, J. Gauss and R. J. Bartlett, J. Chem. Phys. 98 8718 (1993).} \\
\text{RCCSD} [T], & \quad \text{UCCSD} [T] \quad \text{corrections are computed without contributions of single excitations (sometimes called CCSD+T(CCSSD)).} \\
\text{RCCSD} - T, & \quad \text{UCCSD} - T \quad \text{triples corrections are computed as defined by M. J. O. Deegan and P. J. Knowles, Chem. Phys. Letters 227 (1994) 321.}
\end{align*}
\]

In fact, all three contributions are always computed and printed. The following variables are used to store the results (here CCSD stands for either UCCSD or RCCSD):

\[
\begin{align*}
\text{ENERGY} & \quad \text{total energy for method specified in the input.} \\
\text{ENERGC} & \quad \text{total CCSD energy without triples.} \\
\text{ENERGT (1)} & \quad \text{total CCSD} (T) \text{ energy.} \\
\text{ENERGT (2)} & \quad \text{total CCSD} [T] \text{ energy.} \\
\text{ENERGT (3)} & \quad \text{total CCSD} - T \text{ energy.}
\end{align*}
\]

It should be noted that in open-shell cases the triples energy slightly depends on the treatment of core orbitals. In MOLPRO pseudo-canonical alpha and beta spin orbitals (Chem. Phys. Letters 186 (1991) 130) are generated by block-diagonalizing the corresponding Fock matrices in the space of valence orbitals, leaving frozen core orbitals untouched. Some other programs include the frozen core orbitals in the canonicalization and transformation. Because of core-valence mixing this leads to slightly different energies. Neither of the two methods can be regarded as better or more justified — it is just a matter of definition. However, the method in MOLPRO is more efficient since the subsequent integral transformation involves only valence orbitals and no core orbitals.

27 The MRCC program of M. Kallay (MRCC)

An interface exists to use the MRCC program of M. Kallay and J. Gauss within Molpro. The license and source code of the MRCC program must be obtained from Mihaly Kallay.
http://www.mrcc.hu/. Currently, only single reference methods with RHF reference functions are supported. Perturbative methods and CCn methods are only available for closed-shell. Furthermore, only serial execution is supported under MOLPRO, i.e. the mpp version cannot be used.

### 27.1 Installing MRCC

Please refer to the MRCC documentation on how to install the MRCC program. The MRCC executables must be found in PATH in order for Molpro to use them.

### 27.2 Running MRCC

The MRCC program is invoked by the command

```
MRCC, options
directives
```

The available options summarized in Table 10. For a detailed description please refer to the MRCC manual of M. Kallay (file “manual” the mrcc directory).

In MOLPRO the method to be used can be given as a string (option METHOD=string). The available methods and the corresponding MRCC input parameters (see MRCC manual) as specified in Table 11.

Directives are usually not necessary, but the CORE, OCC, ORBITAL, MAXIT, directives work as in the MOLPRO CCSD program. In addition, the number of states can be given on a STATE directive and this has the same meaning as the EOM_NSTATES option.
Table 10: Options for MRCC

<table>
<thead>
<tr>
<th>Option</th>
<th>Alias</th>
<th>Default value</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>METHOD</td>
<td>CALC</td>
<td>CC(n)</td>
<td>Computational method. See Table 11</td>
</tr>
<tr>
<td>EXCITATION</td>
<td>LEVEL</td>
<td>-1</td>
<td>Excitation level in cluster operator</td>
</tr>
<tr>
<td>RESTART_CC</td>
<td>RESTART</td>
<td>0</td>
<td>Restart option. If 1, restart with previous amplitudes.</td>
</tr>
<tr>
<td>DIRECTORY</td>
<td>DIR</td>
<td>''</td>
<td>Subdirectory in which MRCC runs (necessary for restart jobs)</td>
</tr>
<tr>
<td>EOM_NSING</td>
<td>NSING</td>
<td>-1</td>
<td>Number of excited singlet states in closed-shell case</td>
</tr>
<tr>
<td>EOM_NTRIP</td>
<td>NTRIP</td>
<td>0</td>
<td>Number of excited triplet states in closed-shell case</td>
</tr>
<tr>
<td>EOM_NSTATES</td>
<td>NDOWN</td>
<td>-1</td>
<td>Number of states in open shell case.</td>
</tr>
<tr>
<td>SYMM</td>
<td>SYMMETRY</td>
<td>-1</td>
<td>Symmetry of excited states</td>
</tr>
<tr>
<td>DENSITY</td>
<td>IDENS</td>
<td>0</td>
<td>Parameter for density calculation</td>
</tr>
<tr>
<td>HF</td>
<td></td>
<td>1</td>
<td>1 for canonical Hartree-Fock orbitals, 0 otherwise</td>
</tr>
<tr>
<td>SPATIAL</td>
<td></td>
<td>1</td>
<td>0 for spin-restricted orbitals, 1 for spin-unrestricted orbitals</td>
</tr>
<tr>
<td>NACTO</td>
<td></td>
<td>0</td>
<td>Number of active occupied orbitals</td>
</tr>
<tr>
<td>NACTV</td>
<td></td>
<td>0</td>
<td>Number of active virtual orbitals</td>
</tr>
<tr>
<td>SACC</td>
<td></td>
<td>0</td>
<td>Spin-adapted coupled cluster</td>
</tr>
<tr>
<td>DBOC</td>
<td></td>
<td>0</td>
<td>Diagonal BO correction</td>
</tr>
<tr>
<td>MEMORY</td>
<td></td>
<td>-1</td>
<td>Memory</td>
</tr>
<tr>
<td>TOL ENERGY</td>
<td>ENERGY</td>
<td>-1.0</td>
<td>Energy convergence threshold</td>
</tr>
<tr>
<td>FREQ</td>
<td></td>
<td>0.0</td>
<td>Frequency for dynamic polarizabilities</td>
</tr>
<tr>
<td>FILE</td>
<td>fort</td>
<td></td>
<td>Name for MRCC fortran files</td>
</tr>
<tr>
<td>CONVER ICONV</td>
<td></td>
<td>0</td>
<td>See mrcc manual</td>
</tr>
<tr>
<td>CS</td>
<td></td>
<td>1</td>
<td>See mrcc manual</td>
</tr>
<tr>
<td>DIAG</td>
<td></td>
<td>0</td>
<td>See mrcc manual</td>
</tr>
<tr>
<td>MAXEX</td>
<td></td>
<td>0</td>
<td>See mrcc manual</td>
</tr>
</tbody>
</table>

a) -1 means default value taken from MOLPRO
<table>
<thead>
<tr>
<th>Key</th>
<th>MRCC parameters</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>CI(n) configuration interaction methods</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CISD</td>
<td>0 2</td>
<td></td>
</tr>
<tr>
<td>CISDT</td>
<td>0 3</td>
<td></td>
</tr>
<tr>
<td>CISDTQ</td>
<td>0 4</td>
<td></td>
</tr>
<tr>
<td>CI (N)</td>
<td>0 N</td>
<td>Specify excitation level N using LEVEL</td>
</tr>
<tr>
<td>CC(N) coupled cluster methods</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CCSD</td>
<td>1 2</td>
<td></td>
</tr>
<tr>
<td>CCSDT</td>
<td>1 3</td>
<td></td>
</tr>
<tr>
<td>CCSDTQ</td>
<td>1 4</td>
<td></td>
</tr>
<tr>
<td>CC (N)</td>
<td>1 N</td>
<td>Specify excitation level N using LEVEL</td>
</tr>
<tr>
<td>CC(N-1)[N] coupled cluster methods</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CCSD [T]</td>
<td>2 3</td>
<td></td>
</tr>
<tr>
<td>CCSDT [Q]</td>
<td>2 4</td>
<td></td>
</tr>
<tr>
<td>CC (N-1) [N]</td>
<td>2 N</td>
<td>Specify excitation level N using LEVEL</td>
</tr>
<tr>
<td>CC(N-1)(N) coupled cluster methods. Also computes [n] corrections</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CCSD(T)</td>
<td>3 3</td>
<td></td>
</tr>
<tr>
<td>CCSDT(Q)</td>
<td>3 4</td>
<td></td>
</tr>
<tr>
<td>CC (N-1) (N)</td>
<td>3 N</td>
<td>Specify excitation level N using LEVEL</td>
</tr>
<tr>
<td>CC(n-1)(n)_L methods (also computes (n) and [n] corrections)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CCSD(T)_L</td>
<td>4 3</td>
<td></td>
</tr>
<tr>
<td>CCSDT(Q)_L</td>
<td>4 4</td>
<td></td>
</tr>
<tr>
<td>CC (N-1) (N)_L</td>
<td>4 N</td>
<td>Specify excitation level N using LEVEL</td>
</tr>
<tr>
<td>CC(n)-1a methods</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CCSDT-1A</td>
<td>5 3</td>
<td></td>
</tr>
<tr>
<td>CCSDTQ-1A</td>
<td>5 4</td>
<td></td>
</tr>
<tr>
<td>CC (N) -1A</td>
<td>5 N</td>
<td>Specify excitation level N using LEVEL</td>
</tr>
<tr>
<td>CC(n)-1b methods</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CCSDT-1B</td>
<td>6 3</td>
<td></td>
</tr>
<tr>
<td>CCSDTQ-1B</td>
<td>6 4</td>
<td></td>
</tr>
<tr>
<td>CC (N) -1B</td>
<td>6 N</td>
<td>Specify excitation level N using LEVEL</td>
</tr>
<tr>
<td>CCn methods (only for ground states)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CC3</td>
<td>7 3</td>
<td></td>
</tr>
<tr>
<td>CC4</td>
<td>7 4</td>
<td></td>
</tr>
<tr>
<td>CCN</td>
<td>7 N</td>
<td>Specify excitation level N using LEVEL</td>
</tr>
<tr>
<td>CC(n)-3 methods</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CCSDT-3</td>
<td>8 3</td>
<td></td>
</tr>
<tr>
<td>CCSDTQ-3</td>
<td>8 4</td>
<td></td>
</tr>
<tr>
<td>CC (N) -3</td>
<td>8 N</td>
<td>Specify excitation level N using LEVEL</td>
</tr>
</tbody>
</table>
Examples: Closed-shell ground-state calculations for H2O:

```
***,mrcc calculations for h2o
memory,8,m
gthresh,energy=1.d-8

geometry={
o;h1,o,r;h2,o,r,h1,theta}
theta=104
r=1 ang
basis=vdz

hf
mrcc,method=cc3;
method(1)=program
e(1)=energy

ccsd(t)
method(2)='CCSD(T) (MOLPRO)'
e(2)=energy

mrcc,method=ccsd(t)
method(3)='CCSD(T) (MRCC)'
e(3)=energy

mrcc,method=ccsdt/dir=mrccdir
method(4)=program
e(4)=energy

mrcc,method=ccsdt(q),restart=1,dir=mrccdir
method(5)=program
e(5)=energy

mrcc,method=CC(n),excitation=4,restart=1,dir=mrccdir
method(6)=program
e(6)=energy

table,method,e
```

http://www.molpro.net/info/current/examples/h2o_mrcc.com

This yields

<table>
<thead>
<tr>
<th>METHOD</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>CC3</td>
<td>-76.23912734</td>
</tr>
<tr>
<td>CCSD (T) (MOLPRO)</td>
<td>-76.23905150</td>
</tr>
<tr>
<td>CCSD (T) (MRCC)</td>
<td>-76.23905150</td>
</tr>
<tr>
<td>CCSDT</td>
<td>-76.23922746</td>
</tr>
<tr>
<td>CCSDT (Q)</td>
<td>-76.23976632</td>
</tr>
<tr>
<td>CCSDTQ</td>
<td>-76.23973043</td>
</tr>
</tbody>
</table>

Excitation energies for H2O:
### h2o excitation energies

```plaintext
memory,8,m
gthresh,energy=1.d-8
go;h1,o,r;h2,o,r,hl,theta
theta=104
r=1 ang
basis=vdz
hf

ii=0
s=2 !number of states in each symmetry
do sym=1,4 !loop over irreps
ccsd;eom,-(s+0.1*sym);$p=molpro;save_energy
mrcc,method=ccsd, symm=sym,nstates=2;$p=mrcc;save_energy
mrcc,method=ccsdt,symm=sym,nstates=2;$p=mrcc;save_energy
s=1
enddo

{table,method,prog,states,e,exc
sort,3}
```

```plaintext
!procedure to save results in variables
!nogprint,variable
e1=energy(1)
do i=1,#energy
ii=ii+1
e(ii)=energy(i)
method(ii)=program
prog(ii)=p
states(ii)=i+0.1*sym
exc(ii)=-(e(ii)-e1)*toev
end do
```

This yields

```
http://www.molpro.net/info/current/examples/h2o_mrcc_eom.com
```

<table>
<thead>
<tr>
<th>METHOD</th>
<th>PROG</th>
<th>STATES</th>
<th>E</th>
<th>EXC</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCSD</td>
<td>MOLPRO 1.1</td>
<td>-76.23580212</td>
<td>0.000</td>
<td></td>
</tr>
<tr>
<td>CCSD</td>
<td>MRCC   1.1</td>
<td>-76.23580212</td>
<td>0.000</td>
<td></td>
</tr>
<tr>
<td>CCSDT</td>
<td>MOLPRO 1.2</td>
<td>-76.23922746</td>
<td>0.000</td>
<td></td>
</tr>
<tr>
<td>CCSD</td>
<td>MRCC   1.2</td>
<td>-76.23580212</td>
<td>0.000</td>
<td></td>
</tr>
<tr>
<td>CCSDT</td>
<td>MOLPRO 1.2</td>
<td>-76.23922746</td>
<td>0.000</td>
<td></td>
</tr>
<tr>
<td>CCSD</td>
<td>MRCC   1.3</td>
<td>-76.23580212</td>
<td>0.000</td>
<td></td>
</tr>
<tr>
<td>CCSDT</td>
<td>MOLPRO 1.4</td>
<td>-76.23922746</td>
<td>0.000</td>
<td></td>
</tr>
<tr>
<td>CCSD</td>
<td>MRCC   1.4</td>
<td>-76.23580212</td>
<td>0.000</td>
<td></td>
</tr>
<tr>
<td>CCSDT</td>
<td>MOLPRO 2.1</td>
<td>-75.85033256</td>
<td>10.489</td>
<td></td>
</tr>
<tr>
<td>CCSD</td>
<td>MRCC   2.1</td>
<td>-75.85033257</td>
<td>10.489</td>
<td></td>
</tr>
<tr>
<td>CCSDT</td>
<td>MOLPRO 2.1</td>
<td>-75.85316687</td>
<td>10.505</td>
<td></td>
</tr>
<tr>
<td>CCSD</td>
<td>MRCC   2.1</td>
<td>-75.85316687</td>
<td>10.505</td>
<td></td>
</tr>
<tr>
<td>CCSDT</td>
<td>MOLPRO 2.2</td>
<td>-75.95093334</td>
<td>7.752</td>
<td></td>
</tr>
<tr>
<td>CCSD</td>
<td>MRCC   2.2</td>
<td>-75.95093335</td>
<td>7.752</td>
<td></td>
</tr>
<tr>
<td>CCSDT</td>
<td>MOLPRO 2.2</td>
<td>-75.95299013</td>
<td>7.789</td>
<td></td>
</tr>
<tr>
<td>CCSD</td>
<td>MRCC   2.2</td>
<td>-75.95299013</td>
<td>7.789</td>
<td></td>
</tr>
<tr>
<td>CCSDT</td>
<td>MOLPRO 2.3</td>
<td>-75.77630664</td>
<td>12.504</td>
<td></td>
</tr>
<tr>
<td>CCSD</td>
<td>MRCC   2.3</td>
<td>-75.77630665</td>
<td>12.504</td>
<td></td>
</tr>
<tr>
<td>CCSDT</td>
<td>MOLPRO 2.3</td>
<td>-75.77972816</td>
<td>12.504</td>
<td></td>
</tr>
<tr>
<td>CCSD</td>
<td>MRCC   2.3</td>
<td>-75.77972816</td>
<td>12.504</td>
<td></td>
</tr>
<tr>
<td>CCSDT</td>
<td>MOLPRO 2.4</td>
<td>-75.87776149</td>
<td>9.743</td>
<td></td>
</tr>
<tr>
<td>CCSD</td>
<td>MRCC   2.4</td>
<td>-75.87776150</td>
<td>9.743</td>
<td></td>
</tr>
</tbody>
</table>
**Open-shell ground-state calculations for O2:**

```plaintext
***,O2 tests
memory,8,m
gthresh,energy=1.d-8

geometry={o1;o2,o1,r1}
r1=2.2
set,state=1,symmetry=4,spin=2 ! Triplet sigma- state
basis=vdz

rhf
uccsd(t)
method(1)='UCCSD(T) MOLPRO'
e(1)=energy

rccsd(t)
method(2)='RCCSD(T) MOLPRO'
e(2)=energy

mrcc,method=ccsdt,dir=mrccdir
method(3)='CCSDT MRCC'
e(3)=energy

mrcc,method=ccsdtq,restart=1,dir=mrccdir
method(4)='CCSDT MRCC'
e(4)=energy

table,method,e

http://www.molpro.net/info/current/examples/o2_mrcc.com
```

This yields

<table>
<thead>
<tr>
<th>METHOD</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>UCCSD(T) MOLPRO</td>
<td>-149.9815472</td>
</tr>
<tr>
<td>RCCSD(T) MOLPRO</td>
<td>-149.9812566</td>
</tr>
<tr>
<td>CCSDT MRCC</td>
<td>-149.9816705</td>
</tr>
<tr>
<td>CCSDT MRCC</td>
<td>-149.9832255</td>
</tr>
</tbody>
</table>
28 The FCIQMC program (FCIQMC)

The FCIQMC program exists through an interface to the NECI codebase, which is actively developed in the group of A. Alavi, and has been integrated into the MOLPRO code. The FCIQMC method is a recently introduced stochastic method which can calculate in principle FCI-quality energies for small to medium-sized molecules. The method should also be suitable for large-scale parallel application across distributed memory architecture. However, it should be noted that since the method relies on random number strings, the exact path of the simulation will change with number of MPI tasks used, although converged results should agree. Since the method is new, the code is also somewhat developmental, and updates and improvements are to be expected. Any user hoping to use the FCIQMC package for a study is welcome to get in contact directly with A. Alavi (asa10@cam.ac.uk), and the lead developer of the code, G. Booth (ghb24@cam.ac.uk), for technical help, advice and access to undocumented options.

It is also highly recommended to invoke the command-line option --no-helper-server, which will ensure that when running in parallel, all MPI processes are utilized. Multiple files are created in addition to the standard output, and dynamic adjustment to the calculation can only take place from the working directory. Therefore it may be useful to assign a convenient working directory from the command-line when MOLPRO is run. This can be done with the -d flag, with -d . setting the current directory as the working directory. Also, since the printing to the output file is buffered, it may be better to view the running simulation from the .xml file.

28.1 The FCIQMC Method

Details of the FCIQMC algorithm are best obtained from various publications on the method, which include:

D. M. Cleland, G. H. Booth, and A. Alavi, J. Chem. Phys. 134, 024112 (2011) (i-FCIQMC) and

and which should be cited in published work resulting from the use of this module.

Briefly, the FCIQMC method involves discretizing the wavefunction amplitudes over the full Slater determinant space into a number of signed ‘walkers’. These walkers represent a coarse-grained snapshot of the wavefunction at any given instant. Through a population dynamics of these walkers evolving in imaginary-time, the ground-state energy and wavefunction can be resolved to arbitrary accuracy (in principle FCI quality), in a time-averaged fashion, without the need for any explicit diagonalization steps. The master equations which are stochastically realized and govern this dynamic, are given by

\[
-\frac{dN_i}{d\tau} = (H_{ii} - E_{\text{ref}} - S)N_i + \sum_{j \neq i} H_{ij}N_j,
\]  

(56)

where \( \tau \) represents the evolution in imaginary-time, \( N_i \) is the walker population on configuration \( i \), and \( S \) is the energy ‘shift’, which can be used as a measure of the correlation energy once the walker population is stable. In the original formulation, this dynamic is integrated exactly over imaginary-time, and converges to the exact basis-set correlation energy of the system within systematically reducible random errors, as long as the number of walkers in the system exceeds a system-dependent number, required to overcome the ‘sign-problem’ present in the space. This number is indicated by the appearance of a plateau in the growth profile of the walkers for a given value of \( S \).
However, in a modification to the algorithm which allows for a generally smooth convergence to the FCIQMC result with increasing walker number, the sum in Eq. 56 is truncated, such that when considering a configuration $i$ whose population is zero, this sum then only runs over those configurations who are deemed ‘initiator’ configurations. These initiator configurations are ones which have an instantaneous population of above a parameter $n_{add}$, or are the chosen ‘reference’ configuration. This modification to the algorithm rigorously converges to the full FCIQMC result in the limit of a large number of walkers, or as $n_{add} \to 0$, and is dubbed ‘$i$-FCIQMC’. This is the default algorithm used in the FCIQMC module.

Note that the choice of reference configuration, or indeed orbital space, should be independent of the final energy obtained, and the method thus constitutes a multiconfigurational correlation treatment, suitable for strongly-correlated problems. However, the choice of reference configuration and orbital space may affect rate of convergence and random error decay.

### 28.2 Running FCIQMC

Although many options and details are provided here, often FCIQMC calculations can be performed using default parameters in a relatively ‘black-box’ fashion, requiring knowledge of only a few key options.

The FCIQMC program is invoked by the command

```
FCIQMC,OPTION=value
```

directives

The simulation will then run within an orbital space obtained from the previous calculation (generally Restricted Hartree–Fock, although MCSCF/CASSCF/localized/unrestricted orbitals, as well as orbital subspaces can also be used with care). The electron number, spin-polarization and symmetry block of the FCIQMC calculation will also be presumed to be the same as specified for this preceding calculation, unless directives specify otherwise, and therefore should result in the FCIQMC module defining a ‘reference’ configuration which is the same as the Hartree–Fock determinant in the previous calculation. The symmetry and energy of this determinant should be checked to avoid slow convergence, or one to an incorrect symmetry solution.

Directives are usually not necessary, but the `CORE`, `OCC`, `ORBITAL` and `WF` directives work as in the MOLPRO CCSD program if core electrons are to be correlated, or if alternative orbital subsets or wavefunctions wish to be defined contrary to the previous mean-field calculation.

The default running procedure is an $i$-FCIQMC calculation, initialized with a single walker at the reference determinant, and the $S$ shift parameter fixed at zero. The number of initial walkers, or value for the shift can be adjusted from their default settings with the `STARTWALKERS` and `FIXEDSHIFT` options. This initial stage should result in an exponential growth of walkers, whose rate of growth depends on the timestep, value of the fixed shift, and the correlation energy of the problem. This phase of the calculation is called ‘fixed shift mode’. Once the total number of walkers has reached a number given by `TARGETWALKERS`, the shift is updated every `INTERVAL` iterations, in order to stabilize the walker growth.

The default behavior is to run for only 100 iterations. This is generally far too short, and should be changed using the `ITERATIONS` command, the `TIME` command, or dynamically with the `CHANGEVARS` facility, which will be detailed in section 28.5. In addition, the timestep will be initially chosen as a reasonable upper-bound, and then dynamically updated through the initial part of the calculation in order to eliminate walker ‘blooming’ events, where multiple walkers (of more than `MAXWALKERBLOOM` are created in a single spawning attempt. However, this initial upper-bound can be a poor guess if the system is especially small, and so alternatively,
the timestep can be specified and fixed for the entire calculation with the TIMESTEP option. Generally this wants to be as large as possible without causing frequent blooming events.

The available options are summarized in Table 12 and those requiring a more detailed explanation are expanded on in section 28.3.

<table>
<thead>
<tr>
<th>Option</th>
<th>Default</th>
<th>Allowed values</th>
<th>Short description</th>
</tr>
</thead>
<tbody>
<tr>
<td>SYMMETRY</td>
<td>ON</td>
<td>‘ON/OFF’</td>
<td>Whether to use point-group symmetry</td>
</tr>
<tr>
<td>SPIN</td>
<td>OFF</td>
<td>‘EVEN/ODD’</td>
<td>Whether to use spin-reversal symmetry</td>
</tr>
<tr>
<td>ITERATIONS</td>
<td>100</td>
<td>INT</td>
<td>Maximum number of iterations</td>
</tr>
<tr>
<td>TIME</td>
<td>OFF</td>
<td>REAL</td>
<td>Runtime in minutes</td>
</tr>
<tr>
<td>TIMESTEP</td>
<td>N/A</td>
<td>REAL</td>
<td>Timestep for use in calculation</td>
</tr>
<tr>
<td>STARTWALKERS</td>
<td>1</td>
<td>INT</td>
<td>Number of initial walkers on reference configuration</td>
</tr>
<tr>
<td>TARGETWALKERS</td>
<td>10,000</td>
<td>INT</td>
<td>Target number of total walkers for entry to variable shift mode</td>
</tr>
<tr>
<td>SEED</td>
<td>-7</td>
<td>INT</td>
<td>Random number seed</td>
</tr>
<tr>
<td>STARTMP1</td>
<td>OFF</td>
<td>INT</td>
<td>Initialize value walkers at MP1 wavefunction distribution</td>
</tr>
<tr>
<td>MAXATREF</td>
<td>OFF</td>
<td>INT</td>
<td>Target number of walkers on reference configuration for variable shift mode</td>
</tr>
<tr>
<td>FIXEDSHIFT</td>
<td>0.0</td>
<td>REAL</td>
<td>Initial value of the fixed shift</td>
</tr>
<tr>
<td>SHIFTDAMPING</td>
<td>0.1</td>
<td>REAL</td>
<td>Damping parameter for adjustment of the shift in variable shift mode</td>
</tr>
<tr>
<td>INTERVAL</td>
<td>10</td>
<td>INT</td>
<td>Iteration interval for writing out statistics and updating of the shift</td>
</tr>
<tr>
<td>PROJE–CHANGEREF</td>
<td>OFF</td>
<td>INT</td>
<td>Percentage increase from the current reference population required to change reference dynamically</td>
</tr>
<tr>
<td>FULL_FCIQMC</td>
<td>False</td>
<td>True/False</td>
<td>Flag to determine whether to run full FCIQMC or i-FCIQMC algorithms</td>
</tr>
<tr>
<td>INITIATOR_THRESH</td>
<td>3</td>
<td>INT</td>
<td>( n_{\text{add}} ) parameter for initiator criterion</td>
</tr>
<tr>
<td>MAXWALKERBLOOM</td>
<td>INIT_THSH</td>
<td>INT</td>
<td>Maximum allowed spawning probability if automatically adjusting timestep</td>
</tr>
<tr>
<td>TRUNCATE</td>
<td>OFF</td>
<td>INT ((n))</td>
<td>Truncate space by excitation level ( n )</td>
</tr>
<tr>
<td>PARTIALFREEZEEOCC</td>
<td>OFF</td>
<td>INT</td>
<td>Number of lowest energy occupied spin-orbitals to partially freeze</td>
</tr>
<tr>
<td>PARTIALFREEZEHOLES</td>
<td>OFF</td>
<td>INT</td>
<td>Number of holes allowed in the ( \text{PARTIALFREEZEEOCC} ) orbital space</td>
</tr>
<tr>
<td>PARTIALFREEZEVIRT</td>
<td>OFF</td>
<td>INT</td>
<td>Number of highest energy virtual spin-orbitals to partially freeze</td>
</tr>
<tr>
<td>PARTIALFREEZEVIRTELECS</td>
<td>OFF</td>
<td>INT</td>
<td>Number of electrons allowed in the ( \text{PARTIALFREEZEVIRT} ) orbital space</td>
</tr>
</tbody>
</table>
Table 13: Options for FCIQMC cont.

<table>
<thead>
<tr>
<th>Option</th>
<th>Default</th>
<th>Allowed values</th>
<th>Short description</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEMORYFACWALKERS</td>
<td>1.5</td>
<td>REAL</td>
<td>Memory factor for main walker array</td>
</tr>
<tr>
<td>MEMORYFACSPAWNED</td>
<td>0.3</td>
<td>REAL</td>
<td>Memory factor for spawned walker arrays</td>
</tr>
<tr>
<td>SINGLESBIAS</td>
<td>OFF</td>
<td>REAL</td>
<td>Singles biasing factor in excitations</td>
</tr>
<tr>
<td>READWALKERS</td>
<td>False</td>
<td>True/False</td>
<td>Option to read in walker distribution from previous run (requires POPSFILEs)</td>
</tr>
<tr>
<td>CONTINUEWALKERGROWTH</td>
<td>False</td>
<td>True/False</td>
<td>If restarting, indicates whether to resume calculation in fixed/variable shift mode</td>
</tr>
<tr>
<td>WRITEPOPSFILE</td>
<td>OFF</td>
<td>INT</td>
<td>Write a restart file (POPSFILE) every value iterations</td>
</tr>
<tr>
<td>POPSFILETIMER</td>
<td>OFF</td>
<td>REAL</td>
<td>Write a restart file (POPSFILE) every value hours</td>
</tr>
<tr>
<td>INCREMENTPOPSFILES</td>
<td>False</td>
<td>True/False</td>
<td>If True preserve previous POPSFILEs</td>
</tr>
<tr>
<td>REBLOCKSHIFT</td>
<td>OFF</td>
<td>INT</td>
<td>Perform error analysis on data from previous calculation with specified iteration equilibration time for shift estimate</td>
</tr>
<tr>
<td>REBLOCKPROJE</td>
<td>OFF</td>
<td>INT</td>
<td>Perform error analysis on data from previous calculation with specified iteration equilibration time for projected energy estimate</td>
</tr>
<tr>
<td>NOMCOUTPUT</td>
<td>False</td>
<td>True/False</td>
<td>Suppress iteration-specific output (Note all data still written to FCIQMCStats file)</td>
</tr>
<tr>
<td>CALCMCSIZESPACE</td>
<td>OFF</td>
<td>INT</td>
<td>Run routine to stochastically calculate size of symmetry-allowed FCI space</td>
</tr>
</tbody>
</table>

28.3 More advanced options

The following section provides more detail on some of the more advanced options described in Table 12.

**SPIN=’EVEN’/’ODD’**

Rather than perform the FCIQMC dynamic in a space of Slater determinants, this option combines each determinant with its spin-flipped partner to create a new space, which exactly spans either the space of even or odd spin eigenfunctions of the system. This effectively halves the number of functions on which the walkers can reside, reducing the overall number of walkers required for a given accuracy, as well as potentially allowing for a larger timestep, and the ability to converge to the lowest energy state of odd and even spin quantum number separately. These functions can be considered a compromise between a determinant and configuration state function space which are true spin eigenfunctions, and thus should reduce the instantaneous spin-contamination of the wavefunction, with only small additional computation overhead. This option is only available for \( M_s = 0 \) states.

**CALCMCSIZESPACE=value**

This option will provide an estimate for the dimensionality of the space in which the FCIQMC dynamic will evolve, prior to
the start of the FCIQMC calculation. This is done via a stochastic sampling of the space, and will write out the evolution of this estimate to a file called 'SpaceMCStats'. The value that this option takes gives the number of iterations (per MPI task) to sample the space for. A final estimate is written to the standard output. All spin and symmetry constraints are considered.

**STARTMP1=value**

This option distributes *value* number of walkers initially at a distribution proportional to that of the MP1 wavefunction. The initial projected energy should therefore agree well with the MP2 energy. This can allow for faster equilibration of the population. If the *value* given here is the same as the TARGETWALKERS, then the simulation will begin in variable shift mode, with the initial shift set to the MP2 energy. Note that this will only work correctly if the orbitals come from a prior RHF calculation.

**MAXATREF=value**

If present, this option provides an additional condition by which the variable shift mode of the calculation can begin. Either if the number of walkers exceeds that specified by TARGETWALKERS, or the number of walkers specifically residing on the reference configuration exceeds the *value* specified in this option, then the shift will be allowed to vary to stabilize walker growth.

**PROJE-CHANGEREF=value**

If present, then this option allows the choice of reference configuration for the calculation of the projected energy to dynamically change during the course of the simulation. As will be seen in section 28.6 the variance of the projected energy estimate is dependent on the choice of reference configuration, but the specifics of the walker dynamic are independent. Therefore, maximizing the population on the reference configuration can be beneficial, especially in strongly-correlated cases where the initial reference (often Hartree–Fock) may have a relatively small weight in the final wavefunction, or where canonical Hartree–Fock orbitals are not used, and so no obvious choice of reference configuration presents itself. The *value* that this option takes is the percentage by which a configuration population is required to exceed the population of the current reference determinant, before the reference is changed to this highest populated configuration, i.e. PROJE-CHANGEREF=15 indicates that if a population on any configuration exceeds 115% of the current reference, it will become the new reference.

**MEMORYFACWALKERS=value**

This is a memory parameter, which determines the available storage for the main walker array. Its value should not affect the calculation if large enough. The *value* given is the fraction of the number of walkers specified by the TARGETWALKERS parameter which can be held in memory (assuming perfect load balancing across MPI tasks). Therefore, the default value of 1.5 should theoretically allow for growth of walkers up to 50% larger than that specified by TARGETWALKERS. This should be more than sufficient for most applications, however if memory errors or unexpected termination of the program are encountered, these memory parameters may need to be increased.

**MEMORYFACSPAWNED=value**

This memory parameter is of a similar type to MEMORYFACWALKERS, but governs the memory allocated for the spawned walker ar-
rays at each iteration. Once again, it is given as a fraction of the walker number specified by \texttt{TARGETWALKERS}, and so the default value of 0.3 should theoretically allow for up to 30\% of the \texttt{TARGETWALKERS} number of walkers to be created each iteration (again assuming perfect load balancing).

As well as specifying orbital subspaces, it is also possible to perform various truncated determinant space calculations within the FCIQMC dynamic, which although not strictly size-consistent, can nevertheless be used to obtain well equilibrated initial walker populations (which can then be read back in), or often accurate approximations to FCI energies in their own right. A common choice of truncated CI space is based on an excitation level criteria, which can be specified with the \texttt{TRUNCATE} keyword.

\texttt{TRUNCATE=value} \hspace{1cm} If present, this truncates the CI space based on the excitation rank of the function from the specified reference determinant. This results in FCIQMC energies which converge on the CIS, CISD, CISDT, CISDTQ, \ldots CI(\textit{value}) hierarchy of approximations.

Another truncated space is one is not in the CI literature to the best of our knowledge, and is based upon either specifying a low-energy occupied orbital space, in which configurations sampled must not contain larger than a given number of holes, and/or a high-energy virtual subspace in which the determinant space must not contain more than a specified number of electrons. Because this reduces to the frozen-core approximation in the case of zero allowed holes in an occupied subspace, or amounts to deleting high-energy virtuals in the limit of no electrons allowed in the virtual subspace, this is denoted ‘partial freezing’. This can also be considered as limiting the excitation level for an electron subset.

\texttt{PARTIALFREEZECC=value} \hspace{1cm} Indicates the number of lowest energy electrons to partially freeze (can be considered a core or semi-core space). Requires the \texttt{PARTIALFREEZEHOLES} option to also be specified.

\texttt{PARTIALFREEZEHOLES=value} \hspace{1cm} Indicates the number of holes allowed in this partially frozen space. Requires the \texttt{PARTIALFREEZECC} option to also be specified.

\texttt{PARTIALFREEZEVERT=value} \hspace{1cm} Indicates the number of highest energy virtual spin-orbitals to partially freeze, restricting the number of electrons which can simultaneously occupy them. Requires the \texttt{PARTIALFREEZEVERTelecs} option to also be specified.

\texttt{PARTIALFREEZEVERTelecs=value} \hspace{1cm} Indicates the number of electrons allowed to simultaneously occupy the highest energy virtual space, as specified in the required \texttt{PARTIALFREEZEVERT} option.

### 28.4 Restarting FCIQMC jobs

Another important facility of the FCIQMC module is the ability to write out restart files (POPS-FILES), detailing the specific number and distribution of the walkers throughout the space. These files can then be copied between systems if desired, and the calculation continued from where it left off. Writing out these POPSFILES is recommended in case further accuracy is required at a later stage. If the previous FCIQMCStats file is also present in the working directory
of the restarted calculation, then the new data obtained will be simply appended to the end of the
previous FCIQMCStats file. Two files are required to restart a calculation: POPSFILEHEAD
and POPSFILEBIN. Options to control their use include:

Writing POPSFILES:

WRITEPOPSFILE=value If this option is specified, then the required POPSFILEs are
written out in the event of a clean exit from the calculation, either via the ITERATIONS or TIME options, or the CHANGEVARS
facility. In addition, the POPSFILEs are written out in iteration intervals specified by the value given. If a value of zero is
given, the POPSFILEs will only be written out at the end of the
calculation.

POPSFILETIMER=value This option will write out POPSFILEs at time intervals of value
hours, as well as the end of the calculation.

INCREMENTPOPSFILES=True This option will ensure that if multiple POPSFILEs are writ-
ten out in one simulation, they will not overwrite previous ver-
sions, but rather append incrementing numerical suffixes to the
filenames, i.e. POPSFILEHEAD.1, POPSFILEHEAD.2, etc. These must be renamed/linked
as files called simply POPSFILEHEAD and POPSFILEBIN
for reading in for subsequent calculations.

Reading POPSFILES:

READWALKERS=True This option must be present in order to read back in walkers
from POPSFILEs.

CONTINUEWALKERGROWTH=True By default, the simulation will resume in variable shift
mode. This option will resume the calculation in variable shift
mode.

28.5 CHANGEVARS facility

The CHANGEVARS facility allows for a real-time dynamic adjustment of many of the parameters
of the FCIQMC calculation. A file (which must be named CHANGEVARS) can be created in the
working directory of the calculation, which contains one or more lines detailing changes to
system parameters, as OPTION new_value (note no '='). Each updated option must be specified
on a separate line. The options available via the CHANGEVARS interface are summarized in
Table 14.

28.6 FCIQMC output

The estimate of the energy is extracted from the simulation in various ways. Once in variable
shift phase of the calculation, where the walker number is stabilised (column 5 in output and
FCIQMCStats file), the shift parameter (column 2) should vary about the correlation energy (S
in Eq. [56] after equilibration. Alternatively, a projected energy estimate can be obtained through
Table 14: Options available via \texttt{CHANGEVARS} interface

<table>
<thead>
<tr>
<th>Option</th>
<th>Allowed argument</th>
<th>Short description</th>
</tr>
</thead>
<tbody>
<tr>
<td>EXIT</td>
<td>NONE</td>
<td>Exit FCIQMC calculation (note: this can also separately exit from \texttt{CALCMCSIZESPACE} calculation</td>
</tr>
<tr>
<td>VARYSHIFT</td>
<td>NONE</td>
<td>Instantaneously leave fixed shift mode and enter variable shift</td>
</tr>
<tr>
<td>ZERO PROJE</td>
<td>NONE</td>
<td>Zero all averaged energy estimators</td>
</tr>
<tr>
<td>ITERATIONS</td>
<td>INT</td>
<td>See table 12</td>
</tr>
<tr>
<td>TIMESTEP</td>
<td>REAL</td>
<td>See table 12</td>
</tr>
<tr>
<td>TRUNCATE</td>
<td>INT</td>
<td>See table 12</td>
</tr>
<tr>
<td></td>
<td>(note: must be increased from current value)</td>
<td></td>
</tr>
<tr>
<td>SHIFT</td>
<td>REAL</td>
<td>Instantaneously change value of shift (available in fixed and variable shift mode)</td>
</tr>
<tr>
<td>SHIFTDAMPING</td>
<td>REAL</td>
<td>See table 12</td>
</tr>
<tr>
<td>INTERVAL</td>
<td>INT</td>
<td>See table 12</td>
</tr>
<tr>
<td>CHANGEREF</td>
<td>NONE</td>
<td>Instantaneously change reference function to highest currently populated</td>
</tr>
<tr>
<td>INITIATOR, THRESH</td>
<td>INT</td>
<td>See table 12</td>
</tr>
<tr>
<td>SINGLESBIAS</td>
<td>REAL</td>
<td>See table 12</td>
</tr>
<tr>
<td>WRITEPOPSFILE</td>
<td>NONE</td>
<td>Instantaneously write out a restart file (POPSFILE)</td>
</tr>
</tbody>
</table>

the projection of the walker distribution onto a reference configuration (column 9, 11 and 23 – see below for details), as

\[
E_{\text{proj}} = \frac{\langle D_0 | H | \Psi_{\text{FCIQMC}} \rangle}{\langle D_0 | \Psi_{\text{FCIQMC}} \rangle} = E_0 + \sum_j \frac{n_j}{n_0} \langle D_0 | H | D_j \rangle
\]

It is clear that this estimate is sensitive to the number of walkers on the reference configuration \((D_0)\), which is why the use of the \texttt{PROJE-CHANGEREF} option is encouraged if it is unclear which the most highly weighted configuration is from the outset of calculation. Initially, this reference will be chosen as the Hartree–Fock determinant, or the configuration resulting from the occupation of the highest weighted orbitals in the case of a prior CASSCF/MCSCF calculation. Unless the system is very strongly correlated and no dominant single reference exists, the projected energy estimate will usually have smaller errorbars, while at convergence the two values should provide relatively independent energy estimates which should agree to within random errors.

The output file contains the following columns of data every \texttt{INTERVAL} iterations from the calculation, unless the \texttt{NOMCOUTPUT} option is given.

1. Iteration number
2. Current shift value
3. Walker change from previous interval
4. Walker growth rate
5. Total walkers
6. Total annihilated walkers over last interval
7. Total walkers that died over last interval
8. Total spawned walkers over last interval
9. Averaged projected correlation energy estimate from beginning of calculation \( \left( \sum_j \frac{\langle n_j H_0 \rangle}{\langle n_0 \rangle} \right) \)
10. Averaged shift correlation energy estimate from 1000 iterations after entry into variable shift mode
11. Instantaneous projected correlation energy estimate averaged only over last \( \text{INTERVAL} \) iterations
12. Number of walkers currently residing on reference configuration
13. Number of walkers currently residing on single or double excitations of reference configuration (that contribute to the sum in Eq. 58)
14. Fraction of spawning attempts which are successful
15. Total number of currently occupied configurations
16. Time taken for last iteration

The end of the output also contains a summary of the most highly weighted configurations at the end of the simulation. The FCIQMCStats file also contains this data, in a way that can easily be plotted, and also contains additional diagnostic information, detailed below

17. Fraction of successful spawning events to single, rather than double excitations
18. Range of occupied configuration number over between MPI processes – a measure of the parallel load-balancing of the simulation
19. Total imaginary-time which has elapsed in the calculation
20. Ignore column
21. Expected shift value obtained in fixed shift mode calculated from rate of growth of reference configuration
22. Expected shift value obtained in fixed shift mode calculated from rate of growth of total walker number
23. Projected total energy estimate averaged only over last \( \text{INTERVAL} \) iterations (col. 11 + reference energy)
24. Denominator of projected energy estimate averaged only over last \( \text{INTERVAL} \) iterations
25. Numerator of projected energy estimate averaged only over last \( \text{INTERVAL} \) iterations
26. Instantaneous normalised weight of reference configuration in FCIQMC wavefunction
27. Instantaneous normalisation factor of FCIQMC wavefunction

In addition to the FCIQMCStats file, unless the full scheme is being used, a file called INITIATORStats is created. Of interest in this file are column 7: the number of ‘initiator’ configurations, column 9: the number of walkers residing on ‘initiator’ configurations and column 11: the number of spawned walkers which were aborted due to the initiator approximation in the last \( \text{INTERVAL} \)
iterations. A NodeFile file is also created for each MPI process. Generally, these files will contain nothing that is not mirrored in the output file, however if the calculation terminates unexpectedly, these files will often contain information on the process-specific reason for this, and should be checked in this instance. At the end of a calculation, the output will print the highest weighted configurations in the calculation, as well as attempting an automatic error analysis on the final energies, which is discussed in the next section.

Especially for initial investigations into a new system, it can be instructive to graphically view the progress of the simulation as it proceeds, to determine whether the simulation can enter the variable shift phase, whether the population on the reference configuration is sufficient, or whether any other parameters should be adjusted via the CHANGEVARS facility. Examples of typical plots starting from a single walker are shown in Fig. 1 and 2.

![Figure 1: Growth in total walker population (column 5), and population on the reference configuration (column 12), obtained from the working directory of the calculation with the GNUPLT package and the command set logscale y; plot 'FCIQMCStats' u 1:5 w l, '' u 1:12 w l.](image1.png)

![Figure 2: Instantaneous total energy estimate from column 23 of the FCIQMCStats file.](image2.png)

### 28.7 FCIQMC error analysis

Since the FCIQMC method is a stochastic simulation, care must be taken in order to obtain reliable energy averages and consequent errorbars. This can be difficult to automate reliably since a knowledge of the equilibration time is required for accurate estimates, as well as requiring serial correlation between the instantaneous estimates to be removed. This is traditionally done using a blocking analysis of the contributions to the energy. An attempt is made to estimate these and provide an automatic error analysis at the end of each FCIQMC calculation, which is then stored in the internal variable FCIQMC_ERR. This may often be good enough, however for production results it is recommended to provide some information manually to increase the accuracy and confidence in these errorbars. This can be done with the REBLOCKSHIFT and REBLOCKPROJE options.

If these options are present, then the FCIQMC calculation will be skipped, and the FCIQMCStats file from the previous calculation will be read back in to perform a blocking analysis. The values that these options take indicate the equilibration time in iterations that is to be given to the shift and projected energy estimates respectively before blocking to obtain accurate averaged energies and errors. These equilibration times can be estimated by plotting iteration against shift (columns 1:2 from the FCIQMCStats file) for the REBLOCKSHIFT value, and iterations against numerator and denominator (columns 1:24 and 1:25) for the REBLOCKPROJE value. It
may be important to consider the equilibration time for both of these columns for the projected energy estimate and give the maximum equilibration time, since the covariance between the quantities in the ratio is needed for an accurate error estimate.

Once these equilibration times have been provided and MOLPRO rerun in the same working directory with these options, a more accurate estimate of the averaged energies and errors will be provided. In addition, files called Blocks_num, Blocks_denom, Blocks_proje and Blocks_shift will be created. By plotting these files, an estimate for whether the random errors are reliable or not can be found, by checking whether the central limit theorem holds when the data is divided up into ‘blocks’ of different length. If column 1 (the number of resummed blocks) is plotted against column 3 (the estimated error between these blocks), with errorbars on the estimated error given in column 4, then a plateau should be observable as the number of blocks decreases. If the error increases continually as the number of blocks decreases, this is a sign that the serial correlation in the data may not have been removed yet, and continued running is advised. A log scale on the x-axis is recommended to observe the full range of block lengths. An example of one of these blocking graphs is shown in Fig. 3. If an incorrect number of blocks is automatically assumed for the plateau height, a more accurate final error can be found for the correct number of blocks in the relevant blocking file (Blocks_proje or Blocks_shift). For the projected energy, the minimum number of blocks should be calculated from the Blocks_num and Blocks_denom files, before the final error read from the corresponding number of blocks in the Blocks_proje file. Note that if the reference configuration changed during the initial run, this is not considered if the blocking is performed manually, and so the correlation energy obtained from manual reblocking will need to be added to previous changed reference energy.

Figure 3: Example of well-converged blocking analysis, with plateau present. This would indicate an error of 0.002 Hartrees in the shift.

28.8 Examples

Examples: Closed-shell ground-state calculations for \( N_2 \) (results from one MPI process):
Nitrogen RHF FCIQMC calculation starting from MP2 distribution
if(.not.modul_neci) then
  skipped
end if
memory, 10, m
basis=cc-pvdz
gem={n1;n2,n1,1.0}
hf
{fciqmc, iterations=5930, spin=even, targetwalkers=100000, \
startmp1=20000, proje-changeref=10, writepopsfile=0, interval=10}
!{fciqmc, reblockshift=1200, reblockproje=1200}

This yields

RESULTS FOR STATE 1.1
----------------------

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current reference energy</td>
<td>-104.125525474439</td>
</tr>
<tr>
<td>Projected correlation energy</td>
<td>-0.200494452975</td>
</tr>
<tr>
<td>Estimated error in Projected correlation energy</td>
<td>0.000267794947</td>
</tr>
<tr>
<td>Shift correlation energy</td>
<td>-0.200119481250</td>
</tr>
<tr>
<td>Estimated error in shift correlation energy</td>
<td>0.00356889015</td>
</tr>
</tbody>
</table>

Projected and shift energy estimates agree within errorbars: $\text{EDiff} = 0.00037497$

Total projected energy $-104.32601993 \pm 0.267795E-03$
Total shift energy $-104.32564496 \pm 0.356889E-02$

!FCIQMC STATE 1.1 ENERGY $-104.326019927414$
!FCIQMC STATE 1.1 FCIQMC_ERR $0.000267794947$

To redo the error analysis, we can run again in the same directory, with the input line changed to include `fciqmc, reblockshift=1200, reblockproje=1200`, set to approximate equilibrated iterations, which returns

RESULTS FOR STATE 1.1
----------------------

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current reference energy</td>
<td>-104.125525474439</td>
</tr>
<tr>
<td>Projected correlation energy</td>
<td>-0.200494452975</td>
</tr>
<tr>
<td>Estimated error in Projected correlation energy</td>
<td>0.000257264982</td>
</tr>
<tr>
<td>Shift correlation energy</td>
<td>-0.198657872098</td>
</tr>
<tr>
<td>Estimated error in shift correlation energy</td>
<td>0.003792051242</td>
</tr>
</tbody>
</table>

Projected and shift energy estimates agree within errorbars: $\text{EDiff} = 0.00189320$

Total projected energy $-104.32607655 \pm 0.257265E-03$
Total shift energy $-104.32418335 \pm 0.379205E-02$

!FCIQMC STATE 1.1 ENERGY $-104.326076546221$
!FCIQMC STATE 1.1 FCIQMC_ERR $0.000257264982$

High spin UHF calculations on atomic Nitrogen, including core correlation, and comparison to FCI (one MPI process):
***, High spin UHF basis iFCIQMC calculation on nitrogen atom, including core correlation
if(.not.modul_neci) then
skipped
end if
memory,50,m
geom={n}
basis=vdz
{uhf;wf,7,8,3}
{fciqmc,iterations=16000,targetwalkers=50000,proje-changeref=10, \writepopsfile=0,interval=10,memoryfacwalkers=2.0,memoryfacspawned=0.7;core}
{fci;core}

http://www.molpro.net/info/current/examples/n_uhf_fciqmc.com

This returns

RESULTS FOR STATE 1.8
---------------------

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Current reference energy</td>
<td>-54.391114562126</td>
</tr>
<tr>
<td>Projected correlation energy</td>
<td>-0.089063298446</td>
</tr>
<tr>
<td>Estimated error in Projected correlation energy</td>
<td>0.000031993101</td>
</tr>
<tr>
<td>Shift correlation energy</td>
<td>-0.088986058082</td>
</tr>
<tr>
<td>Estimated error in shift correlation energy</td>
<td>0.000239973111</td>
</tr>
</tbody>
</table>

Projected and shift energy estimates agree within errorbars: EDiff = 0.00007724

Total projected energy | -54.48017786 +/- 0.319931E-04 |
Total shift energy     | -54.48010062 +/- 0.239973E-03 |

!FCIQMC STATE 1.8 ENERGY | -54.480177860572 |
!FCIQMC STATE 1.8 FCIQMC_ERR | 0.000031993101 |

RESULTS FOR STATE 1.8
---------------------

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Correlation energy</td>
<td>-0.089000492121</td>
</tr>
<tr>
<td>!FCI STATE 1.8 Energy</td>
<td>-54.480115054246</td>
</tr>
</tbody>
</table>

Excited spin state calculations of Be₂ using the SPIN option. With spin=odd set, it will converge to the lowest odd 5 spin state (one MPI process):

***, FCIQMC calculation on the lowest odd spin state of Be₂
if(.not.modul_neci) then
skipped
end if
geom={Be1;Be2,Be1,2.0}
basis=cc-pvdz
{hf;wf,8,1,0}
{fciqmc,iterations=18410,spin=odd,targetwalkers=100000, \proje-changeref=10,writepopsfile=0,memoryfacwalkers=1.4,memoryfacspawned=0.3}

http://www.molpro.net/info/current/examples/be2_highspin_fciqmc.com

This returns
RESULTS FOR STATE 1.1
---------------------

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current reference energy</td>
<td>-28.418109510728</td>
</tr>
<tr>
<td>Projected correlation energy</td>
<td>-0.145376051508</td>
</tr>
<tr>
<td>Estimated error in Projected correlation energy</td>
<td>0.000214957903</td>
</tr>
<tr>
<td>Shift correlation energy</td>
<td>-0.145621476634</td>
</tr>
<tr>
<td>Estimated error in shift correlation energy</td>
<td>0.000167618454</td>
</tr>
</tbody>
</table>

Projected and shift energy estimates agree within errorbars: EDiff = 0.00024543

Total projected energy                | -28.56348556 +/- 0.214958E-03 |
Total shift energy                    | -28.56373099 +/- 0.167618E-03 |
!FCIQMC STATE 1.1 ENERGY             | -28.563730987362             |
!FCIQMC STATE 1.1 FCIQMC_ERR          | 0.000167618454               |

which agrees with the fifth state (no symmetry) obtained with FCI:

RESULTS FOR STATE 5.1
---------------------

!FCI STATE 5.1 Energy                | -28.563629184909             |
29 The DMRG program of the Chan group (BLOCK)

An interface exists to use the DMRG BLOCK program of the Chan group within Molpro. The source code of BLOCK can alternatively be obtained from WEBSITE. The parallel version is fully supported under MOLPRO. To use BLOCK in parallel, the flag

```
--no-helper-server
```

should be included on the MOLPRO command line.

29.1 Installing BLOCK

MOLPRO fetches a copy of the most recent stable BLOCK code, and compiles it. For this, the

```
--enable-Block
```

flag must be called when running ./configure.

29.2 Running BLOCK

29.2.1 Directives

The BLOCK program is invoked by the command

```
BLOCK, options directives
```

The available options are summarized in Table 15. For more detailed descriptions, please refer to the BLOCK manual at WEBSITE.

To run a DMRG calculation with default settings, first specify the orbitals to correlate (the active space), using the CORE, OCC, and ORBITAL directives, similar to other correlated methods in MOLPRO. Then specify the maximum number of renormalized states to keep with MAXM. This runs a DMRG calculation with the default sweep schedule and a default orbital ordering. The default orbital ordering is determined by using the Fiedler vector method.

There may be times when one wants finer control of the DMRG calculation. In such cases, it is possible to specify the sweep schedule manually. A sweep schedule is set by directives, for example,

```
schedule, 0 50 1.0e-6 1e-06
schedule, 4 150 1e-6 1e-6
schedule, 6 200 1e-6 1e-6
schedule, 8 500 1e-8 0.0
```

Column 1 is the sweep number at which to change the parameters of the calculation, column 2 is the number of renormalized states, column 3 is the tolerance of the Davidson diagonalization, and column 4 is the noise to be added to the density matrix.

For finer control of the orbital ordering, we also provide a genetic algorithm minimization method of a weighted exchange matrix. The genetic algorithm usually provides a sensible orbital ordering, although it can take a long time for large numbers of orbitals.

To control the orbital ordering manually use the reorder directive with the indices of the reordered orbitals,
reorder, 3, 2, 6, 1, 5, 4

If one wishes to use the Molpro storage order *(i.e. no reorder)*, add the following option:
reorderorb=0.

To set non-default weights in state-averaged calculations, use the `weights` directive,
weights, 0.3, 0.7

### 29.2.2 Restarting calculations

The BLOCK program periodically checkpoints the calculation. To restart a DMRG calculation
from a saved checkpoint, use the following command,

```
restart, FCIDUMP=dumpfile_name, SCRATCH=dir_name
```

where `dumpfile_name` and `dir_name`, are the name of the orbitals file and scratch directory, re-
spectively.

<table>
<thead>
<tr>
<th>Option</th>
<th>Alias</th>
<th>Default value</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAXM</td>
<td>500</td>
<td></td>
<td>Maximum size of blocks; must always be specified</td>
</tr>
<tr>
<td>FIEDLER</td>
<td>1</td>
<td></td>
<td>Default ordering optimization</td>
</tr>
<tr>
<td>GAOPT</td>
<td>0</td>
<td></td>
<td>Orbital ordering optimization</td>
</tr>
<tr>
<td>REORDERORB</td>
<td>1</td>
<td></td>
<td>If 0, turn off all orbital ordering</td>
</tr>
<tr>
<td>MAXITER</td>
<td>30</td>
<td></td>
<td>Maximum no. of sweep iterations</td>
</tr>
<tr>
<td>SWEEP_TOL</td>
<td>1E-09</td>
<td></td>
<td>Sets the final DMRG tolerance</td>
</tr>
<tr>
<td>ONEDOT</td>
<td>0</td>
<td></td>
<td>One-dot sweeps only</td>
</tr>
<tr>
<td>TWODOT</td>
<td>0</td>
<td></td>
<td>Two-dot sweeps only</td>
</tr>
<tr>
<td>ONEPDM</td>
<td>0</td>
<td></td>
<td>Calculates the 1-PDM</td>
</tr>
<tr>
<td>TWPDM</td>
<td>0</td>
<td></td>
<td>Calculates the 2-PDM</td>
</tr>
<tr>
<td>DRYRUN</td>
<td>0</td>
<td></td>
<td>Writes FCIDUMP and DMRG input file only</td>
</tr>
<tr>
<td>RESTART</td>
<td>0</td>
<td></td>
<td>DMRG restart</td>
</tr>
<tr>
<td>FCIDUMP</td>
<td>NA</td>
<td></td>
<td>For restart only. Specify name of dump file</td>
</tr>
<tr>
<td>SCRATCH</td>
<td>NA</td>
<td></td>
<td>For restart only. Specify name of the scratch directory</td>
</tr>
<tr>
<td>IRREP</td>
<td>1</td>
<td></td>
<td>Irreducible representation of state</td>
</tr>
<tr>
<td>NROOTS</td>
<td>1</td>
<td></td>
<td>Number of roots in state-averaged calculation</td>
</tr>
<tr>
<td>OUTPUTLEVEL</td>
<td>0</td>
<td></td>
<td>Set to -1 for more verbose molpro output, 1 for full output</td>
</tr>
<tr>
<td>NELEC</td>
<td>-1</td>
<td></td>
<td>Number of electrons</td>
</tr>
<tr>
<td>TWODOT_TO_ONEDOT</td>
<td>-1</td>
<td></td>
<td>Switch from two-dot to one-dot</td>
</tr>
</tbody>
</table>

*a) -1 means default value taken from BLOCK*
Examples:

Closed-shell ground-state calculations for sto-3g(10e⁻, 7o) H₂O using default parameters.

```
angstrom
geomtyp=xyz
geometry=
  O  0.000000  0.000000  0.000000
  H  0.700000  0.000000  0.700000
  H -0.700000  0.000000  0.700000
}
basis=sto-3g
{rhf}
{dmrg, maxm=50
  core, 0, 0, 0, 0
  occ, 4, 2, 1, 0
}
```

![Link to examples](http://www.molpro.net/info/current/examples/h2o_dmrg.com)

**METHOD**

<table>
<thead>
<tr>
<th></th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>-74.961135</td>
</tr>
<tr>
<td>DMRG (M=50)</td>
<td>-75.017832</td>
</tr>
<tr>
<td>FCI (comparison)</td>
<td>-75.017832</td>
</tr>
</tbody>
</table>

Closed-shell ground-state calculations for the localized π-active space (8e⁻, 8o) of octatetraene in minimal basis using default parameters.
symmetry, nosym
gemx = xyz
angstrom
geometry = {
  C 2.35401  -6.07788  -0.00000
  C 3.40526  -5.24546  -0.00000
  C 3.28692  -3.88730  -0.00000
  C 4.33880  -3.04529  -0.00000
  C 4.21017  -1.68428  -0.00000
  C 5.26204  -0.84227  -0.00000
  C 5.14370   0.51589  -0.00000
  C 6.19495   1.34830  -0.00000
  H 1.42023  -5.73687  -0.00000
  H 2.49445  -7.06217  -0.00000
  H 4.31219  -5.65764  -0.00000
  H 2.36872  -3.49894  -0.00000
  H 5.25770  -3.43408  -0.00000
  H 3.29126  -1.29550  -0.00000
  H 6.18025  -1.23064  -0.00000
  H 4.23677   0.92806  -0.00000
  H 7.12873   1.00730  -0.00000
  H 6.05451   2.33259  -0.00000
}
basis=sto-3g
{rhf}
{locali, pipek, locmethod=3
thresh, 1d-12, 1e-5
core, 25
occ, 33
save, 2102.2
}
{dmrg, maxm=250
orbital, 2102.2
core, 25
occ, 33
}

http://www.molpro.net/info/current/examples/octatetraene_dmrg.com

METHOD E
HF  -304.80229195
DMRG -304.97074163
FCI (comparison) -304.97074163

An example of a non-default orbital ordering and non-default scheduling for the localized \( \pi \)-active space (18\( \epsilon^- \), 18\( \sigma \)) of tetracene in minimal basis.
angstrom
symmetry, nosym
geomtyp = xyz
geometry = {
  C  5.7789001801  -1.5248905095  0.0000000000
  C  7.0401293170  -2.2085591442  0.0000000000
  C  8.2184825553  -0.0829976070  0.0000000000
  C  8.2184829496   0.6081247534  0.0000000000
  C  7.0401299670   0.6111988751  0.0000000000
  C  5.7789904096   0.0722677743  0.0000000000
  C  4.5632188446   0.6081247534  0.0000000000
  C  3.3272486621   0.6111988751  0.0000000000
  C  3.3272486617  -1.5250913599  0.0000000000
  C  4.5632186002  -2.2054838807  0.0000000000
  H  7.0387315422  -3.2964281036  0.0000000000
  H  9.1661920542  -2.0465927646  0.0000000000
  H  9.1661927656   0.4492313275  0.0000000000
  H  7.0387324522   1.6990678777  0.0000000000
  H  4.5629588592   1.6967700679  0.0000000000
  H  4.5629585552  -3.2941290592  0.0000000000
  C  2.0912785157   0.6081247534  0.0000000000
  C  2.0912787599  -2.2054838807  0.0000000000
  C  0.8755071337  -1.5248905103  0.0000000000
  C  0.8755069045  -0.0722677743  0.0000000000
  H  2.0915384850   1.6967700763  0.0000000000
  H  2.0915387880  -3.2941290672  0.0000000000
  C  -0.3856326333   0.6111988735  0.0000000000
  C  -1.5639856245  -0.0829976283  0.0000000000
  C  -1.5639852310  -1.5143631626  0.0000000000
  C  -0.3856319836  -2.2085591425  0.0000000000
  H  -0.3842351293   1.6990678801  0.0000000000
  H  -2.5116954264   0.4492313184  0.0000000000
  H  -2.5116947162  -2.0465927555  0.0000000000
  H  -0.3842342185  -3.2964281058  0.0000000000
}
basis=sto-3g
{rhf}
{merge orbital, 2100.2
move
rotate, 54.1, 48.1, 90
rotate, 52.1, 46.1, 90
rotate, 70.1, 69.1, 90
save, 2100.2
}
{rhf
maxit, 1}
{locali, pipek, locmethod=3
thresh, 1d-12, 1e-5
core, 51
occ, 69
save, 2102.2
}
{dmrg, maxiter=8, outputlevel=1
orbital, 2102.2
core, 51
occ, 69
reorder, 9,8,13,17,7,10,15,6,5,11,14,4,3,18,16,12,2,1
schedule, 0, 100, 1e-05, 1e-04
schedule, 4, 250, 1e-05, 1e-04
}

http://www.molpro.net/info/current/examples/tetracene_dmrng.com
<table>
<thead>
<tr>
<th>METHOD</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>-680.245827</td>
</tr>
<tr>
<td>DMRG (M=100)</td>
<td>-680.349299</td>
</tr>
<tr>
<td>DMRG (M=250)</td>
<td>-680.578887</td>
</tr>
</tbody>
</table>
AB INITIO MULTIPLE SPAWNING DYNAMICS

AIMS is a multi-state first-principles dynamics program written by Benjamin G. Levine, Joshua D. Coe, Aaron M. Virshup, Hongli Tao, Christian R. Evenhuis, William J. Glover, Toshifumi Mori, Michal Ben-Nun and Todd J. Martinez.

Bibliography:


All publications resulting from use of this program must acknowledge the above. See also:


The AIMS module implements the Ab Initio Multiple Spawning method to perform dynamics calculations on multiple electronic states. Although the program was designed for non-adiabatic dynamics with CASSCF wavefunctions, it can be used quite generally for first principles molecular dynamics, provided that nuclear gradients are available.

AIMS provides a description of a time-evolving molecular wavepacket with a multi-configurational, product gaussian function basis. To allow the size of the basis set to remain small while describing the wavepacket dynamics, the centers of the full-dimensional gaussian functions follow classical trajectories while their widths are kept fixed (the frozen Gaussian approximation). When these classical trajectories encounter regions of large non-adiabatic coupling to another electronic state, new basis functions are spawned on the coupled state and the Time Dependent Schrödinger Equation is solved in order to describe population transfer between the electronic states. In this way, the description of the wavepacket can be systematically improved by increasing the number of initial trajectory basis functions, while reducing the coupling threshold at which trajectories spawned. Alternatively, spawning can be disabled, and the method will reduce to traditional first-principles classical molecular dynamics when a single trajectory basis function is used.

30.1 Compilation

AIMS is compiled as a component of Molpro; however, it requires a fortran 2003 compiler and is disabled unless the preprocessor variable MOLPRO_f2003 is defined, which depends on the version of your compiler.
30.2 Structure of the input

The AIMS program is controlled by the Molpro input deck and a number of external text files:

30.2.1 Molpro input deck

The AIMS program is invoked by the command AIMS. The details of the electronic structure are defined in specifically named procedures. At a minimum, for first principles dynamics, AIMS requires the following structure to the input deck:

SYMMETRY, nosym
ORIENT, noorient
GEOMTYP=xyz
GEOMETRY={
  Initial atom specifications. Must match ordering of Geometry.dat, but need not be the same geometry
}
BASIS={Basis specifications.}
MPINIT={
  Electronic structure routines for initial wavefunction
}
MPCALC={
  Electronic structure routines for dynamics calculations. At a minimum, must include:
  ener(1)=energy(1)
  ener(2)=energy(2) etc
  force
}
AIMS, dir

where

dir (string) Relative directory to AIMS input files. (Default is working directory).

Note: the above is appropriate only for first-principles dynamics (without spawning). CASSCF spawning calculations require additional procedures and a specific structure to the MPINIT and MPCALC procedures. See the examples in section 30.5.
### 30.2.2 Control.dat

Control.dat is a fortran NAMELIST file storing the main parameters (in au) of an AIMS simulation. At the end of the file, one can optionally specify user-defined atom types (see below).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Options (Default)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Required parameters:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NumStates</td>
<td>Integer</td>
<td>Number of electronic states.</td>
</tr>
<tr>
<td>InitState</td>
<td>Integer</td>
<td>Initial electronic state.</td>
</tr>
<tr>
<td>NumParticles</td>
<td>Integer</td>
<td>Number of atoms.</td>
</tr>
<tr>
<td><strong>Common parameters:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IMethod</td>
<td>0</td>
<td>First principles dynamics (No NACV).</td>
</tr>
<tr>
<td></td>
<td>(1)</td>
<td>CASSCF dynamics, with NACV.</td>
</tr>
<tr>
<td>IRestart</td>
<td>(0)/1</td>
<td>Restart the calculation when set to 1.</td>
</tr>
<tr>
<td>RestartTime</td>
<td>Real (-100.0)</td>
<td>Time from which to restart in Checkpoint.txt</td>
</tr>
<tr>
<td></td>
<td></td>
<td>If disabled, use Last_Bundle.txt.</td>
</tr>
<tr>
<td>IRndSeed</td>
<td>Integer (0)</td>
<td>Initial condition random number seed.</td>
</tr>
<tr>
<td>InitialCond</td>
<td>(’NoSample’)</td>
<td>Read initial conditions from Geometry.dat.</td>
</tr>
<tr>
<td></td>
<td>’Wigner’</td>
<td>Sample from the Wigner distribution of harmonic normal modes in Frequencies.dat.</td>
</tr>
<tr>
<td></td>
<td>’Quasiclassical’</td>
<td>As above, for the Quasiclassical distribution.</td>
</tr>
<tr>
<td></td>
<td>’Boltzmann’</td>
<td>As above, for the Boltzmann distribution.</td>
</tr>
<tr>
<td>Temperature</td>
<td>Real (0.0)</td>
<td>Temperature (Kelvin) of the initial conditions.</td>
</tr>
<tr>
<td><strong>Expert parameters:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>InitBright</td>
<td>Logical (.false.)</td>
<td>Select optically brightest of InitState and IDark as initial state.</td>
</tr>
<tr>
<td>InitDark</td>
<td>Logical (.false.)</td>
<td>As above, but for darkest state.</td>
</tr>
<tr>
<td>IDark</td>
<td>Integer (-1)</td>
<td>See above.</td>
</tr>
<tr>
<td>InitGap</td>
<td>Real (0.0)</td>
<td>Select initial ground-excited energy gap to within ( \pm 0.5 \times \text{InitGapWidth} ).</td>
</tr>
<tr>
<td></td>
<td></td>
<td>See above.</td>
</tr>
<tr>
<td>InitGapWidth</td>
<td>Real (0.0)</td>
<td>See above.</td>
</tr>
<tr>
<td>IRestartTraj</td>
<td>Integer array (0)</td>
<td>Subset of trajectories to restart from. Can restart a single dead trajectory.</td>
</tr>
<tr>
<td>NumInitBasis</td>
<td>Integer (1)</td>
<td>Number of initial coupled basis functions.</td>
</tr>
<tr>
<td>FirstGauss</td>
<td>Logical (.false.)</td>
<td>Place the first basis function at the molecular origin (that of Geometry.dat), with zero momentum.</td>
</tr>
<tr>
<td>MirrorBasis</td>
<td>Logical (.false.)</td>
<td>Mirror the initial basis on another electronic state, MirrorState.</td>
</tr>
<tr>
<td>MirrorState</td>
<td>Integer (1)</td>
<td>See above.</td>
</tr>
<tr>
<td>EnergyAdjust</td>
<td>Logical (.false.)</td>
<td>Adjust momenta of mirrored basis (along NACV) to match original basis energy.</td>
</tr>
<tr>
<td>SharpEnergy</td>
<td>Logical (.false.)</td>
<td>Adjust momenta of all initial basis functions to match first basis function energy.</td>
</tr>
</tbody>
</table>
### Table 17: Integration and numerics

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Options (Default)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Required parameters:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TimeStep</td>
<td>Real</td>
<td>Simulation timestep.</td>
</tr>
<tr>
<td>SimulationTime</td>
<td>Real</td>
<td>Simulation length.</td>
</tr>
<tr>
<td><strong>Common parameters:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ExShift</td>
<td>Real (0.0)</td>
<td>Apply a shift of $+\text{ExShift}$ to diagonals of Hamiltonian to improve amplitude/phase propagation. Good choice is average potential energy of ground and excited states.</td>
</tr>
<tr>
<td>CoupTimeStep</td>
<td>Real (TimeStep/4)</td>
<td>Timestep to use in regions of large nonadiabatic coupling.</td>
</tr>
<tr>
<td><strong>Expert parameters:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TimeStepRejection</td>
<td>Logical (.true.)</td>
<td>Enables adaptive time-stepping when encountering integration problems.</td>
</tr>
<tr>
<td>MinTimeStep</td>
<td>Real (CoupTimeStep/4)</td>
<td>Minimum timestep to use when adaptive time-stepping.</td>
</tr>
<tr>
<td>DieOnMinStep</td>
<td>Logical (.true.)</td>
<td>Stop calculation if minimum timestep is reached.</td>
</tr>
<tr>
<td>EnergyStepCons</td>
<td>Real (0.005)</td>
<td>Allowed violation of classical energy conservation before timestep is rejected.</td>
</tr>
<tr>
<td>NormCons</td>
<td>Real (0.25)</td>
<td>Permitted deviation in Norm from beginning of simulation.</td>
</tr>
<tr>
<td>RejectAllStateFlip</td>
<td>Logical (.true.)</td>
<td>Reject a timestep if any two electronic states flip. If .false. then only reject if state is coupled to occupied state.</td>
</tr>
<tr>
<td>OlapThresh</td>
<td>Real (0.001)</td>
<td>Threshold overlap between two trajectories below which matrix elements not calculated.</td>
</tr>
<tr>
<td>RegThresh</td>
<td>Real (0.0001)</td>
<td>Threshold to regularize the overlap matrix before inversion.</td>
</tr>
<tr>
<td>Constrain</td>
<td>Logical (.false.)</td>
<td>Apply geometric contraints? If yes, supply Constraints.dat</td>
</tr>
</tbody>
</table>
Table 18: Spawning

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Options (Default)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Common parameters:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CSThresh</td>
<td>Real (0.1)</td>
<td>Threshold Coupling, above which to spawn.</td>
</tr>
<tr>
<td>PopToSpawn</td>
<td>Real (0.1)</td>
<td>Minimum population a trajectory must have before it can spawn.</td>
</tr>
<tr>
<td>OMax</td>
<td>Real (0.8)</td>
<td>Prevent spawning if overlap of spawned trajectory with existing basis greater than Omax.</td>
</tr>
<tr>
<td>MaxTraj</td>
<td>Real (100)</td>
<td>Maximum number of allowed trajectories. Above which, spawning is disabled.</td>
</tr>
<tr>
<td>IgnoreState</td>
<td>Integer (0)</td>
<td>Stop dynamics of trajectories on IgnoreState if not coupled for at least DecoherenceTime. Choose 1 if only interested in excited states.</td>
</tr>
<tr>
<td>MaxEDiff</td>
<td>Real (0.03)</td>
<td>Energy gap threshold for calculating nonadiabatic couplings, above which, coupling taken to be zero.</td>
</tr>
<tr>
<td><strong>Expert parameters:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DecoherenceTime</td>
<td>Real (200.0)</td>
<td>See above.</td>
</tr>
<tr>
<td>SpawnCoupV</td>
<td>Logical (.false.)</td>
<td>Use Coup.velocity as criterion for spawning rather than Coupling magnitude alone.</td>
</tr>
<tr>
<td>EShellOnly</td>
<td>Logical (.true.)</td>
<td>Require spawned trajectories to have same classical energy as parent by adjusting momentum along NACV.</td>
</tr>
</tbody>
</table>
### Table 19: Output

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Options (Default)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Common parameters:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>zAllText</td>
<td>Logical (.false.)</td>
<td>Write all output files?</td>
</tr>
<tr>
<td>zEDatFile</td>
<td>Logical (.true.)</td>
<td>Write Energy file?</td>
</tr>
<tr>
<td>zNDatFile</td>
<td>Logical (.true.)</td>
<td>Write Population file?</td>
</tr>
<tr>
<td>zTrajFile</td>
<td>Logical (.false.)</td>
<td>Write Trajectory files?</td>
</tr>
<tr>
<td>zAmpFile</td>
<td>Logical (.false.)</td>
<td>Write Amplitude files?</td>
</tr>
<tr>
<td>zPotEnFile</td>
<td>Logical (.false.)</td>
<td>Write Potential Energy files?</td>
</tr>
<tr>
<td>zXYZ</td>
<td>Logical (.false.)</td>
<td>Write XYZ Geometry files?</td>
</tr>
<tr>
<td>zCoupFile</td>
<td>Logical (.false.)</td>
<td>Write Coupling files?</td>
</tr>
<tr>
<td>zChargeFile</td>
<td>Logical (.false.)</td>
<td>Write Charge files?</td>
</tr>
<tr>
<td>zDipoleFile</td>
<td>Logical (.false.)</td>
<td>Write Dipole files?</td>
</tr>
<tr>
<td>zTDipoleFile</td>
<td>Logical (.false.)</td>
<td>Write Transition Dipole files?</td>
</tr>
<tr>
<td>zQMRRFile</td>
<td>Logical (.false.)</td>
<td>Write $\langle r^2 \rangle$ quadrupole moment files?</td>
</tr>
<tr>
<td>zCIVecFile</td>
<td>Logical (.false.)</td>
<td>Write CI Vector files?</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(Not recommended for large CI)</td>
</tr>
<tr>
<td>zCorrfile</td>
<td>Logical (.false.)</td>
<td>Write Correlation function file?</td>
</tr>
<tr>
<td>zBundMatFile</td>
<td>Logical (.false.)</td>
<td>Write Matrices (H, S, etc)?</td>
</tr>
<tr>
<td>WriteMolden</td>
<td>Logical (.false.)</td>
<td>Write Molden files?</td>
</tr>
<tr>
<td>MoldenStep</td>
<td>Integer (200)</td>
<td>How often (every number of timesteps) Molden files are written.</td>
</tr>
<tr>
<td>RestartStep</td>
<td>Integer (4)</td>
<td>How often (every number of timesteps) Restart files are written.</td>
</tr>
<tr>
<td><strong>Expert parameters:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NStepToPrint</td>
<td>Integer (1)</td>
<td>How often (every number of timesteps) output files are written.</td>
</tr>
<tr>
<td>WriteEveryStep</td>
<td>Logical (.true.)</td>
<td>Write output every timestep,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>including subtimesteps of adaptive propagation.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Overrides NStepToPrint.</td>
</tr>
<tr>
<td>NBonds</td>
<td>Integer (0)</td>
<td>Number of bond lengths to print. Define IBond below.</td>
</tr>
<tr>
<td>IBond(2,NBonds)</td>
<td>Integer (0)</td>
<td>List of atom indices that are bonded. See NBonds above.</td>
</tr>
<tr>
<td>NAngles</td>
<td>Integer (0)</td>
<td>Number of bond angles to print. Define IAngle below.</td>
</tr>
<tr>
<td>IAngle(3,NAngles)</td>
<td>Integer (0)</td>
<td>List of atom indices that define bond angles.</td>
</tr>
<tr>
<td>NDihedrals</td>
<td>Integer (0)</td>
<td>Number of dihedral angles to print. Define IDihedral below.</td>
</tr>
<tr>
<td>IDihedral(4,NDihedrals)</td>
<td>Integer (0)</td>
<td>List of atom indices that define dihedral angles.</td>
</tr>
<tr>
<td>NPyrams</td>
<td>Integer (0)</td>
<td>Number of pyramidalization angles to print. Define IPyram below.</td>
</tr>
<tr>
<td>IPyram(4,NPyrams)</td>
<td>Integer (0)</td>
<td>List of atom indices that define pyramidalization angles.</td>
</tr>
</tbody>
</table>
User-defined atom types

AIMS recognizes the atoms H, C, N, O, S, F, Cl and assigns appropriate masses and gaussian width parameters for these atoms. If you wish to modify these defaults, or if your system contains other atoms, you can define custom atom types at the end of Control.dat. The format is (in atomic units):

\begin{verbatim}
  n
  AtomName(1) AtomicNumber(1) AtomicMass(1) GaussianWidth(1)
  ... : AtomName(n) AtomicNumber(n) AtomicMass(n) GaussianWidth(n)
\end{verbatim}

30.2.3 Geometry.dat

Geometry.dat contains the molecular geometry that will be used in the generation of initial conditions. Optionally, the momenta can also be specified, which is useful if \texttt{InitialCond='NoSample'}:

\begin{verbatim}
  UNITS=ANG or UNITS=BOHR
  natom
  AtomName(1) x(1) y(1) z(1)
  ... : AtomName(natom) x(natom) y(natom) z(natom)
  Momenta:
  AtomName(1) px(1) py(1) pz(1)
  ... : AtomName(natom) px(natom) py(natom) pz(natom)
\end{verbatim}

\footnote{For definition, see J. Phys. Chem. A 113, 12815 (2009)}
30.2.4 FrequenciesMP.dat

FrequenciesMP.dat contains the normal-mode frequencies and displacements of the molecule in its initial geometry and electronic state (usually the ground state). This information is used in the generation of initial conditions. If InitialCond\neq \text{'NoSample'} then either this file, Hessian.dat or Frequencies.dat (Sections 30.2.5 and 30.2.6 respectively) must be present. The format of FrequenciesMP.dat follows the Molpro output of a Frequencies calculation:

<table>
<thead>
<tr>
<th>Wavenumbers [cm⁻¹]</th>
<th>1 A</th>
<th>2 A</th>
<th>3 A</th>
<th>4 A</th>
<th>5 A</th>
</tr>
</thead>
<tbody>
<tr>
<td>1116.71</td>
<td>1725.49</td>
<td>1728.47</td>
<td>3435.76</td>
<td>3566.01</td>
<td></td>
</tr>
<tr>
<td>Intensities [km/mol]</td>
<td>157.34</td>
<td>17.93</td>
<td>16.24</td>
<td>1.67</td>
<td>0.53</td>
</tr>
<tr>
<td>Intensities [relative]</td>
<td>100.00</td>
<td>11.40</td>
<td>10.32</td>
<td>1.06</td>
<td>0.33</td>
</tr>
<tr>
<td>GX1</td>
<td>-0.10597</td>
<td>-0.00088</td>
<td>-0.00021</td>
<td>-0.03801</td>
<td>-0.00009</td>
</tr>
<tr>
<td>GY1</td>
<td>0.00067</td>
<td>-0.05838</td>
<td>-0.02628</td>
<td>-0.00017</td>
<td>-0.07554</td>
</tr>
<tr>
<td>GZ1</td>
<td>0.00004</td>
<td>0.02639</td>
<td>-0.05807</td>
<td>0.00078</td>
<td>0.00226</td>
</tr>
<tr>
<td>GX2</td>
<td>0.49134</td>
<td>-0.14946</td>
<td>0.19728</td>
<td>0.17300</td>
<td>-0.07729</td>
</tr>
<tr>
<td>GY2</td>
<td>0.03972</td>
<td>0.54519</td>
<td>0.46553</td>
<td>-0.12339</td>
<td>0.02439</td>
</tr>
<tr>
<td>GZ2</td>
<td>-0.19161</td>
<td>0.21763</td>
<td>-0.00782</td>
<td>0.51879</td>
<td>-0.19043</td>
</tr>
<tr>
<td>GX3</td>
<td>0.49290</td>
<td>-0.09010</td>
<td>-0.22955</td>
<td>0.17771</td>
<td>-0.20720</td>
</tr>
<tr>
<td>GY3</td>
<td>0.13665</td>
<td>0.43154</td>
<td>-0.28739</td>
<td>-0.39612</td>
<td>0.35792</td>
</tr>
<tr>
<td>GZ3</td>
<td>0.13722</td>
<td>-0.52910</td>
<td>0.11024</td>
<td>-0.37702</td>
<td>0.36169</td>
</tr>
<tr>
<td>GX4</td>
<td>0.48838</td>
<td>0.25184</td>
<td>0.03520</td>
<td>0.17755</td>
<td>0.28570</td>
</tr>
<tr>
<td>GY4</td>
<td>-0.18573</td>
<td>-0.16545</td>
<td>0.18702</td>
<td>0.52182</td>
<td>0.66736</td>
</tr>
<tr>
<td>GZ4</td>
<td>0.05376</td>
<td>-0.05521</td>
<td>0.70450</td>
<td>-0.15258</td>
<td>-0.20268</td>
</tr>
</tbody>
</table>

Note: Only the real, non-zero frequencies should be included in this file (i.e. those corresponding to vibrations). The first line of the file must be the number of frequencies. See section 47 for details on how to perform a normal-mode frequencies calculation in Molpro.

30.2.5 Hessian.dat

As an alternative to FrequenciesMP.dat, AIMS can generate the normal mode frequencies after reading in the Hessian from Hessian.dat. The format of this file is:

```plaintext
natom
Hess(1,1) Hess(2,1) ... Hess(3*natom,3*natom)
```

Note: the Hessian should not be mass weighted. It is permissible to have carriage returns in the list of Hessian components.
30.2.6 Frequencies.dat

As an alternative to FrequenciesMP.dat and Hessian.dat, AIMS can read in normal-mode frequencies and vectors in AIMS format in Frequencies.dat. The format of this file is:

\[
\text{natom } \text{nmodes} \\
\text{freq(1) freq(2) ... freq(nmodes)} \\
\text{modevec(1,1) modevec(2,1) ... modevec(3*natom,nmodes)}
\]

Note: Frequencies must be in cm\(^{-1}\), but normal mode vectors can be mass scaled or not- AIMS will detect. Also, it is permissible to have carriage returns in the list of frequencies and mode vectors. This file is generated by AIMS if either FrequenciesMP.dat or Hessian.dat is used initially.

30.2.7 Constraints.dat

If Constraint= .true., then Constraints.dat must be supplied. This is a fortran NAMELIST file that defines the geometric constraints in the system. These constraints are enforced with the RATTLE algorithm. The parameters contained in this file are:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Options (Default)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>NumBonds</td>
<td>Integer (0)</td>
<td>Number of bond lengths to constrain Define IBondPtcles below.</td>
</tr>
<tr>
<td>IBondPtcles(2,NumBonds)</td>
<td>Integer (0)</td>
<td>List of atom indices that are bonded. See NumBonds above.</td>
</tr>
<tr>
<td>NumAngles</td>
<td>Integer (0)</td>
<td>Number of bond angles to constrain Define IAnglePtcles below.</td>
</tr>
<tr>
<td>IAnglePtcles(3,NumAngles)</td>
<td>Integer (0)</td>
<td>List of atom indices that define bond angles.</td>
</tr>
<tr>
<td>NComAtoms</td>
<td>Integer (0)</td>
<td>Number of atoms that define the center-of-mass constraint. Define ICOMPtcles below.</td>
</tr>
<tr>
<td>ICOMPtcles(NComAtoms)</td>
<td>Integer (0)</td>
<td>List of atom indices that define the center of mass.</td>
</tr>
<tr>
<td>Toler</td>
<td>Real (1E-4)</td>
<td>Rattle tolerance</td>
</tr>
<tr>
<td>MaxIts</td>
<td>Integer (10000)</td>
<td>Maximum number of Rattle iterations</td>
</tr>
</tbody>
</table>

Note, a maximum of 1000 constraints is allowed.

30.3 Running a CASSCF spawning calculation

This section gives an overview of how to set up and run a CASSCF ab initio multiple spawning calculation.

1) The first step is to create a molpro input deck that controls how the CASSCF electronic structure calculations are performed. AIMS requires a fairly complicated structure to the molpro deck and it is highly recommended that you use the ethylene CASSCF example as a starting point (section 30.5). Control.dat should then be modified for your system and desired simulation parameters (section 30.2.2).
2) Next, the initial conditions should be defined. This involves providing an initial geometry in Geometry.dat (section 30.2.3) and normal-mode frequencies and displacements in FrequenciesMP.dat (section 30.2.4), which will be used to generate a phase-space distribution that the initial conditions sample. Alternatively, one can also provide momenta in Geometry.dat and set InitialCond='NoSample' in Control.dat, and directly specify the initial conditions.

3) The AIMS calculation is then initiated by running molpro on the input deck, in the usual fashion. In order to sample different initial conditions, multiple AIMS simulations should be run with different values of the random number seed IRndSeed (or different Geometry.dat files) - each of these should be run in a unique directory.
30.4 Output

Beyond the regular molpro output, which contains the electronic structure output, AIMS writes to a number of text files, depending on the output parameters in Control.dat (section 30.2.2). All values are given in atomic units unless otherwise specified. Electronic properties of a trajectory are evaluated at the center geometry of the trajectory basis function.

**FMS.out**
Current progress of simulation and any warning/error messages.

**E.dat**
Wavepacket energies. QM energies are expectation values of the quantum operators, including coherences between the trajectory basis functions. CL energies are averages of the trajectories’ classical energies, weighted by the amplitude norm of each trajectory.

**N.dat**
Electronic populations, the sum of which should be conserved.

**TrajDump.i**
Dynamic variables for trajectory i.

**Amp.i**
Amplitudes of trajectory i. Note: since the product Gaussian basis is non-orthogonal, the amplitude norms do not necessarily sum to 1.

**PotEn.i**
Electronic energies for trajectory i. The last column displays the total classical energy of the trajectory, which should be conserved.

**positions.i.xyz**
Snapshots of trajectory i’s center geometry in XYZ format (Angstrom).

**Coup.i**
Nonadiabatic couplings of each state to the occupied state for trajectory i. The first nstate columns contain the magnitude of coupling vectors and the last nstate columns contain the projection of the coupling onto the velocity vector.

**Charge.i**
Partial atomic charges corresponding to the occupied electronic state of trajectory i. The molpro input deck must contain a Mulliken population analysis directive in the **MPCALC** procedure.

**Dipole.i**
Dipole moments of each electronic state for trajectory i.

**TDip.i**
Transition dipoles from ground to excited states for trajectory i.

**QMRR.i**
Isotropic quadrupole moment $⟨r^2⟩$ of each electronic state for trajectory i. The molpro input deck must contain **EXPEC,QMRR**.

**CIVec.i**
CI Vectors for each state of trajectory i.

**CFxn.dat**
The overlap correlation function $⟨Ψ(t)|Ψ(0)⟩$.

**H.dat**
Hamiltonian matrix.

**S.dat**
Overlap matrix. Note: the overlap between trajectories on different states is zero, but is displayed here as if they were on the same state.

**SDot.dat**
The time derivative of the Overlap matrix.

**i.j.molf**
Molden file for trajectory i at time j.

**Checkpoint.txt**
Restart file with history.

**Last_Bundle.txt**
Restart file for the last written timestep.

**Spawn.log**
Details of successful spawns.
FailSpawn.log          Details of unsuccessful spawns.
Spawn.i               XYZ file of geometry where trajectory i was spawned.

**30.5 Examples**

The following two examples show how AIMS can be run in either single-state first-principle molecular dynamics mode, or multi-state spawning mode. The parameters found in these input files were chosen for illustrative purposes and are not necessarily appropriate for your system of interest. It is recommended the literature be consulted before performing AIMS simulations.

**Ethylene Hartree-Fock First-Principles Molecular Dynamics**

See examples/aims_ethyl_HF

**Ethylene CASSCF Spawning Dynamics**

See examples/aims_ethyl_CASSCF

**31 SMILES**


This code is not included in binary versions of Molpro, and by default the code is not included when building from source code; one should use the `--enable-slater` configure option to enable compilation of the code.

The SMILES module is invoked by the `intyp='SLATER'` card. Name for ancillary files generated by the package can be supplied by `SLFILES=filename`. Default name is ‘slscratch’.

Three-center two-electron integrals of types $(AB|AC)$ and $(AB|CD)$ are computed by means of Gaussian expansions (STO-nG). The default length of the expansions is 9 (STO-9G). However, integrals obtained with STO-9G expansions may have not sufficient accuracy for post-HF calculations, specially with high quality basis sets. In these cases, the length of the expansions can be changed setting the variable `NGSSTO= number of gaussians`. Though a maximum of `NGSSTO=30` is allowed, the lengths of the expansions actually available in the package depend on the $(n,l)$ quantum numbers. If an expansion not included is required, the program takes the largest currently available.

Program limitations: In the current version, a maximum of 511 basis functions is allowed, and contracted functions cannot be used.

**31.1 INTERNAL BASIS SETS**

The following internal basis sets are available.
Table 21: Internal basis sets in SMILES

<table>
<thead>
<tr>
<th>Basis set</th>
<th>H-He</th>
<th>Li-Be</th>
<th>B-Ne</th>
<th>Na-Ar</th>
</tr>
</thead>
<tbody>
<tr>
<td>VB1</td>
<td>[3,1]</td>
<td>[5,1]</td>
<td>[5,3,1]</td>
<td>—</td>
</tr>
<tr>
<td>CVB1</td>
<td>[3,1]</td>
<td>[6,2]</td>
<td>[6,4,1]</td>
<td>—</td>
</tr>
<tr>
<td>FVB1</td>
<td>[3,2,1]</td>
<td>[5,3,1,1]</td>
<td>[5,4,2,1]</td>
<td>—</td>
</tr>
<tr>
<td>ZVB1</td>
<td>[3,1]</td>
<td>[4,3,1]</td>
<td>[4,3,1]</td>
<td>[6,5,1]</td>
</tr>
<tr>
<td>VB2</td>
<td>[4,2,1]</td>
<td>[6,2,1]</td>
<td>[6,4,2,1]</td>
<td>—</td>
</tr>
<tr>
<td>CVB2</td>
<td>[4,2,1]</td>
<td>[7,3,2]</td>
<td>[7,5,3,1]</td>
<td>—</td>
</tr>
<tr>
<td>ZVB2</td>
<td>[4,2,1]</td>
<td>[5,4,2,1]</td>
<td>[5,4,2,1]</td>
<td>[7,6,2,1]</td>
</tr>
<tr>
<td>VB3</td>
<td>[5,3,2,1]</td>
<td>[7,3,2,1]</td>
<td>[7,5,3,2,1]</td>
<td>—</td>
</tr>
<tr>
<td>CVB3</td>
<td>[5,3,2,1]</td>
<td>[8,4,3,2]</td>
<td>[8,6,4,3,1]</td>
<td>—</td>
</tr>
<tr>
<td>ZVB3</td>
<td>[5,3,2,1]</td>
<td>[6,5,3,2,1]</td>
<td>[6,5,3,2,1]</td>
<td>[8,7,3,2,1]</td>
</tr>
</tbody>
</table>

31.2 EXTERNAL BASIS SETS

External basis sets can be supplied in a file that must be located in the working directory. Each record will contain the following data (free format):

I N L EXP NG

where:

I: atom type index (integer)
N: principal quantum number (integer)
L: angular quantum number (integer)
EXP: exponent (double precision)
NG: number of gaussians for the \((AB|AC)\) and \((AB|CB)\) integrals (integer)

Atom type index is used to establish the correspondence between the basis functions and the centers (atoms). All records having the same value of I will define the basis set for all the atoms of the corresponding type.

Example:

For a calculation on the \(\text{CO}_2\) molecule with the following geometry data:

```
Geometry={
  3
  C1, 0.000000000000E+00, 0.000000000000E+00, 0.000000000000E+00
  O2, 0.000000000000E+00, 0.000000000000E+00,-0.117963799946E+01
  O3, 0.000000000000E+00, 0.000000000000E+00, 0.117963799946E+01
}
```

Clementi and Roetti’s Single Zeta basis set could be supplied in an external file like:

```
1 1 0 5.67263 12
1 2 0 1.60833 12
1 2 1 1.56788 12
2 1 0 7.65781 12
2 2 0 2.24588 12
2 2 1 2.22662 12
```
The first three records define the basis set for atoms of the first type (carbon in this example), and the following three, the basis set for atoms of the second type (oxygen).

NG is mandatory even in case of diatomics, though gaussian expansions will not be used, the value of NG being irrelevant in this case.

### 31.3 Example

Example using internal basis set for H\(_2\)O.

```plaintext
memory,20,m
if(.not.modul_slater) then
  exit
end if

geomtyp=zmat
gometry={
o;h1,o,r;h2,o,r,h1,theta
}
r=0.96 ang
theta=102

intyp='SLATER'
basis=VB1

hf
ccsd(t)
multi
mrci
```

[http://www.molpro.net/info/current/examples/slater.com](http://www.molpro.net/info/current/examples/slater.com)

### 32 LOCAL CORRELATION TREATMENTS

#### 32.1 Introduction

The local correlation program of MOLPRO can currently perform closed-shell LMP2, LMP3, LMP4(SDTQ), LCISD, LDCSD, LQCISD(T), and LCCSD(T) calculations. For large molecules, all methods scale linearly with molecular size, provided very distant pairs are neglected, and the integral-direct algorithms are used.

Much higher efficiency is achieved by using density fitting (DF) approximations to compute the integrals. Density fitting is available for all local methods up to LCCSD(T), as well as for analytical LMP2 gradients. Only iterative triples methods like LCCSDT-1b can currently not be done with density fitting.

The errors introduced by DF are negligible, and the use of the DF methods is highly recommended. Linear scaling can be obtained in DF-LMP2 using the LOCFIT option (see Ref. 11); in DF-LCCSD(T), the most important parts also scale linearly, but some transformation steps scale quadratically.

Energy gradients are available for LMP2, DF-LMP2, DF-SCS-LMP2, and LQCISD (in the latter case only for LOCAL=1, i.e. the local calculation is simulated using the canonical program, and savings only result from the reduced number of pairs).
Local explicitly correlated methods (DF-LMP2-R12 and DF-LMP2-F12 are described in section 35).

Before using these methods, it is strongly recommended to read the literature in order to understand the basic concepts and approximations. A recent review [1] and Ref. [2] may be suitable for an introduction.

References:

Review:

General local Coupled Cluster:

Multipole treatment of distant pairs:

Linear scaling local MP2:

Density fitted local methods:

LMP2 Gradients and geometry optimization:

**LMP2 vibrational frequencies:**

**Intermolecular interactions and the BSSE problem:**

**Improved treatment of intermolecular pairs in local coupled cluster methods (beyond LMP2):**

### 32.2 Getting started

The local correlation treatment is switched on by preceding the command name by an *L*, i.e., by using the *LMP2, LMP3, LMP4, LQCISD, LCCSD, LCDSD, or LCISD* commands.

The *LQCISD* and *LCCSD* commands can be appended by a specification for the perturbative treatment of triple excitations (e.g., *LCCSD(T0)*):

- **(T)** Use the default triples method. Currently this is T0.
- **(T0)** Non-iterative local triples. This is the fastest triples option. It is usually sufficiently accurate and recommended to be used in most cases.
- **(T1)** T0 plus one perturbative update of the triples amplitudes. If the accuracy of T0 is insufficient (very rarely the case!), this can be used to improve the accuracy. The computational cost is at least twice as large as for T0. In contrast to T0, the triples amplitudes must be stored on disk, which can be a bottleneck in calculations for large molecules. Also the memory requirements are substantially larger than for T0.
- **(T1C)** As T1, but a caching algorithm is used which avoids the simultaneous storage of all triples amplitudes on disk (as is the case for *(T1) or *(TF))*). Hence, T1C requires less disk space but more CPU-time than T1. The more disk space is made available for the caching algorithm (using the T1DISK option on the local card, see below), the less CPU time is used.
(TF) Full iterative triples calculation. With full domains and without weak pair approximations this gives the same result as a canonical (T) calculation. Typically, 3-5 iterations are needed, and therefore the computational effort is 2-3 times larger than for (T1). The disk and memory requirements are the same as for T1. The T0 energy is also computed and printed. TFULL and FULL are aliases for TF.

(TA) As TF, but the T1 energy is also computed. Since the first iteration is different for T1, the convergence of the triples iterations is slightly different with TF and TA (TF being somewhat faster in most cases). TALL and ALL are aliases for TA.

Density fitting can be invoked by prepending the command name by DF-, e.g. DF-LMP2, DF-LCCSD(T0) etc. In density fitting calculations an additional auxiliary basis set is needed. Details about choosing such basis sets and other options for density fitting are described in sections 32.10 and 15.

The general input for local coupled LMP2 or coupled cluster calculations is:

- **LMP2, options** Local MP2 calculation
- **LCCSD, options** Local CCSD calculation
- **LDCSD, options** Local DCSD calculation
- **LCCSD (T0), options** Local CCSD(T0) calculation

The same options as on the command line can also be given on subsequent LOCAL and MULTP directives. Instead of using the MULTP directive, the MULTP option on the command line can also be used.

In the following, we will first give a summary of all options and directives. These will be described in more detail in the subsequent sections. For new users it is recommended to read section 32.9 at the end of this chapter before starting calculations.

### 32.3 Summary of options

Many options can be specified on the command line. For all options appropriate default values are set, and so these options must usually be modified only for special purposes. For convenience and historical reasons, alias names are available for various options, which often correspond to the variable name used in the program. Table 22 summarizes the options, aliases and default values. In the following, the parameters will be described in more detail.
### Table 22: Summary of `local` options and their default values

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Alias</th>
<th>Default value</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>General Parameters:</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LOCAL</td>
<td></td>
<td>4</td>
<td>determines which program to use.</td>
</tr>
<tr>
<td>MULTP</td>
<td></td>
<td>0</td>
<td>turns on multipole approximations for distant pairs.</td>
</tr>
<tr>
<td>SAVEDOM</td>
<td>SAVE</td>
<td>0</td>
<td>specifies record for saving domain info.</td>
</tr>
<tr>
<td>RESTDOM</td>
<td>START</td>
<td>0</td>
<td>specifies record for reading domain info.</td>
</tr>
<tr>
<td>LCOORB</td>
<td></td>
<td>0</td>
<td>activates or deactivates orbital localization.</td>
</tr>
<tr>
<td>LOC_METHOD</td>
<td></td>
<td></td>
<td>specifies which localization method to use.</td>
</tr>
<tr>
<td>CANONICAL</td>
<td></td>
<td>0</td>
<td>allows to use canonical virtual orbitals (for testing).</td>
</tr>
<tr>
<td>PMDEL</td>
<td>CPLDEL</td>
<td>0</td>
<td>discards contributions of diffuse functions in PM localization.</td>
</tr>
<tr>
<td>SAVORB</td>
<td>SAVLOC</td>
<td>0</td>
<td>specifies record for saving local orbitals.</td>
</tr>
<tr>
<td>DOMONLY</td>
<td></td>
<td>0</td>
<td>if 1, only domains are made.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>if 2, only orbital domains are made.</td>
</tr>
<tr>
<td><strong>Parameters to define domains:</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>THRBP</td>
<td>DOMSEL</td>
<td>0.98</td>
<td>Boughton-Pulay selection criterion for orbital domains.</td>
</tr>
<tr>
<td>NPASEL</td>
<td></td>
<td>0</td>
<td>charge used in the NPA selection criterion for orbital domains.</td>
</tr>
<tr>
<td>CHGMIN</td>
<td></td>
<td>0.01</td>
<td>determines the minimum allowed atomic charge in domains.</td>
</tr>
<tr>
<td>CHGMINH</td>
<td></td>
<td>0.03</td>
<td>as CHGMIN, but used for H-atoms (default 0.03).</td>
</tr>
<tr>
<td>CHGMAX</td>
<td></td>
<td>0.40</td>
<td>If the atomic charge is larger than this value, the atom is always included in the domain.</td>
</tr>
<tr>
<td>MAXANG</td>
<td>MAXL</td>
<td>99</td>
<td>angular momentum restriction for BP domain selection.</td>
</tr>
<tr>
<td>MAXBP</td>
<td></td>
<td>0</td>
<td>determines how atoms are ranked in BP procedure.</td>
</tr>
<tr>
<td>MULLIKEN</td>
<td>LOCMUL</td>
<td>0</td>
<td>determines the method to determine atomic charges.</td>
</tr>
<tr>
<td>MERGEDOM</td>
<td></td>
<td>0</td>
<td>merges overlapping domains.</td>
</tr>
<tr>
<td>DELCOR</td>
<td>IDLCOR</td>
<td>2</td>
<td>delete projected core AOs up to certain shell.</td>
</tr>
<tr>
<td>DELBAS</td>
<td>IBASO</td>
<td>0</td>
<td>determines how to remove redundancies.</td>
</tr>
<tr>
<td><strong>Distance criteria for domain extensions:</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>REXT</td>
<td></td>
<td>0</td>
<td>criterion for all pair domains.</td>
</tr>
<tr>
<td>REXTS</td>
<td></td>
<td>0</td>
<td>criterion for strong pair domains.</td>
</tr>
<tr>
<td>REXTC</td>
<td></td>
<td>0</td>
<td>criterion for strong and close pair domains.</td>
</tr>
<tr>
<td>REXTW</td>
<td></td>
<td>0</td>
<td>criterion for strong, close, and weak pair domains.</td>
</tr>
<tr>
<td><strong>Connectivity criteria for domain extensions:</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IEXT</td>
<td></td>
<td>0</td>
<td>criterion for all pair domains.</td>
</tr>
<tr>
<td>IEXTS</td>
<td></td>
<td>0</td>
<td>criterion for strong pair domains.</td>
</tr>
<tr>
<td>IEXTC</td>
<td></td>
<td>0</td>
<td>criterion for strong and close pair domains.</td>
</tr>
<tr>
<td>IEXTW</td>
<td></td>
<td>0</td>
<td>criterion for strong, close, and weak pair domains.</td>
</tr>
<tr>
<td><strong>Parameters to select pair classes:</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>USE_DIST</td>
<td></td>
<td>1</td>
<td>determines if distance of connectivity criteria are used.</td>
</tr>
<tr>
<td>RCLOSE</td>
<td>CLOSEP</td>
<td>1</td>
<td>distance criterion for selection of weak pairs.</td>
</tr>
<tr>
<td>RWEAK</td>
<td>WEAKP</td>
<td>3</td>
<td>distance criterion for selection of weak pairs.</td>
</tr>
<tr>
<td>RDIST</td>
<td>DISTP</td>
<td>8</td>
<td>distance criterion for selection of distant pairs.</td>
</tr>
<tr>
<td>RVDIST</td>
<td>VERYD</td>
<td>15</td>
<td>distance criterion for selection of very distant pairs.</td>
</tr>
<tr>
<td>ICLOSE</td>
<td></td>
<td>1</td>
<td>connectivity criterion for selection of weak pairs.</td>
</tr>
<tr>
<td>IWEAK</td>
<td></td>
<td>2</td>
<td>connectivity criterion for selection of weak pairs.</td>
</tr>
<tr>
<td>IDIST</td>
<td></td>
<td>5</td>
<td>connectivity criterion for selection of distant pairs.</td>
</tr>
<tr>
<td>IVDIST</td>
<td></td>
<td>8</td>
<td>connectivity criterion for selection of very distant pairs.</td>
</tr>
<tr>
<td>CHGMIN_PAIRS</td>
<td>CHGMINP</td>
<td>0.20</td>
<td>determines minimum charge of atoms used for pair classification.</td>
</tr>
<tr>
<td>KEEPCL</td>
<td></td>
<td>0</td>
<td>determines if close pairs are included in LCCSD.</td>
</tr>
<tr>
<td>Parameter</td>
<td>Alias</td>
<td>Default value</td>
<td>Meaning</td>
</tr>
<tr>
<td>-----------</td>
<td>-------</td>
<td>---------------</td>
<td>---------</td>
</tr>
<tr>
<td>DSTMLT</td>
<td></td>
<td>3</td>
<td>multipole expansion level for distant pairs</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IEPART</td>
<td></td>
<td>0</td>
<td>If nonzero: do energy partitioning.</td>
</tr>
<tr>
<td>EPART</td>
<td></td>
<td>3.0</td>
<td>cutoff parameter for determining individual monomers.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TYPECHECK</td>
<td>TYPECHK</td>
<td>1</td>
<td>activates basis function type restrictions.</td>
</tr>
<tr>
<td>DELSHL</td>
<td>IDLSHL</td>
<td>1</td>
<td>determines if whole shells are to be deleted.</td>
</tr>
<tr>
<td>DELEIG</td>
<td>IDLEIG</td>
<td>1</td>
<td>determines how to select redundant functions.</td>
</tr>
<tr>
<td>DELCMin</td>
<td>CDELMIN</td>
<td>0.1</td>
<td>parameter for use with DELEIG=1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OPDOM</td>
<td>IOPDOM</td>
<td>5</td>
<td>determines how operator domains are determined for LCCSD</td>
</tr>
<tr>
<td>RMAXJ</td>
<td></td>
<td>8</td>
<td>distance criterion for J-operator list.</td>
</tr>
<tr>
<td>RMAXK</td>
<td></td>
<td>8</td>
<td>distance criterion for K-operator list.</td>
</tr>
<tr>
<td>RMAXL</td>
<td></td>
<td>15</td>
<td>distance criterion for L-operator list.</td>
</tr>
<tr>
<td>RMAXX</td>
<td></td>
<td>5</td>
<td>distance criterion for 3-ext integral list.</td>
</tr>
<tr>
<td>RDOMJ</td>
<td></td>
<td>0</td>
<td>distance criterion for K-operator domains.</td>
</tr>
<tr>
<td>RDOMK</td>
<td></td>
<td>8</td>
<td>distance criterion for J-operator domains.</td>
</tr>
<tr>
<td>IMAXJ</td>
<td></td>
<td>5</td>
<td>connectivity criterion for J-operator list.</td>
</tr>
<tr>
<td>IMAXK</td>
<td></td>
<td>5</td>
<td>connectivity criterion for K-operator list.</td>
</tr>
<tr>
<td>IMAXL</td>
<td></td>
<td>8</td>
<td>connectivity criterion for L-operator list.</td>
</tr>
<tr>
<td>IMAXX</td>
<td></td>
<td>3</td>
<td>connectivity criterion for 3-ext integral list.</td>
</tr>
<tr>
<td>IDOMJ</td>
<td></td>
<td>0</td>
<td>connectivity criterion for K-operator domains.</td>
</tr>
<tr>
<td>IDOMK</td>
<td></td>
<td>5</td>
<td>connectivity criterion for J-operator domains.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SKIPDIST</td>
<td>SKIPD</td>
<td>3</td>
<td>determines at which stage weak and distant pairs are eliminated</td>
</tr>
<tr>
<td>ASYDOM</td>
<td>JITERM</td>
<td>0</td>
<td>parameter for use of asymmetric domains</td>
</tr>
<tr>
<td>LOCSING</td>
<td>LOCSNG</td>
<td>0</td>
<td>determines virtual space used for singles</td>
</tr>
<tr>
<td>PIPKAO</td>
<td>LOCAO</td>
<td>0</td>
<td>activates AO localization criterion</td>
</tr>
<tr>
<td>NONORM</td>
<td></td>
<td>2</td>
<td>determines whether projected functions are normalized</td>
</tr>
<tr>
<td>LMP2ALGO</td>
<td>MP2ALGO</td>
<td>3</td>
<td>if nonzero, use low-order scaling method in LMP22 iterations</td>
</tr>
<tr>
<td>OLDDEF</td>
<td></td>
<td>0</td>
<td>allows to revert to older defaults</td>
</tr>
<tr>
<td>T1DISK</td>
<td></td>
<td>10</td>
<td>maximum disk space (in GByte) for T1 caching algorithm</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>THRBP</td>
<td></td>
<td>0.98</td>
<td>Threshold Boughton-Pulay method.</td>
</tr>
<tr>
<td>THRIP1P</td>
<td></td>
<td>1.d-12</td>
<td>Threshold for Pipek-Mezey localization.</td>
</tr>
<tr>
<td>THRORB</td>
<td></td>
<td>1.d-6</td>
<td>Threshold for eliminating projected orbitals with small norm.</td>
</tr>
<tr>
<td>THRLOC</td>
<td></td>
<td>1.d-6</td>
<td>Threshold for eliminating redundant projected orbitals.</td>
</tr>
<tr>
<td>THRCor</td>
<td></td>
<td>1.d-1</td>
<td>Threshold for eliminating projected core orbitals.</td>
</tr>
<tr>
<td>THRMP2</td>
<td></td>
<td>1.d-8</td>
<td>Threshold for neglecting small fock matrix elements in the LMP2 iteration.</td>
</tr>
</tbody>
</table>
32.4 Summary of directives

The same standard directives as in the canonical programs, e.g., \texttt{OCC}, \texttt{CLOSED}, \texttt{CORE}, \texttt{WF}, \texttt{ORBITAL} are also valid in the local methods. In addition, there are some directives which only apply to local calculations:

- **LOCAL** \texttt{=local} Invokes local methods and allows to specify the same options as on the command line.
- **MULTP** As \texttt{LOCAL}, but multipole approximations are used for distant pairs.
- **DOMAIN** Define domains manually (not recommended).
- **MERGEDOM** Allows to merge domains
- **REGION** Allows to select regions of a molecule to be treated at a certain level of theory.
- **ENEPART** Analysis of pair energies.
- **SAVE** Save domains and LCCSD amplitudes.
- **START** Restart with domains and LCCSD amplitudes from a previous calculation.

32.5 General Options

- **LOCAL**=\texttt{local} Determines which method is used:
  - \texttt{LOCAL=0}: Conventional (non-local) calculation.
  - \texttt{LOCAL=1}: Local method is simulated using canonical MOs. The local basis is used only at an intermediate stage to update the amplitudes in each iteration (only for testing).
  - \texttt{LOCAL=2}: Calculation is done in local basis, but without using local blocking (i.e. full matrices are used). This is the most expensive method and only for testing.
  - \texttt{LOCAL=3}: Fully local calculation (obsolete).
  - \texttt{LOCAL=4}: Fully local calculation (default). This is the fastest method for large molecules with many weak pairs and requires minimum memory.

- **LOCORB**=\texttt{option} If this option is given and \texttt{option}>0, the orbitals are localized using the Pipek-Mezey technique. If this option is not given or \texttt{option}=0 (default), the orbitals are localized unless localized orbitals are found in the orbital record (cf. \texttt{ORBITAL} directive and \texttt{LOCALI} command). In the latter case, the most recent localized orbitals are used. Setting \texttt{option}=-1 switches the localization off. If \texttt{option}>1 the localized orbitals are printed. Note: Boys localization can only be performed using the \texttt{LOCALI} command. The program will use the Boys orbitals if they are found in the orbital record and the \texttt{LOCORB} option is absent or \texttt{option} \leq 0.

- **LOC\_METHOD**=\texttt{method} This option allows to select between Pipek-Mezey (\texttt{method=}\texttt{PM}) or Natural Orbitals (\texttt{method=}\texttt{NBO}) localization. If Pipek-Mezey orbitals are requested, the default Boughton-Pulay domain selection will be used. When \texttt{method=}\texttt{NBO}, the domain selection will be based on the NPA charges, with \texttt{NPASEL=}0.03 (by default). In both cases, the domain selection parameter can be explicitly given (cf. \texttt{DOMSEL} and
NPASEL options) in order to use another domain criterion. If localized orbitals are found in the orbital record, but the type does not coincide, the orbitals are again localized according to method and used in the calculation.

SAVORB=record

Allows the localized and projected orbitals to be saved in record=name.ifil for later use (e.g. plotting). The two orbital sets are stored in the same dump record and can be restored at later stages using

ORBITAL,record,[TYPE=]LOCAL or ORBITAL,record,[TYPE=]PROJECTED, respectively.

DOMONLY=value

If value > 0 only domains are made, but no energy is computed. This can be used to check and save the domains for later use.

DSTMLT=level

Determines the expansion level of the multipole expansion of distant pairs (e.g. 1 means dipole approximation, 2 quadrupole approximation and so on). The default for MULTP is 3.

INTERACT

Automatically determine individual molecules in a calculation and set appropriate pair lists for computing interaction energies. See section 22.9.8 for more details.

Parameters for energy partitioning:

IEPART=value

enables/disables energy partitioning.

iepart=0: Energy partitioning is disabled.

iepart=1: Energy partitioning is enabled.

iepart=2: Energy partitioning is enabled. Additionally, a list of all pair energies and their components is printed.

EPART=cutoff

Cutoff parameter to determine individual monomers in a cluster (i.e. centre groups). Should be somewhat larger than the largest intramolecular bond length (given in a.u.).

Miscellaneous options:

SKIPDIST=skipdist

Test-parameter. Its value should only affect the efficiency but not influence the results.

skipdist=-1: Weak and distant pairs are set to zero after MP2 but are not eliminated from the pair list and not skipped in any loop.

skipdist=0: No pairs are deleted from pair list, but weak and distant pairs are skipped in the loops were appropriate.

skipdist=1: Very distant pairs are neglected from the beginning. Distant pairs are eliminated after MP2.

skipdist=2: As skipdist=1, but also weak pairs are eliminated after MP2.

skipdist=3: As skipdist=2, but distant pairs are eliminated from the operator list in case of LMP2 with multipole approximations for distant pairs. This is the default.

ASYDOM=jiterm

Experimental test parameter. Enables the use of asymmetric domains for distant pairs. The asymmetric domain approximation supplements the multipole approximation for distant pairs, as it suppresses the treatment of configurations for which no integrals can be computed by multipole expansion. This leads to computational savings and improved numerical stability.

jiterm=0: Disable asymmetric domains.

jiterm=-1: Enable asymmetric domains (default).
**jiterm=-2**: Enable a variation of the asymmetric domain formalism: Exchange operators will initially be projected to the asymmetric domain instead of simply packed.

**LOCING=locsing**

If `locsing.ne.0`, the single excitations use the full space, i.e., they are not treated locally. This is only works for `LOCAL=1`.

**MAXANG=imax**

The purpose of this experimental option is to reduce the basis set sensitivity of the Boughton-Pulay (BP) method for domain selection. Only basis functions with angular momentum up to `imax-1` are included when computing the overlap of the approximate and exact orbitals. For example, `MAXANG=2` means to omit all contributions of $d$, $f$ and higher angular momentum functions. To obtain reasonable domains, the value of `THRBPF` must often be reduced (to 0.97 or so). This option should only be used with care!

**PIPEKAO=option**

If `option ≥ 0`, the orbitals are localized my maximizing the coefficients of basis functions of a given type at a given atom. Normally, this is only useful to uniquely define degenerate orbitals in atoms. For instance, when this option is used to localize the orbitals for a dimer like $(Ar)_2$ at a very long distance, clean $s$, $p_x$, $p_y$, and $p_z$ atomic orbitals will be obtained. It is not recommended to use this option for molecular calculations!

**NONORM=value**

Determines if projected functions are normalized (not recommended).
- `value=-1`: projected orbitals are normalized before redundancy check.
- `value=0`: projected orbitals are normalized after redundancy check (default).
- `value=1`: projected orbitals are normalized in redundancy check, afterwards unnormalized.
- `value=2`: projected orbitals are never normalized (default in gradient calculations).

**LMP2ALGO=value**

If nonzero, use low-order scaling method in LMP2 iterations. Values can be 1, 2, or 3, and 3 is usually fastest if large basis sets are used.

**OLDDEF=value**

For compatibility with older versions: if nonzero, revert to old defaults. Options set before this may be overwritten.

**Thresholds:**

**THRPIL=thresh**

Threshold for Pipek-Mezey localization. The localization is assumed to be converged if all $2 \times 2$ rotation angles are smaller than `thresh`. The default is $1.d-12$. It can also be modified globally using `GTHRESH`, `LOCALI=thresh`.

**THRORB=thresh**

Threshold for eliminating functions from pair domains whose norm is smaller than `thresh` after projecting out the occupied space. The default is `throrb=1.d-6`.

**THRLOC=thresh**

Threshold for eliminating redundant basis functions from pair domains. For each eigenvalue of $\tilde{S} \leq \text{thresh}$ one function is deleted. The default is $1.d-6$. The method used for deleting functions depends on the parameters `IDLEIG` and `IBASO`.

**THRMP2=thresh**

Threshold for neglecting small fock matrix couplings in the LMP2 iterations (default 1.d-8). Specifying a larger threshold speeds up the iterations but may lead to small errors in the energy. In the initial iterations, a larger threshold is chosen automatically. It is gradually reduced to the specified final value during the iterations.
Threshold for deleting projected core orbitals. The functions are only deleted if their norm is smaller than \textit{thresh} (default 0.1)

The thresholds can also be specified on the \texttt{THRESH} directive.

\section*{32.6 Options for selection of domains}

The following sections describe the most important options which affect the domains.

\subsection*{32.6.1 Standard domains}

Standard domains are always determined first. They are used to define strong, close, weak, and distant pairs. More accurate results can be obtained with extended domains, as described in section \ref{sec:extended-domains}.

\texttt{THRBP=\textit{value}}

Threshold for selecting the atoms contributing to orbital domains using the method of Boughton and Pulay (BP). As many atoms as needed to fulfill the BP criterion are included in a domain. The order in which atoms are considered depends on the parameter \texttt{MAXBP}, see below. The default is \texttt{THRBP=0.98}. \texttt{THRBP=1.0} includes all atoms into each orbital domain, i.e., leads to full domains. If no pairs are neglected, this should yield the canonical MP2 energy.

The criterion is somewhat basis dependent. See section \ref{sec:recommended-values} for recommended values of this threshold.

\texttt{CHGMIN=\textit{value}}

determines the minimum allowed Mulliken (or Löwdin) charge for an atom (except H) in a domain, i.e., atoms with a smaller (absolute) charge are not included, even if the \texttt{THRBP} criterion is not fulfilled (default 0.01).

\texttt{CHGMINH=\textit{value}}
as \texttt{CHGMIN}, but used for H-atoms (default 0.03).

\texttt{CHGMAX=\textit{value}}

If the atomic charge is larger than this value, the atom is included, independent of any ranking.

\texttt{MAXBP=\textit{maxbp}}

If \texttt{maxbp=1}, the atoms are ranked according to their contribution to the Boughton-Pulay overlap. If \texttt{maxbp=0} (default), the atoms are ranked according to atomic charges. In both cases atoms with charges greater than \texttt{CHGMAX} are always included, and atoms with the same charges are added as groups.

\texttt{MULLIKEN=option}

determines the method to determine atomic charges. \texttt{MULLIKEN=0} (default): squares of diagonal elements of \(\mathbf{S}^2\) are used (Löwdin charges); \texttt{MULLIKEN=1}: Mulliken gross charges are used. The first choice is less basis set dependent and more reliable with diffuse basis sets.

\texttt{MERGEDOM=\textit{number}}

If \texttt{number} is greater than zero, all orbital domains containing \texttt{number} or more atoms in common are merged (\texttt{number=1} is treated as \texttt{number=2}, default 0). This is particularly useful for geometry optimizations of conjugated or aromatic systems like, e.g., benzene. In the latter case, \texttt{MERGEDOM=1} causes the generation of full \(\pi\)-domains, i.e., the domains for all three \(\pi\)-orbitals comprise all carbon basis functions. Note that the merged domains are generated after the above
print of orbital domains, and information about merged domains is printed separately. See section 32.9.7 for further discussion of geometry optimizations.

There are some other options which should normally not be modified:

**DELBAS=ibaso**
This parameter determines the method for eliminating redundant functions of pair domains.

- **ibaso=0**: The space of normalized eigenvectors of $\tilde{S}_{ij}$, which correspond to small eigenvalues, is eliminated (default). Any other value is not recommended and not further documented.

**DELCOR=nshell**
Activates elimination of basis functions corresponding to core orbitals. If **nshell=1**, only 1s-functions are eliminated from projected space. If **nshell=2** (default) 1s functions on first-row atoms, and 1s, 2s, and 2p-functions are eliminated on second-row atoms. Nothing is eliminated on H or He atoms. If effective core potentials are used, nothing is deleted at the corresponding atom. Also, functions are only deleted if the norm of the projected function is below **THRCOR** (default 0.1).

### 32.6.2 Extended domains

There are two alternative modes for domain extensions: either **distance criteria** REXT, REXTS, REXTC, or REXTW can be used. These are in Bohr and refer to the minimum distance between any atom in a standard orbital domain $[ij]$ and another atom. If an atom is found within the given distance, all PAOs at this atom are added to the domain $[ij]$. Alternatively, **connectivity criteria** IEXT, IEXTS, IEXTC, or IEXTW can be used. These refer to the number of bonds between any atom contained in the standard domain $[ij]$ and another atom. The advantage of distance criteria is that they select also atoms within the given radius which are not connected to the present domain by bonds. On the other hand, the connectivity criteria are independent of different bond lengths, e.g., for first and second-row atoms. Only one of the two possibilities can be used, i.e., they are mutually exclusive.

- **REXT=value** Distance criterion for extension of all pair domains.
- **REXTS=value** Distance criterion for extension of strong pair domains.
- **REXTC=value** Distance criterion for extension of strong and close pair domains.
- **REXTW=value** Distance criterion for extension of strong, close, and weak pair domains.
- **IEXT=value** Connectivity criterion for extension of all pair domains.
- **IEXTS=value** Connectivity criterion for extension of strong pair domains.
- **IEXTC=value** Connectivity criterion for extension of strong and close pair domains.
- **IEXTW=value** Connectivity criterion for extension of strong, close, and weak pair domains.

By default, domains are not extended, i.e., the default values of all parameters listed above are zero. Note that the pair classes are determined on the basis of the standard domains, and therefore domain extensions have no effect on the pair lists.
Also note that the computational effort increases with the fourth power of the domain sizes and can therefore increase quite dramatically when extending domains. This does not affect the linear scaling behaviour in the asymptotic limit.

### 32.6.3 Manually Defining orbital domains (\texttt{DOMAIN})

It is possible to define the domains “by hand”, using the \texttt{DOMAIN} directive:

\texttt{DOMAIN,orbital,atom1,atom2 ...}

where \texttt{orbital} has the form \texttt{i orb.isym}, e.g., \texttt{3.1} for the third orbital in symmetry 1, and \texttt{atomi} are the atomic labels as given in the Z-matrix geometry input, or, alternatively, the Z-matrix row numbers. All basis functions centred at the given atoms are included into the domain. For instance

\texttt{DOMAIN,3.1,C1,C2}

defines a domain for a bicentric bond between the carbon atoms \texttt{C1} and \texttt{C2}. The \texttt{DOMAIN} directive must be given after any \texttt{OCC}, \texttt{CLOSED}, or \texttt{CORE} directives. Note that the order of the localized orbitals depends on the localization procedure, and could even change as function of geometry, and therefore manual \texttt{DOMAIN} input should be used with great care. The domains of all orbitals which are not explicitly defined using \texttt{DOMAIN} directive are determined automatically as usual.

### 32.7 Options for selection of pair classes

There are two alternative modes for defining the pair classes: either distance criteria \texttt{RCLOSE}, \texttt{RWEAK}, \texttt{RDIST}, \texttt{RVDIST} can be used. These are in Bohr and refer for a given orbital pair \((i,j)\) to the minimum distance \(R^{(i,j)}\) between any atom in the standard orbital domains \([i]\) and any atom in the standard orbital domains \([j]\). Alternatively, the connectivity criteria \texttt{ICLOSE}, \texttt{IWEAK}, \texttt{IDIST}, \texttt{IVDIST} can be used. These refer to the minimum number of bonds between any atom contained in the standard domain \([i]\) and any atom contained in the standard domain \([j]\). The advantage of using connectivity criteria is the independence of the bond lengths, while the advantage of distance criteria (default) is that they are also effective in non-bonding situations. Only one of the two possibilities can be used, i.e., they are mutually exclusive. The use of distance criteria is the default. Using connectivity criteria for pair selection requires to set the option \texttt{USE_DIST=0}.

\texttt{USE_DIST} (default 1) If nonzero, use distance criteria, otherwise connectivity criteria.

\texttt{CHGMIN_PAIRS} Only atoms in the primary domains are considered for the pair classification if the atomic Löwdin charge is larger than \texttt{CHGMIN_PAIRS} (default value 0.2). This criterion was introduced in order to reduce the dependence of the pair selection on localization tails.

\texttt{RCLOSE} (default 1) Strong pairs are defined by \(0 \leq R^{(i,j)} < \text{RCLOSE}\). Close pairs are defined by \texttt{RCLOSE} \(\leq R^{(i,j)} < \text{RWEAK}\).

\texttt{RWEAK} (default 3) Weak pairs are defined by \texttt{RWEAK} \(\leq R^{(i,j)} < \text{RDIST}\).

\texttt{RDIST} (default 8) Distant pairs are defined by \texttt{RDIST} \(\leq R^{(i,j)} < \text{RVDIST}\).

\texttt{RVDIST} (default 15) Very distant pairs for which \(R^{(i,j)} \geq \text{RVDIST}\) are neglected.
(default 1) Strong pairs are separated by less than \( I_{\text{CLOSE}} \) bonds. Close orbital pairs are separated by at least \( I_{\text{CLOSE}} \) bonds but less than \( I_{\text{WEAK}} \) bonds.

(\text{default 2}) Weak orbital pairs are separated by at least \( I_{\text{WEAK}} \) bonds but less than \( I_{\text{DIST}} \) bonds.

(\text{default 5}) Distant orbital pairs are separated by at least \( I_{\text{DIST}} \) bonds but less than \( I_{\text{VDIST}} \) bonds.

(\text{default 8}) Very distant orbital pairs (neglected) are separated by at least \( I_{\text{VDIST}} \) bonds.

(\text{default 0}) If \( \text{KEEPCL} = 1 \), the LMP2 amplitudes of close pairs are included in the computation of the strong pair LCCSD residuals. If \( \text{KEEPCL} = 2 \) all close pairs are fully included in the LCCSD (this does not affect the triples list). This option is not yet implemented as efficiently as it could, and can therefore lead to a significant increase of the CPU time.

Setting \( R_{\text{CLOSE}} \) or \( R_{\text{WEAK}} \) to zero means that all pairs up to the corresponding class are treated as strong pairs (\( R_{\text{WEAK}} = 0 \) implies \( R_{\text{CLOSE}} = 0 \)). For instance, \( R_{\text{CLOSE}} = 0 \) means that strong and close pairs are fully included in the LCCSD (in this case \( \text{KEEPCL} = 1 \) has no effect). Note, however, that setting \( R_{\text{CLOSE}} = 0 \) increases the length of the triples list. Setting \( R_{\text{DIST}} = 0 \) means that all distant pairs are treated as weak pairs. This does not affect \( R_{\text{WEAK}} \) and \( R_{\text{CLOSE}} \) and has no effect unless multipole approximations are used for distant pairs. Setting \( R_{\text{VDIST}} = 0 \) means that no very distant pairs are neglected. Again, this has no effect on the other distance parameters.

### 32.8 Directives

#### 32.8.1 The LOCAL directive

The LOCAL directive can be used to specify options for local calculations. If this directive is inside the command block of a local calculation, the options are used only for the current calculation, and this is entirely equivalent as if they were specified on the command line. The LOCAL directive can also be given outside a command block, and in this case the options are used for all subsequent local correlation calculations in the same input.

Example:

```
DF-LMP2,THRBP=0.985
```

is equivalent to

```
(DF-LMP2
 LOCAL,THRBP=0.985)
```

In the following example the LOCAL directive is global and acts on all subsequent local calculations, i.e. both calculations will use THRBP=0.985

```
LOCAL,THRBP=0.985
DF-LMP2    !local MP2 calculation
OPTG       !geometry optimization using the DF-LMP2 energy
DF-LCCSD(T) !local coupled cluster at the optimized structure.
```
32.8.2 The \texttt{MULTP} directive

The \texttt{MULTP} directive turns on the multipole approximations for distant pairs, as described in Ref. [8]. Further options can be given as described above for the \texttt{LOCAL} directive.

\texttt{LOCAL, MULTP, options}

is equivalent to

\texttt{MULTP, options}

The level of the multipole approximation can be chosen using option \texttt{DSTMLT} (default 3) (1 means dipole approximation, 2 quadrupole approximation and so on).

The multipole approximation reduces the computational cost of LMP2 calculations for very large molecules, but leads to some additional errors, see Ref. [8]. It is normally not recommended to be used in coupled-cluster calculations and should never be used for computing intermolecular forces. It can also not be used in geometry optimizations or gradient calculations.

32.8.3 Saving the wavefunction (\texttt{SAVE})

The wavefunction can be saved for later restart using

\texttt{SAVE, record}

where \texttt{record} has the usual form, e.g., 4000.2 means record 4000 on file 2. If this directive is given, the domain information as well as the amplitudes are saved (for MPn the amplitudes are not saved). If just the domain information should be stored, the \texttt{SAVE} option on the \texttt{LOCAL} directive must be used (cf. section 32.3).

32.8.4 Restarting a calculation (\texttt{START})

Local CCSD, DCSD or QCISD calculations can be restarted using

\texttt{START, record}

The record given must have been saved in a previous local calculation using the \texttt{SAVE} directive (otherwise this directive is ignored). If the \texttt{START} directive is given, the domain information as well as the amplitudes of the previous calculation are used for restart. It is possible, for instance, to start a local CCSD calculation with the amplitudes previously saved for a local QCISD calculation (but of course it is not possible to use a record saved for a non-local CCSD or QCISD calculation). If it is intended only to use the domain information but not the amplitudes for a restart, the \texttt{START} option on the command line or \texttt{LOCAL} directive must be used (cf. section 32.3).

32.8.5 Correlating subsets of electrons (\texttt{REGION})

In large molecules, it may be sufficient to correlate only the electrons in the vicinity of an active group, and to treat the rest of the molecule at the SCF level. This approach can even be extended, different correlation levels may be used for different sections of the system. The \texttt{REGION} directive allows the specification of a subset of atoms:

\texttt{REGION, METHOD=method, [DEFAULT=default_method], [TYPE=INCLUSIVE|EXCLUSIVE], \texttt{atom1, atom2} . . .}
The orbitals located at these atoms will be treated at the level specified in \textit{method}. The remaining orbitals will be treated as defined in \textit{default}. If not given by the user, the latter option will be set to \textit{HF}.

The orbital selection can be done in two ways. If \textit{type} is set to \textit{INCLUSIVE}, any orbital containing one of the atoms in its domain centre list will be included. If \textit{type} is set to \textit{EXCLUSIVE}, the program will only add orbitals whose domains are exclusively covered by the given atoms. Any local correlation treatment can be given as \textit{method}, with the restriction that only \textit{MP2} and \textit{HF} can be used as \textit{default method}. Up to two \textit{REGION} directives may be included in a single calculation, ordered according to the correlation level (\textit{method}) specified for the region. The highest level region should be given last.

It is advisable to check the region orbital list and the orbital domains printed by the program. The use of regions may significantly reduce the computation time, and, provided the active atoms are sensibly chosen, may give still sufficiently accurate results for the \textit{active group}, e.g. bond lengths and bond angles.

\subsection*{32.8.6 Domain Merging (MERGEDOM)}

The restriction of the virtual space in local calculations may result in discontinuities for reaction path calculations due to changes of the geometry dependent domains. This may be avoided by the use of a \texttt{MERGEDOM} directive

\begin{verbatim}
MERGEDOM,[NEIGHBOUR=value],[CENTERS=[atom1, atom2...]], [RECORD=...],CHECK
\end{verbatim}

This directive provides augmented domains, which can be saved (using option or directive \texttt{SAVE}, see section \[32.8.3\]) for later use in reaction paths or in single point calculations (in cases where the orbital domain description is unbalanced). The use of the \textit{neighbour} option works in the same way as the local option \texttt{MERGEDOM}, with \textit{value} specifying the number of coincident centres. If the \textit{centres} option is used, an atom list should be given (enclosed by square brackets). The domains of all orbitals located exclusively at these atoms will be merged, and the resulting merged domains will be used for all these orbitals.

One may also give a \textit{record} number from a previously saved local calculation. The domain list contained in the record will be matched to the current one, and orbital domains augmented (merged) to include both sets. This domain definition should then be adequate for calculations on both points (and all those in between). This procedure can be repeated to include more geometries. In this way domains can be defined that are appropriate for a whole range of geometries (e.g. a reaction path), and if these domains are used in all calculations a strictly smooth potential energy surface is obtained.

\subsection*{32.8.7 Energy partitioning for molecular cluster calculations (ENEPART)}

The local character of occupied and virtual orbitals in the local correlation treatment also offers the appealing possibility to decompose the intermolecular interaction energy of molecular clusters into individual contributions of different excitation classes. This allows to distinguish between intramolecular-, dispersive-, and ionic components of the correlation contribution to the interaction energy (cf. M. Schütz, G. Rauhut and H.J. Werner, J. Phys. Chem. 102, 5197 (1998)). The energy partitioning algorithm is activated either by supplying the \texttt{ENEPART} directive:

\begin{verbatim}
ENEPART,[epart],[iepart]
\end{verbatim}

or by giving the parameters as options on the command line.
The `epart` parameter determines the cutoff distance for (intramolecular) bond lengths (in a.u., default 3 a.u.) and is used to automatically determine the individual monomer subunits of the cluster. The `iepart` parameter enables the energy partitioning, if set to a value larger than zero (default 1). Additionally, if `iepart` is set to 2, a list of all intermolecular pair energies and their components is printed.

The output section produced by the energy partitioning algorithm will look similar to the following example:

```
energy partitioning enabled!
centre groups formed for cutoff [au] = 3.00
 1 :O1 H11 H12
 2 :O2 H21 H22
energy partitioning relative to centre groups:
intramolecular correlation:  -0.43752663
  exchange dispersion :   0.00000037
  dispersion energy     :   0.00022425
  ionic contributions   :   0.0007637
```

The centre groups correspond to the individual monomers determined for `epart=3`. In the present example, two water monomers were found. The correlation energy is partitioned into the four components shown above. The exchange dispersion, dispersion and ionic components reflect directly the related intermolecular components of the complex, while the intramolecular correlation contribution to the interaction energy has to be determined by a super-molecular calculation, i.e. by subtracting the (two) corresponding monomer correlation energies from the intramolecular correlation component of the complex given in the output.

Alternatively, the following form can be used:

```
ENEPART,RMAX=[r1,r2,r3,...]
```

and the program will then print the energy contributions of all pairs in the ranges between the given distances (in bohr, enclosed by square brackets, e.g., `ENEPART,RMAX=[0,3,5,7,9,11]`). A second list in which the contributions are given as a function of the number of bonds between the pair domains will also be printed.

### 32.9 Doing it right

The local correlation methods in MOLPRO employ localized molecular orbitals (LMOs). Pipek-Mezey localization is recommended, but Boys localization is also possible. The virtual orbital space is spanned by non-orthogonal projected atomic orbitals (PAOs). The local character of this basis makes it possible to introduce two distinct approximations: first, excitations are restricted to `domains`, which are subspaces of (PAOs) that are spatially close to the orbitals from which the electrons are being excited. Secondly, the orbital pairs are classified according to their importance (based on distance or connectivity criteria), and only `strong pairs` are treated at the highest level (e.g. CCSD). The remaining `weak` and `distant` pairs are treated at the LMP2 level, and `very distant` pairs are neglected. These approximations lead to linear scaling of the computational resources as a function of the molecular size.

Naturally, such approximation can introduce some errors, and therefore the user has to be more careful than with standard black box methods. On the other hand, the low-order scaling makes it possible to treat much larger systems at high levels of theory than it was possible so far.

This section summarizes some important points to remember when performing local correlation calculations.
32.9.1 Basis sets

For numerical reasons, it is useful to eliminate projected core orbitals, since these may have a very small norm. By default, projected core orbitals are eliminated if their norm is smaller than 0.1 (this behaviour can be changed using the DELCOR and THRCOR options). For local calculations we recommend the use of generally contracted basis sets, e.g., the correlation consistent cc-pVnZ sets of Dunning and coworkers. For these basis sets the core basis functions are uniquely defined, and will always be eliminated if the defaults for DELCOR and THRCOR are used.

The correlation consistent basis sets are also recommended for all density fitting calculations, since optimized fitting basis sets are available for each basis.

32.9.2 Symmetry and Orientation

1. Turn off symmetry! Otherwise, you won’t get appropriately localized orbitals (local orbitals will tend to be symmetry equivalent instead of symmetry adapted). Symmetry can be used only if all atoms are symmetry unique. This allows the local treatment of planar molecules in \( C_\text{\textit{s}} \) symmetry. But note that neither the multipole program nor the density fitting programs support symmetry at all, so choose always \( C_1 \) symmetry for DF-calculations or with the MULTP option.

To turn off symmetry, specify NOSYM as the first line of your geometry input, e.g.

```plaintext
geometry={
  nosym
  O1
  H1,O1,roh
  H2,O1,roh,h1,hoh
}
```

Alternatively, add

```plaintext
SET,ZSYMEL=NOSYM
```

before the geometry block.

2. Use NOORIENT! We recommend to use the NOORIENT option in the geometry input, to avoid unintended rotations of the molecule when the geometry changes. This is particularly important for geometry optimizations and for domain restarts in calculations of interaction energies (see section 32.9.8).

32.9.3 Localization

By default, Pipek-Mezey localization is used and performed automatically in the beginning of a local correlation calculation. Thus

```plaintext
df-hf !Hartree-Fock with density fitting
df-lmp2 !LMP2 using the Pipek-Mezey LMOs
```

is equivalent to

```plaintext
df-hf !Hartree-Fock with density fitting
locali,pipek !Orbital localization using the Pipek-Mezey criterion
df-lmp2 !LMP2 using the Pipek-Mezey LMOs
```
Boys localization can be used as well, but in this case the localization must be done beforehand, e.g.

\begin{verbatim}
  df-hf !Hartree-Fock with density fitting
  locali,boys !Orbital localization using the Boys criterion
  df-lmp2 !LMP2 using the Boys LMOs
\end{verbatim}

Poor localization is sometimes an intrinsic problem, in particular for strongly conjugated systems or when diffuse basis sets are used. This is caused by localization tails due to the overlapping diffuse functions. The problem is particularly frequent in calculations of systems with short bonds, e.g., aromatic molecules. It can be avoided using directive

\texttt{PIPEK,DELETE=\textit{n}}

with \textit{n} = 1 or 2. This means that the contributions of the \textit{n} most diffuse basis functions of each angular momentum type are ignored in the localization. This often yields much better localized orbitals when diffuse basis sets are used. For aug-cc-pVTZ, \textit{n} = 2 has been found to work very well, while for aug-cc-pVDZ \textit{n}=1.

In rare cases it might also happen that the localization procedure does not converge. It is then possible to choose a second-order Newton-Raphson localization scheme, using the directive

\texttt{PIPEK,METHOD=2,[DELETE=\textit{n}]}\[
\texttt{PIPEK,METHOD=3,[DELETE=\textit{n}]}\[

which first performs a few standard Pipek-Mezey iterations and then invokes the second-order localization scheme. This then usually converges very quickly.

### 32.9.4 Orbital domains

The orbital domains are determined automatically using the procedure of Boughton and Pulay, J. Comput. Chem., 14, 736 (1993) and J. Chem. Phys. 104, 6286 (1996). For higher accuracy the domains can be extended, and in this way the canonical result can be systematically approached (cf. Ref. [1] and section 32.6.2). Details are described in section 32.6.

In most cases, the domain selection is uncritical for saturated molecules. Nevertheless, in particular for delocalized systems, it is recommended always to check the orbital domains, which are printed in the beginning of each local calculation. For such checking, the option \texttt{DOMONLY=1} can be used to stop the calculation after the domain generation. The orbital domains consist of all basis functions for a subset of atoms. These atoms are selected so that the domain spans the corresponding localized orbital with a preset accuracy (alterable with option \texttt{THRBP}). A typical domain output, here for water, looks like this:

\begin{verbatim}
Orbital domains
Orb.  Atom Charge Crit.
  2.1  O1  1.17  0.00
  3    H2  0.84  1.00
  3.1  O1  2.02  1.00
  4.1  O1  1.96  1.00
  5.1  O1  1.17  0.00
  2    H1  0.84  1.00
\end{verbatim}

This tells you that the domains for orbitals 2.1 and 5.1 comprise the basis functions of the oxygen atom and one hydrogen atom, while the domains for orbitals 3.1 and 4.1 consist...
of the basis function on oxygen only. The latter ones correspond to the oxygen lone pairs, the former to the two OH bonds, and so this is exactly what one would expect. For each domain of AOs, corresponding projected atomic orbitals (PAOs) are generated, which span subspaces of the virtual space and into which excitations are made. Options which affect the domain selection are described in section 32.6. Improper domains can result from poorly localized orbitals (see section 32.9.3 or a forgotten NOSYM directive. This does not only negatively affect performance and memory requirements, but can also lead to unexpected results.

The default for the selection criterion THRBP is 0.98. This works usually well for small basis sets like cc-pVDZ. For larger basis sets like cc-pVTZ we recommend to use a slightly larger value of 0.985 to ensure that enough atoms are included in each domain. For cc-pVQZ recommend THRBP=0.990 is recommended. In cases of doubt, compare the domains you get with a smaller basis (e.g., cc-pVDZ).

The choice of domains usually has only a weak effect on near-equilibrium properties like equilibrium geometries and harmonic vibrational frequencies. More critical are energy differences like reaction energies or barrier heights. In cases where the electronic structure strongly changes, e.g., when the number of double bonds changes, it is recommended to compare DF-LMP2 and DF-MP2 results before performing expensive LCCSD(T) calculations. More balanced results and smooth potentials can be obtained using the MERGEDOM directive, see section 32.8.6.

### 32.9.5 Freezing domains

In order to obtain smooth potential energy surfaces, domains must be frozen. The domain information can be stored using the SAVE option and recovered using the START option. Alternatively, the SAVE and START can be used, see section 32.8.3. In the latter case, also the CCSD amplitudes are saved/restarted. Freezing domains is particularly important in calculations of intermolecular interactions, see section 32.9.8. Domains that are appropriate for larger ranges of geometries, such as reaction pathways, can be generated using the MERGEDOM directive, section 32.8.6. The domains are automatically frozen in geometry optimizations and frequency calculations, see section 32.9.7. Note, however, that this automatic procedure only works if a single local calculation is involved in the optimization. In case of optimizations with counterpoise correction the domains for the complex and each monomer must be frozen individually in different records using the SAVE and START directives.

### 32.9.6 Pair Classes

The strong, close, weak and distant pairs are selected using distance or connectivity criteria as described in more detail in section 32.7. Strong pairs are treated by CCSD, all other pairs by LMP2. In triples calculations, all orbital triples \((ijk)\) are included for which \((ij), (ik), \text{and} (jk)\) are close pairs. In addition, one of these pairs is restricted to be strong. The triples energy depends on the strong and close pair amplitudes. The close pair amplitudes are taken from the LMP2 calculation. Thus, increasing the distance or connectivity criteria for close and weak pairs will lead to more accurate triples energies. While for near equilibrium properties like geometries and harmonic vibrational frequencies the default values are normally appropriate, larger distance criteria are sometimes needed when computing energy differences, in particular barrier heights. In cases of doubt, RWEAK should first be increased until convergence is reached, and then RCLOSE can be varied as well. Such tests can be performed with small basis sets like cc-pVDZ, and the optimized values then be used in the final calculations with large basis sets.
32.9.7 Gradients and frequency calculations

Geometry optimizations [15-17] and numerical frequency calculations [18-20] can be performed using analytical energy gradients [15-17] for local MP2. LMP2 geometry optimizations are particularly attractive for weakly bound systems, since virtually BSSE free structures are obtained (see section 32.9.8 and Refs. [21-23]). For reasons of efficiency it is strongly advisable to use the DF-LMP2 Gradient [17] for all geometry optimizations. Setting SCSGRD=1 on the DF-LMP2 command or DFIT directive activates the gradient with respect to Grimmes SCS scaled MP2 energy functional (see also section DFIT). Analytical energy gradients are not yet available for the multipole approximation of distant pairs, and therefore MULTP cannot be used in geometry optimizations or frequency calculations.

In geometry optimizations, the domains are allowed to vary in the initial optimization steps. When the stepsize drops below a certain threshold (default 0.01) the domains are automatically frozen. In numerical Hessian or frequency calculations the domains are also frozen. It is therefore not necessary to include SAVE and START options.

Particular care must be taken in optimizations of highly symmetric aromatic systems, like, e.g., benzene. In $D_6h$ symmetry, the localization of the $\pi$-orbitals is not unique, i.e., the localized orbitals can be rotated around the $C_6$ axis without changing the localization criterion. This redundancy is lost if the symmetry is slightly distorted, which can lead to sudden changes of the localized orbitals. If now the domains are kept fixed using the SAVE and START options, a large error in the energy might result. On the other hand, if the domains are not kept fixed, their size and quality might change during the optimization, again leading to spurious energy changes and divergence of the optimization.

The best way to avoid this problem is to use the MERGEDOM=1 option (see section 32.6). If this option is given, the domains for the $\pi$ orbitals will comprise the basis functions of all six carbon atoms, and the energy will be invariant with respect to unitary transformations among the three $\pi$ orbitals. Note that this problem does not occur if the symmetry of the aromatic system is lowered by a substituent.

Redundant orbital rotations can also lead to convergence difficulties of the Pipek-Mezey localization. This can be overcome by using

\[
\text{PIPEK, METHOD=2}
\]

or

\[
\text{PIPEK, METHOD=3}
\]

With METHOD=2, the second derivatives of the localization criterion with respect to the orbital rotations is computed and diagonalized, and rotations corresponding to zero eigenvalues are eliminated. This method converges quadratically. With METHOD=3 first a few iterations with the standard Pipek-Mezey method are performed, then the second-order method is invoked. This appears to be the most robust and accurate localization method.

Finally, we note that the LMP2 gradients are quite sensitive to the accuracy of the SCF convergence (as is also the case for MP2). If very accurate structures are required, or if numerical frequencies are computed from the gradients, the default SCF accuracy might be insufficient. We recommend in such cases to add an ACCU,14 directive (possibly even ACCU,16) after the HF command. Indicative of insufficient SCF accuracy are small positive energy changes near the end of the geometry optimization.
32.9.8 Intermolecular interactions

Local methods are particularly useful for the calculation of weak intermolecular interactions since the basis set superposition error (BSSE) is largely reduced [1,13,14] and counterpoise corrections are usually not necessary (provided the BSSE of the underlying Hartree-Fock is small). However, one must be careful to define the domains properly and to include all intermolecular pairs at the highest computational level. A convenient way to define appropriate domains and pair lists is to use the option INTERACT=1. If this option is given, individual molecules are identified automatically and all intermolecular pairs are automatically treated as strong pairs and included in the LCCSD. Similarly, appropriate triples lists are generated for LCCSD(T) calculations. It is required that all orbital domains are located on individual molecules. Note however that the inclusion of the intermolecular pairs strongly increases the number of strong pairs and triples, and therefore high-level calculations can become very expensive.

For calculations of interaction potentials of weakly interacting systems, the domains of the sub-systems should be determined at a very large distance and saved using the SAVE=record option on the LOCAL or MULTP directive, or the SAVE directive (see section 32.8.3). If the asymptotic energy is not needed it is sufficient to do this initial calculation using option DOMONLY=1). These domains should then be reused in the subsequent calculations at all other intermolecular distances by using the START=record option or the START directive (see section 32.8.4). Only in this way the basis set superposition error is minimized and normally negligible (of course, this does not affect the BSSE for the SCF, and therefore the basis set should be sufficiently large to make the SCF BSSE negligible).

Usually, diffuse basis functions are important for obtaining accurate intermolecular interactions. When diffuse basis sets are used, it may happen that the Pipek-Mezey localization does not yield well localized orbitals. This problem can in most cases be overcome by using the directive

PIPEK,DELETE=n

as described in section 32.9.3

A final warning concerns local density fitting (see sections 32.10 and 15): local fitting must not be used in counterpoise calculations, since no fitting functions would be present on the dummy atoms and this can lead to large errors.

For examples and discussions of these aspects see Refs. [21-23]

32.9.9 Efficient and accurate treatment of close pairs in local CCSD(T)

As discussed above, efficient LCCSD(T) calculations employ a hierarchical treatment of the LMO pairs, which are distinguished into the pair classes strong, close, weak, and very distant. Only the strong pairs are actually treated at the full coupled cluster level, while for close and weak pairs only LMP2 is used (and very distant pairs are omitted altogether). Consequently, intermolecular pairs in bigger molecules or clusters, which are usually not strong, are only treated at the LMP2 level, which is often poor (since van der Waals interactions are only captured at the lowest level of perturbation theory) and compromises the otherwise high accuracy of coupled cluster like LCCSD(T). By setting the keyword how_treatclswk on the local card appropriately, it is possible to treat the close pairs at a higher level than LMP2, i.e.,

how_treatclswk=1 local MP2
how_treatclswk=2 direct local RPA
how_treatclswk=3 local ring-CCD3
how_treatclswk=4  local ring-CCD
how_treatclswk=5  local CCD[S]-R^{-6}

These methods for close pairs are discussed in detail in Refs. [24-25]. The philosophy is to include all diagrams with \( R^{-6} \) decay behavior up to a certain order of perturbation theory. E.g., LringCCD3 denotes local ring CCD up to third-order diagrams, and LCCD[S]-R^{-6} is full local CCD with a perturbative singles correction, yet omitting all diagrams with decay behavior quicker than \( R^{-6} \) (like ladder diagrams). As shown in Ref. [25], the LCCD[S]-R^{-6} provides excellent intermolecular interaction energies, virtually indistinguishable from LCCSD, at a much lower cost (mainly due to the omission of ladders). We therefore recommend to use either LringCCD3 or LCCD[S]-R^{-6}. Note that it is essential to couple strong and close pairs in such calculations, i.e., to set keepcls=1 (vide supra). As an example, the input segment to set all intermolecular pairs to close and treat them at the level of LCCD[S]-R^{-6} is

local,keepcls=1,interact=1,interpair=1,how_treatclswk=5

See also the input example h2o_dimer_lccsdhybrids.com.

### 32.10 Density-fitted LMP2 (DF-LMP2), LDCSD (DF-LDCSD), and coupled cluster (DF-LCCSD(T0))

Density-fitting LMP2, LDCSD and LCCSD calculations can be performed by adding the prefix DF- to the command name. The input is as follows:

DF-LMP2,[\textit{options}]
DF-LCCSD(T),[\textit{options}]

Options for density fitting can be mixed with any options for LOCAL. Options for density fitting can also be given on a DFIT directive (see section [15]).

The most important options for density fitting in local methods are

\textbf{BASIS\_MP2=\textit{string}}

Fitting basis set used in LMP2 and in LCCSD for integrals with up to 2 external orbitals. If a correlation consistent basis set is used (e.g. cc-pVTZ) the corresponding fitting basis for MP2 us used by default (cc-pVTZ/MP2FIT). Otherwise the fitting basis set must be defined in a preceding basis block (see section [11]).

\textbf{BASIS\_CCSD=\textit{string}}

Fitting basis set used in LCCSD for integrals over 3- and 4-external orbitals. The default is BASIS\_MP2 and this is usually sufficient. However, the accurate approximation of 4-external integrals in LCCSD requires larger fitting basis sets than LMP2. Therefore, in order to minimize fitting errors, it is recommended to use the next larger fitting basis, e.g., BASIS\_CCSD=VQZ for orbital basis VTZ.

\textbf{LOCFIT=value:}

If LOCFIT=1 local fitting is enabled. This is necessary to achieve linear scaling in DF-LMP2 (see Refs. [11-14]). The errors introduced by local fitting are usually very small, but there are some exceptions. For instance, LOCFIT=1 must not be used in counterpoise calculations, see section [32.9.8]. Note that for small molecules LOCFIT=1 can be more expensive than LOCFIT=0.

For further details and options for density fitting see section [15].
33 PNO-LMP2 and PNO-LMP2-F12

In this section local correlation methods that use pair natural orbitals (PNOs) are described. This program is entirely distinct from the older PAO-based methods that were described in the previous section. It is designed for parallel execution, and disk I/O is avoided as much as possible. This means that more memory is required than in other programs. However, the data are distributed over all computing cores, and the memory requirement per core is inversely linear in the number of cores used. Therefore, it is normally not recommended to use these programs on a single core. Depending on the molecular size, parallelization works well up to 100-200 cores using multiple nodes, provided a fast network (Infiniband or similar) is available.

Appropriate default values are set which normally yield results that are close to the canonical ones. In particular, sub-kJ/mol accuracy of relative energies is usually achieved with PNO-LMP2-F12 (relative to MP2-F12).

Currently the PNO program of MOLPRO can perform closed-shell PNO-LMP2 and PNO-LMP2-F12 calculations. We strongly recommend that the user reads the following references for the concepts and local approximations used in the PNO program.


The point group symmetry support of the PNO-LMP2 method is described in


More references on the correlation methods, including some reviews suitable for an introduction, are listed in Sec. 32.

The PNO program is currently under active development. More features, including a PNO-LCCSD method, and performance improvements, will be available in future releases.

33.1 Getting started

The program is invoked using

```
PNO-LMP2, options
```

or, for the explicitly correlated variants

```
PNO-LMP2-F12, options
```

Available options are described in later sections of this manual. An example input file can be found in examples/h2odimer_pno_lmp2_f12.com.
33.2 Fundamental options

In this section we describe the parameters most relevant to the accuracy and performance of the PNO program. We note that our team has carefully selected the default options through benchmark calculations, and the options only need to be modified for special cases.

Options for PAO/OSV/PNO generation:

- **THRNPA=value** Charge threshold for selection of primary PAO domains when using IBOs or NBOs (default 0.2).
- **IEXT=value** Domain extension using connectivity. value corresponds to the number of bonds by which the primary domains are extended. The default is IEXT=2.
- **REXT=value** Domain extension using distance. value is the radius in \( a_0 \) from any atom in the primary domain. IEXT and REXT can be combined. If both are given all atoms are included that are selected by one or the other criterion. The default is REXT=5.
- **THROSV=threshold** OSV selection threshold based on occupation numbers (default 1.d-9).
- **THRPNO=threshold** PNO selection threshold based on the energy criterion (default 0.998). If thresh is smaller than 0.1 it refers to the natural occupation numbers, otherwise it refers to the fraction of OSV pair energies to be recovered. It is also possible to specify 3 values for strong+close, weak, and distant pairs as THRPNO=[thrstrong, thrweak, thrdist].
- **THRPNO_OCC=threshold** PNO selection threshold based on occupation numbers (default 1.d-8). If THRPNO is also given, a PNO is selected only when both criteria are fulfilled.

Options for F12 calculations:

- **BB_F12** (logical). If true use the local and parallel F12 energy routines (default .true.). Otherwise F12 routines relying on hard disk I/O (and therefore shall be run on a single computer node) will be used. This option shall only be set false if problems (such as insufficient memory available) arise from the parallel F12 routines.
- **BB_F12_PNO=value** If BB_F12_PNO=0, both OSV- and PNO-LMP2-F12 energy will be computed; If BB_F12_PNO=1, only PNO-LMP2-F12 energy will be computed; If BB_F12_PNO=2, only OSV-LMP2-F12 correction will be computed and the resulting energy will be set to PNO-LMP2 energy plus OSV-LMP2-F12 correction (default 1).
- **THRF12=threshold** LMP2 pair energy threshold for selecting pairs for which F12 corrections are computed. The default value is 1.d-4.

Options for domain approximations and orbital screening:

- **LOCFIT=0** Disables local fitting (default is LOCFIT=1).
- **IDFDOM=value** Fitting domain extension using connectivity. The default is 3.
- **RDFDOM=value** Fitting domain extension using distances in \( a_0 \). The default is 7. If both IDFDOM and RDFDOM are given, the DF functions at a center will be included when either criterion is fulfilled.
LOCRI=0 Disables local RI (default is LOCRI=1).

IRIDOM=value RI domain extension using connectivity. The default is 3.

RRIDOM=value RI domain extension using distances in \(a_0\). The default is 7. If both IRIDOM and RRIDOM are given, the RI basis functions at a center will be included when either criterion is fulfilled.

FITLMO=threshold In the PNO program LMOs are truncated if the square sum of the coefficients at one center is smaller than \(threshold\) (default 1.d-6). The remaining LMO coefficients are fitted to the original LMO.

FITPAO=threshold In the PNO program PAOs at one center are truncated when none of the PAOs at the center has a square sum of coefficients greater than \(threshold\) (default 1.d-6). The remaining PAO coefficients are fitted to the original PAOs.

BB_F12_THRVAL=value The MP2 pair energy threshold in determining the LMO domains \([ij]_{\text{LMO}}\) used in the F12 strong orthogonality projector (default 1.d-4). This option only applies to the selection of the valence occupied orbitals in the LMO domains.

ICOREDOM_F12=value, RICOREDOM_F12=value The connectivity and distance (in \(a_0\)) criteria in determining the LMO domains \([ij]_{\text{LMO}}\) used in the F12 strong orthogonality projector (defaults are 2 and 5.0, respectively). This option only applies to the selection of the core orbitals in the LMO domains.

Options for symmetry:

LOCSYM=1 Use point group symmetry (default is LOCSYM=0). Note that the PNO-LMP2-F12 program does not support point group symmetry.

### 33.3 Advanced options

In this section we list some advanced options to the PNO program. These options exist for technical or historical reasons and we do not recommend modifying the default values in general.

The following options are available for the orbital localization:

LOC_METHOD=method Localization method. \(method\) can be IBO (intrinsic bond orbitals, default), PM (Pipek-Mezey), or NBO (natural bond orbitals). IBO is strongly recommended, as it is most efficient and stable. The PNO-LMP2-F12 method only supports IBO presently.

IBTYPE=value Projector type for generation of intrinsic atomic orbitals. \(value\) can be 1 or 2 (default).

IBOEXP=value Exponent used in the PM-like localization functional. \(value\) can be 2 or 4 (default).

Options for PAO domain selection:

THRBP=value Boughton-Pulay completeness criterion for selection of primary PAO domains when using PM.

Options for OSV generation:
OSV_AMPL=PAO|CAN|OPT Amplitudes to used to generate OSVs. PAO (default) means to use semi-canonical amplitudes in the PAO domains; CAN means semi-canonical in the full virtual space; OPT means fully optimized LMP2 amplitudes in the full virtual space.

Options for PNO generation:

PNO_AMPL=OSV|OSV(OPT)|PAO|PAO(OPT) Amplitudes to used to generate PNOs. OSV (default) means to use semi-canonical (non-iterative) OSV amplitudes; PAO means semi-canonical (non-iterative) PAO amplitudes; if (OPT) is appended the amplitudes are iteratively optimized (can be expensive with OSV(OPT) and very expensive with PAO(OPT)).

PNO_DIAG (logical). If true, use PNO domain selection criterion also for diagonal pairs. Otherwise OSV domains are used for diagonal pairs. If PNO_DIAG=true the threshold THROSV only affects the distant pair multipole treatment.

The PNO program devides basis functions to blocks for integral screening. The following options are available for defining the block sizes. A smaller block size encourages more efficient integral screening and improves the parallel efficient, while a larger block size improves the performance of matrix operations and reduces the bookkeeping cost.

BB_BLOCKS_AO=value Target blocking size in the AO basis (default 32).
BB_BLOCKS_DF_F12=value Target blocking size in the DF basis for the F12 calculations (default 32). The option does not affect PNO-LMP2 calculations.
BB_BLOCKS_RI=value Target blocking size in the RI basis for the F12 calculations (default 128).

In addition, the following options control the integral screening thresholds:

BB_THRESH=value Block screening threshold (default 1.d-5).
BB_RADIUS=value Block screening radius (default 4).

The following options controls some technical details of the PNO program.

BLOCKING (logical) If true use the blocked density fitting routines when possible (default).
BB_F12_CACHE=value Whether a local cache is used in combination with globalarrays (GA). Default value is 1, i.e., loading from GA is buffered.

33.4 Technical issues

For large molecules, we recommend using the density-fitted Hartree–Fock program (DF–HF) for the proceeding Hartree–Fock calculation. Presently the program is not well parallelized over multiple computer nodes. We therefore suggest running DF–HF calculations separately and using the save option to dump the molecular orbitals to disk for the electron correlation calculations. A parallel local density-fitted Hartree–Fock program is being developed and will be available in the near future.
The PNO program stores large data structure in distributed memory through the globalarrays toolkit. The toolkit has memory allocation mechanisms independent of Molpro. When running the PNO program, one should not allocate all available physical memory to Molpro using the memory command in an input file, so that the globalarrays toolkit could allocate sufficient memory when needed. In some cases it is helpful to pass the \(-G\) [ga_mem] option in the molpro command line. This allows the allocation of ga_mem megawords of memory for globalarrays at the beginning of execution. Without doing this, globalarrays may crash when the distributed data structure gets large, most likely due to an upstream bug. The total amount of memory used by molpro and globalarrays on a node, in MB, can be estimated from \(n_{core}(8M_{molpro} + 1000) + 8M_{GA}/n_{node}\), where \(n_{core}\) is the number of cores per node, \(n_{node}\) is the number of nodes, \(M_{molpro}\) is the memory set by the memory command in the input file, and \(M_{GA}\) is the memory set with the \(-G\) option. The total amount of memory used shall not exceed available memory on a node, otherwise runtime errors due to insufficient memory are likely.

## 34 LOCAL METHODS FOR EXCITED STATES

### 34.1 Local CC2 and ADC(2)

Bibliography:

**General local CC2 for excited states:**


**Laplace transformed local CC2 for excited states:**


**Analytical nuclear gradients for ground and excited states:**


**Previous work on local methods for excited states (LEOM-CCSD):**


All publications resulting from use of this program must acknowledge Ref. [3] (calculations of singlet states) and [5] (calculations of triplet states and properties).

The command `LT-DF-LCC2` calls the Laplace transformed LCC2 program, and `LT-DF-LADC(2)` calls LADC(2). The excited states of interest should be specified on the EOM card.
34 LOCAL METHODS FOR EXCITED STATES

34.2 Options for EOM

see also section 25.1.

In the case of LT-DF-LCC2/ADC(2) multistate calculations are possible, and it is recommended to calculate more states as needed.

The parameters on the EOM card:

EOM,-n.1,key1=value1,key2=value2,...

where \( n.1 \) is the last state of interest, e.g., with EOM,-5.1 the four lowest excited states will be calculated. The following keywords \( \text{key} \) are possible:

**SINGLET=ising** If set to 1, singlet states will be calculated (default).

**TRIPLET=trip** If set to 1, triplet states will be calculated (not implemented for ADC(2)).

**EXFILE=record.ifil** Record for converged CIS eigenvectors (default 6100.2).

**SAVE=record.ifil** Record for save of restart information.

**SAVET=record.ifil** Record for restart information for triplet states (if calculated together with singlet states).

**START=record.ifil** Record for restart of previous calculation.

**STARTT=record.ifil** Record for restart of previous calculation (if calculated together with singlet states).

**NSRCH4ST=nest** In the first \( nst \) iterations in the Davidson diagonalisation the excited state domains are determined for each basis vector in the Davidson subspace (“search for states”) (default 7).

**THRLCH=thrlnch** threshold for the Davidson procedure. If smaller than zero, the Davidson procedure is skipped and DIIS is started directly instead (possible only for restart, SAVE and START have to be identical).

**THRLCD=thrlcd** threshold for DIIS.

**ADC2=adc2** if = 1, do ADC(2) calculation instead of CC2.

**LTGS=ltgs** if = 1, use LT-DF-LMP2 for the ground state.

Default local approximations are defined according to procedure described in Ref. [3] (Laplace domains).

**INTFRAC=fracint** Rough criterion for specifying eom-domains from laplace-transformed integrals (default 0.8).

**INTEXC=excint** Criterion for specifying important orbitals from laplace-transformed integrals (default 0.999).

**REALFRAC=fracreal** Exact criterion for specifying eom-domains from laplace-transformed integrals (default 0.98).

**FULLFRAC=fracfull** Check for all orbital domains (complete sum over all orbitals) (default 0.95).

To switch to local approximations calculated according to Ref. [9] (Boughton-Pulay procedure for excited states), set INTFRAC to zero.

Occupied orbital pair lists are calculated from important orbitals (Refs. [1,5]).
EWEAKPAIR = ewpair  Distance criterion for excited state orbital pairs definition (default 5).

ALLSTRONG = allstr  Different possibilities for excited state orbital pairs:
  0: \([ij] \leq \text{ewpair}, [im] \leq \text{ewpair}, [mn] \leq \text{ewpair}\);
  1: \(\forall [ij], [im], [mn] \leq \text{ewpair}\);
  2: \(\forall [ij], [im] \leq \text{ewpair}, [mn] \leq \text{ewpair}\) (default);

where \(i, j\) are important orbitals and \(m, n\) non-important. More detailed see Ref. [1].

One can try to improve the convergence of iterative procedures by changing following parameters

PRECOND = prec  Type of preconditioner in LT-DF-LCC2/ADC(2) and DF-CIS:
  0: canonical orbital energies;
  3: solving linear equations including diagonal part of \((H - F)^{\text{CIS}}\) with MINRES (default).

HSCAL = hscl  Scaling factor for diagonal part of \((H - F)^{\text{CIS}}\) matrix in the case of linear equations preconditioner (default 0.7).

Properties are also activated on the EOM card:

PROPES = prop  States for which properties (dipole moments) should be calculated, e.g., PROPES = -3.1 + 5.1 - 8.1 + 15.1

TRANES = tran  States for which transition moments should be calculated, syntax like for properties. Is not implemented for ADC(2) and for triplet states.

DENSAVE = rec. ifil  Record, where densities calculated for states prop can be saved (for printing, see 34.4).

Note that ADC(2) transition moments require second-order ground-state singles and doubles amplitudes [see e.g. G. Wälz, D. Kats, D. Usyvat, T. Korona and M. Schütz, Phys. Rev. A 86, 052519 (2012); ADC(2) is equivalent to TD-UCC[2]-H]. This is done by carrying out a partial local MP4 calculation, with second-order doubles restricted to strong pairs. For ADC(2) excitation energies or first-order properties just the first-order LMP2 amplitudes are required. Strong, close, and weak pairs actually all enter the subsequent excited state calculations.

By default, orbital un-relaxed properties are computed. In order to calculate also orbital relaxed properties the option ORBREL on the LOCAL card should be set to 1, i.e.,

LOCAL, ORBREL = 1

This also applies to the calculation of nuclear gradients. Options concerning nuclear gradients, which are also activated on the EOM card, are

GSONLY = 0 or 1  1: only ground state gradient is calculated

GRADSTATE = gradstate  Excited state for which the gradient is to be calculated, e.g., GRADSTATE = 2.1;
  must be combined with GSONLY = 0

GRADDIIS = 0 or 1  0: DIIS after Davidson diagonalization is switched off for all states except gradstate

NOFOLLOWGRAD = 0 or 1  0: tries to follow a state in a geometry optimization after crossing on the basis of the overlap with eigenvector of previous geometry; 1: calculate gradient of state number gradstate regardless of crossing
ONLYTOTLM = 0 or 1: only total, rather than ground- and excited state Lagrange multipliers for orbital variations are computed. Hence, only one set of CPL and CPHF equations need to be solved rather than two. However, orbital relaxed properties are then not available.

34.3 Parameters on LAPLACE card

NPOINTS Number of quadrature points (default (for CC2) 3).

NPOINTS_CC2S Number of quadrature points in CC2 in "search for states" (default 1).

DISTRF Type of distribution function in functional for determination of Laplace points:
0: integral with $f_x = 1$;
4: sum of distributions $f_x$ (default).

NULLPOINT If larger than zero, use also a Laplace-point with $t=0$. In case of CC2 is always zero.

34.4 Print options

Setting GPRINT,CIVECTOR=1 prints the ten largest canonical contributions from singles vectors in each iteration.

For EOMPRINT card:

LOCEOM $\geq$ 0: print eom domain informations

POPUL $\leq$ 0: dont print population analysis

The densities saved with DENS SAVE can be written into a cube file. Corresponding commands in CUBE module are

DENSITY,rec.ifil,cc2 Creates a cube file from the ground state density saved on record rec.ifil.

DENSITY,rec.ifil,full,state=st. 1 Creates a cube file from the excited state density of state st. 1.

DENSITY,rec.ifil,diff,state=st. 1 Creates a cube file from the difference density (full - cc2) for state st. 1.

34.5 Examples

Example 1:

***,The five lowest singlet excited states of water molecule
memory,64,m
gdirect
symmetry,nosym;orient,noorient
geometry={
o ,, 0.000, 0.000, 0.119
h1,, 1.423, 0.000, -0.947
h2,, -1.423, 0.000, -0.947 }
basis={
default,vdz
set,mp2fit
default,vdz/mp2fit
set,jkfit
The excitation energies (in eV) stand after the calculation in array $\text{OMEGAF}_S$ for singlet states and in $\text{OMEGAF}_T$ for triplet states.

Example 2:

***, The five lowest triplet excited states and properties
memory,64,m
gdirect
symmetry, nosym; orient, noorient
geometry={
o ,, 0.000, 0.000, 0.119
h1,, 1.423, 0.000, -0.947
h2,, -1.423, 0.000, -0.947 }
basis={
default, vdz
set, mp2fit
default, vdz/mp2fit
set, jkfit
default, vdz/jkfit }

hf
{lt-df-lcc2 }  !ground state CC2
!five lowest triplet states, dipole moments for four lowest, density saved:
eom, -6.1, triplet=1, singlet=0, propes=-5.1, densave=5000.2
eomprint, popul=-1, loceom=-1 }  !minimize the output
!ground state density, file h2o0_density.cube:
{cube, h2o0,, 80, 80, 80
density, 5000.2, cc2 }
!difference excited state density, file h2o1_density.cube:
{cube, h2o1,, 80, 80, 80
density, 5000.2, diff, state=2.1 }

In order to set up an input for a geometry optimization of an excited state we recommend to use the input examples furan_opt_ltdflcc2lr.com (for local CC2) and furan_opt_ltdflucc2lr.com (for local ADC(2) aka TD-LUCC[2]-H) as templates. Provided that second-order methods like CC2 or ADC(2) are appropriate for the state to be optimized, it is recommended to use local ADC(2) rather than local CC2, since the former is considerably faster. Even if a local CC2 optimized geometry of an excited state is required, it is wise to preoptimize with local ADC(2). For a comparison of the performance of these two methods in geometry optimizations we refer to Ref. [8].

35  EXPLICITLY CORRELATED METHODS

Explicitly correlated calculations provide a dramatic improvement of the basis set convergence of MP2, CCSD, CASPT2, and MRCI correlation energies. Such calculations can be performed using the commands of the form

$command, options$

where $command$ can be one of the following:

MP2-F12  Closed-shell canonical MP2-F12. By default, the fixed amplitude ansatz ($\text{FIX}$, see below) is used, but other ansätze are also possible. The F12-corrections is com-
computed using density fitting, and then added to the MP2 correlation energy obtained without density fitting.

DF-MP2-F12 As MP2-F12, but the DF-MP2 correlation energy is used. This is less expensive than MP2-F12.

DF-LMP2-F12 Closed-shell DF-MP2-F12 with localized orbitals. Any method and ansatz as described in J. Chem. Phys. 126, 164102 (2007) can be used (cf. sections 35.2, 35.7).

DF-RMP2-F12 Spin-restricted open-shell DF-RMP2-F12 using ansatz 3C. Any method as described in J. Chem. Phys. 128, 154103 (2008) can be used (cf. sections 35.2, 35.7).

CCSD-F12 Closed-shell CCSD-F12 approximations as described in J. Chem. Phys. 127, 221106 (2007). By default, the fixed amplitude ansatz is used and the CCSD-F12A and CCSD-F12B energies are computed. Optionally, the command can be appended by A or B, and then only the corresponding energy is computed. For more details see section 35.10.

CCSD-F12c Closed-shell CCSD(F12*) approximation as proposed by Hättig, Tew and Köhn. In Molpro this is denoted f12c. As compared to CCSD-F12a/b it requires additional computational effort. Since in some parts the implementation is brute-force without paging algorithms, large memory may be required. In most cases there is no gain in accuracy as compared to f12b and therefore the use of this method is normally not recommended. Currently CCSD-F12c is not available for open-shell cases.

CCSD(T)-F12 Same as CCSD-F12, but perturbative triples are added.

CCSD(T)-F12c Same as CCSD-F12c, but perturbative triples are added.

UCCSD-F12 Open-shell unrestricted UCCSD-F12 approximations as described by G. Knizia, T. B. Adler, and H.-J. Werner, J. Chem. Phys. 130, 054104 (2009). Restricted open-shell Hartree-Fock (RHF) orbitals are used. Optionally, the command can be appended by A or B, and then only the corresponding energy is computed. For more details see section 35.10.

UCCSD(T)-F12 Same as UCCSD-F12, but perturbative triples are added.

RCCSD(T)-F12 Similar to UCCSD(T)-F12, but the partially spin-adapted scheme is used.

DCSD-F12 Closed-shell CCSD-F12 approximations applied to DCSD method, see CCSD-F12 for more details.

UDCSD-F12 Open-shell unrestricted CCSD-F12 approximations applied to DCSD method, see UCCSD-F12 for more details.

RDCSD-F12 Open-shell partially spin-adapted CCSD-F12 approximations applied to DCSD method.


Published work arising from these methods should cite the following:

(for the density fitting approximations in linear R12 methods)

(for the frozen geminal expansions)


In the following, we briefly summarize the ansätze and approximations that can be used in single-reference treatments. For more details and further references to related work of other authors see H.-J. Werner, T. B. Adler, and F. R. Manby, General orbital invarient MP2-F12 theory, J. Chem. Phys. 126, 164102 (2007) (in the following denoted I). More information about MRCI-F12 calculations are given in section 20.8

### 35.1 Reference functions

The MP2-F12, CCSD-F12, and UCCSD-F12 methods must use conventional (non-density fitted) spin-restricted Hartree-Fock reference functions (HF or RHF). DF-HF cannot be used for these methods. This restriction is necessary to ensure that the Fock matrix is diagonal and consistent with the integrals used in these methods. For DF-MP2-F12, DF-LMP2-F12, and
DF-RMP2-F12 either HF or DF-HF reference functions can be used. Currently, only finite dipole fields can be applied, other perturbations are not yet supported. ECPs can be used, but this is still experimental and not extensively benchmarked. The Douglas-Kroll-Hess or eXact-2-Component Hamiltonians cannot currently be used in combination with F12 methods.

### 35.2 Wave function Ansätze

The so called "ansatz" determines the definition of the explicitly correlated wave function. This is to be distinguished from the various approximations that can be used to approximate the Hamiltonian matrix elements. Generally, we use ansatz 3 (cf. I), for which the projector has the form

\[
\hat{Q}_{12} = (1 - \hat{o}_1)(1 - \hat{o}_2)(1 - \hat{v}_1\hat{v}_2),
\]

where \(\hat{o}_i\) is a one-electron projector for electron \(i\) onto the occupied space, and \(\hat{v}_i\) projects onto the virtual orbital space. In the case that domain approximations are used in local explicitly correlated wave functions, the operators \(\hat{v}\) are replaced by operators \(\hat{d}_{ij}\) that project just onto the domain for the orbital pair \(ij\).

In MOLPRO the following wave function ansätze can be used:

#### 35.2.1 The general ansatz

The conventional external pair functions are augmented by terms of the form

\[
|u_{ijp}^{F12}\rangle = \sum_{p = \pm 1} \sum_{kl} T_{ijp}^{kl} \hat{Q}_{12} \hat{F}_{12} |kl\rangle
\]

This ansatz is orbital invariant (i.e., the same results are obtained with canonical or localized orbitals), but it often suffers from geminal basis set superposition errors. Furthermore, singularities may occur in the zeroth-order Hamiltonian, in particular for larger systems. Therefore, this ansatz is normally not recommended.

#### 35.2.2 The diagonal ansatz (D)

The sum over \(kl\) in equation (59) is restricted to \(ij\). This ansatz is not orbital invariant and size consistent only when localized orbitals are used. However, geminal basis set superposition errors are absent and therefore the results are often more accurate than with the general ansatz.

#### 35.2.3 The fixed amplitude ansatz (FIX)

The diagonal ansatz is used and the amplitudes of the explicitly correlated configurations are determined by the wavefunction cusp conditions, i.e.

\[
T_{ij}^{ij,1} = \frac{1}{2}, \quad T_{ij}^{ij,-1} = \frac{1}{4}
\]

This ansatz is orbital invariant, size consistent and free of GBSSE.
35.3 RI Approximations

Various approximations such as A, B, C, HY1, HY2 exist for the matrix elements of the first-order Hamiltonian (see I). They differ in the way the RI approximations are made. In the limit of a complete RI basis, approximations B and C are identical and yield the exact result for a given wave function ansatz. We generally recommend approximation C, which is simpler and more efficient than approximation B. Normally, the union of the AO and RI basis sets is used to approximate the resolution of the identity (CABS approach). In the hybrid approximations (HY1, HY2, HX) only the AO basis is used in some less important terms. Together with the recommended approximation C, HY1 or HY2 can be used; HY2 is more accurate, HY1 more efficient. In most cases, approximation 3C(HY1) provides an excellent compromise between accuracy and efficiency. In approximation A, all terms involving exchange operators are neglected. This approximation is used along with local approximations in our low-order scaling LMP2-F12/3*A(loc) method that can be applied to large molecules (cf. section 35.11).

If the extended Brillouin condition (EBC, see I) is assumed, the explicitly correlated and conventional amplitude equations decouple and can be solved independently. These approximations are denoted by a star, e.g. 3*C.

35.4 Basis sets

In MOLPRO the F12 integrals can only be computed using density fitting (DF) approximations. The many electron integrals are approximated by resolutions of the identity (RI) expansions. Thus, F12 calculations require three different basis sets: the orbital (AO) basis, the DF basis, and the RI basis.

We recommend as AO basis sets the augmented correlation consistent basis sets (denoted AVnZ) or the specially optimized correlation consistent F12 basis sets (denoted VnZ-F12, cf. K.A. Peterson and H.-J. Werner, J. Chem. Phys. 128, 084102 (2008)). Normally, triples zeta basis sets (AVTZ or VTZ-F12) yield excellent results that are close to the basis set limit. Diffuse basis functions are rather essential both for the HF and MP2-F12 energies, and therefore the standard VTZ sets are not recommended. If the AVnZ or VnZ-F12 orbital basis sets are used, suitable density fitting (DF) basis and resolution of the identity (RI) basis sets are automatically chosen. For the AVnZ orbital basis sets, AVnZ/MP2FIT and VnZ/JKFIT basis sets are used by default for the DF and RI, respectively. The associated optimized CABS basis set of Peterson et al. can be chosen by specifying RI_BASIS=OPTRI. For the VnZ-F12 orbital basis, the associated CABS (OPTRI) basis sets are used by default. Other basis sets can be chosen using the DF_BASIS, DF_BASIS_EXCH and RI_BASIS options (cf. section 35.6). See section 15 for more details about density fitting.

This is an example for using multiple basis sets for density fitting and resolution of the identity.
The following two examples yield identical results:

```plaintext
***, h2o
geom={o;
     h1,o,r;
     h2,o,r,h1,theta}
r=0.97 ang
theta=104

basis={
  default, avtz
  set, df
  default, avtz/mp2fit !density fitting basis
  set, jk
  default, avtz/jkfit !density fitting basis for Fock and exchange matrices
  set, ri
  default, avtz/optri !ri cabs basis
}
hf
ccsd(t)-f12, df_basis=df, df_basis_exch=jk, ri_basis=ri

http://www.molpro.net/info/current/examples/h2o_basissets1.com
```

```plaintext
***, h2o
geom={o;
     h1,o,r;
     h2,o,r,h1,theta}
r=0.97 ang
theta=104

basis={
  default, avtz
  set, df, context=mp2fit
  default, avtz !density fitting basis
  set, jk, context=jkfit
  default, avtz !density fitting basis for Fock and exchange matrices
  set, ri, context=optri
  default, avtz !ri cabs basis
}
hf
ccsd(t)-f12, df_basis=df, df_basis_exch=jk, ri_basis=ri

http://www.molpro.net/info/current/examples/h2o_basissets2.com
```

```plaintext
***, h2o
geom={o;
     h1,o,r;
     h2,o,r,h1,theta}
r=0.97 ang
theta=104

basis=avtz
hf
ccsd(t)-f12, df_basis=avtz, df_basis_exch=avtz/jkfit, ri_basis=avtz/optri

http://www.molpro.net/info/current/examples/h2o_basissets3.com
```

In the latter example the specifications MP2FIT and JKFIT could be omitted, i.e. the input
```
ccsd(t)-f12, df_basis=avtz, df_basis_exch=avtz/jkfit, ri_basis=avtz/optri
```
would be equivalent. In fact, since default density fitting basis sets are used
ccsd(t)-f12, ri_basis=optri

would be sufficient. Note, however, that without the specification OPTRI the avtz/jkfit basis set would be used for the RI. For example,

```
basis=avtz
hf
cccsd(t)-f12
```

is equivalent to

```
basis=avtz
hf
cccsd(t)-f12,df_basis=avtz/mp2fit,df_basis_exch=vtz/jkfit,ri_basis=vtz/jkfit
```

If the VnZ-F12 basis sets are used, the OPTRI sets are used by default, i.e.,

```
basis=vtz-f12
hf
cccsd(t)-f12
```

is equivalent to

```
basis=vtz-f12
hf
cccsd(t)-f12,df_basis=avtz/mp2fit,df_basis_exch=vtz/jkfit,\  ri_basis=vtz-f12/optri
```

### 35.5 Symmetry

Symmetry cannot be used in DF-LMP2-F12 calculations. However, in MP2-F12, DF-MP2-F12, DF-RMP2-F12, CCSD(T)-F12 and UCCSD(T)-F12 calculations Abelian symmetry can be used as usual; in these cases the preceding DF-MP2-F12 calculations will be automatically performed without symmetry, and the integrals that are necessary for subsequent CCSD-F12 or UCCSD-F12 calculations will be transformed to the symmetry adapted basis. This is fully automatic and transparent to the user. Note, however, that the prefix DF- turns off symmetry automatically, and if you want to use symmetry in the HF calculations preceding the DF-MP2-F12 or DF-MP2-F12 calculations the symmetry elements (or `AUTO`) must be specified using the SYMMETRY directive (setting `SYMMETRY,AUTO` works fine).

### 35.6 Options

There are many options available, but these are hardly needed. Normally, when standard orbital basis sets such as aug-cc-PVTZ or VTZ-F12 are used, appropriate defaults are used and no further options are needed. A typical input simply reads

```
basis=vtz-f12
hf
cccsd(t)-f12
```

We recommend to specify options only when necessary and when it is well understood what they mean!

Options for canonical and local versions:
**DF_BASIS**=basis Select the basis for density fitting (see section [35] for details). *basis* can either refer to a set name defined in the basis block, or to a default MP2 fitting basis (e.g., **DF_BASIS**=VTZ generates the VTZ/MP2FIT basis). By default, the MP2FIT basis that corresponds to the orbital basis is used.

**DF_BASIS_EXCH**=basis Select the density fitting basis for computing the exchange and Fock operators. By default, the JKFIT basis sets which correspond to the orbital basis are used.

**RI_BASIS**=basis Select the basis for the resolution of the identity (RI). This can refer to a default basis set or a set name defined in a basis block. For F12 methods the Hartree-Fock JKFIT basis sets perform well for the RI, despite having been optimized for other purposes. These sets are used by default for the AVnZ orbital basis sets. The basis type can be appended to the basis name after a slash, e.g., **RI_BASIS**=AVQZ/JKFIT would use the specified JKFIT set, or **RI_BASIS**=AVQZ/OPTRI would use the optimized CABS basis sets of Peterson et al. These are recommended for the AVnZ and VnZ-F12 basis sets and used by default for the latter ones. Note that each OPTRI basis is associated to a specific orbital basis. Therefore, the name of the OPTRI basis must either be the same as that of the orbital basis, or be omitted, e.g., **RI_BASIS**=OPTRI selects automatically the correct set for the current orbital basis.

In case of R12-methods (which are not recommended to be used), the RI basis should be chosen to be a large uncontracted AO basis (at least AVQZ). Contraction/uncontraction can be forced appending **(CONTRACT)** or **(UNCONTRACT)** to the basis name, e.g., **RI_BASIS**=AVQZ(UNCONTRACT)/ORBITAL. If other options are given in parenthesis, these can be separated by commas, e.g., **RI_BASIS**=AVQZ(f/d,UNCONTRACT)/ORBITAL. Alternative forms, which should work as well, are **RI_BASIS**=AVQZ(f/d)(UNCONTRACT)/ORBITAL or **RI_BASIS**=AVQZ(f/d)/ORBITAL(UNCONTRACT).

**CONTEXT**=context Can be used to change the default type for the RI basis, e.g., **CONTEXT**=OPTRI will use the OPTRI basis sets that correspond to the VnZ-F12 or AVnZ basis sets.

**ANSATZ**=ansatz Select the explicitly correlated ansatz ansatz methods. See section [35.7] for the possibilities and further details.

**GEM_BASIS** Basis set name for geminal expansion; atom labels are ignored. This can either be **OPTFULL** (full nonlinear fit of the geminal expansion), **EVEN** (even tempered fit), or refer to a set name defined in a previous **BASIS** block. Default is **OPTFULL**.

**GEM_TYPE** Frozen geminal type: **LINEAR** or **SLATER**, default is **SLATER**.

**GEM_NUMBER** Number of Gaussian geminal functions (default 6).

**GEM_CENTRE** Centre of even tempered geminal exponents, if **GEM_BASIS**=EVEN (default 1.0).

**GEM_RATIO** Ratio of even tempered geminal exponents, if **GEM_BASIS**=EVEN (default 3.0).

**GEM_BETA** Exponent for Slater-type frozen geminal, or parameter for weight function in other frozen geminal models (default 1.0 $a_0^{-1}$). It is possible to specify extra exponents for core-core and core-valence correlation. If two values are given (in square brackets), the first is used for valence pairs, the second for core-core (cc) and core-
valence (cv) pairs. If three values are given, the first is used for vv, the second for
cv, and the third for cc correlation.

GEM_OMEGA Exponent for weighting function (default -1, which means a value derived from
GEM_BETA).

GEM_MOM Exponent for r in omega fitting (default 0).

GEM_M Exponent for r in weighting function (default 0).

GEM_MAXIT Max. number of iterations in geminal optimization (default 200).

GEM_PRINT Print parameter for geminal optimization (default 0).

GEM_DEBUG Debug option for geminal optimization (default 0).

GEM_FAC Convergence threshold for geminal line search (default 0.001).

GEM_METHOD Geminal optimization method (augmented Hessian (AH) or Newton-Raphson
(NR), default AH).

GEM_TRUST Trust ratio in AH geminal optimization (default 0.4).

GEM_SHIFT Hessian shift in AH geminal optimization (default 0).

GEM_NUMERICAL Flags numerical integration in geminal optimization (default 0).

GEM_PLOT Geminal plot file (default blank).

GEM_OPT_FULL If nonzero (default), fit each geminal independently to Gaussians (if several
exponents are used). If zero, the first exponent is fitted, unless GEM_BETA_OPT is
specified.

GEM_BETA_OPT Exponent used to fit the Gaussian expansion.

SIM_MULTGEM Only for calculation with multiple exponents: if nonzero, loop externally over
integral program for different exponents. This is implied automatically if each
geminal is fitted independently. If the same Gaussian exponents are used for each
Slater exponent, SIM_MULTGEM=0 can be used (default). In this case the integral
program handles the general contractions (slightly faster).

PRINT=ipri Select output level:

<table>
<thead>
<tr>
<th>ipri</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Standard output</td>
</tr>
<tr>
<td>1</td>
<td>Standard output plus more detailed information about integral evaluations.</td>
</tr>
<tr>
<td>2</td>
<td>Debugging output</td>
</tr>
</tbody>
</table>

THRBINV Threshold below which non-physical eigenvalues are projected from approximate
B matrices

THRAOF12 Threshold for integral screening contribution.

35.7 Choosing the ansatz and the level of approximation

The Ansatz can be chosen using the ANSATZ option and/or by options on the command line.

3A Ansatz 3A;
3*A Ansatz 3A with EBC approximation
3B Ansatz 3B
3*B Ansatz 3B with EBC approximation
The ansatz can be further detailed by appending options in parenthesis, e.g.

\[ \text{ANSATZ}=3\text{B}(D) \]

These options can be one of

- **D**: Use diagonal ansatz
- **FIX**: Use diagonal ansatz with fixed amplitudes (orbital invariant)
- **FIXC**: Use diagonal ansatz with fixed amplitudes and canonical orbitals
- **DX**: Use diagonal ansatz and assume X-matrix to be diagonal (only for Ansatz 3A)
- **GBC**: Use GBC approximation (only for 3B, default in 3A)
- **EBC**: Use EBC approximation (same as *)
- **HX1**: Use HX1 approximation (only for 3B).
- **HY1**: Use HY1 approximation (only for 3B and 3C).
- **HY2**: Use HY2 approximation (only for 3B and 3C).
- **HY**: Default hybrid approximation. HX1 and HY2 approximation in 3B, HY2 in 3C.
- **NOZ**: Neglect Z terms (only for 3B and 3C).
- **NOX**: Neglect X terms (only for 3A and 3B).

Several options separated by commas can be given. For instance

\[ \text{ANSATZ}=3\text{C}(\text{FIX}, \text{HY1}) \]

uses the diagonal ansatz 3C(D) with fixed coefficients and the hybrid (HY1) approximation. Alternatively or in addition, the following options can be given on the command line:

- **DIAG=1**: Use diagonal ansatz.
- **DIAGX=1**: Use diagonal ansatz and assume X-matrix to be diagonal.
- **GBC=1**: Use GBC approximation (only for 3B, default in 3A).
- **EBC=1**: Use EBC approximation (same as *).
- **HYPRID=n**: Use HYn approximation.
- **HYPRIDX=1**: Use HX1 approximation.
- **NOZ=1**: Neglect Z terms (only 3B and 3C).
- **NOX=1**: Neglect X terms (only 3A and 3B).
- **FIX=1**: Use diagonal ansatz with fixed coefficient approximation (orbital invariant).
- **FIX=2**: Use diagonal ansatz with fixed coefficient approximation. Evaluate only first order energy expression, not the Hylleraas functional. Very fast but less accurate and reliable!
- **FIXCAN=1**: Use diagonal ansatz with fixed coefficient approximation and canonical orbitals. A non-iterative method is used to evaluate the energy. This is equivalent to \[ \text{FIX}=1, \text{CANONICAL}=1 \] and is most efficient.
- **FIXCAN=-1**: As \( \text{FIXCAN}=1 \), but equations are solved iteratively (test purpose only).
35  EXPLICITLY CORRELATED METHODS

CABS=1 Use CABS (default). If CABS=0 is given, CABS is disabled. However, if RI_BASIS=OPTRI, the orbital and OPTRI basis sets are automatically merged, and then exactly the same results as with CABS=1 are obtained.

ORTHO_CABS=1 Construct CABS basis from orthogonal MOs and ABS basis rather than AO and RI basis.

THRABS=thrabs Threshold for smallest eigenvalue of S in auxiliary ABS (only used with ORTHO_CABS=1; default=THRCABS).

THRCABS=thrabs Threshold for smallest eigenvalue of S in CABS (default 1.d-8).

THRCABS_REL=thrabs_rel Relative CABS threshold (default 1.d-9). The actual threshold is max(thrabs,eigmax*thrabs_rel, where eigmax is the largest eigenvalue of the overlap matrix.

PRINT=level Print parameter. PRINT=1 give information about all computed integrals and the iterations.

DEBUG=level Can be used to obtain extended debug print.

SOLVE=0 Use a most efficient pair-specific fully iterative method (default).

SOLVE=1 Use simple fully iterative method.

SOLVE=2 Use pair specific iterative method (more expensive).

SOLVE=3 Use pair specific non iterative method (most expensive, only with canonical orbitals).

CANONICAL=1 Use canonical orbitals and full domains.

DOMSEL=1 Use full domains and localized orbitals (unless CANONICAL=1 is given).

SCALE_TRIP=1 Scale triples energy as explained in section 35.10

SINGLES If set to one, include CABS singles correction (default=1)

CORE_SINGLES If set to one, include CABS singles correction for core orbitals (default=0)

EXTGEN For open-shell systems: If 1 (default, recommended), include all occupied valence orbital pairs for \( mn \) in \( T_{mn}^{ij} \), independent of spin (as described in J. Chem. Phys. 130, 054104 (2009), section II.E). If 0, use only pairs \( mn \) where the spins of \( i \) and \( m \), and \( j \) and \( n \) are equal.

For instance

\[ \text{ANSATZ}=3C, \text{fix}=1, \text{hybrid}=1, \text{canonical}=1 \]

implies a canonical 3C calculation with diagonal ansatz 3C, using fixed coefficient and hybrid approximations. The combination of the options \text{fix}=1 \text{ and canonical}=1 implies a non-iterative calculation of the energy and is recommended. The above is equivalent to all of the following:

\[ \text{ANSATZ}=3C(\text{FIXC},\text{HY1}) \]
\[ \text{ANSATZ}=3C(D,\text{FIXC},\text{HY1}) \]
\[ \text{ANSATZ}=3C(D,\text{HY1},\text{FIX}),\text{canonical}=1 \]

Note that the HF convergence threshold should be rather strict to obtain accurate results (use ACCU, 14 in the HF).

Numerous further options are for specialist use only and not described here. See \text{explicit.registry} for a full list.
35.8 CABS Singles correction

By default, the perturbative CABS singles correction as described in J. Chem. Phys. 127, 221106 (2007) and J. Chem. Phys. 128, 154103 (2008) is included in the reference energy of all MP2-F12 and CCSD-F12 calculations (closed and open-shell, except for LMP2-F12/3*A(loc), which is done with a different program). The corrected reference energy is stored in variable ENERGR, so that ENERGY-ENERGR are the total correlation energies. For the setting of other variables by the F12 programs see section 35.12.

The singles correction can be turned off by option SINGLES=0, e.g.

MP2-F12, SINGLES=0

The contribution of core orbitals to the singles energy is not included by default, but can be turned on by option CORE_SINGLES, e.g.

MP2-F12, CORE_SINGLES=1

However, we do not recommended the use of core singles, because they depend sensitively on the CABS basis construction and do not offer significant improvements in relative energies.

35.9 Pair specific geminal exponents

Different Slater exponents can be used for core-core, core-valence and valence-valence pairs as described in H.-J. Werner, G. Knizia, and F. R. Manby (Mol. Phys. 2010, DOI: 10.1080/00268976.2010.526641). The exponents are specified using the GEM_BETA option, e.g., GEM_BETA=[1.0, 1.7, 2.5] (see options, section 35.6). The three values are used for vv, cv, cc pairs, respectively. In most cases, core pairs can be defined by using the CORE directive: all orbitals that are not core and do not belong to the default valence shell are then treated as core. If part of the default valence shell is to be taken as core (e.g., the 3d shell in first-row transition metals), the core can be defined via the PRCORE variable, e.g., prcore=[4,2,2,1,4,2,2,1] for Cu2. This variable must then be defined before the F12 calculation that should use it. The following example shows calculation for Br2, in which the 3d shell is treated as core.
memory, 32, m
qthresh, energy = 1. d-8
geometry = (br; br, br, rmin)

rmin = 2.281 ANG

basis = {
  ecp, Br, ecp10mdf
  sp, Br, aug-cc-pVTZ-PP; c;
  d, Br, 338.996, 103.217, 42.3638, 18.4356, 8.37254, 3.80222, 1.68677, 0.677520
  c, 1. 0, 0.001524, 0.015673, 0.072400, 0.186303, 0.323881, 0.374534, 0.257418, 0.068051
  d, Br, 2.9173, 0.6300, 0.2228
  f, Br, 1.4417
}

set, dfmp
a, Br, 40.9778, 22.0940, 14.1569, 6.30933, 3.49893, 2.07145, 1.224111, 0.706125, 0.421245, 0.235424, 0.133419
b, Br, 31.5779, 17.7012, 10.3673, 5.56829, 3.34725, 1.86205, 1.12814, 0.520803, 0.290648, 0.155863
c, Br, 35.4419, 14.4095, 7.13728, 4.02429, 2.19901, 1.18121, 0.537101, 0.320289, 0.151982
f, Br, 16.6283, 7.92639, 3.69263, 1.89967, 1.02171, 0.418748
g, Br, 58.3022, 21.9356, 7.85160, 5.60937, 2.04334, 1.37529
h, Br, 7.5153, 3.15089

set, ri
a, Br, 18.7563, 9.07737, 4.87021, 2.00555, 0.900841, 0.080149
b, Br, 26.0294, 17.4042, 9.55778, 3.70554, 2.47230, 1.18351, 0.511543, 0.177391
c, Br, 15.9542, 11.4584, 8.89027, 1.44361, 0.945611, 0.334128
d, Br, 42.4889, 15.5186, 10.3279, 6.36172, 2.80704, 0.961178, 0.415934
e, Br, 24.3260, 9.29525, 3.78033, 1.65385, 0.919948
f, Br, 18.4810, 7.54637, 2.84990, 0.966374
i, Br, 11.4466

} explicit, ri_basis = ri, df_basis = dfmp, df_basis_exch = def2-qzvpp/jkfit

hf; accu, 16
i = 1
(mp2-f12, gem_beta = [1.25]; core, 2, 1, 1)
emp2f12(i) = energy - energr
ef12_vv(i) = energ_vv
ef12_cv(i) = energ_cv
ef12_cc(i) = energ_cc
$beta(i) = [1.25]'
i = i + 1
(mp2-f12, gem_beta = [0.8, 1.7]; core, 2, 1, 1)
emp2f12(i) = energy - energr
ef12_vv(i) = energ_vv
ef12_cv(i) = energ_cv
ef12_cc(i) = energ_cc
$beta(i) = [0.8, 1.7]'
i = i + 1
(mp2-f12, gem_beta = [0.8, 1.7, 2.2]; core, 2, 1, 1)
emp2f12(i) = energy - energr
ef12_vv(i) = energ_vv
ef12_cv(i) = energ_cv
ef12_cc(i) = energ_cc
$beta(i) = [0.8, 1.7, 2.2]'

table, beta, ef12_cc, ef12_cv, ef12_vv, emp2f12
Title, Results for Br2, basis vdz-f12

http://www.molpro.net/info/current/examples/br2_f12_multgem.com
CCSD(T)-F12

The CCSD-F12 and UCCSD-F12 programs first do DF-MP2-F12/3C(FIX) (closed-shell) or DF-RMP2-F12/3C(FIX) (open-shell) calculations, and then perform the CCSD-F12 (UCCSD-F12) without density fitting. By default, the CCSD-F12A and CCSD-F12B energies are both computed. A specific method can be requested by appending A or B to the -F12 suffix. Furthermore, instead of the 3C(FIX) ansatz, different ansätze (e.g. 3C) can be used. In this case the amplitudes of the explicitly correlated terms are determined in the MP2-F12 calculation and kept fixed in the CCSD-F12.

It should be noted that these methods involve approximations and do not yield the exact CCSD-F12 energies. Preliminary experience has shown that the CCSD-F12A method slightly overestimates the correlation energies, while CCSD-F12B underestimates them. For AVDZ or AVTZ basis sets, CCSD-F12A usually gives very good results, but for larger basis sets it may overestimate the basis set limit and converge from below to the limit. Thus, convergence may not be monotonic, and extrapolation of the correlation energies should not be attempted. CCSD-F12B usually converges monotonically from below to the limit and gives best results for AVQZ and larger basis sets. Thus, we currently recommend CCSD-F12A for AVDZ and AVTZ basis sets, and CCSD-F12B for larger basis sets (rarely needed).

The perturbative triples correction can be invoked by using CCSD(T)-F12 or UCCSD(T)-F12. There is no direct F12 correction to the triples, and therefore the basis set error of the triples is not affected by the F12 (small changes of the triples energy arise from the fact that the doubles amplitudes are affected by the F12 terms). In many cases, a simple and pragmatic improvement of the triples energy can be obtained by scaling the triples energy contribution as

$$\Delta E_{(T^*)} = \Delta E_{(T)} * \frac{E_{MP2}^{corr}-F12}{E_{corr}^{MP2}}$$

This can be done automatically by setting option SCALE_TRIP=1, i.e.

CCSD(T)-F12, SCALE_TRIP=1

DF-LMP2-F12 calculations with local approximations

Local variants of the DF-MP2-F12 and CCSD(T)-F12 methods are invoked by the commands DF-LMP2-F12, DF-LCCSD-F12, DF-LCCSD(T)-F12 with ansatz 3*A(LOC) [for DF-LCCSD-F12 fixed amplitudes are used, i.e., the default is 3*A(LOC,FIX)]. These calculations are performed with a different program than non-local calculations. The (LOC) option implies that the LMP2 calculation with domain approximations is performed, and by default a local projector as first described in H.-J. Werner, J. Chem. Phys. 129, 101103 (2008) is used [see also T. B. Adler, F. R. Manby, and H.-J. Werner, J. Chem. Phys. 130, 054106 (2009); T. B. Adler and H.-J. Werner, J. Chem. Phys. 130, 241101 (2009); T. B. Adler and H.-H. Werner, J. Chem. Phys. 135, 144117 (2011)]

This yields very similar results as the corresponding canonical methods at much lower cost\(^3\) and the method can be applied to quite large molecules.

Special options for these local variants are (local RI works only with ansatz 3*A):

PAIRS Specifies which pairs to be treated by R12 or F12
(STRONG|CLOSE|WEAK|ALL; pairs up to the given level are included). The

---

\(^3\) ANSATZ=3*A(LOC,FIX) is exactly equivalent to ANSATZ=3*A(FIX,NOX),PROJF=2,CABS=0,SINGLES=0, but if the latter options are used the non-local program is used to compute the F12 correction and local approximations are only simulated. CABS singles can then be included by omitting the SINGLES=0 option.
default is ALL. Note that even with ALL very distant pairs are neglected if these are neglected in the LMP2 as well.

**USEVRT**
If zero, the \(1 - pp + po + op - p'o - op'\) form of the projector is used, and local RI approximations apply to \(p\) and \(p'\). If set to 1, the \(1 + oo - vv - p'o - op'\) form of the projector is used; any local RI approximation then applies only to the RI contribution \(p'\).

**USEPAO**
If USEPAO=1 use pair-specific local projectors instead of \(vv\). This is the default if either the ansatz contains '(LOC)' or if domain approximations are made in the LMP2 (i.e., DOMSEL<1 is explicitly specified). Otherwise the default is USEPAO=0. USEPAO=1 automatically implies USEVRT=1, i.e. local RI approximations only affect the RI contributions \(p'\). Furthermore, if USEPAO=1 is specified and DOMSEL is not given, default domains are assumed in the LMP2. If USEPAO=0, full domains (DOMSEL=1) will be used.

**FULLAO**
if USEVRT=0 and FULLAO=1, local RI approximations only apply to the RI contributions \(p'\). This should give the same results as USEVRT=1 (only applies if USEPAO=0).

**DEBUG**
Parameter for debug print.

**LOCFIT_F12**
If set to one, use local fitting. Default is no local fitting (LOCFIT_F12=0)

**LOCFIT_R12**
Alias for LOCFIT_F12. Local fitting is not recommended in R12 calculations.

**FITDOM**
Determine how the base fitting domains are determined (only applies if LOCFIT_F12=1):
0: Fitdomains based on united operator domains;
1: Fitdomains based on orbital domains (default);
2: Fitdomains based on united pair domains using strong pairs;
3: Fitdomains based on united pair domains using strong, close and weak pairs.
Note: This is the only option implemented in the DF-LMP2 program. Therefore, the DF-LMP2 and DF-LMP2-F12 programs might give slightly different results if default values are used.

**RDOMAUX**
Distance criterion for density fitting domain extensions in case of local fitting. The default depends on FITDOM.

**IDOMAUX**
Connectivity criterion for density fitting domain extensions in case of local fitting.

**RAODOM**
Distance criterion for RI domain extensions. Zero means full RI basis (default). If USEPAO=1 or USEVRT=1 or FULLAO=1 a value of 5 bohr is recommended. In other cases the local RI domains must be very large (RAODOM>12) and the use of local RI approximations is not recommended.

**IAODOM**
Connectivity criterion for RI domain extensions. Zero means full RI basis (default). Values greater or equal to 2 should lead to sufficiently accurate results, provided the local projector (USEPAO=1) is used.

**THRAO**
Screening threshold for coulomb integrals in the AO or RI basis.

**THRAOF12**
Screening threshold for F12 integrals.

**THRMO**
Screening threshold for half transformed integrals.

**THRPROD**
Product screening threshold in the first half transformation.

**NOMP2**
If set to 1, only the F12 calculation is performed, and the LMP2 is skipped. This is sometimes useful if full domains are used, since the iterative LMP2 then causes a big overhead and needs a lot of memory. It is then more efficient to do the a DF-MP2 calculation separately and compute the total energy as the sum of the DF-MP2 energy and the F12 energy.
Values greater than 0 invoke the local projector. \( \text{PROJF}=1 \) project vv parts only (this is formally the most accurate case but only possible with the canonical program \([\text{ANSATZ}=3*\text{A}(\text{FIX}, \text{NOX})] \). \( \text{PROJF}=2 \) project vv and vo parts (default). This is unavoidable if the local program is used \([\text{ANSATZ}=3*\text{A}(\text{LOC})] \).

If \( > 0 \), core contributions are neglected in the projector. This is a necessary approximation in order to compute the LCCSD-F12 coupling terms efficiently (implementation not yet finished). Setting \( \text{MODOMC}=0 \) avoids the approximation. Note that the results in J. Chem. Phys. 135, 144117 (2011) have been obtained using \( \text{MODOMC}=0 \).

Further options for density fitting are described in section [15] and further options to choose the ansatz in section [35.7].

Typical inputs for calculations with local approximations are:

diagram

This would perform a local MP2 with a Boughton-Pulay domain completeness criterion of 0.985. In the F12 part, distant pairs are not included \( \text{(PAIRS=WEAK)} \) and the local projector is used \( \text{(USEPAO=1, default).} \) Local density fitting and local RI approximations are used. A corresponding non-local calculation (still using localized orbitals and the diagonal ansatz) would be

![Diagram]

Note: The use of local DF and RI domains is still experimental and should be used with care!

### 35.12 Variables set by the F12 programs

The following variables are set by the F12 programs:

**ENERGR**
Reference energy. This includes the perturbative CABS singles correction if computed.

**ENERGY**
Total energy of the requested method (including the F12 and singles corrections). \( \text{ENERGY(1)} \) and \( \text{ENERGY(2)} \) hold the F12A and F12B values, respectively (if both are computed).

**ENERGC**
Total CCSD-F12 energies in ccisd-f12 or uccsd-f12 calculations. \( \text{ENERGC(1)} \) and \( \text{ENERGC(2)} \) hold the F12A and F12B values, respectively (if both are computed). The difference of \( \text{ENERGY} \) and \( \text{ENERGC} \) is the triples energy contribution.

**ENERGT**
Triples energy contribution. This is a vector. The corresponding methods are stored in \( \text{METHODT} \) (strings).

**EMP2**
Total MP2 energy (excluding F12 correction, but including the singles correction).
EMP2_SCS  Total SCS-MP2 energy (excluding F12 correction, but including the singles correction).
EMP2_SING  Singlet MP2 correlation energy (excluding F12 correction).
EMP2_TRIP  Triplet MP2 correlation energy (excluding F12 correction).
EMP2_STRONG  Strong pair contribution to the LMP2 correlation energy (where applicable).
EMP2_CLOSE  Close pair contribution to the LMP2 correlation energy (where applicable).
EMP2_WEAK  Weak pair contribution to the LMP2 correlation energy (where applicable).
EMP2_DIST  Distant pair F12 contribution to the LMP2-F12 correlation energy (where applicable).

EF12  F12 contribution to the MP2-F12 correlation energy for the requested ansatz.
EF12S  F12 contribution to the MP2-F12 correlation energy using EBC approximation for the requested ansatz.
EF12D  F12 contribution to the MP2-F12 correlation energy using EBC approximation and diagonal (DX) approximation for the requested ansatz.
EF12_SING  Singlet F12 contribution to the MP2-F12 correlation energy for the requested ansatz.
EF12_TRIP  Triplet F12 contribution to the MP2-F12 correlation energy for the requested ansatz.
EF12_STRONG  Strong pair F12 contribution to the LMP2-F12 correlation energy (where applicable).
EF12_CLOSE  Close pair F12 contribution to the LMP2-F12 correlation energy (where applicable).
EF12_WEAK  Weak pair F12 contribution to the LMP2-F12 correlation energy (where applicable).
EF12_DIST  Distant pair F12 contribution to the LMP2-F12 correlation energy (where applicable).
EF12_SCS  F12 contribution to the MP2-F12 correlation energy for the requested ansatz.
EF12_SINGLES  Total CABS singles contribution (in closed-shell case equal to EF12_RHFRELAX).
EF12_RHFRELAX  CABS singles correction of the reference energy (only the spin-free contribution is used).
ANSATZ  The requested ansatz (string variable)

Variables corresponding to EF12_* exist also for EF12S_* and EF12D_*.

In case of doubt or problems, try in a test calculation
SHOW, ENERG*, EMP2*, EF12*

This should show all relevant variables that exist. Note that system variables are internally stored with an underscore as a prefix, and this may be shown by the SHOW command. The variables can be accessed with or without underscore (but if the user defines a variable with the same name then the underscore is needed to access the system variable and not the user variable).

36  THE FULL CI PROGRAM

This module is the determinant full CI program, as described in

Published work resulting from the use of this program should cite these references.
The program in normal use finds the lowest eigenvector of the complete CI hamiltonian matrix; more sophisticated use is possible, but not documented here. The program is interfaced to free standing versions such as supplied in the CPC program library by use of the DUMP option.
The program is called with the command FCI.

36.1 Defining the orbitals

ORBIT, name.file;
name.file specifies the record from which orbitals are read. The default is the set of orbitals from the last SCF, MCSCF or CI calculation.

36.2 Occupied orbitals

OCC, n\textsubscript{1}, n\textsubscript{2}, \ldots, n\textsubscript{8};
n\textsubscript{i} specifies numbers of occupied orbitals (including CORE) in irreducible representation number i. If not given, the default is the complete basis set.

36.3 Frozen-core orbitals

CORE, n\textsubscript{1}, n\textsubscript{2}, \ldots, n\textsubscript{8};
n\textsubscript{i} is the number of frozen-core orbitals in irrep number i. These orbitals are doubly occupied in all configurations, i.e., not correlated. If no CORE card is given, the program uses the same core orbitals as the last CI calculation; if there was none, then the atomic inner shells are taken as core. To avoid this behaviour and correlate all electrons, specify

CORE

36.4 Defining the state symmetry

The number of electrons and the total symmetry of the wavefunction are specified on the WF card:

WF, elec, sym, spin

where

elec: is the number of electrons
sym: is the number of the irreducible representation
spin: defines the spin symmetry, spin= 2S (singlet=0, doublet=1, triplet=2, etc.)
36.5 Density matrix

The 1-electron density matrix can be computed with
\[ DM,record,file \]
and then subsequently used to calculate one-electron properties using the PROP program.

36.6 Excited states

\[ STATE,value; \]
Specifies the number of states to be sought (default 1).

36.7 Convergence threshold

\[ THR,value; \]
Convergence threshold (default \( 10^{-5} \)). If changes in the normalised wavefunction become less than this value, then the iterative eigenvector solver terminates.

36.8 Printing options

\[ PRINT,code,value; \]
Print options. Generally, the value determines how much intermediate information is printed. \( value=1 \) means no print (default for all codes). if \( value \) is omitted, it is taken as zero, which is usually appropriate. Specification of higher values will generate more output. The following codes are allowed:

- ORBITAL: Print molecular orbitals
- INTEGRAL: Print integrals
- TIMING: Print extra timing information
- DIAGONAL: Print diagonal elements of Hamiltonian
- HAMILTONIAN: Print much intermediate information

36.9 Interface to other programs

\[ DUMP; \]
causes the FCI diagonalization to be bypassed, with input information and transformed integrals being written to a formatted file FCIDUMP. The format is as described in Comp. Phys. Commun. 54 (1989) 75, and in an external program should be accessed using the FCIdump class or module available from [https://bitbucket.org/pjknowles/fcidump](https://bitbucket.org/pjknowles/fcidump).
37 SYMMETRY-ADAPTED INTERMOLECULAR PERTURBATION THEORY

37.1 Introduction

The SAPT (symmetry-adapted intermolecular perturbation theory) program calculates the total interaction energy between closed-shell molecules as a sum of individual first and second order interaction terms, namely electrostatic $E_{\text{pol}}^{(1)}$, induction $E_{\text{ind}}^{(2)}$ and dispersion $E_{\text{disp}}^{(2)}$ accompanied by their respective exchange counterparts ($E_{\text{exch}}^{(1)}$, $E_{\text{exch-ind}}^{(2)}$ and $E_{\text{exch-disp}}^{(2)}$). The latter ones arise due to electron exchange between the monomers when the molecules are close to each other and are sometimes denoted as Pauli repulsion. Since all above terms are accessible through density matrices and static and dynamic density-density response functions of the monomers, in principle (see section 37.4) no calculation of the dimer wave function is required. Therefore SAPT is free from the basis set superposition error which occurs in the supermolecular approach.

References:

General Symmetry-adapted perturbation theory and many-body SAPT:

DFT-SAPT:

Density fitting DFT-SAPT (DF-DFT-SAPT):

Density fitting DFT-SAPT for arbitrary monomer basis sets (DFSAPT):

(See also:
and references therein for a related approach to DFT-SAPT termed SAPT(DFT))

37.2 First example

A typical input for SAPT has the following form:

```
r=5.6
geometry={nosym; he1; he2,he1,r}
basis=avqz
!
wf records
ca=2101.2
cb=2102.2
!
monomer A
dummy,he2
{hf; save,$ca}
```
Here the `sapt;monomerA/B` store some informations about the two monomers which are needed in the subsequent SAPT calculation invoked by `sapt;intermol`. The individual interaction energy terms are stored (in millihartree) in distinct variables and may be collected in arrays for producing potential energy surfaces. For example the input

```plaintext
geometry={nosym; he1; he2,he1,r}
basis=avtz

!wf records
cb=2101.2
ca=2102.2

!distances
dist=[4.5,5.0,5.5,5.6,6.0,6.5,7.0]
do i=1,#dist
   r=dist(i)
   
   !monomer A
dummy,he2
   {hf; start,atdens; save,$ca}
sapt;monomerA

   !monomer B
dummy,he1
   {hf; start,atdens; save,$cb}
sapt;monomerB

   !interaction contributions
sapt;intermol,ca=$ca,cb=$cb

   elst(i)=E1pol; exch(i)=E1ex
   ind(i)=E2ind; exind(i)=E2exind
   disp(i)=E2disp; exdisp(i)=E2exdisp
   etot(i)=E12tot

   data,truncate,$ca
endo
data,dist,elst,exch,ind,exind,disp,exdisp,etot

{table,dist,elst,exch,ind,exind,disp,exdisp,etot
 ftyp,d,d,d,d,d,d,d,d,d,d
 plot}
```

yields the plot.
Currently SAPT only accepts single-determinant wave functions for the monomers, i.e. from Hartree-Fock or Kohn-Sham DFT (see next section) calculations. This means that if Hartree-Fock wave functions are used for monomer, the following quantity is obtained (zero in superscript denotes that no intramonomer correlation is accounted for) [1].

\[
E_{\text{SAPT}} = E^{(10)}_{\text{pol}} + E^{(10)}_{\text{exch}} + E^{(20)}_{\text{ind,resp}} + E^{(20)}_{\text{exch-ind,resp}} + E^{(20)}_{\text{disp}} + E^{(20)}_{\text{exch-disp}}
\]

No point group symmetry can be exploited in a SAPT calculation.

### 37.3 DFT-SAPT

It is of crucial importance to account for the *intra*molecular correlation effects of the individual SAPT terms since Hartree-Fock theory often yields poor first- and second-order electrostatic properties. While this can be done using many-body perturbation theory [1] (in a double perturbation theory ansatz) a more efficient way is to use static and time-dependent DFT theory. This variant of SAPT, termed as DFT-SAPT [2-6], has in contrast to Hartree-Fock-SAPT the appealing feature that the polarisation terms \( E^{(1)}_{\text{pol}}, E^{(2)}_{\text{ind}}, E^{(2)}_{\text{disp}} \) are potentially exact, i.e. they come out exactly if the exact exchange-correlation (xc) potential and the exact (frequency-dependent) xc response kernel of the monomers were known. On the other hand, this does not hold for the exchange terms since Kohn-Sham theory can at best give a good approximation to the exact density matrix of a many-body system. It has been shown [6] that this is indeed the case and therefore DFT-SAPT has the potential to produce highly accurate interaction energies comparable to high-level supermolecular many-body perturbation or coupled cluster theory. However, in order to achieve this accuracy, it is of crucial importance to correct the wrong asymptotic behaviour of the xc potential in current DFT functionals [3-5]. This can be done by using e.g.:

\{(ks,lda; asymp,<shift>)\}

which activates the gradient-regulated asymptotic correction approach of Grüning et al. (J. Chem. Phys. 114, 652 (2001)) for the respective monomer calculation. The user has to supply a shift parameter \( (\Delta_{\text{xc}}) \) for the bulk potential which should approximate the difference between the HOMO energy \( (\varepsilon_{\text{HOMO}}) \) obtained from the respective standard Kohn-Sham calculation and the (negative) ionisation potential of the monomer (IP):

\[
\Delta_{\text{xc}} = \varepsilon_{\text{HOMO}} - (-\text{IP})
\]
This method accounts for the derivative discontinuity of the exact \( \text{xc} \)-potential and that is missing in approximate ones. Note that this needs to be done only once for each system. (See also section 37.7.2 for an explicit example).

Concerning the more technical parameters in the DFT monomer calculations it is recommended to use lower convergence thresholds and larger intergration grids compared to standard Kohn-Sham calculations.

### 37.4 High order terms

It has been found that third and higher-order terms become quite important if one or both monomers are polar. As no higher than second-order terms are currently implemented in SAPT, one may use a non-correlated estimation of those terms by using supermolecular Hartree-Fock (see e.g. [7]). This can be done by adapting the following template:

```plaintext
!dimer
hf
edm=energy

!monomer A
dummy,<monomer2>
(hf; save,$ca)
ema=energy
sapt;monomerA

!monomer B
dummy,<monomer1>
(hf; start,atdens; save,$cb)
emb=energy
sapt;monomerB

!interaction contributions
sapt,sapt_level=2;intermol,ca=$ca,cb=$cb

esup=(edm-ema-emb)*1000. mH
dHF=esup-e1pol-e1ex-e2ind-e2exind
```

which stores the resulting \( \delta(\text{HF}) \) term in \( dHF \).

### 37.5 Density fitting

In order to be able to study interactions between extended monomers one can use density fitting to approximate the integrals in SAPT [7]. For this one may use the input:

```plaintext
{sapt;intermol,ca=$ca,cb=$cb,fitlevel=3
dfit,basis_coul=jkfit,basis_exch=jkfit,basis_mp2=mp2fit,cfit_scf=3}
```

with in the basis section defined \( jkfit \) and \( mp2fit \) fitting basis sets (see section 15).

Currently only the ALDA \( \text{xc} \)-kernel is implemented for the case \( \text{SAPTLEVEL}=3 \) and \( \text{SAPT_FITLEVEL}=3 \). This means that a corresponding SAPT calculation would be incompatible with hybrid-DFT monomer orbitals/orbital energies. Therefore it is recommended to use nonhybrid functionals in the case the dispersion/exchange-dispersion energy terms are requested in a DF-DFT-SAPT run. Another possibility is to localise the \( \text{xc} \)-potential via, e.g., the OEP method (see also example in section 37.7.3).
37.6 SAPT with ECP’s

If effective core potentials (ECP’s) are used in the monomer calculations, it is important to add the \( \delta \) (HF) term to the SAPT interaction energy (see K. Patkowski, K. Szalewicz, *J. Chem. Phys.* 127 (2007) 164103). For examples for the calculation of \( \delta \) (HF) see sections 37.4 and 37.7.

37.7 Examples

37.7.1 HF-SAPT calculation of the H\(_2\)O dimer using the \( \delta \) (HF) correction

```
qthresh,energy=1.d-8,orbital=1.d-8,grid=1.d-8
symmetry,nosym
orient,noorient
GEOMETRY=
  1,O1,,0.00000000,0.00000000,0.00000000
  2,H1,,0.00000000,0.00000000,1.83606000
  3,H2,,1.77604000,0.00000000,-0.4656040
  4,O2,,-0.6605540,0.00000000,5.54064000
  5,H3,,-1.6582100,-1.4536300,6.05324000
  6,H4,,-1.6582100,1.45363000,6.05324000
}
basis=avdz
!sapt files
cb=2102.2

!dimer
hf
edm=energy

!monomer A
dummy,o2,h3,h4
{hf; save,$ca}
ema=energy
{sapt;monomerA}

!monomer B
dummy,o1,h1,h2
{hf; start,atdens; save,$cb}
emb=energy
{sapt;monomerB}

!interaction contributions
{sapt,SAPT_LEVEL=3;intermol,ca=$ca,cb=$cb,icpks=1}

!HF supermolecular interaction energy and delta(HF) contribution
eint_HF=(edm-ema-emb)*1000 mH
delta_HF=eint_HF-e1pol-e1ex-e2ind-e2exind

!add E2disp + E2exch-disp to HF interaction energy
eint_sapt=eint_HF+e2disp+e2exdisp
```

http://www.molpro.net/info/current/examples/h2odimer_sapt_hf.com
37.7.2 DFT-SAPT calculation of the NeAr dimer using the $\delta$(HF) correction

```plaintext
gthresh,energy=1.d-8,orbital=1.d-8,grid=1.d-8
symmetry,nosym
orient,noorient
geometry={
  Ne,,0.0,0.0,0.0
  Ar,,0.0,0.0,6.5)
basis=avtz

!=========delta(HF) contribution for higher order interaction terms====
!sapt files
cb=2101.2
cb=2102.2
!dimer
hf
!monomer A
dummy,ar
{hf; save,$ca}
ema=energy
{sapt;monomerA}

!monomer B
dummy,ne
{hf; start,atdens; save,$cb}
emb=energy
{sapt;monomerB}

!interaction contributions
{sapt,SAPT_LEVEL=2;intermol,ca=$ca,cb=$cb,icpks=1}

!calculate high-order terms by subtracting 1st+2nd order energies
eint_hf=(edm-ema-emb)*1000 mH
delta_hf=eint_hf-e1pol-e1ex-e2ind-e2exind

!=========DFT-SAPT at second order intermol. perturbation theory====
!sapt files
cb=2103.2
cb=2104.2
!shifts for asymptotic correction to xc potential
eps_homo_pbe0_ar=-0.440936 !HOMO(Ar)/PBE0 functional
eps_homo_pbe0_ne=-0.589207 !HOMO(Ne)/PBE0
ip_ar=0.5792 !exp. ionisation potential
ip_ne=0.7925 !exp. ionisation potential
shift_ar=ip_ar+eps_homo_pbe0_ar !shift for bulk xc potential (Ar)
shift_ne=ip_ne+eps_homo_pbe0_ne !shift for bulk xc potential (Ne)

!monomer A
dummy,ar
{ks,pbe0; asymp,shift_ne; save,$ca}
{sapt;monomerA}

!monomer B
dummy,ne
{ks,pbe0; start,atdens; asymp,shift_ar; save,$cb}
{sapt;monomerB}

!interaction contributions
{sapt,intermol,ca=$ca,cb=$cb,icpks=0}
!add high-order approximation to obtain the total interaction energy
eint_dftsapt=e12tot+delta_hf
```

http://www.molpro.net/info/current/examples/near_sapt_acdft.com
37.7.3 DF-DFT-SAPT calculation of the NeAr dimer using the $\delta$(HF) correction

```plaintext
gdirect; gthresh,energy=1.d-8,orbital=1.d-8,grid=1.d-8
symmetry,nosym
orient,nosym
geometry={
Ne,,0.0,0.0,0.0
Ar,,0.0,0.0,6.5}
basis=
set,orbital; default,avtz  !for orbitals
set,jkfit; default,avtz/jkfit  !for JK integrals
set,mp2fit; default,avtz/mp2fit  !for E2disp/E2exch-disp
set,dflhf; default,avtz/jkfit  !for LHF
}

!=========delta(HF) contribution for higher order interaction terms====
ca=2101.2; cb=2102.2  !sapt files

dimer
{df-hf,basis=jkfit,locorb=0}
edm=energy

!monomer A
dummy,ar
{df-hf,basis=jkfit,locorb=0; save,$ca}
ema=energy
{sapt;monomerA}

!monomer B
dummy,ne
{df-hf,basis=jkfit,locorb=0; save,$cb}
emb=energy
{sapt;monomerB}

!interaction contributions
{sapt,SAPT_LEVEL=2;intermol,ca=$ca,cb=$cb,icpks=1,fitlevel=3
dfit,basis_coul=jkfit,basis_exch=jkfit,cfit_scf=3}

eint_hf=(edm-ema-emb)*1000 mH
delta_hf=eint_hf-e1pol-e1ex-e2ind-e2exind

!=========DFT-SAPT at second order intermol. perturbation theory====
ca=2103.2; cb=2104.2  !sapt files;

!shifts for asymptotic correction to xc potential
eps_homo_pbe0_ar=-0.440936  !HOMO(Ar)/PBE0 functional
eps_homo_pbe0_ne=-0.589207  !HOMO(Ne)/PBE0
ip_ar=0.5792  !exp. ionisation potential
ip_ne=0.7925  !exp. ionisation potential
shift_ar=ip_ar+eps_homo_pbe0_ar  !shift for bulk xc potential (Ar)
shift_ne=ip_ne+eps_homo_pbe0_ne  !shift for bulk xc potential (Ne)

!monomer A, perform LPBE0AC calculation
dummy,ar
{df-ks,pbex,pw91c,lhf; dftfac,0.75,1.0,0.25; asymp,shift_ne; save,$ca}
{sapt;monomerA}

!monomer B, perform LPBE0AC calculation
dummy,ne
{df-ks,pbex,pw91c,lhf; dftfac,0.75,1.0,0.25; start,atdens; asymp,shift_ar; save,$cb}
{sapt;monomerB}

!interaction contributions
{sapt,SAPT_LEVEL=3;intermol,ca=$ca,cb=$cb,icpks=0,fitlevel=3,nlexfac=0.0
dfit,basis_coul=jkfit,basis_exch=jkfit,cfit_scf=3}

!add high-order approximation to obtain the total interaction energy
eint_dftsapt=e12tot+delta_hf
```

37.8 Options

**SAPT_LEVEL** Set to 1 for first-order terms ($E^{(1)}_{\text{pol}}$ and $E^{(1)}_{\text{exch}}$), to 2 for additional second order (exchange-)induction terms ($E^{(2)}_{\text{ind}}$ and $E^{(2)}_{\text{exch-ind}}$) and 3 for all first- and second-order terms (including then also $E^{(2)}_{\text{disp}}$ and $E^{(2)}_{\text{exch-disp}}$) (default 3)

**SAPT_FITLEVEL** Level of density fitting approximations in SAPT which can have values 0 to 3 (default 0)

**SAPT_ICPKS** Switch between iterative (=1) and non-iterative (=0) solution of coupled-perturbed Kohn-Sham equations (default 0)

**SAPT_CPKSTHR** Threshold for density matrix convergency in the coupled-perturbed Kohn-Sham program (default 1.d-6).

**SAPT_CPKMAXIT** Maximum number of iterations in the coupled-perturbed Kohn-Sham program (default 50).

**SAPT_FROZENA** Number of frozen electrons in the response calculations for monomer A (default 0)

The following parameters are of importance if **SAPT_FITLEVEL>0**:

**SAPT_NFRQ_DISP** Number of frequencies for the Casimir-Polder integration (default 12)

**SAPT_NORM_DISP** Norm for the density fitting which can be either **COULOMB** or **NATURAL** (default **COULOMB**)

**SAPT_DISP_N4** Can speedup the calculation of the dispersion energy by $N^4$ scaling (default 1)

**THR_XCKERN** Density threshold for the xc kernel matrix elements (default 1.d-8)

**FIT_XCKERN** Fit both sides of the xc kernel (default 0)

**SAPT_DISK** If 0 write all dimer amplitudes to file, if 1 write 3-index response propagators to file and if 2 write 3-index response propagators compressed to file. The latter two variants save disk space but need more CPU time to compute $E^{(2)}_{\text{exch-disp}}$ (default 0)

**COMPRESS_THR** If **SAPT_DISK=2** this value determines the compression cutoff (default 1d-12)

**UNCoupled** If **SAPT_DISK>0** calculate also uncoupled (exchange-)dispersion energies (default false)

**THRAO** Threshold for AO 3-index integrals (default 1.d-12)

**THRMO** Threshold for MO 3-index integrals (default 1.d-8)

**THRROV** Threshold for AO 2-index integrals (default 1.d-10)

**THRPROD** Product threshold for first half transformation (default 1.d-8)

**THRSW** Threshold for Schwarz screening (default 1.d-5)

**C6** Calculate dispersion coefficients for the two monomers (Note that the full dimer basis set is used in each case and that a closer distance of the monomers can perturb the result).

**XCKERN NBLOCK** number of grid points treated together as a block for $(\text{aux}|f_{xc}|\text{occ}\times\text{virt})$ integrals (default 128)

**CFAC** factor for VWN correlation in ALDA xc-kernel (default 1.d0)
The last threshold values for the 2- and 3-index integrals should not be set higher in density fitting calculations as this can cause lower accuracies in the interaction terms. In addition SAPT knows the following subcommands:

**MONOMERA** Stores informations (like number of electrons, etc.) about previous monomer A calculation

**MONOMERB** See above

**INTERMOL** Starts the SAPT calculation

**INTERMOL** may have the following subkeywords:

- **CA** Record number of wave function for monomer A (always needed)
- **CB** Record number of wave function for monomer B (always needed)
- **SAPTLEVEL** See above
- **FITLEVEL** See above
- **ICPKS** See above
- **FROZA** See above
- **FROZB** See above
- **NLEXFAC** Amount of nonlocal exact exchange in hybrid DFT-SAPT calculations
- **CPKSTHR** Threshold for density matrix convergency in the coupled-perturbed Kohn-Sham program.
- **CPKSMAXIT** Maximum number of iterations in the coupled-perturbed Kohn-Sham program.

### 37.9 DFSAPT: a density-fitting DFT-SAPT program for arbitrary monomer basis sets

DFSAPT is an alternative density-fitting DFT-SAPT program which works with arbitrary monomer basis sets and which can be used for extended dimer systems of about 800 electrons, see Ref.[8].

For a standard DFSAPT calculation using a dimer centered basis set the Molpro input file looks very similar to a corresponding DF-DFT-SAPT calculation, see example `h2o_2-dfsapt.com` (section [37.9.1]). There are, however, two important points to be taken care of:

**important #1** Set `oldnorm=1` before any call to the DFSAPT program.

**important #2** Add numbers to atom labels in the geometry blocks. These have to have a subsequent ordering, see examples [37.9.1][37.9.4]

A corresponding calculation, in which the water monomers are calculated in their own local basis set (monomer centered basis set calculation) is presented in example `h2o_2-mc-dfsapt.com` (section [37.9.2]). Note, however, that very large basis sets are required to converge the individual interaction energy contributions. In order to improve the basis set convergence, additional mid-bond functions can be added as is exemplified in example `h2o_2-mcplus-dfsapt.com` (section [37.9.3]). Here the def2-TZVP basis functions for the Neon atom were positioned in between the O···H hydrogen bridge.

A complete (DCBS) DFSAPT calculation with additional $\delta$(HF) correction and using the PBE0AC(BRJ) xc potential (with automatic asymptotic correction) is shown in section [37.9.4].
Note that in contrast to the DFT-SAPT/DF-DFT-SAPT programs the exchange-dispersion energy is not calculated on the coupled level. Instead, the coupled $E^{(2)}_{\text{exch\textendash}\text{disp}}$ energies are estimated by scaling the uncoupled ones with a factor which has been obtained from a linear fit to exact results, see Ref.[8].

The following list shows all options which can be used with the DFSAPT program:

- **E1P**: Calculate $E^{(1)}_{\text{pol}}$ (default: 1).
- **E1X**: Calculate $E^{(1)}_{\text{exch}}$ (default: 1).
- **E2I**: Calculate $E^{(2)}_{\text{ind}}$ (default: 0).
- **E2XI**: Calculate $E^{(2)}_{\text{exch\textendash}\text{ind}}$ (default: 0).
- **E2D**: Calculate $E^{(2)}_{\text{disp}}$ (default: 0).
- **E2XD**: Calculate $E^{(2)}_{\text{exch\textendash}\text{disp}}$ (default: 0).
- **ALL**: Calculate all SAPT contributions (up to 2nd order) (default: 0).
- **AUXBAS**: Auxiliary basis set (default: MP2FIT).
- **NFREQ**: Number of frequencies for computing the monomer response matrices (default: 10).
- **GRIDTHR**: Threshold for grid accuracy (default: 1d-10).
- **THRKERN**: Threshold for density in xc kernel calculation (default: 1d-12).
- **PRINT**: Print flag (default: 0).
- **W0**: Value effects Gauss-Legendre quadrature for computing the response function (see Amos,Handy,Knowles,Rice,Stone, *J. Phys. Chem.* 89 (1985) 2186) (default: 2d0)
- **FEXX**: Exact exchange factor in response calculations (default: 0d0).
- **FXC**: Exchange-correlation factor in response calculations (default: 0d0).
- **FCOUL**: Coulomb contribution factor in response calculations (default: 0d0).
- **XFAC**: Exchange factor in XC kernel (default: 1d0).
- **CFAC**: Correlation factor in XC kernel (default: 1d0).
- **AUXMAX**: Maximum block size of auxiliary function space for three-index integrals of the type (aux|orb.orb) (default: 50).
- **MOMAX**: Maximum block size of orbital function space for three-index integrals of the type (orb|orb.aux) (default: 50).
- **FXCSING**: Singularity correction for XC kernel matrix (default: 0)
- **THRDUM**: Threshold for density calculated at dummy function gridpoints (which can serve as a singularity correction for the calculation of the XC kernel matrix) (default: 1d-4).
- **COMP**: Write 3-index integrals compressed to disk (to save disk space) (default: 0).
- **THRC**: Threshold for 3-index integral calculations (integrals which are smaller than the given threshold are not written to disk) (default: 1d-10).
- **MINB**: Minimal bytelength for integral compression (default: 1).
- **MODE**: Switch for alternative DFSAPT driver which can use integral compression (to be evoked by MODE=2) (default: 1).
- **FXCFIT**: Use density fitting for computation of XC contributions in CPKS calculation (default: 0).
CPKS  
Switch for different CPKS solvers (default: 1).

CDIRECT  
Use integral direct algorithm for computing the (exact) exchange contributions in CPKS calculations, otherwise intergrals of the type (aux|vir.vir) are written to disk (default: 0).

MAXIT  
Maximum number of iterations in CPKS (default: 60).

THRCG  
Threshold for CG/GMRES solver in CPKS calculations (default: 1d-8).

NSYSOLVE  
Switch for BiCG (NSYSOLVE=1) or GMRES (NSYSOLVE=2) solver in CPKS calculations (default: 2).

NSUB  
Subspace size in GMRES solver (default: 50).

T678  
Switch for 3 different computation modes for $E^{(2)}_{\text{exch-disp}}$. T678=3 is recommended for the calculation of large systems but requires more disk space to store intermediate quantities (default: 1).

### 37.9.1 DFSAPT calculation of the water dimer using a DCBS basis set

```text
***,h2o-dimer DCBS
gthresh,energy=1.d-8,orbital=1.d-8,grid=1.d-8
oldnorm=1

c=2101.2
lb=2102.2

basis=
set,orbital
default,def2-tzvpp
default,def2-tzvpp/jkfit
set,mp2fit
default,def2-tzvpp/mp2fit
}
symmetry,nosym
angstrom
geometry=({
  1,O1,, -1.551007, -0.114520, 0.000000
  2,H2,, -1.934259, 0.762503, 0.000000
  3,H3,, -0.599677, 0.040712, 0.000000
  4,O4,, 1.350625, 0.111469, 0.000000
  5,H5,, 1.680398, -0.373741, -0.758561
  6,H6,, 1.680398, -0.373741, 0.758561
})
dummy,4,5,6
{ks,pbe; save,$ca}
monomerA,orb=$ca,core=1
dummy,1,2,3
{ks,pbe; start,atdens; save,$cb}
monomerB,orb=$cb,core=1
(grid; gridthr,1d-8)
dfsapt,all=1,fcoul=1.0,fxc=1.0

http://www.molpro.net/info/current/examples/h2o_2-dfsapt.com
```
37.9.2 DFSAPT calculation of the water dimer using an MCBS basis set

```bash
***, h2o-dimer MCBS
gthresh, energy=1.d-8, orbital=1.d-8, grid=1.d-8
oldnorm=1
c=2101.2
cb=2102.2

symmetry, nosym
angstrom
oxorient
gometry={
    1, O1,, -1.551007, -0.114520, 0.000000
    2, H2,, -1.934259, 0.762503, 0.000000
    3, H3,, -0.599677, 0.040712, 0.000000
}
basis={
    set, orbital
default, def2-tzvpp
}

{ks, pbe; save, $ca}
monomerA, orb=$ca, core=1

symmetry, nosym
angstrom
noorient
gometry={
    4, O4,, 1.350625, 0.111469, 0.000000
    5, H5,, 1.680398, -0.373741, -0.758561
    6, H6,, 1.680398, -0.373741, 0.758561
}

{ks, pbe; start, atdens; save, $cb}
monomerB, orb=$cb, core=1

symmetry, nosym
angstrom
noorient
gometry={
    1, O1,, -1.551007, -0.114520, 0.000000
    2, H2,, -1.934259, 0.762503, 0.000000
    3, H3,, -0.599677, 0.040712, 0.000000
    4, O4,, 1.350625, 0.111469, 0.000000
    5, H5,, 1.680398, -0.373741, -0.758561
    6, H6,, 1.680398, -0.373741, 0.758561
}
basis={
    set, orbital
default, def2-tzvpp
    set, jkfit
default, def2-tzvpp/jkfit
    set, mp2fit
default, def2-tzvpp/mp2fit
}

{grid; gridthr, 1d-8}
dfsapt, all=1, fcoul=1.0, fxc=1.0

http://www.molpro.net/info/current/examples/h2o_2-mc-dfsapt.com
```
37.9.3 DFSAPT calculation of the water dimer using an MC+BS basis set

```plaintext
***, h2o-dimer MC+BS

ca=2101.2
cb=2102.2

basis={
  set, orbital
  default, def2-tzvpp
}

symmetry, nosym

geometry={
  1, O1,, -1.551007, -0.114520, 0.000000
  2, H2,, -1.934259, 0.762503, 0.000000
  3, H3,, -0.599677, 0.040712, 0.000000
  4, Ne7,, 0.375474, 0.076091, 0.000000
}

dummy, ne7

{ks, pbe; save, $ca}

monomerA, orb=$ca, core=1

symmetry, nosym

geometry={
  4, O4,, 1.350625, 0.111469, 0.000000
  5, H5,, 1.680398, -0.373741, -0.758561
  6, H6,, 1.680398, -0.373741, 0.758561
  7, Ne7,, 0.375474, 0.076091, 0.000000
}

dummy, ne7

{ks, pbe; start, atdens; save, $cb}

monomerB, orb=$cb, core=1

symmetry, nosym

geometry={
  1, O1,, -1.551007, -0.114520, 0.000000
  2, H2,, -1.934259, 0.762503, 0.000000
  3, H3,, -0.599677, 0.040712, 0.000000
  4, O4,, 1.350625, 0.111469, 0.000000
  5, H5,, 1.680398, -0.373741, -0.758561
  6, H6,, 1.680398, -0.373741, 0.758561
  7, Ne7,, 0.375474, 0.076091, 0.000000
}

basis={
  set, orbital
  default, def2-tzvpp
  set, jkfit
  default, def2-tzvpp/jkfit
  set, mp2fit
  default, def2-tzvpp/mp2fit
}

dummy, ne7

{grid; gridthr, 1d-8}

dfsapt, all=1, fcoul=1.0, fxc=1.0

http://www.molpro.net/info/current/examples/h2o_2-mcplus-dfsapt.com
```
37.9.4 **DFSAPT calculation of the water dimer with additional $\delta$(HF) correction**

```
gdirect

qthresh,energy=1d-8,orbital=1d-7,grid=1d-8

symmetry,nosym
angstrom

geometry={
  1,O,   1.551007, -0.114520,  0.000000
  2,H,   1.934259,  0.762503,  0.000000
  3,H,   0.599677, -0.040712,  0.000000
  4,O,   1.350625,  0.111469,  0.000000
  5,H,   1.680398, -0.373741, -0.758561
  6,H,   1.680398, -0.373741,  0.758561
}
basis=
  set,orbital
  default,avdz
  set,jkfit
  default,avdz/jkfit
  set,mp2fit
  default,avdz/mp2fit
}
oldnorm=1
ca=2110.2
cb=2120.2
nkerna=1
nkernb=1

{df-hf,basis=jkfit; save,2100.2}
edm_hf=energy
dummy,4,5,6
{df-hf,basis=jkfit; save,cb; start,atdens}
em_hf=energy
monomerA,orb=$cb,core=$nkernb

dummy,1,2,3
{df-hf,basis=jkfit; save,ca; start,atdens}
emb_hf=energy
monomerB,orb=$ca,core=$nkerna

{grid; gridthr,1d-6}
{dfsapt,elp=1,eix=1,e2i=1,e2xi=1,auxbas='jkfit',fexx=1.0,fcoul=1.0,mode=1,cdirect=1,thrcg=1d-6}
{grid; gridthr,1d-8}
eint_hf=(edm_hf-ema_hf-emb_hf)*1000e0 mH
delta_hf=eint_hf-e12tot
dummy,4,5,6
lxgamma=1.15
{df-ks,lxbecke,pbex,pbec,basis=jkfit; dftfac,0.25,0.75,1.0; asymp,0d0; save,ca; start,atdens}
monomerA,orb=$ca,core=$nkernb

dummy,1,2,3
lxgamma=1.15
{df-ks,lxbecke,pbex,pbec,basis=jkfit; dftfac,0.25,0.75,1.0; asymp,0d0; save,cb; start,atdens}
monomerB,orb=$cb,core=$nkernb

{grid; gridthr,1d-6}
{dfsapt,all=1,auxbas='mp2fit',fxc=1.0,fcoul=1.0,mode=1,cpks=2,fxcfit=1,fxcsing=1,t678=3}
eint_sapt=e12tot+delta_hf
```

[http://www.molpro.net/info/current/examples/h2o_2-dfsapt2.com](http://www.molpro.net/info/current/examples/h2o_2-dfsapt2.com)
37.10 SAPT(CCSD)

SAPT with monomers described on the CCSD level is available for small complexes. In SAPT(CCSD) monomer density matrices and density-density matrix response functions from expectation-value CCSD theory are utilized. A high cost of SAPT(CCSD) results from the necessity of calculation of the CCSD response functions. Cumulant contributions from two-electron density matrices for \( E_{\text{exch}}^{(2)} \) and \( E_{\text{exch-ind}}^{(2)} \) are also available. The calculations can be performed for dimer-centered or monomer-centered-plus basis sets (the latter for all components but \( E_{\text{exch-disp}}^{(2)} \)). \( E_{\text{disp}}^{(2)} \) and \( E_{\text{exch-disp}}^{(2)} \) are usually calculated from density-fitted response functions in order to reduce the CPU time (from \( O(N^8) \) to \( O(N^7) \), where \( N \) is the molecular size). Some input examples can be found in the Molpro testjobs directory (note that \( E_{\text{disp}}^{(2)} \) and \( E_{\text{exch-disp}}^{(2)} \) are calculated separately from other SAPT components). It is important to note that SAPT(CCSD) and DFT-SAPT from Chapter 37.1 are completely different codes.

References:

Review of SAPT(CCSD):


38 PROPERTIES AND EXPECTATION VALUES

38.1 The property program

The property program allows the evaluation of one-electron operators and expectation values. Normally, the operators are computed automatically when using the global GEXPEC directive (see section 6.13) or the EXPEC or TRAN commands in the SCF, MCSCF, and CI programs. The explicit use of the property program is only necessary in the rare case that the user is interested in an orbital analysis of the properties.

38.1.1 Calling the property program (PROPERTY)

PROPERTY

invokes the property program.

38.1.2 Expectation values (DENSITY)

DENSITY [.record.file] [.specifications]
If this card is present, the density matrix will be read from record \textit{record.file} and property expectation values will be calculated. If the specification \textit{record.file} is omitted, the last dump record is used. Density matrices for specific states can be selected using \textit{specifications}, as explained in section 4.11. Note that the density matrices are stored in the same record as the orbitals.

### 38.1.3 Orbital analysis (\texttt{ORBITAL})

\texttt{ORBITAL[,record.file] [,specifications]}

If this card is present, the orbitals are read from record \textit{record.file} and an orbital analysis of the expectation values is printed (the density matrix must also be provided!). If \textit{record.file} is omitted, the last dump record is used. This is only meaningful for diagonal density matrices (SCF or natural orbitals). Natural orbitals for specific states can be selected using \textit{specifications}, as explained in section 4.11.

### 38.1.4 Specification of one-electron operators

The required operators are specified by code words. Optionally, the geometry or the nuclear centre at which the operator is computed can be specified.

For each operator, an input card of the following form is required:

\texttt{code,centre,x,y,z,,factor}

\textit{code} specifies the property. The available operators are given in section 6.13.

The other parameters have the following meaning:

- \textit{centre} row number of Z-matrix or atomic symbol defining the centre at which property shall be calculated; if \textit{centre} \neq 0 you need not read in coordinates.
- \textit{x,y,z} cartesian coordinates of the point (only if \textit{centre}=0).
- \textit{factor} the operator is multiplied by this factor. The default is \textit{factor}=1 except for \texttt{REL}. In this cases proper factors for relativistic corrections are used unless \textit{factor} is given. The two commas before factor are needed to preserve compatibility with \texttt{Molpro96}.

### 38.1.5 Printing options

\texttt{PRINT,print}

This card is used to control output, mainly for debugging purposes.

\textit{print} = 0 no test output (default)

\textit{print} > 0 operators are printed.

### 38.1.6 Examples

The following example computes the dipole quadrupole moments of water and prints an orbital analysis. By default, the origin is at the centre of mass, and this is taken as origin for the quadrupole moments.
38 PROPERTIES AND EXPECTATION VALUES

***,h2o properties
geometry={o;h1,o,r;h2,o,r,h1,theta} !Z-matrix geometry input
r=1 ang !bond length
theta=104 !bond angle
hf !do scf calculation
property !call property program
orbital !read scf orbitals
density !read scf density matrix
dm !compute dipole moments and print orbital contributions
qm !compute quadrupole moments and print orbital contributions
{multi;wf;state,2;dm !do full-valence CASSCF
natorb,state=1.1 !compute natural orbitals for state 1.1
natorb,state=2.1} !compute natural orbitals for state 2.1

http://www.molpro.net/info/current/examples/h2o_property.com

Alternatively, the dipole and quadrupole moments can be computed directly in the SCF and MCSCF programs, but in this case no orbital contributions are printed:

***,h2o properties
geometry={o;h1,o,r;h2,o,r,h1,theta} !Z-matrix geometry input
gexpc,dm,qm !global request of dipole and quadrupole moments
r=1 ang !bond length
theta=104 !bond angle
hf !do scf calculation
{multi;wf;state,2 !do full-valence CASSCF
natorb,state=1.1 !compute natural orbitals for state 1.1
natorb,state=2.1} !compute natural orbitals for state 2.1

http://www.molpro.net/info/current/examples/h2o_gexpcc1.com

38.2 Distributed multipole analysis

Any density matrix can be analysed using the distributed multipole analysis described by Stone, Chem. Phys. Letters (1981), 83, 233. The multipole moments arising from the overlap of each pair of primitives are calculated with respect to the overlap centre, and then shifted to the nearest of a number of multipole sites. By default these comprise all atoms specified in the integral input. However the list of multipole sites can be modified by deleting and/or adding sites, and also by restricting the rank of multipole which may be transferred to any given site. The atomic charges are stored in the MOLPRO variable ATCHARGE. The i’th element in ATCHARGE corresponds to the i’th row of the Z-matrix input.

Options may appear in any order, except DENSITY, which must be first if given.

The present version does not allow generally contracted AO basis sets.
38.2.1 Calling the DMA program (DMA)

DMA;

This command initializes the DMA program.

38.2.2 Specifying the density matrix (DENSITY)

DENSITY,record.file [,specifications]

The density matrix to be analysed is that found in record record on file file. If omitted, record.file defaults to current orbital record. If specified, DENSITY must appear first in the input. Density matrices for specific states can be selected using specifications, as explained in section 4.11.

38.2.3 Linear molecules (LINEAR, GENERAL)

GENERAL;

(default) invokes the normal program, which copes with any geometry.

LINEAR

invokes a faster program which can be used when all the atoms are arranged parallel to the z-axis and only the \( m = 0 \) components of the multipoles are required.

38.2.4 Maximum rank of multipoles (LIMIT)

LIMIT,name,lm\( \text{ax} \);

\( l_{\text{max}} \) is the highest rank of multipole that is to be calculated by the program. Default (and maximum) is 10 for the general program and 20 for the linear one. If name is specified, the limit applies only to multipole site name.

38.2.5 Omitting nuclear contributions (NONUCLEAR)

NONUCLEAR

The nuclear contributions to properties are not to be evaluated.

38.2.6 Specification of multipole sites (ADD, DELETE)

ADD,name,x,y,z,lm\( \text{ax} \),radius;

Add a new site at \((x, y, z)\) with the name specified. The multipole rank is limited to \( l_{\text{max}} \) if a value is specified, otherwise the value of \( l_{\text{max}} \) specified by the LIMIT directive is used. No account is taken of symmetry; every site in a symmetry-equivalent set must be specified explicitly. The radius of the site may also be specified (default 1.0).

DELETE,name

Delete all atoms with the name given from consideration as a multipole site. Note that original atoms from the integral program have names 1, 2, 3, \ldots as printed in integral output. DELETE, ALL deletes all atoms and gives the multipoles with respect to the origin only.
38.2.7 Defining the radius of multipole sites (RADIUS)

RADIUS, name, r;

Assign radius $r$ to all sites with the name given. The program moves multipoles at an overlap centre $P$ to the site $S$ for which the value of $|P - S|/r(S)$ is smallest. In the absence of a RADIUS directive, all sites are given radius 1.

38.2.8 Notes and references

The multipoles produced by this analysis are given in their spherical harmonic definitions. Explicit formulae for translating between the cartesian and spherical harmonic definitions of the multipole moments are given in, *Explicit formulae for the electrostatic energy, forces and torques between a pair of molecules of arbitrary symmetry*, S. L. Price, A. J. Stone, and M. Alderton, Molec. Phys., 52, 987 (1984).


38.2.9 Examples

The following input calculates SCF multipole moments for water.

```plaintext
***, h2o distributed multipole analysis
geometry={o;h1,o,r;h2,o,r,h1,theta} !Z-matrix geometry input
r=1 ang !bond length
theta=104 !bond angle
basis=6-311g**
hf !do scf calculation
{dma;limit,,4} !results for total multipoles are

http://www.molpro.net/info/current/examples/h2o_dma.com
```

38.3 Mulliken population analysis

38.3.1 Calling the population analysis program (POP)

POP;

Invokes Mulliken analysis program, which analyses any density matrix into its contributions from s,p,d,... basis functions on each atom. The density matrix is taken from the last dump record, unless overridden with the DENSITY card. The subcommands may be abbreviated by the first four characters. The atomic charges are stored in the MOLPRO variable ATCHARGE. The i'th element in ATCHARGE corresponds to the i'th row of the Z-matrix input.

38.3.2 Defining the density matrix (DENSITY)

DENSITY, record.file [, specifications]

Take density matrix to be analysed from record record on file file. Density matrices for specific states can be selected using specifications, as explained in section 4.11. Note that the density matrices are stored in the same record as the orbitals.
38.3.3 Populations of basis functions (INDIVIDUAL)

INDIVIDUAL;

38.3.4 Example

```plaintext
***, h2o population analysis
geometry={o;h1,o;r;h2,o;r,h1,theta} !Z-matrix geometry input
r=1 ang !bond length
theta=104 !bond angle
basis=6-311g** !do scf calculation
pop; !Mulliken population analysis using mcscf density
individual !give occupations of individual basis functions

http://www.molpro.net/info/current/examples/h2o_pop.com
```

If specified, the Mulliken populations of each individual basis function are printed.

38.4 Natural Bond Orbital Analysis

38.4.1 Calling the Natural Bond Orbital analysis program (NBO)

```plaintext
NBO,[WITH_CORE=core_option],[LEVEL=level],[KEEP_WBI=wbi_option];
```

The Natural Bond Orbital Analysis of Weinhold and coworkers (J. Chem. Phys. 83 (1985)
the use of the NBO card. It reads from a density or orbital record, and performs the necessary
transformations to Natural Atomic Orbitals (NAO), Natural Bond Orbitals (NBO) and Natural
Localized Molecular Orbitals (NLMO). The latter can also be saved to a record and later used
in local correlation treatments (cf. Section 32). By default, the full orbital space is used. The
core orbitals can, however, be left out of the procedure if core_option=0.

One can choose to truncate the transformation series (e.g., only compute the NAO orbitals), with
help of the LEVEL keyword. If level=1, only the NAO transformation will be carried out. For
level=2 the NBO transformation is performed, and for 3 the NLMO (default).

Sometimes, the NBO procedure will not converge due to a bad ordering on the 2-center bond
search. The first run is based on the Wiberg bond index, but the algorithm switches to the atom
ordering on the subsequent runs. This can be avoided by the use of the option KEEP_WBI. If
wbi_option=1, the Wiberg bond index is used in all iterations.

38.4.2 Saving the NLMO orbitals (SAVE)

```plaintext
SAVE, record.file;
```

The NLMO orbitals are saved in the specified record, together with the NPA charges.

38.5 Finite field calculations

Dipole moments, quadrupole moments etc. and the corresponding polarizabilities can be ob-
tained as energy derivatives by the finite difference approximation. This is most easily done
with the DIP, QUAD, or FIELD commands. An error will result if the added perturbation is not totally symmetric (symmetry 1). Note that the orbitals must be recomputed before performing a correlation calculation.

38.5.1 Dipole fields (DIP)

DIP, xfield, yfield, zfield;
DIP+, xfield, yfield, zfield;

Add a finite dipole field to the one electron Hamiltonian and the core energy. The field strength is given by xfield, yfield, zfield. DIP+ adds to any existing field, otherwise any previous field is removed.

38.5.2 Quadrupole fields (QUAD)

QUAD, xxfield, yyfield, zzfield, xyfield, xzfield, yzfield;
QUAD+, xxfield, yyfield, zzfield, xyfield, xzfield, yzfield;

Exactly as the DIP command, but adds a quadrupole field.

38.5.3 General fields (FIELD)

FIELD, oper1, fac1, oper2, fac2, …;
FIELD+, oper1, fac1, oper2, fac2, …;

Adds one-electron operators oper1, oper2, … with the corresponding factors fac1, fac2, … to the one-electron hamiltonian. The available operators are given in section 6.13. An error will result if the added perturbation is not totally symmetric (symmetry 1).

FIELD+ adds to any existing field, otherwise any previous field is removed.

Note that FIELD does currently not modify core polarization potentials (CPP). If CPPs are present, only DIP and QUAD should be used.

38.5.4 Examples

The first examples shows various possibilities to add perturbations to the one-electron hamiltonian.
The second example shows how to compute dipole moments and polarizabilities using finite fields.
38 PROPERTIES AND EXPECTATION VALUES

---

```plaintext
***, H2O finite field calculations

r=1.85, theta=104 !set geometry parameters
geometry=(O;
    H1,O,r;
    H2,O,r,H1,theta)

basis=avtz !define default basis
field=[0,0.005,-0.005] !define finite field strengths
$method=[hf,mp4,ccsd(t),casscf,mrci]

k=0
do i=1,#field !loop over fields
dip,,,field(i) !add finite field to H
do m=1,#method !loop over methods
    k=k+1
    $method(m) !calculate energy
    e(k)=energy !save energy
endo
enddo

k=0
n=#method
do m=1,#method
    k=k+1
    energ(m)=e(k)
    dipmz(m)=(e(k+n)-e(k+2*n))/(field(2)-field(3)) !dipole moment as first energy derivative
dpolz(m)=(e(k+n)+e(k+2*n)-2*e(k))/((field(2)-field(1))*(field(3)-field(1))) !polarizability
endo

dipmz=energ(m)
dpolz=energ(m)
table,method,energ,dipmz,dpolz

title, results for H2O, r=$R, theta=$theta, basis=$basis

---

http://www.molpro.net/info/current/examples/h2o_field.com

38.6 Relativistic corrections

Relativistic corrections may be calculated within the Cowan-Griffin approach by computing expectation values of the mass-velocity and 1-electron Darwin integrals; these should be generated using the property integral program with keyword REL. The expectation values can be computed within the SCF, MCSCF and CI programs in the usual way using the EXPECT command, again with the keyword REL. The mass-velocity and Darwin terms, and their sum are subsequently available through the MOLPRO variables MASSV, DARW and EREL respectively.
```
38.6.1 Example

***,ar2
geometry={ar1;ar2,ar1,r} !geometry definition
r=2.5 ang !bond distance
{hf; !non-relativistic scf calculation
expec,rel,darwin,massv} !compute relativistic correction using Cowan-Griffin operator
e_nrel-energy !save non-relativistic energy in variable enrel
show,masvv,darwin,erel !show individual contribution and their sum

http://www.molpro.net/info/current/examples/ar2_rel.com

38.7 CUBE — dump density or orbital values

CUBE, filename, iflag, n1, n2, n3

calls a module which dumps the values of various properties on a spatial parallelopipedal grid
to an external file. The purpose is to allow plotting of orbitals, densities and other quantities by
external programs. The format of the file is intended to be the same as that produced by other
programs.

filename is the unix path name of the file to be written, and its specification is mandatory.
iflag If iflag is negative (default), a formatted file will be written, otherwise unformatted
fortran i/o will be used.
n1, n2, n3 specify the number of grid points in each of three dimensions. If not specified,
sensible defaults are chosen.

By default, the last density computed is evaluated on the grid, and written to filename. This
behaviour can be modified by one or more of the following subcommands.

38.7.1 STEP — setting the point spacing

STEP,[stepx],[stepy], [stepz]

stepx, stepy, stepz specify the point spacing in each of three axis directions. By default, the value
of stepx, stepy, stepz is determined by the number of grid points, the Bragg radii of the atoms,
and some related parameters.

38.7.2 DENSITY — source of density

DENSITY,[density-source]
GRADIENT,[density-source]
LAPLACIAN,[density-source]

Compute the density and, optionally, its gradient and laplacian. <density-source> may be a
record number containing the required density, and may contain further qualification, such as
set number, in the usual way. By default, the last computed density is taken.
38.7.3 ORBITAL — source of orbitals

ORBITAL,[orbital-list],[RECORD=orbital-source]

<orbital-list> is a list of one or more orbital numbers of the form number:symmetry or keywords chosen from HOMO, LUMO, OCC (all occupied orbitals), ALL. If nothing is specified, the default is HOMO. <orbital-source> may be a record number containing the required density, and may contain further qualification, such as set number, in the usual way. By default, the last computed orbitals are taken.

Note that the CUBE file format precludes simultaneous orbital and density dumps, but that this may be achieved in the GOPENMOL format (see 38.8).

38.7.4 AXIS — direction of grid axes

AXIS,x,y,z

x,y,z specify the unnormalised direction cosines of one of the three axes defining the grid. Up to three AXIS commands can be given, but none is required. Axes need not be orthogonal. By default, the first axis is the cartesian x, the second is orthogonal to the first and to the cartesian z, and the third is orthogonal to the first two.

38.7.5 BRAGG — spatial extent of grid

Based on the direction of the coordinate axes, a parallelopiped (in the usual case of orthogonal axes, a cuboid) is constructed to contain the molecule completely. The atoms are assumed to be spherical, with an extent proportional to their Bragg radii, and the constant of proportionality can be changed from the default value using

BRAGG, scale

After the parallelopiped has been constructed, the grid is laid out with equal spacing to cover it using the number of points specified on the CUBE command.

38.7.6 ORIGIN — centroid of grid

ORIGIN,x,y,z

x,y,z specify the centroid of the grid. It is usually not necessary to use this option, since the default should suffice for most purposes.

38.7.7 TITLE — user defined title

TITLE,title

Set a user defined title in the cube file.

38.7.8 DESCRIPTION — user defined description

DESCRIPTION, description

Set a user defined description in the cube file.
38.7.9 Format of cube file

The formatted cube file contains the following records:

- **(A)** job title.
- **(A)** brief description of the file contents.
- **(I5, 3F12.6)** number of atoms, coordinates of grid origin (bohr).
- **(I5, 3F12.6)** number of grid points \( n_1 \), step vector for first grid dimension.
- **(I5, 3F12.6)** number of grid points \( n_2 \), step vector for second grid dimension.
- **(I5, 3F12.6)** number of grid points \( n_3 \), step vector for third grid dimension.
- **(I5, 4F12.6)** atomic number, charge and coordinates; one such record for each atom.
- **(6E13.5)** \( n_1 \times n_2 \) records of length \( n_3 \) containing the values of the density or orbital at each grid point. With default choice of the axes, the inner loop will be over \( n_3 \) points along the cartesian \( z \) axis, and the outer loop over \( n_1 \) points along the cartesian \( x \) axis.
  
  In the case of a number of orbitals \( m \), the record length is \( m \times n_3 \), with the data for a single grid point grouped together. In the case of the density gradient, there is first a record of length \( n_3 \) containing the density, then one of length \( 3n_3 \) containing the gradient, with the three cartesian components contiguous. For the laplacian, there is a further record of length \( n_3 \).

38.8 GOPENMOL — calculate grids for visualization in gOpenMol

GOPENMOL, filename, iflag, n1, n2, n3

The syntax and sub-options are exactly the same as for CUBE, except that the files produced are in a format that can be used directly in the gOpenMol visualization program. The following should be noted:

- Only the base name (up to the last '.') in filename is used, and is appended by different suffixes to create several different files:

  - **.crd** A CHARMm CRD-format file containing the coordinates is always produced, and may be used in the invocation of gOpenMol:
    
    rungOpenMol -i filename.crd

  - **.density.plt** If DENSITY is given, then the file filename.density.plt is produced and contains the density grid in gOpenMol internal format.

  - **.orbital_number.symmetry.plt** If ORBITAL is given, then for each orbital number, symmetry specified, the file filename_orbital_number.symmetry.plt is produced and contains the orbital grid in gOpenMol internal format.

- The default is not to produce any orbitals or densities, and so only the atomic coordinates are dumped.

- The default is to use unformatted binary files, and this should not normally be changed.

- The ORIGIN and AXIS commands should not be used.
• If
  \texttt{INTERACT}

is given in the input, when all the grids have been calculated, an attempt is made to
start \texttt{gOpenMol} by executing the Unix command \texttt{rungOpenMol}. If \texttt{rungOpenMol}
is not in $\texttt{PATH}$, then nothing happens. Otherwise, \texttt{gOpenMol} should start and display
the molecule. Any \texttt{.plt} files produced can be added to the display by following the
\texttt{Plot;Contour} menu item. The name of the Unix command may be changed from the
default \texttt{rungOpenMol} by specifying it as the first argument to the \texttt{INTERACT} directive.
By default, \texttt{gOpenMol} is not started, and this is equivalent to giving the command \texttt{BATCH}.

39 RELATIVISTIC CORRECTIONS

There are three ways in \texttt{MOLPRO} to take into account scalar relativistic effects:

1. Use the Douglas-Kroll-Hess or eXact-2-Component (X2C) relativistic one-electron inte-
grals.

2. Compute a perturbational correction using the Cowan-Griffin operator (see section 6.13).

3. Use relativistic effective core potentials (see section 12).

39.1 Using the Douglas–Kroll–Hess or eXact-2-Component Hamiltonians

For all-electron calculations, the preferred way is to use either the Douglas–Kroll–Hess (DKH)
or eXact-2-Component (X2C) Hamiltonians, the former of which is available up to (in principle)
arbitrary order in \texttt{MOLPRO}. DKH is activated by setting any of

\begin{verbatim}
SET,DKROLL=1
SET,DKHO=n, (n = 2,...,99),
SET,DKHP=m, (m = 1,...,5)
\end{verbatim}

or for X2C by setting

\begin{verbatim}
SET,DKHO=101
\end{verbatim}

somewhere in the input before the first energy calculation.

Alternatively, these values can be given as options on the \texttt{INT} command:

\begin{verbatim}
INT,[DKROLL=1],DKHO=n,DKHP=m.
\end{verbatim}

or

\begin{verbatim}
INT,DKHO=101
\end{verbatim}

The DKH option \texttt{DKROLL} is available for compatibility with earlier versions of \texttt{MOLPRO}. If
only \texttt{DKROLL=1} is given, the default for \texttt{DKHO} is 2. Setting \texttt{DKROLL=0} disables DKH and
X2C, independently of the setting of \texttt{DKHO}. DKH is also disabled by setting \texttt{DKHO=0}, unless
\texttt{DKROLL=1} is set. In order to avoid confusion, it is recommended only to use \texttt{DKHO} and never
set \texttt{DKROLL}.

The value of \texttt{DKHP} specifies the parametrization for the DKH treatment (it has no effect for
X2C):
DKHP=1: Optimum parametrization (OPT, default)
DKHP=2: Exponential parametrization (EXP)
DKHP=3: Square-root parametrization (SQR)
DKHP=4: McWeeny parametrization (MCW)
DKHP=5: Cayley parametrization (CAY)

Example:

```
SET,DKHO=8  ! DKH order = 8
SET,DKHP=2  ! choose exponential parametrization for unitary transformations (recommended)
```

Up to fourth order (DKHO=4) the DKH Hamiltonian is independent of the chosen parametrization. Higher-order DKH Hamiltonians depend slightly on the chosen parameterization of the unitary transformations applied in order to decouple the Dirac Hamiltonian.

For details on the infinite-order DKH Hamiltonians see

M. Reiher, A. Wolf, JCP 121, 2037–2047 (2004),

For details on the different parametrizations of the unitary transformations see

The current implementation is the polynomial-cost algorithm by Peng and Hirao: D. Peng, K. Hirao, JCP 130, 044102 (2009).

A detailed comparison of the capabilities of this implementation as well as the current implementation of the X2C approach is provided in:


39.2 Example for computing relativistic corrections

```
***,ar2
geometry=(ar1;ar2,ar1,r)  !geometry definition
r=2.5 ang  !bond distance
(hf;  !non-relativisitic scf calculation
expec,rel,darwin,massv) !compute relativistic correction using Cowan-Griffin operator
e_nrel-energy  !save non-relativistic energy in variable enrel
show,massv,darwin,erel  !show individual contribution and their sum

dkroll=1  !use douglas-kroll one-electron integrals
hf;  !relativistic scf calculation
e_dk-energy  !save relativistic scf energy in variable e_dk.
show,massv,darwin,erel  !show mass-velocity and darwin contributions and their sum
show,e_dk-e_nrel  !show relativistic correction using Douglas-Kroll
```

http://www.molpro.net/info/current/examples/ar2_rel.com

40 DIABATIC ORBITALS

In order to construct diabatic states, it is necessary to determine the mixing of the diabatic states in the adiabatic wavefunctions. In principle, this mixing can be obtained by integration of the non-adiabatic coupling matrix elements. Often, it is much easier to use an approximate
method, in which the mixing is determined by inspection of the CI coefficients of the MCSCF or CI wavefunctions. This method is applicable only if the orbital mixing is negligible. For CASSCF wavefunctions this can be achieved by maximizing the overlap of the active orbitals with those of a reference geometry, at which the wavefunctions are assumed to be diabatic (e.g. for symmetry reasons). The orbital overlap is maximized using the new DIAB command in the MCSCF program.

This procedure works as follows: first, the orbitals are determined at the reference geometry. Then, the calculations are performed at displaced geometries, and the "diabatic" active orbitals, which have maximum overlap with the active orbitals at the reference geometry, are obtained by adding a DIAB directive to the input:

Old form (Molpro96, obsolete):

\texttt{DIAB,orbref, orbsav, orb1,orb2,pri}

New form:

\texttt{DIAB,orbref[type=orbtype],STATE=state [SPIN=spin],MS2=ms2],SAVE=orbsav [ORB1=orb1,ORB2=orb2],PRINT=pri}

Here \texttt{orbref} is the record holding the orbitals of the reference geometry, and \texttt{orbsav} is the record on which the new orbitals are stored. If \texttt{orbsav} is not given (recommended!) the new orbitals are stored in the default dump record (2140.2) or the one given on the ORBITAL directive (see section \ref{sec:19.5.4}). In contrast to earlier versions of \texttt{MOLPRO} it is possible that \texttt{orbref} and \texttt{orbsav} are the same. The specifications \texttt{TYPE}, \texttt{STATE}, \texttt{SPIN} can be used to select specific sets of reference orbitals, as described in section \ref{sec:4.11}. \texttt{orb1}, \texttt{orb2} is a pair of orbitals for which the overlap is to be maximized. These orbitals are specified in the form \texttt{number.sym}, e.g. \texttt{3.1} means the third orbital in symmetry 1. If \texttt{orb1}, \texttt{orb2} are not given, the overlap of all active orbitals is maximized. \texttt{pri} is a print parameter. If this is set to 1, the transformation angles for each orbital are printed for each jacobi iteration.

Using the defaults described above, the following input is sufficient in most cases:

\texttt{DIAB,orbref}

Using \texttt{Molpro98} is is not necessary any more to give any \texttt{GEOM} and \texttt{DISPL} cards. The displacements and overlap matrices are computed automatically (the geometries are stored in the dump records, along with the orbitals).

The diabatic orbitals have the property that the sum of orbital and overlap contributions in the non-adiabatic coupling matrix elements become approximately zero, such that the adiabatic mixing occurs only through changes of the CI coefficients. This allows to determine the mixing angle directly from the CI coefficients, either in a simple way as described for instance in J. Chem. Phys. \textbf{89}, 3139 (1988), or in a more advanced manner as described by Pacher, Cederbaum, and Köppel in J. Chem. Phys. \textbf{89}, 7367 (1988).

Below we present an example for the first two excited states of H$_2$S, which have $B_1$ and $A_2$ symmetry in $C_{2v}$, and $A''$ symmetry in $C_{S}$. We first perform a reference calculation in $C_{2v}$ symmetry, and then determine the diabatic orbitals for displaced geometries in $C_{S}$ symmetry. Each subsequent calculation uses the previous orbitals as reference. One could also use the orbitals of the $C_{2v}$ calculation as reference for all other calculations. In this case one would have to take out the second-last input card, which sets \texttt{reforb=2141.2}. 


41 NON ADIABATIC COUPLING MATRIX ELEMENTS

Non-adiabatic coupling matrix elements can be computed by finite differences for MCSCF or CI wavefunctions using the DDR program. For state-averaged MCSCF wavefunctions, they can also be computed analytically (cf. section 19.9.2).

Note that present numerical procedure has been much simplified relative to Molpro96. No GEOM and DISPL input cards are needed any more, and the three necessary calculations can be done in any order.

41.1 The DDR procedure

In order to compute the coupling matrix elements by finite differences, one has to compute and store the wavefunctions at two (first-order algorithm) or three (second-order algorithm) slightly displaced geometries. The order of these calculations is arbitrary.

The typical strategy is as follows:

1.) Compute the wavefunction at the reference geometry. The wavefunctions for both states have to be stored using the SAVE command of the CI program. If the matrix elements are computed for MCSCF wavefunctions, it is necessary to recompute the wavefunction with the CI
program, using the NOEXC option. The transition density matrix is stored using the DM directive of the CI program.

2.) Compute the wavefunctions at the (positively) displaced geometry and store the CI wavefunction in a second record.

3.) If the second-order (three-point) method is used, step (2) is repeated at a (negatively) displaced geometry.

4.) Compute the transition density matrices between the states at the reference geometry and the displaced geometries. This is done with the TRANS directive of the CI program.

5.) Finally, the DDR program is used to assemble the matrix element. Using the first-order two-point method, only a single input line is needed:

\[ DDR, dr, orb1, orb2, trdm2 \]

where \( dr \) is the geometry increment used as denominator in the finite difference method, \( orb1 \) is the record holding the orbitals of the reference geometry, \( orb2 \) is the record holding the orbitals of the displaced geometry, and \( trdm2 \) is the record holding the transition density matrix computed from the CI-vectors at \( R \) and \( R+DR \).

If central differences (three points) are used, the input is as follows:

\[ DDR, 2*dr \]
\[ ORBITAL, orb1, orb2, orb3 \]
\[ DENSITY, trdm1, trdm2, trdm3 \]

where \( dr, orb1, orb2 \) are as above, and \( orb3 \) is the record holding the orbitals at the negatively displaced geometry.

\( trdm1, trdm2, trdm3 \) are the records holding the transition densities \( \gamma(R|R) \), \( \gamma(R|R+DR) \), and \( \gamma(R|R-DR) \), respectively.

If more than two states are computed simultaneously, the transition density matrices for all pairs of states will be stored in the same record. In that case, and also when there are just two states whose spatial symmetry is not 1, it is necessary to specify for which states the coupling is to be computed using the STATE directive:

\[ STATE, state_1, state_2 \]

where \( state_i \) is of the form \( istate.isym \) (the symmetries of both states must be the same, and it is therefore sufficient to specify the symmetry of the first state).

As an example the input for first-order and second-order calculations is given below. The calculation is repeated for a range of geometries, and at the end of the calculation the results are printed using the TABLE command.

In the calculation shown, the "diabatic" CASSCF orbitals are generated in the two CASSCF calculations at the displaced geometries by maximizing the overlap with the orbitals at the reference geometry. This is optional, and (within the numerical accuracy) does not influence the final results. However, the relative contributions of the orbital, overlap and CI contributions to the NACME are modified. If diabatic orbitals are used, which change as little as possible as function of geometry, the sum of overlap and orbital contribution is minimized, and to a very good approximation the NACME could be obtained from the CI-vectors alone.
This calculation produces the following table:

<table>
<thead>
<tr>
<th>R</th>
<th>NACME1P</th>
<th>NACME1M</th>
<th>NACMEAV</th>
<th>NACME2</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.0</td>
<td>-0.22828936</td>
<td>-0.22328949</td>
<td>-0.22578942</td>
<td>-0.22578942</td>
</tr>
<tr>
<td>10.5</td>
<td>-0.51777034</td>
<td>-0.50728914</td>
<td>-0.51252974</td>
<td>-0.51252974</td>
</tr>
<tr>
<td>11.0</td>
<td>0.76672943</td>
<td>0.76125391</td>
<td>0.76399167</td>
<td>0.76399167</td>
</tr>
<tr>
<td>11.5</td>
<td>0.42565202</td>
<td>0.42750263</td>
<td>0.42657733</td>
<td>0.42657733</td>
</tr>
<tr>
<td>12.0</td>
<td>0.19199878</td>
<td>0.19246799</td>
<td>0.19223338</td>
<td>0.19223338</td>
</tr>
</tbody>
</table>

Note that the sign changes because of a phase change of one of the wavefunctions. In order to keep track of the sign, one has to inspect both the orbitals and the ci-vectors.

42 QUASI-DIABATIZATION

The DDR procedure can also be used to generate quasi-diabatic states and energies for MRCI wavefunctions (CASSCF case can be treated as special case using the NOEXC directive in the MRCI). The quasi-diabatic states have the property that they change as little as possible relative to a reference geometry; with other words, the overlap between the states at the current geometry with those at a reference geometry is maximized by performing a unitary transformation among the given states. Preferably, the adiabatic and diabatic states should be identical at the reference geometry, e.g., due to symmetry. For instance, in the examples given below for the \( ^1B_1 \) and \( ^1A_2 \) states of \( H_2S \), \( C_2v \) geometries are used as reference, and at these geometries the states are unmixed due to their different symmetry. At the displaced geometries the molecular symmetry is reduced to \( C_S \). Both states now belong to the \( ^1A'' \) irreducible representation and are strongly mixed. For a description and application of the procedure described below, see D. Simah, B. Hartke, and H.-J. Werner, J. Chem. Phys. 111, 4523 (1999).

This diabatization can be done automatically and requires two steps: first, the active orbitals of a CASSCF calculation are rotated to maximize the overlap with the orbitals at the reference geometry. This is achieved using the DIAB procedure described in section 19.5.9. Secondly, the DDR procedure can be used to find the transformation among the CI vectors.

The following input is required:

DDR calls the DDR procedure.

ORBITAL, \( orb1, orb2 \) \( orb1 \) and \( orb2 \) are the (diabatic) orbitals at the current and reference geometry, respectively.

DENSITY, \( trdm1, trdm2 \) \( trdm1 \) and \( trdm2 \) are transition densities computed at the current geometry. \( trdm2 \) are transition densities computed using the wavefunctions of the current (bra) and reference (ket) geometries.

MIXING, \( state1, state2, \ldots \) The given states are included in the diabatization.

ENERGY, \( e1, e2, \ldots \) Adiabatic energies of the states. If this input card is present, the Hamiltonian in the basis of the diabatic states is computed and printed. Alternatively, the energies can be passed to DDR using the Molpro variable EADIA.

The results are printed and stored in the following Molpro variables, provided the ENERGY directive or the EADIA variable is found:

Results including the first-order orbital correction:
<table>
<thead>
<tr>
<th>Variable</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>SMAT</strong></td>
<td>The first $nstate \times nstate$ elements contain the state overlap matrix (bra index ranks fastest).</td>
</tr>
<tr>
<td><strong>UMAT</strong></td>
<td>The first $nstate \times nstate$ elements contain the transformation matrix.</td>
</tr>
<tr>
<td><strong>HDIA</strong></td>
<td>The first $nstate \cdot (nstate + 1)/2$ elements contain the lower triangle of the diabatic Hamiltonian.</td>
</tr>
<tr>
<td><strong>MIXANG</strong></td>
<td>Non-adiabatic mixing angle in degree. This is available only in the two-state case.</td>
</tr>
</tbody>
</table>

The corresponding results obtained from the CI-vectors only (without orbital correction) are stored in the variables [SMATCI], UMATCI, HDIACI, and MIXANGCI.

The way it works is most easily demonstrated for some examples. In the following input, the wavefunction is first computed at the $C_2v$ reference geometry, and then at displaced geometries.
***, h2s Diabatization
memory, 3, m

gprint, orbitals, civector

symmetry, x
orient, noorient ! noorient should always be used for diabatization
gprint, orbitals, civector

geometry={
h1, s, r1;
h2, s, r2, h1, theta
}
basis=avdz ! This basis is too small for real application
r1=2.5 ! Reference geometry
theta=[92]
r={2.50, 2.55, 2.60} ! Displaced geometries
reforb=2140.2 ! Orbital dump record at reference geometry
refci=6000.2 ! MRCI record at reference geometry
savci=6100.2 ! MRCI record at displaced geometries
text, compute wavefunction at reference geometry (C2v)
r2=r1
(hf; occ, 9, 2; wf, 18, 2, 4;
orbital, 2100.2)

{multi; occ, 9, 2; closed, 4, 1;
wf, 18, 2; state, 2;
natorb, reforb ! Save reference orbitals on reforb
noextra ! Dont use extra symmetries}

{ci; occ, 9, 2; closed, 4, 1;
wf, 18, 2, 0; state, 2;
orbital, diab, reforb ! Use orbitals from previous CASSCF
save, savci} ! Save MRCI wavefunction

Text, Displaced geometries
do i=1, # r ! Loop over different r values
data, truncate, savci+1 ! Truncate dump file after reference
r2=r(i) ! Set current r2

{multi; occ, 9, 2; closed, 4, 1;
wf, 18, 2, 0; state, 2;
start, reforb ! Starting orbitals
orbital, diab, 3140.2 ! Dump record for orbitals
diab, reforb ! Generate diabatic orbitals relative to reference geometry
noextra ! Dont use extra symmetries}

{ci; occ, 9, 2; closed, 4, 1;
wf, 18, 2, 0; state, 2;
orbital, diabatic ! Use diabatic orbitals
save, savci} ! Save MRCI for displaced geometries

el(i)= energy(1) ! Save adiabatic energies
e2(i)= energy(2)

{ci; trans, savci, savci ! Compute transition densities at R2
dm, 7000.2} ! Save transition densities on this record
{ci; trans, savci, refci; dm, 7100.2} ! Compute transition densities between R2 and R1
{dm} ! Save transition densities on this record
density, 7000.2, 7100.2 ! Densities for <R2||R2> and <R2||R1>
orbital, 3140.2, 2140.2 ! Orbitals for <R2||R2> and <R2||R1>
energy, el(i), e2(i) ! Adiabatic energies
mixing, 1.2, 2.2 ! Compute mixing angle and diabatic energies
This calculation produces the following results:

Diabatic energies for H$_2$S, obtained from CI-vectors

<table>
<thead>
<tr>
<th>R</th>
<th>E1</th>
<th>E2</th>
<th>H11CI</th>
<th>H22CI</th>
<th>H21CI</th>
<th>MIXCI</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.50</td>
<td>-398.64296319</td>
<td>-398.63384782</td>
<td>-398.64296319</td>
<td>-398.63384782</td>
<td>0.00000000</td>
<td>0.00</td>
</tr>
<tr>
<td>2.55</td>
<td>-398.64572746</td>
<td>-398.63666636</td>
<td>-398.64509901</td>
<td>-398.63729481</td>
<td>-0.00230207</td>
<td>15.27</td>
</tr>
<tr>
<td>2.60</td>
<td>-398.64911752</td>
<td>-398.63771802</td>
<td>-398.64662578</td>
<td>-398.64020976</td>
<td>-0.00471125</td>
<td>27.87</td>
</tr>
</tbody>
</table>

Diabatic energies for H$_2$S, obtained from CI-vectors and orbital correction

<table>
<thead>
<tr>
<th>R</th>
<th>E1</th>
<th>E2</th>
<th>H11</th>
<th>H22</th>
<th>H21</th>
<th>MIXTOT</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.50</td>
<td>-398.64296319</td>
<td>-398.63384782</td>
<td>-398.64296319</td>
<td>-398.63384782</td>
<td>0.00000000</td>
<td>0.00</td>
</tr>
<tr>
<td>2.55</td>
<td>-398.64572746</td>
<td>-398.63666636</td>
<td>-398.64509941</td>
<td>-398.63729441</td>
<td>-0.00230139</td>
<td>15.26</td>
</tr>
<tr>
<td>2.60</td>
<td>-398.64911752</td>
<td>-398.63771802</td>
<td>-398.64662526</td>
<td>-398.64021027</td>
<td>-0.00471160</td>
<td>27.88</td>
</tr>
</tbody>
</table>

The results in the first table are obtained from the CI-contribution to the state-overlap matrix only, while the ones in the second table include a first-order correction for the orbitals. In this case, both results are almost identical, since the DIAB procedure has been used to minimize the change of the active orbitals. This is the recommended procedure. If simply natural orbitals are used without orbital diabatization, the following results are obtained from the otherwise unchanged calculation:

Diabatic energies for H$_2$S, obtained from CI-vectors

<table>
<thead>
<tr>
<th>R</th>
<th>E1</th>
<th>E2</th>
<th>H11CI</th>
<th>H22CI</th>
<th>H21CI</th>
<th>MIXCI</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.50</td>
<td>-398.64296319</td>
<td>-398.63384782</td>
<td>-398.64296319</td>
<td>-398.63384782</td>
<td>0.00000000</td>
<td>0.00</td>
</tr>
<tr>
<td>2.55</td>
<td>-398.64572742</td>
<td>-398.63666630</td>
<td>-398.64509512</td>
<td>-398.63763760</td>
<td>-0.00280315</td>
<td>19.11</td>
</tr>
<tr>
<td>2.60</td>
<td>-398.64911746</td>
<td>-398.63771803</td>
<td>-398.64521031</td>
<td>-398.64162518</td>
<td>-0.00541050</td>
<td>35.83</td>
</tr>
</tbody>
</table>

Diabatic energies for H$_2$S, obtained from CI-vectors and orbital correction

<table>
<thead>
<tr>
<th>R</th>
<th>E1</th>
<th>E2</th>
<th>H11</th>
<th>H22</th>
<th>H21</th>
<th>MIXTOT</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.50</td>
<td>-398.64296319</td>
<td>-398.63384782</td>
<td>-398.64296319</td>
<td>-398.63384782</td>
<td>0.00000000</td>
<td>0.00</td>
</tr>
<tr>
<td>2.55</td>
<td>-398.64572742</td>
<td>-398.63666630</td>
<td>-398.64509146</td>
<td>-398.63730226</td>
<td>-0.00231474</td>
<td>15.36</td>
</tr>
<tr>
<td>2.60</td>
<td>-398.64911746</td>
<td>-398.63771803</td>
<td>-398.64648358</td>
<td>-398.64035190</td>
<td>-0.00480493</td>
<td>28.73</td>
</tr>
</tbody>
</table>

It is seen that the mixing obtained from the CI vectors only is now very different and meaningless, since the orbitals change significantly as function of geometry. However, the second calculations, which accounts for this change approximately, still gives results in quite good agreement with the calculation involving diabatic orbitals.

The final examples shows a more complicated input, which also computes the non-adiabatic coupling matrix elements. In a two-state model, the NACME should equal the first derivative of the mixing angle. In the example, the NACME is computed using the 3-point DDR method (NACMECI), and also by finite difference of the mixing angle (DCHI).
***, h2s Diabatization and NACME calculation
memory, 3, m
gprint, orbitals, civector

symmetry, x
orient, noorient  ! noorient should always be used for diabatization
group= 
  s;
  h1, s, r1;
  h2, s, r2, h1, theta}
basis=avdz  ! This basis is too small for real application
r1=2.5  ! Reference geometry
theta=[92]  
r=[2.55, 2.60]  ! Displaced geometries
dr=[0, 0.01, -0.01]  ! Small displacements for finite difference NACME calculation
reforb1=2140.2  ! Orbital dump record at reference geometry
refci=6000.2  ! MRCI record at reference geometry
savci=6100.2  ! MRCI record at displaced geometries
text, compute wavefunction at reference geometry (C2v)
r2=r1

{hf; occ, 9, 2; wf, 18, 2, 4; orbital, 2100.2}

{multi; occ, 9, 2; closed, 4, 1;
wf, 18, 2; state, 2;  ! 1B1 and 1A2 states
natorb, reforb1  ! Save reference orbitals on reforb1
noextra}  ! Don't use extra symmetries

{ci; occ, 9, 2; closed, 4, 1;  ! MRCI at reference geometry
wf, 18, 2, 0; state, 2;
orbital, reforb1  ! Use orbitals from previous CASSCF
save, refci}  ! Save MRCI wavefunction

Text, Displaced geometries
do i=1, #r  ! Loop over different r values
data, truncate, savci+1  ! Truncate dumpfile after reference
reforb=reforb1
do j=1, 3  ! Loop over small displacements for NACME
r2=r(i)+dr(j)  ! Set current r2

{multi; occ, 9, 2; closed, 4, 1;
wf, 18, 2, 0; state, 2;  ! Wavefunction definition
start, reforb
orbital, 3140.2+j;  ! Dump record for orbitals
diab, reforb
noextra}  ! Don't use extra symmetries
reforb=3141.2  ! Use orbitals for j=1 as reference for j=2, 3

{ci; occ, 9, 2; closed, 4, 1;
wf, 18, 2, 0; state, 2;
orbital, diabatic
save, savci+j}  ! Use diabatic orbitals
save, savci+j  ! Save MRCI for displaced geometries
eadia=energy
if(j.eq.1) then
  el(i)=energy(1)
e2(i)=energy(2)
end if

{ci; trans, savci+j, savci+j;  ! Compute transition densities at R2+DR(j)
dm, 7000.2+j}  ! Save transition densities on this record
{ci; trans, savci+j, refci;  ! Compute transition densities between R2+DR(j) and R1

enddo
The calculation produces the following table

<table>
<thead>
<tr>
<th>R</th>
<th>MIXCI</th>
<th>MIXTOT</th>
<th>DCHI</th>
<th>NACMECI</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.55</td>
<td>15.2694</td>
<td>15.2644</td>
<td>-5.2226</td>
<td>-5.2365</td>
</tr>
<tr>
<td>2.60</td>
<td>27.8740</td>
<td>27.8772</td>
<td>-3.4702</td>
<td>-3.4794</td>
</tr>
</tbody>
</table>

Diabatic energies for H2S, obtained from CI-vectors

<table>
<thead>
<tr>
<th>R</th>
<th>E1</th>
<th>E2</th>
<th>H11CI</th>
<th>H22CI</th>
<th>H21CI</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.55</td>
<td>-398.64572746</td>
<td>-398.63666636</td>
<td>-398.64509901</td>
<td>-398.63729481</td>
<td>-0.00230207</td>
</tr>
<tr>
<td>2.60</td>
<td>-398.64911752</td>
<td>-398.63771802</td>
<td>-398.64662578</td>
<td>-398.64020976</td>
<td>-0.00471125</td>
</tr>
</tbody>
</table>

Diabatic energies for H2S, obtained from CI-vectors and orbital correction

<table>
<thead>
<tr>
<th>R</th>
<th>E1</th>
<th>E2</th>
<th>H11</th>
<th>H22</th>
<th>H21</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.55</td>
<td>-398.64572746</td>
<td>-398.63666636</td>
<td>-398.64509941</td>
<td>-398.63729441</td>
<td>-0.00230139</td>
</tr>
<tr>
<td>2.60</td>
<td>-398.64911752</td>
<td>-398.63771802</td>
<td>-398.64662526</td>
<td>-398.64021027</td>
<td>-0.00471160</td>
</tr>
</tbody>
</table>

As expected the coupling matrix elements obtained from the 3-point DDR calculation (NACMECI) and by differentiating the mixing angle (DCHI) are in close agreement.
43 THE VB PROGRAM CASVB

CASVB is a general program for valence bond calculations written by T. Thorsteinsson and D. L. Cooper (1996–2005).

This program can be used in two basic modes:

a) variational optimization of quite general types of nonorthogonal MCSCF or modern valence bond wavefunctions

b) representation of CASSCF wavefunctions in modern valence form, using overlap- (relatively inexpensive) or energy-based criteria.

Bibliography:


All publications resulting from use of this program should acknowledge relevant publications. There is a more complete bibliography at [http://www.liv.ac.uk/dlc/CASVB.html](http://www.liv.ac.uk/dlc/CASVB.html)

43.1 Structure of the input

All CASVB sub-commands may be abbreviated by four letters. The general input structure can be summarized as follows:

a) For generating representations of CASSCF wavefunctions, the program is invoked by the command CASVB. For variational optimization of wavefunctions it is normally invoked inside MULTI by the sub-command VB (see [19.10]).

b) Definition of the CASSCF wavefunction (not generally required).

c) Definition of the valence bond wavefunction.

d) Recovery and/or storage of orbitals and vectors.

e) Manual input of starting guess (optional).

f) Optimization control.

g) Definition of molecular symmetry and possible constraints on the VB wavefunction.

h) Wavefunction analysis.

i) Further general options.

Items a) and b) should precede everything else in the input; apart from this, commands may come in any order.
43.2 Defining the CASSCF wavefunction

*CASVB* is interfaced with the determinant part of *MULTI* (i.e., `CONFIG, CSF;` must not be specified). When this program is run prior to *CASVB*, the CI vector must dumped using one of the directives `SAVE, NATORB, CANONICAL, or LOCALI` (see section 19.5.5). The three latter are recommended.

43.2.1 The VBDUMP directive

`VBDUMP[vbdump];`

If present, the `VBDUMP` card must occur first in the *CASVB* input. It is not required for variational calculations.

Note that in the majority of cases (e.g., if a *CASVB* run occurs immediately after *MULTI*, or for variational calculations), explicit specification of dump records with `vbdump` is not required.

Wavefunction definitions may be restored here using `VBDUMP` cards (see also Section 19.8.6). The default record name (`vbdump`) is 4299.2. If a `VBDUMP` card is not present and record 4299.2 does not exist, then *CASVB* will attempt to generate the wavefunction information automatically based on the latest MCSCF calculation (however, `STATE` and `WEIGHT` information will not be restored in such a case).

43.3 Other wavefunction directives

The definitions of the CASSCF wavefunction may also be specified manually using some or all of the directives:

- **OCC**: Occupied orbitals.
- **CLOSED**: Closed-shell orbitals.
- **FROZEN**: Frozen-core orbitals.
- **WF**: Wavefunction card.
- **STATE**: Number of states for this wavefunction symmetry.
- **WEIGHT**: Weights of states.

For the exact definition of these cards see sections 19.2 and 19.3. These commands may also be used to modify the values defined in `VBDUMP`. The information given on these cards should correspond to the CI vector saved in the CASSCF calculation. The cards, and their ordering, should therefore coincide with those used in *MULTI*, except for the `WEIGHT` cards which may differ. At present, the VB wavefunction must correspond to a well-defined number of electrons and total spin. Other states may be present, but an error condition will occur if non-zero weights are specified for wavefunction symmetries with varying values of `elec` or `spin`.

43.4 Defining the valence bond wavefunction

43.4.1 Specifying orbital configurations

The number of core and active orbitals (`mcore, mact`), active electrons (`Nact`), and the value of the total spin will be identical to that defined for the CASSCF wavefunction. The spatial VB
configurations are defined in terms of the active orbitals only, and may be specified using one or more CON cards (note that the RESTRICT and SELECT keywords are not used in CASVB):

\[ \text{CON} n_1, n_2, n_3, n_4, \ldots ; \]

The configurations can be specified by occupation numbers, exactly as in MULTI (see section 19.4.3), so that \( n_i \) is the occupation of the \( i \)th valence bond orbital. Alternatively a list of \( N_{\text{act}} \) orbital numbers (in any order) may be provided – the program determines which definition applies. The two cards \[ \text{CON}, 1, 0, 1, 2; \]
and \[ \text{CON}, 1, 3, 4, 4; \]
are thus equivalent.

If no configurations are specified the single covalent configuration \( \phi_1 \phi_2 \cdots \phi_{N_{\text{act}}} \) is assumed.

### 43.4.2 Selecting the spin basis

\[ \text{SPINBASIS}, \text{key}; \]

\text{key} may be chosen from \text{KOTANI} (default), \text{RUMER}, \text{PROJECT} or \text{LTRUMER}, specifying the basis of spin eigenfunctions used in the definition of valence bond structures. \text{PROJECT} refers to spin functions generated using a spin projection operator, \text{LTRUMER} to Rumer functions with the so-called “leading term” phase convention.

### 43.5 Recovering CASSCF CI vector and VB wavefunction

The appropriate MOLPRO records may be specified explicitly using the \text{START} directive (an alternative is the \text{vbdump} mechanism described in section 43.2.1):

\[ \text{START}, \text{ci}, \text{vb}, \text{orb}, \text{trnint}; \]

\text{ci}: record name for the CASSCF CI vector. The CI vector must have been dumped previously using either of the \text{SAVE}, \text{NATORB}, \text{CANONICAL}, or \text{LOCALI} directives (see section 19.5.5). A default value for \text{ci} is determined from the most recent \text{vbdump} record(s).

Note that if the \text{ci} record is not found, only an energy-based optimization of the VB wavefunction can be carried out.

\text{vb}: record name for the valence bond orbitals and structure coefficients, as saved by a previous CASVB calculation. If the VB wavefunction was previously saved in the AO basis the orbitals will be projected onto the present active space (note that it is necessary to specify a record name for the molecular orbitals (\text{orb} below) for this to be possible).

\text{orb}: record name for the molecular orbitals defining the CASSCF wavefunction. This information is necessary if one wants to output the valence bond orbitals in the atomic orbital basis.

\text{trnint}: record name for the transformed CASSCF integrals. These are required for the energy-based criteria (i.e., if \text{CRIT,ENERGY} is specified), and can be saved inside MULTI by the \text{TRNINT} sub-command (see 19.8.7). The default record name, both here and in \text{MULTI}, is 1900.1.

### 43.6 Saving the VB wavefunction

\[ \text{SAVE}, \text{vb}, \text{civb}; \]

\text{vb}: record name for VB wavefunction (default is first available record after 3200.2), i.e., orbitals and structure coefficients.
**43.7 Specifying a guess**

**GUESS; key-1...; key-2...;...**

The `GUESS` keyword initiates the input of a guess for the valence bond orbitals and structure coefficients. `key-i` can be either `ORB`, `STRUC` or `READ`. These keywords modify the guess provided by the program, or specified by the `START` directive. It is thus possible to modify individual orbitals in a previous solution to construct the starting guess.

**43.7.1 Orbital guess**

**ORB, i, c_1, c_2,..., c_{mact};**

Specifies a starting guess for valence bond orbital number `i`. The guess is specified in terms of the `mact` active MOs defining the CASSCF wavefunction. (Note that the definition of these MOs will depend on how the CI vector was dumped – i.e. which of the `SAVE`, `NATORB`, `CANONICAL`, or `LOCALI` directives was used (see section 19.5.5). Use of one of the three latter keywords is recommended.)

**43.7.2 Guess for structure coefficients**

**STRUC, c_1, c_2,..., c_{NVB};**

Specifies a starting guess for the `NVB` structure coefficients. If this card is not provided, and no guess specified by `START`, the perfect-pairing mode of spin coupling is assumed for the spatial configuration having the least number of doubly occupied orbitals. Note that the definition of structures depends on the value of `SPINBASIS`. Doubly occupied orbitals occur first in all configurations, and the spin eigenfunctions are based on the singly occupied orbitals being in ascending order.

**43.7.3 Read orbitals or structure coefficients**

The `READ` keyword can take one of the following forms:

**READ,ORB,iorb1[,TO,iorb2] [,AS,iorb1[,TO,iorb2]] [,FROM,record];**

**READ,STRUC,istruc1[,TO,istruc2] [,AS,istruc1[,TO,istruc2]] [,FROM,record];**

**READ,ALL [,FROM,record];**

In this way a subset of orbitals and/or structure coefficients may be picked out from a previous calculation. Renumbering of orbitals or structures can be done using the “AS” construct as outlined above. If the VB wavefunction was previously saved in the AO basis, the orbitals will be projected onto the present active space (note that it is necessary to specify a record name for the molecular orbitals (`orb` in the `START` command) for this to be possible).

Default for `record` is the `vb` record name specified in keyword `START` (if applicable).
43.8 Permuting orbitals

ORBPERM,i1,...,i_{nuc};

Permutes the orbitals in the valence bond wavefunction and changes their phases according to $\phi'_j = \text{sign}(i_j)\phi_{\text{abs}(i_j)}$. The guess may be further modified using the GUESS keyword. Also the structure coefficients will be transformed according to the given permutation (note that the configuration list must be closed under the orbital permutation for this to be possible).

43.9 Optimization control

43.9.1 Optimization criterion

CRIT,method;

Specifies the criterion for the optimization. method can be OVERLAP or ENERGY (OVERLAP is default). The former maximizes the normalized overlap with the CASSCF wavefunction:

$$\max \left( \frac{\langle \Psi_{\text{CAS}} | \Psi_{\text{VB}} \rangle}{\sqrt{\langle \Psi_{\text{VB}} | \Psi_{\text{VB}} \rangle}} \right)$$

and the latter simply minimizes the energy:

$$\min \left( \frac{\langle \Psi_{\text{VB}} | \hat{H} | \Psi_{\text{VB}} \rangle}{\langle \Psi_{\text{VB}} | \Psi_{\text{VB}} \rangle} \right) .$$

43.9.2 Number of iterations

MAXITER,N_{iter};

Specifies the maximum number of iterations in the second order optimizations. Default is $N_{\text{iter}} = 50$.

43.9.3 CASSCF-projected structure coefficients

(NO)CASPROJ;

With this keyword the structure coefficients are picked from the transformed CASSCF CI vector, leaving only the orbital variational parameters. For further details see the bibliography. This option may be useful to aid convergence.

43.9.4 Saddle-point optimization

SADDLE,n;

Defines optimization onto an $n^{\text{th}}$-order saddle point. See also T. Thorsteinsson and D. L. Cooper, Int. J. Quant. Chem. 70, 637–50 (1998).
43.9.5 Defining several optimizations

More than one optimization may be performed in the same CASVB deck, by the use of OPTIM keywords:

OPTIM[;...;FINOPTIM];

The subcommands may be any optimization declarations defined in this section, as well as any symmetry or constraints specifications described in section 43.10. Commands given as arguments to OPTIM will be particular to this optimization step, whereas commands specified outside will act as default definitions for all subsequent OPTIM keywords.

If only one optimization step is required, the OPTIM keyword need not be specified.

When only a machine-generated guess is available, CASVB will attempt to define a sequence of optimization steps chosen such as to maximize the likelihood of successful convergence and to minimize CPU usage. To override this behaviour, simply specify one or more OPTIM cards.

43.9.6 Multi-step optimization

A loop over two or more optimization steps may be specified using:

ALTERN,Niter;...;FINALTER

With this specification the program will repeat the enclosed optimization steps until either all optimizations have converged, or the maximum iteration count, Niter, has been reached.

43.10 Point group symmetry and constraints


43.10.1 Symmetry operations

SYMELM,label,sign;

Initiates the definition of a symmetry operation referred to by label (any three characters). sign can be + or −; it specifies whether the total wavefunction is symmetric or antisymmetric under this operation, respectively. A value for sign is not always necessary but, if provided, constraints will be put on the structure coefficients to ensure that the wavefunction has the correct overall symmetry (note that the configuration list must be closed under the orbital permutation induced by label for this to be possible).

The operator is defined in terms of its action on the active MOs as specified by one or more of the keywords IRREPS, COEFFS, or TRANS (any other keyword will terminate the definition of this symmetry operator). If no further keyword is supplied, the identity is assumed for label. The alternative format SYMELM,label,sign;key-1;...;key-2;...;... may also be used.

43.10.2 The IRREPS keyword

IRREPS,i_1, i_2;...;
The list $i_1, i_2, \ldots$ specifies which irreducible representations (as defined in the CASSCF wave-
function) are antisymmetric with respect to the *label* operation. If an irreducible representation
is not otherwise specified it is assumed to be symmetric under the symmetry operation.

### 43.10.3 The COEFFS keyword

**COEFFS,$i_1, i_2, \ldots$**

The list $i_1, i_2, \ldots$ specifies which individual CASSCF MOs are antisymmetric with respect to
the *label* operation. If an MO is not otherwise specified, it is assumed to be symmetric under the
symmetry operation. This specification may be useful if, for example, the molecule possesses
symmetry higher than that exploited in the CASSCF calculation.

### 43.10.4 The TRANS keyword

**TRANS,$n_{dim}, i_1, \ldots i_{n_{dim}}, c_{11}, c_{12}, \ldots c_{n_{dim}n_{dim}}$**

Specifies a general $n_{dim} \times n_{dim}$ transformation involving the MOs $i_1, \ldots i_{n_{dim}}$, specified by the
c coefficients. This may be useful for systems with a two- or three-dimensional irreducible
representation, or if localized orbitals define the CASSCF wavefunction. Note that the specified
transformation must always be orthogonal.

### 43.10.5 Symmetry relations between orbitals

In general, for a VB wavefunction to be symmetry-pure, the orbitals must form a representa-
tion (not necessarily irreducible) of the symmetry group. Relations between orbitals under the
symmetry operations defined by SYMELM may be specified according to:

**ORBREL,$i_1, i_2, label1, label2, \ldots$**

Orbital $i_1$ is related to orbital $i_2$ by the sequence of operations defined by the *label* specifications
(defined previously using SYMELM). The operators operate right to left. Note that $i_1$ and $i_2$ may
coincide. Only the minimum number of relations required to define all the orbitals should be
provided; an error exit will occur if redundant ORBREL specifications are found.

### 43.10.6 The SYMPROJ keyword

As an alternative to incorporating constraints, one may also ensure correct symmetry of the
wavefunction by use of a projection operator:

**(NO)SYMPROJ[,irrep1,irrep2,\ldots]**

The effect of this keyword is to set to zero coefficients in unwanted irreducible representations.
For this purpose the symmetry group defined for the CASSCF wavefunction is used (always a
subgroup of $D_{2h}$). The list of irreps in the command specifies which components of the wave-
function should be kept. If no irreducible representations are given, the current wavefunction
symmetry is assumed. In a state-averaged calculation, all irreps are retained for which a non-
zero weight has been specified in the wavefunction definition. The SYMPROJ keyword may
also be used in combination with constraints.
43.10.7 Freezing orbitals in the optimization

\textbf{FIXORB}, i_1, i_2, \ldots ;

This command freezes the orbitals specified in the list $i_1, i_2, \ldots$ to that of the starting guess. Alternatively the special keywords \textbf{ALL} or \textbf{NONE} may be used. These orbitals are eliminated from the optimization procedure, but will still be normalized and symmetry-adapted according to any \textbf{ORBREL} keywords given.

43.10.8 Freezing structure coefficients in the optimization

\textbf{FIXSTRUC}, i_1, i_2, \ldots ;

Freezes the coefficients for structures $i_1, i_2, \ldots$. Alternatively the special keywords \textbf{ALL} or \textbf{NONE} may be used. The structures are eliminated from the optimization procedure, but may still be affected by normalization or any symmetry keywords present.

43.10.9 Deleting structures from the optimization

\textbf{DELSTRUC}, i_1, i_2, \ldots; [\textbf{ALL}],[\textbf{NONE}];

Deletes the specified structures from the wavefunction. The special keywords \textbf{ALL} or \textbf{NONE} may be used. A structure coefficient may already be zero by symmetry (as defined by \textbf{SYMELM} and \textbf{ORBREL}), in which case deleting it has no effect.

43.10.10 Orthogonality constraints

\textbf{ORTHCON}; \textit{key-1}, \ldots ; \textit{key-2}, \ldots ; \ldots

The \textbf{ORTHCON} keyword initiates the input of orthogonality constraints between pairs of valence bond orbitals. The sub-keywords \textit{key-i} can be one of \textbf{ORTH}, \textbf{PAIRS}, \textbf{GROUP}, \textbf{STRONG} or \textbf{FULL} as described below. Orthogonality constraints should be used with discretion. Note that orthogonality constraints for an orbital generated from another by symmetry operations (using the \textbf{ORBREL} keyword) cannot in general be satisfied.

\textbf{ORTH}, i_1, i_2, \ldots ;

Specifies a list of orbitals to be orthogonalized. All overlaps between pairs of orbitals in the list are set to zero.

\textbf{PAIRS}, i_1, i_2, \ldots ;

Specifies a simple list of orthogonalization pairs. Orbital $i_1$ is made orthogonal to $i_2$, $i_3$ to $i_4$, etc.

\textbf{GROUP}, \textit{label}, i_1, i_2, \ldots ;

Defines an orbital group to be used with the \textbf{ORTH} or \textbf{PAIRS} keyword. The group is referred to by \textit{label} which can be any three characters beginning with a letter a–z. Labels defining different groups can be used together or in combination with orbital numbers in \textbf{ORTH} or \textbf{PAIRS}. $i_1$, $i_2$, \ldots specifies the list of orbitals in the group. Thus the combination \textbf{GROUP},AZZ,1,2; \textbf{GROUP},BZZ,3,4; \textbf{ORTH},AZZ,BZZ; will orthogonalize the pairs of orbitals 1-3, 1-4, 2-3 and 2-4.

\textbf{STRONG};
This keyword is short-hand for strong orthogonality. The only allowed non-zero overlaps are between pairs of orbitals \((2n-1, 2n)\).

**FULL;**

This keyword is short-hand for full orthogonality. This is mainly likely to be useful for testing purposes.

### 43.11 Wavefunction analysis

#### 43.11.1 Spin correlation analysis

**(NO)SCORR;**

With this option, expectation values of the spin operators \((\hat{s}_\mu + \hat{s}_\nu)^2\) are evaluated for all pairs of \(\mu\) and \(\nu\). Default is \texttt{NOSCORR}. The procedure is described by: G. Raos, J. Gerratt, D. L. Cooper and M. Raimondi, Chem. Phys. 186, 233–250 (1994); ibid, 251–273 (1994); D. L. Cooper, R. Ponec, T. Thorsteinsson and G. Raos, Int. J. Quant. Chem. 57, 501–518 (1996).

At present this analysis is only implemented for spin-coupled wavefunctions.

#### 43.11.2 Printing weights of the valence bond structures

For further details regarding the calculation of weights in CASVB, see T. Thorsteinsson and D. L. Cooper, J. Math. Chem. 23, 105-26 (1998).

**VBWEIGHTS,key1,key2,…**

Calculates and outputs weights of the structures in the valence bond wavefunction \(\Psi_{VB}\). \texttt{key} specifies the definition of nonorthogonal weights to be used, and can be one of:

- **LOWDIN** Performs a symmetric orthogonalization of the structures and outputs the corresponding weights.
- **ALL** All of the above.
- **NONE** Suspends calculation of structure weights.

The commands **LOWDIN** and **INVERSE** require the overlap matrix between valence bond structures, and some computational overhead is thus involved.

#### 43.11.3 Printing weights of the CASSCF wavefunction in the VB basis

For further details regarding the calculation of weights in CASVB, see T. Thorsteinsson and D. L. Cooper, J. Math. Chem. 23, 105-26 (1998).

**CIWEIGHTS,key1,key2,…,[N_{conf}];**

Prints weights of the CASSCF wavefunction transformed to the basis of nonorthogonal VB structures. For the \texttt{key} options see \texttt{VBWEIGHTS} above. Note that the evaluation of inverse overlap weights involves an extensive computational overhead for large active spaces. Weights are
given for the total CASSCF wavefunction, as well as the orthogonal complement to $\Psi_{VB}$. The default for the number of configurations requested, $N_{\text{conf}}$, is 10. If $N_{\text{conf}}=-1$ all configurations are included.

### 43.12 Controlling the amount of output

```
PRINT,i1, i2,...;
```

Each number specifies the level of output required at various stages of the execution, according to the following convention:

-1 No output except serious, or fatal, error messages.
0 Minimal output.
1 Standard level of output.
2 Extra output.

The areas for which output can be controlled are:

- $i_1$: Print of input parameters, wavefunction definitions, etc.
- $i_2$: Print of information associated with symmetry constraints.
- $i_3$: General convergence progress.
- $i_4$: Progress of the 2nd order optimization procedure.
- $i_5$: Print of converged solution and analysis.
- $i_6$: Progress of variational optimization.
- $i_7$: Usage of record numbers on file 2.

For all, the default output level is +1. If $i_5 \geq 2$ VB orbitals will be printed in the AO basis (provided that the definition of MOs is available); such output may be especially useful for plotting of orbitals.

### 43.13 Further facilities

Calculations can also be performed for various types of direct product wavefunctions and/or with strictly localized orbitals. Details are available from the authors. These facilities will be documented in a later release.

### 43.14 Service mode

```
SERVICE;
```

This keyword takes precedence over any others previously defined to CASVB. It provides simple facilities for retrieving orbital coefficients and VB structure coefficients. It should not be used during a run of CASVB that has been invoked from inside MULTI.

```
START,record.file;
```

Coefficients are taken from `record.file`. The default value is `2100.2`.

```
WRITE,iwrite;
```

Vectors in the symmetry orbital basis are written to channel `iabs(iwrite)`. The default action is
to write these vectors to the standard output. If \texttt{iwrite} is negative, then the vectors are instead written to a binary file as a single record.

\texttt{SPECIAL,$idim1,idim2,idim3,idim4$;}

If present, this keyword must come last. The program attempts to retrieve from \texttt{record.file} a vector of length $idim1 \times idim2 + idim3$, after first skipping $idim4$ elements. The vector is written according to the setting of \texttt{iwrite}. (Default \texttt{idim} values are zero.)

### 43.15 Examples

\texttt{***, ch2} ! A1 singlet state
\texttt{geometry={angstrom}
\texttt{c}
\texttt{h1,c,1.117}
\texttt{h2,c,1.117,h1,102.4}}
\texttt{int hf}
\texttt{(multi; occ,4,1,2; closed,1} ! 6 in 6 CASSCF
\texttt{natorb,,ci,save=3500.2; vbdump)}
\texttt{(casvb,,ci,save=3500.2; vbdump)
\texttt{(casvb, save,3200.2)} ! Overlap-based VB using
\texttt{(casvb, save,3200.2; save,3220.2)} ! the spin-coupled wavefunction
\texttt{(casvb, save,3220.2)} ! Energy-based VB calculation
\texttt{(casvb, save,3220.2; save,3240.2; print,,,,,2)}
---

\texttt{***, n2s2 (model a)} ! Variational calculation for N2S2.
\texttt{v=2.210137753 bohr} ! NOTE: other choices of active space
g\texttt{geometry={ n, -v, 0, 0;}
\texttt{n, +v, 0, 0;}
\texttt{s, 0, -v, 0;}
\texttt{s, 0, +v, 0}}
\texttt{basis=VTZ}
\texttt{hf}
\texttt{(multi; occ,7,4,5,2,4,2,2,0; closed,7,4,5,2,1,0,1,0; natorb,,ci,save=3500.2}
\texttt{(multi; occ,7,4,5,2,4,2,2,0; closed,7,4,5,2,1,0,1,0;}
\texttt{(vb; start,,3500.2; scorr)}}
---

\texttt{***, lih} ! Fully-variational VB calculation
\texttt{r=2.8 bohr} ! and geometry optimization.
g\texttt{geometry=(li;h,li,r)}
b\texttt{asis=VTZ}
\texttt{hf}
\texttt{(multi; occ,4,0,0,0; closed,0,0,0,0; natorb,,ci,save=3500.2)
\texttt{(multi; occ,4,0,0,0; closed,0,0,0,0;}
\texttt{(vb; start,3500.2))}
o\texttt{optg}---
44 SPIN-ORBIT-COUPLING

44.1 Introduction

Spin-orbit matrix elements and eigenstates can be computed using either the Breit-Pauli (BP) operator or spin-orbit pseudopotentials (ECPs). The state-interacting method is employed, which means that the spin-orbit eigenstates are obtained by diagonalizing $\hat{H}_d + \hat{H}_{SO}$ in a basis of eigenfunctions of $\hat{H}_d$. The full Breit-Pauli SO-operator can be used only for MCSCF wavefunctions. For MRCI wavefunctions, the full BP operator is used for computing the matrix elements between internal configurations (no electrons in external orbitals), while for contributions of external configurations a mean-field one-electron fock operator is employed. The error caused by this approximation is usually smaller than 1 cm$^{-1}$.

The program allows either the computation of individual spin-orbit matrix elements for a given pair of states, or the automatic setting-up and diagonalization of the whole matrix for a given set of electronic states. In the latter case, matrix elements over one-electron operators are also computed and transformed to the spin-orbit eigenstates (by default, the dipole matrix elements are computed; other operators can be specified on the GEXPEC or EXPEC cards, see section 6.13). Since it may be often sufficient to compute the spin-orbit matrix elements in a smaller basis than the energies, it is possible to replace the energy eigenvalues by precomputed values, which are passed to the spin-orbit program by the MOLPRO variable HLSDIAG.

44.2 Calculation of SO integrals

The one- and two-electron spin-orbit integrals over the BP Hamiltonian can be precomputed and stored on disk using the command

```
LSINT [X][Y][Z][ONECENTER][;TWINT;][;PREFAC;]
```

X, Y, and Z specify the components to be computed. If none of these is given, all three are evaluated. The advantage of precomputing the integrals is that they can then be used in any number of subsequent SO calculations, but this may require a large amount of disk space (note that there are 6 times as many integrals as in an energy calculation). If the LSINT card is not given, the integrals are computed whenever needed. The keyword ONECENTER activates the one-center approximation for one- and two- electron spin-orbit integrals. This can reduce drastically the computing time for large molecules. TWINT and PREFAC can be used to control the accuracy of spin-orbit integrals. These thresholds are similar to TWINT and PREFAC for standard integrals. The default value for PREFAC is TWINT/100, and the default value for TWINT is 10$^{-7}$. In the case when no integrals are precomputed, these thresholds can be specified as options for HLSMAT or TRANLS cards, see below.

The input for spin-orbit ECPs is described in section 12. Of course, in ECP-LS calculations the LSINT card is not needed.

44.3 Calculation of individual SO matrix elements

Individual spin-orbit matrix elements can be computed within the MRCI program using

```
TRANLS,record1.file, record2.file, bra2ms, ket2ms, lsop;
```

where
record1.file Record holding the bra-wavefunction.

record2.file Record holding the ket-wavefunction. Both records must have been generated using the \texttt{SAVE} directive of the MRCI program.

\texttt{bra2ms} \quad 2 \times M_S \text{ value of the bra-wavefunction.}

\texttt{ket2ms} \quad 2 \times M_S \text{ value of the ket-wavefunction.}

\texttt{lsop} \quad \text{Cartesian component of the Spin-orbit Hamiltonian.}

This can be one of \texttt{LSX}, \texttt{LSY}, or \texttt{LSZ} in all electron calculations, and \texttt{ECPLSX}, \texttt{ECPLSY}, or \texttt{ECPLSZ} in ECP calculations. Starting from the MOLPRO version 2008.1, more types are available which control the approximation level. These are described in section 44.4.

Since the spin-orbit program is part of the MRCI program, the \texttt{TRANLS} card must be preceded by a [MR]CI card. For the case that the matrix elements are computed for MCSCF wavefunctions, one has to recompute and save the CI-vectors using the MRCI program (see chapter 20), using the \texttt{NOEXC} directive to avoid inclusion of any further excitations out of the MCSCF reference function. If in the MRCI step several states of the same symmetry are computed simultaneously using the \texttt{STATE} directive, the matrix elements are computed for all these states. Note that the \texttt{OCC} and \texttt{CLOSED} cards must be the same for all states used in a \texttt{TRANLS} calculation.

The selection rules for the $M_S$ values are $\Delta M_S = \pm 1$ for the \texttt{LSX} and \texttt{LSY} operators, and $\Delta M_S = 0$ for the \texttt{LSZ} operator. Note that $2M_S$ has to be specified, and so the selection rules applying to the difference of the input values are 0 or 2.

In all-electron SO calculations the value of the calculated spin-orbit matrix element is saved (in atomic units) in the MOLPRO variables \texttt{TRLSX}, \texttt{TRLSY} and \texttt{TRLSZ} for the \texttt{x}, \texttt{y}, and \texttt{z} components respectively. For ECP-LS calculations the variables \texttt{TRECPLSX}, \texttt{TRECPLSY}, and \texttt{TRECPLSZ} are used. Note that for imaginary matrix elements (i.e., for the \texttt{x} and \texttt{z} components of the SO Hamiltonian) the matrix elements are imaginary and the stored real values have to be multiplied by $i$. If matrix elements for several states are computed, all values are stored in the respective variable-arrays with the bra-states running fastest.

### 44.4 Approximations used in calculating spin-orbit integrals and matrix elements

Recently, more sophisticated approximations were introduced to simplify spin-orbit calculations for larger molecules. These are controlled by specifying the spin-orbit operator type \texttt{lsop} as follows (we omit suffixes \texttt{X}, \texttt{Y}, \texttt{Z} which specify the component):

\textbf{LS} \quad \text{Standard spin-orbit calculations.}

\textbf{ALS} \quad \text{The one-center approximation is used for one- and two-electron spin-orbit integrals.}

\textbf{FLS} \quad \text{The effective Fock-matrix approximation is used for the internal part too.}

\textbf{AFLS} | \textbf{AMFI} \quad \text{The one-center approximation is used for one- and two-electron spin-orbit integrals, and the effective Fock-matrix approximation for the internal part.}

\textbf{ECPLS} \quad \text{Effective core potentials are used for all atoms at which they are defined; contributions of all other atoms are neglected (see below).}

In case that the effective Fock matrix is used for all contributions, and no spin-orbit integrals are pre-calculated and stored on disk (i.e., the \texttt{LSINT} command is not given), the Fock matrices are evaluated in direct mode and no integrals are stored on disk. When this is combined with
the one-center approximation (AMFI), the computing and I/O times are drastically reduced, and this makes spin-orbit calculations quite fast even for larger molecules.

Also, the treatment of ECP-type of spin-orbit interaction has been changed and now allows for treating both ECP and non-ECP atoms in one calculation. Thus, in molecules containing both heavy and light atoms, the heavy atoms can be described using ECPs and the light atoms using all-electron basis sets. If the operator type is LS, ALS, FLS, or AFLS, then for the atoms having an ECP spin-orbit operator defined in the basis input the ECP operator is used, while the full BP-operator is used for all other atoms (couplings are neglected). Both one-center and AMFI approximations can be used in this case. If, on the other hand, one specifies the operator type as ECPLS, then the behavior is the same as in the previous versions, i.e., only the ECP contributions are considered and the contributions from all other atoms are neglected.

44.5 Calculation and diagonalization of the entire SO-matrix

\texttt{HLSMAT, type, record1, record2, record3, ...}

Computes the entire SO matrix and diagonalizes it using all states which are contained in the records record1, record2, record3, .... All records must have been generated using the SAVE directive of the MRCI program. \texttt{type} may be either LS for Breit-Pauli calculations, or ECP for ECP-LS calculations. By default, the eigenvalues and dipole transition matrix elements between the ground and excited states are printed.

As with the \texttt{TRANLS} card, the \texttt{HLSMAT} is recognized only by the MRCI program and must be preceded by a \texttt{CI} card. Also, the \texttt{OCC} and \texttt{CLOSED} cards must be the same for all states used in a \texttt{HLSMAT} calculation.

44.6 Modifying the unperturbed energies

Often it may be sufficient to compute the spin-orbit matrix elements in a smaller basis or at a lower computational level than the energies. It is therefore possible to replace the energy eigenvalues by precomputed values, which are passed to the spin-orbit program by the MOLPRO variable \texttt{HLSDIAG}. The energy values in \texttt{HLSDIAG} must be in exactly the same order as the states in the records given on the \texttt{HLSMAT} card. Before any spin-orbit calculation, the variable \texttt{HLSDIAG} must either be undefined or cleared (then the original energies are used), or must contain exactly the number of energies as the number of states treated in the subsequent spin-orbit calculation (use \texttt{CLEAR, HLSDIAG} to clear any previous values in the variable). It is the user’s responsibility that the order of the energies in \texttt{HLSDIAG} is correct!

44.6.1 Print Options for spin-orbit calculations

\texttt{PRINT, option1=value1, option2=value2, ...}

where option can be

\begin{itemize}
  \item \texttt{HLS} \; \texttt{HLS=-1} only the SO energies and transition matrix elements between ground and excited states are printed (default).
  \item \texttt{HLS} \; \texttt{HLS=0} The SO matrix is printed.
  \item \texttt{HLS} \; \texttt{HLS=1} The property matrices are printed.
  \item \texttt{HLS} \; \texttt{HLS=2} The individual matrix elements are printed (same as \texttt{OPTION, MATEL}).
  \item \texttt{HLS} \; \texttt{HLS=3} Debugging information is printed.
\end{itemize}
VLS  

VLS=-1: No print of eigenvectors (default).
VLS≥0: The eigenvectors are printed.

### 44.6.2 Options for spin-orbit calculations

Some options can be set using the **OPTION** directive (in any order)

**OPTIONS** [WIGNER=value] [HLTRANS=value] [MATEL=value]

where

**WIGNER**  This option determines whether the Wigner-Eckart theorem should be used when the SO matrix is determined. **WIGNER=1** (default) uses the theorem, **WIGNER=0** calculates each SO matrix element individually. This option is needed for test purposes only.

**HLTRANS**  This option determines whether a SO matrix calculation should be performed in the not spin-symmetry adapted basis set (**HLTRANS=0**), in the spin-symmetry adapted basis set (**HLTRANS=1**, default) or with both basis sets (**HLTRANS=2**). At present, symmetry adaption can only be performed for triplet states, where the following notation is used to indicate the symmetry adapted spin functions:  

\[ |S,M_S\rangle_+ = \frac{1}{\sqrt{2}} (|S,M_S\rangle + |S,-M_S\rangle), \]

\[ |S,M_S\rangle_- = \frac{1}{\sqrt{2}} (|S,M_S\rangle - |S,-M_S\rangle). \]

If only singlet and triplet states are considered, the spin-orbit matrix is blocked according to double-group symmetry and the eigenvalues for each each block are printed separately. In all other cases the **HLTRANS** option is ignored.

**MATEL**  If the entire SO matrix is calculated using **HLSMAT**, the individual matrix elements are normally not shown. When the option **MATEL=1** is given, the individual matrix elements and the contributions of the internal and external configuration classes are printed.
44.7 Examples

44.7.1 SO calculation for the S-atom using the BP operator

```bash
**,** SO calculation for the S-atom
geometry={s}
basis={spd,s,vtz}   !use uncontracted basis

{rhf;occ,3,2,2,2;wf,16,4,2}   !rhf for 3P state

{multi}
wf,16,4,2;wf,16,6,2;wf,16,7,2;wf,16,1,0;state,3;   !1D and 1S states
wf,16,4,0;wf,16,6,0;wf,16,7,0}   !3P states

{ci;wf,16,1,0;save,3010.1;state,3;noexc}
{ci;wf,16,4,0;save,3040.1;noexc}
{ci;wf,16,6,0;save,3060.1;noexc}
{ci;wf,16,7,0;save,3070.1;noexc}
{ci;wf,16,4,2;save,3042.1;noexc}
{ci;wf,16,6,2;save,3062.1;noexc}
{ci;wf,16,7,2;save,3072.1;noexc}

{ci;wf,16,1,0;save,4010.1;state,3}
ed=energy(1)   !save energy for 1D state in variable ed
es=energy(3)   !save energy for 1S state in variable es
ep=energy      !save energy for 3P state in variable ep

{ci;hlsmat,ls,3010.1,3040.1,3042.1,3060.1,3062.1,3070.1,3072.1,3042.1,3062.1,3072.1}   !All states, casscf

lsint          !compute so integrals

{ci;hlsmat,ls,4042.1,4062.1,4072.1}   !Only triplet states, casscf

text,3P states, mrci

{ci;hlsmat,ls,4042.1,4062.1,4072.1}   !Only triplet states, mrci

{ci;hlsmat,ls,3010.1,3040.1,3070.1,3042.1,3062.1,3072.1,3042.1,3062.1,3072.1}   !All states, casscf

{ci;hlsmat,ls,3010.1,3040.1,3060.1,3070.1,3042.1,3062.1,3072.1,3042.1,3062.1,3072.1}
```

http://www.molpro.net/info/current/examples/s_so.com
44.7.2 SO calculation for the I-atom using ECPs

***,I
memory,5,M;
gprint,orbitals,civector,basis;
gthresh,energy=1.d-8,coeff=1.d-8;
geometry={I};

basis={

! Iodine-ECP (Dirac-Fock) with SO-coupling
!
ecp,I,46,4,3;
1; 2, 1.00000000, 0.00000000; ! lokal term = 0
2; 2, 3.50642001, 83.09814545; 2, 1.74736492, 5.06370919; ! s-terme
3; 2, 2.99860773, 1/3* 81.88444526; 2, 3.01690894, 2/3* 83.41280402; ! p-terms with weight
4; 2, 1.59415934, 1/3* 2.32392477; 2, 1.19802939, 2/3* 2.72079843; ! d-terme with weight
4; 2, 1.03813792, 2/5* 6.40131754; 2, 1.01158599, 3/5* 6.21328827; ! p-terms with weight
2, 2.04193864, 2/5* 19.11604172; 2, 1.99631017, 3/5* 19.08465909; ! d-terms with weight
4; 2, 2.64971585,-3/7* 24.79106489; 2, 2.75335574,-4/7* 24.98147319; ! f-terms with weight
2, 0.49970082,-3/7* 0.27936581; 2, 0.79638982,-4/7* 0.70184261; ! ECP-SO for p-terms
4; 2, 2.99860773,-2/3* 81.88444526; 2, 1.59415934,-2/3* 2.32392477; ! ECP-SO for d-terms
4; 2, 1.03813792,-2/5* 6.40131754; 2, 1.01158599, 3/5* 6.21328827; ! ECP-SO for f-terms
2, 2.04193864,-2/5* 19.11604172; 2, 1.99631017, 3/5* 19.08465909; ! ECP-SO for d-terms
4; 2, 2.64971585, 2/7* 24.79106489; 2, 2.75335574,-2/7* 24.98147319; ! ECP-SO for f-terms
2, 0.49970082, 2/7* 0.27936581; 2, 0.79638982, 2/7* 0.70184261; ! ECP-SO for f-terms
!
! Iodine-basis
!
s,1,0.2027624,0.4080619,0.8212297,1.6527350,3.3261500;
c,1.5,-0.4782372,-0.5811680,0.2617769,0.4444120,-0.1596560;
s,1,0.05,0.2027624,0.4080619,0.8212297,1.6527350,3.3261500;
c,1.5,0.4251589,0.2995618,0.0303167,-0.2064228,0.0450858;
p,1,0.05,0.2027624,0.4080619,0.8212297,1.6527350,3.3261500;
c,1.5,0.2451589,0.2995618,0.0303167,-0.2064228,0.0450858;
f,1,0.3;
d,1,0.2,0.4;
}

{hf;occ,1,1,1,,1;wf,7,5,1} !scf for 2Pz
{multi;occ,1,1,1,,1;wf,7,5,1} !casscf with minimal active space
{ci;wf,7,2,1;wf,7,3,1;wf,7,5,1} !average 2P states
{ci;wf,7,2,1;noexc;save,5000.2} !save casscf vector for 2Px state
{ci;wf,7,3,1;noexc;save,5100.2} !save casscf vector for 2Py state
{ci;wf,7,5,1;noexc;save,5200.2} !save casscf vector for 2Pz state
{ci;wf,7,2,1;save,6000.2} !mrci for 2Px state
{ci;wf,7,3,1;save,6100.2} !mrci for 2Py state
{ci;wf,7,5,1;save,6200.2} !mrci for 2Pz state
{multi;occ,1,2,2,,2} !casscf with larger active space
{ci;wf,7,2,1;wf,7,3,1;wf,7,5,1} !average 2P states
{ci;wf,7,2,1;noexc;save,5010.2} !save casscf vector for 2Px state
{ci;wf,7,3,1;noexc;save,5110.2} !save casscf vector for 2Py state
{ci;wf,7,5,1;noexc;save,5210.2} !save casscf vector for 2Pz state
{ci;wf,7,2,1;save,6010.2} !mrci for 2Px state
{ci;wf,7,3,1;save,6110.2} !mrci for 2Py state
{ci;wf,7,5,1;save,6210.2} !mrci for 2Pz state

text,casscf, occ,1,1,1,,1
{ci;hlsmat,ecp,5000.2,5100.2,5200.2} !do spin-orbit calculations
text,casscf, occ,1,2,2,,2
{ci;hlsmat,ecp,5010.2,5110.2,5210.2}
text,mrci, occ,1,1,1,,1
{ci;hlsmat,ecp,6000.2,6100.2,6200.2}
text,mrci, occ,1,2,2,,2
{ci;hlsmat,ecp,6010.2,6110.2,6210.2}
45 ENERGY GRADIENTS

45.1 Analytical energy gradients

MOLPRO uses different gradient programs:

The CADPAC gradient program is based on the CADPAC integral routines by R. D. Amos. Currently, this program works for closed shell SCF, high spin RHF, and (state averaged) MCSCF. In the MCSCF case the wavefunction must either be fully optimized, or frozen core orbitals must be taken from a closed-shell SCF calculation (but this does not work in the case of state-averaged MCSCF). Note that CADPAC does not work with generally contracted basis functions.

The ALASKA gradient program is based on the SEWARD integral routines by R. Lindh. It allows the calculation of gradients of generally contracted basis functions for closed shell SCF, open shell RHF, UHF, RKS, UKS, MCSCF, MP2, LMP2, DF-LMP2, QCISD, QCISD(T), CCSD, DCSD and RS2 (CASPT2). Gradients for state averaged MCSCF wave functions can be evaluated using the RS2 gradient program, see section 45.1.5. For details about CASPT2 gradients, see section 21.7.

The AIC density fitting integral program written by G. Knizia computes two- and three-index integrals and integral derivatives. This program is used for computing gradients for the DF-MP2, DF-LMP2, state averaged DF-MCSCF, and DF-CASPT2 methods.

By default, the program uses ALASKA gradients whenever possible. However, it is possible to force the use of a particular gradient program by defining the variable GRADTYP before calling the gradient program:

GRADTYP=ALASKA
GRADTYP=CADPAC

The gradient program is called using the FORCE command:

FORCE

Normally, the FORCE command is not needed, since geometry optimizations should be performed using the OPTG procedure. An exception is the optimization of counterpoise corrected energies, which requires several force calculations (cf. section 46.4.7).

If no further data cards are given, the default is to evaluate the gradient for the last optimized wavefunction. In this case no further input is needed for ordinary gradient cases (the program remembers the records on which the wavefunction information is stored). An exception is the unusual case that several different CPMCSCF calculations have been formed in a previous MC-SCF calculation. In this case the SAMC directive must be used to select the desired record. If analytical gradients are not available for the last wavefunction, the gradient is computed numerically. For more details regarding numerical energy gradients see section 45.2.

45.1.1 Adding gradients (ADD)

ADD,factor,[NOCHECK];

If this card is present, the current gradient and energy are added to the previous ones using the given factor. This is useful for the optimization of counterpoise corrected energies (cf. 46.4.7). By default, the program will stop with an error message unless NOORIENT has been specified in the geometry input. This behaviour can be disabled by the NOCHECK option. This option should only be given if all gradients which are added are evaluated at exactly the same nuclear geometry; otherwise wrong results could result due to unintended rotations of the system.
45.1.2 Scaling gradients (SCALE)

\texttt{SCALE,factor;}

If this card is present, the current gradient and energy are scaled by the give factor. This is sometimes useful for the optimization of counterpoise corrected energies (cf. 46.4.7).

45.1.3 Defining the orbitals for SCF gradients (ORBITAL)

\texttt{ORBITAL,record.file;}

In the SCF case, \texttt{record.file} specifies the location of the orbitals, which are used for constructing density matrices, etc. This card is only needed if the SCF for which the gradient is to be computed was not the most recent energy calculation.

For MCSCF wavefunctions, the \texttt{ORBITAL} card is not needed, because the location of the orbitals is stored in the MCSCF dump record.

45.1.4 MCSCF gradients (MCSCF)

\texttt{MCSCF,record.file;}

Triggers code for MCSCF gradient. \texttt{record.file} specifies the location of information dumped from the MCSCF program, using a \texttt{SAVE,GRD=recmc.filmc} card. This card is not needed if the \texttt{FORCE} command appears directly after the corresponding MCSCF input, since the program automatically remembers where the MCSCF information was stored. The same is true if \texttt{OPTG} is used.

45.1.5 State-averaged MCSCF gradients with SEWARD

SA-MCSCF gradients can be computed using segmented or generally contracted basis sets using \texttt{SEWARD} and the RS2 gradient program. The \texttt{NOEXC} directive has to be used in the RS2 input, but no \texttt{CPMCSCF} card is required in \texttt{MULTI}. The RS2 gradient program does the CP-MCSCF automatically.

Example: compute SA-CASSCF gradients for $^2\Pi$ and $^2\Sigma^+$ state of OH.

\begin{verbatim}
geometry={o;h,o,r}
r=1.83
{multi;wf,9,2,1;wf,9,3,1;wf,9,1,1} !state averaged casscf for X(2PI) and A(2SIGMA)
{rs2;noexc;wf,9,1,1} !compute A(2SIGMA) energy
forces !energy gradient for A(2SIGMA) state
{rs2;noexc;wf,9,2,1} !compute A(2PI) energy
forces !energy gradient for A(2PI) state
\end{verbatim}

http://www.molpro.net/info/current/examples/oh_samcforce.com

Without the \texttt{NOEXC} directive, the RS2 (CASPT2) gradient would be evaluated, using the state-averaged orbitals.
State-averaged MCSCF gradients with CADPAC

Normally, no further input is required for computing gradients for state-averaged MCSCF when CADPAC is used. Note, however, that a `CPMCS CF, GRAD.state` directive is required in the SA-MCSCF calculation (see Section [19.9]). The gradients are then computed automatically for the state specified on the `CPMCS CF` card. The same is true for difference gradients (`CPMCS CF, DGRAD.state1, state2`) and non-adiabatic coupling matrix elements (`CPMCS CF, NACM.state1, state2`). It is possible to do several coupled-perturbed MCSCF calculations one after each other in the same MCSCF. In this case FORCE would use the last solution by default. The information from the CPMCS CF is passed to the FORCE program in a certain records (default 5101.1, 5102.1, ...). If several CPMCS CF calculations are performed in the same MCSCF, several such records may be present, and a particular one can be accessed in the FORCE program using the `SAMC` directive:

```
SAMC,record.
```

An alias for `SAMC` is `CPMC`. For compatibility with earlier versions one can also use

```
NACM,record
```

for non-adiabatic couplings or

```
DEMC,record
```

for difference gradients.

Example:

```
multi;
....
state,3
  cpmcs cf,nacm,1.1,2.1,save=5101.1 !do cpmcs cf for coupling of states 1.1 - 2.1
  cpmcs cf,nacm,1.1,3.1,save=5102.1 !do cpmcs cf for coupling of states 1.1 - 3.1
  cpmcs cf,nacm,2.1,3.1,save=5103.1 !do cpmcs cf for coupling of states 2.1 - 3.1
force;samc,5101.1; !compute NACME for states 1.1 - 2.1
force;samc,5102.1; !compute NACME for states 1.1 - 3.1
force;samc,5103.1; !compute NACME for states 2.1 - 3.1
```

Non-adiabatic coupling matrix elements (NACM)

see Section [45.1.6]

Difference gradients for SA-MCSCF (DEMC)

see Section [45.1.6]
45.1.9 Example

***, Calculate Gradients for Water
alpha=104 degree !set geometry parameters
r=1 ang
geometry={O; !define z-matrix
H1,o,r;
H2,o,r,H1,alpha}
basis=vdz !basis set
hf !do scf
forces !compute gradient for SCF
mp2 !mp2 calculation
forces !mp2 gradients
multi !casscf calculation
forces !casscf gradient

http://www.molpro.net/info/current/examples/h2o_forces.com

45.2 Numerical gradients

It is possible to compute gradients by finite differences using
FORCE, NUMERICAL, options

Numerical gradients are computed automatically if no analytical gradients are available for the last energy calculation. By default, no further input are needed, and the gradient will be computed for the last energy calculation. The following options can be given on the FORCE command or on subsequent directives (see subsequent sections):

STARTCMD=command The input between command and the current FORCE command defines the energy calculation for which the gradient is computed. This input section is executed for each displacement.

PROC=procname specifies a procedure to be executed for each displacement. This must define a complete energy calculation and must not contain gradient or Hessian calculations.

VARIABLE=varname Compute the gradient of the value of variable varname. This implies numerical gradients. The variable must be set in the corresponding energy calculation.

COORD=ZMAT|CART|3N coordinates with respect to which the gradient is evaluated. See section 45.2.1 for more information.

DISPLACE=ZMAT|SYM|UNIQUE|CART Displacement coordinates to be used for numerical gradient. The default is ZMAT if the geometry is given as a zmatrix which depends on variables, and SYM (symmetrical displacement coordinates) otherwise. See section 45.2.1 for more information.

SYMMETRY=AUTO|NOSYM Symmetry to be used in wavefunction calculations of numerical gradients. This option is only relevant if DISPLACE=UNIQUE|CART. If AUTO is given, the maximum possible symmetry is used for each displacement. This implies that the energy is independent of the symmetry used. Note that this often not the case in MRCI or CASPT2 calculations. The option can also not be used in local correlation calculations.

AUTO (logical). Same as SYMMETRY=AUTO
ZMAT (logical). Same as COORD=ZMAT
OPT3N (logical). Same as COORD=3N

RSTEP=rstep Step length for distances in numerical gradient calculations (in bohr). The default is 0.01.

DSTEP=dstep Step length for symmetrical displacements (in bohr). The default is 0.01.

ASTEP=astep Step length for angles in numerical gradient calculations (in degree). The default is 1.

CENTRAL (logical). Use 2-point central formula; needs $2M$ energy calculations for $M$ degrees of freedom.

FORWARD (logical). Use forward gradients (needs only $M+1$ energy calculations, but less accurate)

FOURPOINT (logical). Use 4-point formula for accurate numerical gradient; needs $4M$ energy calculations.

NUMERICAL (logical). Force the use of numerical gradients, even if gradients are available.

VARSAV (logical). Save gradient in variables GRADX, GRADY, GRADZ.

Example

```
hf
ccsd(t)
forces,numerical
```

The program will then automatically repeat HF and CCSD(T) at as many geometries as needed for evaluating the gradient. This is equivalent to

```
hf
ccsd(t)
forces,numerical,startcmd=hf
```

or, using a procedure

```
forces,numerical,proc=runccsdt
...
runccsdt=

hf
ccsd(t)
```

45.2.1 Choice of coordinates (COORD)

By default, the numerical gradients are computed relative to all variables on which the z-matrix depends. If the z-matrix depends on no variables or on $3N$ variables, the gradient is computed for all $3N$ coordinates and symmetrical displacement coordinates are used to evaluate the gradient. This yields the minimum computational effort.

These defaults can be modified using the COORD directive:

```
COORD,coord_type,[displacement_type]
```

where coord_type can be one of the following:

- **ZMAT** Compute the numerical gradients for all variables on which the geometry depends (default).
Compute the gradients for all $3N$ nuclear coordinates. This is the default if the $z$-matrix does not depend on variables or if the $xyz$ input format is used. If this option is used and the original geometry is given in $z$-matrix form, the $z$-matrix is lost.

The specification of `displacement_type` is optional and only affects the numerical calculation of the gradient for $3N$ coordinates. It can also be given using `DISPLACE, displacement_type`

`displacement_type` can be one of the following:

- **SYM**: Use symmetrical displacements. This yields the minimum number of displacements and always preserves the symmetry of the wavefunction. This is the default and only recommended option.
- **CART**: Displacements are generated for all $3N$ Cartesian coordinates. This is normally not recommended, since in cases in which molecular symmetry is present it generates far more displacements than needed. Also, the wavefunction symmetry is not preserved, and the calculation must be done in C1 symmetry.
- **UNIQUE**: As CART, but symmetry-equivalent displacements are eliminated. Not recommended either.

### 45.2.2 Numerical derivatives of a variable

Numerical derivatives of the value of a variable can be computed using `VARIABLE, name`

The default is to compute the gradient of the current energy.

### 45.2.3 Step-sizes for numerical gradients

By default, the numerical step sizes are 0.01 bohr for distances or Cartesian coordinates, and 1 degree for angles. These defaults can be changed using `RSTEP, dr` and `ASTEP, da`

where $dr$ is the displacement for distances (or Cartesian coordinates) in bohr, and $da$ is the displacement for angles in degree. The value of `RSTEP` is used for symmetrical displacements. The step sizes for individual variables can be modified using `VARSTEP, varname=value,...`

where the `value` must be in atomic units for distances and in degree for angles.

### 45.2.4 Active and inactive coordinates

By default, numerical gradients are computed with respect to all variables on which the $Z$-matrix depends, or for all $3N$ coordinates if there are no variables or $XYZ$ input style is used. One can define subsets of active variables using `ACTIVE, variables`
If this card is present, all variables which are not specified are inactive. Alternatively, `INACTIVE` variables
In this case all variables that are not given are active.

### 45.3 Saving the gradient in variables

If the directive

```
VARSAV
```

is given, the gradient is saved in variables `GRADX`, `GRADY`, `GRADZ`. `GRADX(n)` is the derivative with respect to `x` for the `n`-th atom. The atoms are in the order as printed. This order can be different from the order in the input `z`-matrix, since the centres are reordered so that all atoms of the same type follow each other.

### 46 GEOMETRY OPTIMIZATION (OPTG)

Automatic geometry optimization is invoked using the `OPTG` command. The `OPT` command available in previous MOLPRO versions is no longer needed and not available any more.

```
OPTG[, key1=value, key2=value, ...]
```

The `OPTG` command can be used to perform automatic geometry optimizations for all kinds of wavefunctions. For minimum searches, it is usually sufficient to give just the `OPTG` command without further options or directives, but many options are available which are described in the following sections.

Various optimization methods can be selected as described in section 46.2.1. MOLPRO allows minimization (i.e. search for equilibrium geometries), transition state optimization (i.e. search for saddle points on energy surfaces), and reaction path following. The standard algorithms are based on the rational function approach and the geometry DIIS approach. Also available is the quadratic steepest descent following method of Sun and Ruedenberg (see J. Sun and K. Ruedenberg, *J. Chem. Phys.* 99, 5257 (1993)). This method is often advantageous in Transition State searches. For a detailed discussion of the various minimization algorithms see F. Eckert, P. Pulay and H.-J. Werner, *J. Comp. Chem* 18, 1473 (1997). Reaction path following is described in F. Eckert and H.-J. Werner, *Theor. Chem. Acc.* 100, 21, (1998). Please refer to the references section for citations of the analytic gradient methods.

When analytical gradients are available for the optimized energy these will be used. See section 45.1 for a list of methods with analytical gradients. Otherwise the gradient will be computed numerically from finite energy differences. Normally, the last computed ground-state energy is used. But the `VARIABLE` directive or option can be used to optimize, e.g., Davidson corrected energies, excited states, or counterpoise corrected energies.

By default the program repeats in each geometry optimization step those commands in the input that are needed to compute the last energy. For example, for MP2 gradients the commands HF and MP2 are needed. The MP2 gradients will then be computed automatically. It is also possible to define procedures for the energy calculation, or to specify the first command from which the input should be repeated in each step (see section 46.1.1). The section of the input which is needed for the geometry optimization must not modify variables that are used in the geometry definition (changes of such variables are ignored, and a warning message is printed).
46.1 Options

Most parameters can be given as options on the OPTG command line, as described in this section. Alternatively, directives can be used, which will be described in section 46.2.

46.1.1 Options to select the wavefunction and energy to be optimized

By default, the last computed energy is optimized, and all commands on which the last energy calculation depends are automatically executed. For certain purposes, e.g., optimization of counter-poise corrected energies or Davidson corrected energies, the following options can be used to alter the default behaviour.

**STARTCMD=command** Specifies a start command. In each geometry optimization step all input beginning with *command* to the current OPTG is processed. This input must not include numerical gradient or Hessian calculations. If numerical gradients are needed, these will be computed for the final energy (or specified variable) by OPTG. It is assumed that these commands have been executed before entering the OPTG program.

**PROC=procname** specifies a procedure to be executed in each geometry optimization step. This must define a complete energy calculation (orbital optimization and correlation treatment), and must not include numerical gradient of Hessian calculations (numerical gradients will be computed automatically for the optimized energy or variable). However, the procedure can include the calculation of analytical gradients, for instance for counter-poise corrected optimizations in which a linear combination of several gradient calculations is needed.

**VARIABLE=varname** Optimize the value of variable *varname*. This implies numerical gradients.

46.1.2 Options for optimization methods

**METHOD=RF|AH|DIIS|QSD|QSDPATH|SRMIN|SRTRANS|STSTEEP** Optimization method to be used. See section 46.2.1 for details.

**ROOT=1|2** Minimum search (1, default) or transition state search (2).

**DIRECTION|IDIR=idir** Determines initial step length and direction in reaction path following, see section 46.2.16.

**STPTOL=value** For reaction path following, see section 46.2.16

**SLMAX=value** For reaction path following, see section 46.2.16

**STEPMAX=value** Max step length in one optimization step. This also affects the step length in reaction path following. For more detailed specifications see section 46.2.12

**TRUST=value** Trust ratio for Augmented Hessian method (default 0.5).

**AHMAX=value** Maximum step size allowed in the Augmented Hessian procedure. This refers to the scaled parameter space (default 0.5).

**CUT=value** Threshold for orthonormalization used in conjugate gradient update of Hessian (default 1.d-3).

**ROTATE** (logical). If .true., the Cartesian coordinates are transformed to minimize rotations (default=.true.)
46.1.3 Options to modify convergence criteria

The standard MOLPRO convergency criterion requires the maximum component of the gradient to be less than \(3 \cdot 10^{-4}\) [a.u.] and the maximum energy change to be less than \(1 \cdot 10^{-6}\) [H] or the maximum component of the gradient to be less than \(3 \cdot 10^{-4}\) [a.u.] and the maximum component of the step to be less than \(3 \cdot 10^{-4}\) [a.u.].

It is also possible to use the convergency criterion of the Gaussian program package. It is somewhat weaker than the MOLPRO criterion and requires the maximum component of the gradient to be less than \(4.5 \cdot 10^{-4}\) [a.u.] and the root mean square (RMS) of the gradient to be less than \(3 \cdot 10^{-4}\) [a.u.] as well as the maximum component of the optimization step to be less then \(0.0018\) [a.u.] and the RMS of the optimization step to be less then \(0.0012\) [a.u.].

MAXIT=\textit{maxit} maximum number of optimization cycles. The default is 50.

GRADIENT=\textit{thgrad} required accuracy of the optimized gradient. The default is \(3 \cdot 10^{-4}\).

ENERGY=\textit{threnerg} required accuracy of the optimized energy. The default is \(1 \cdot 10^{-6}\).

STEP=\textit{thstep} convergence threshold for the geometry optimization step. The default is \(3 \cdot 10^{-4}\).


GAUSSIAN (logical). Use Gaussian convergency criteria.

SRMS=\textit{thsrms} sets (for Gaussian convergency criterion) the required accuracy of the RMS of the optimization step. The default is 0.0012.

GRMS=\textit{thrgrms} sets (for Gaussian convergency criterion) the required accuracy of the RMS of the gradient. The default is \(3 \cdot 10^{-4}\).

FREEZE=\textit{thrfreez} Freeze DFT grid and domains in local calculations if the step length is smaller than \textit{thrfreez} (default 0.01).

Note: The defaults for the convergence parameters can also be changed by using a global GTHRESH directive, i.e.

\texttt{GTHRESH, OPTSTEP=\textit{step}, OPTGRAD=\textit{grad}, ENERGY=\textit{energy};}

46.1.4 Options to specify the optimization space

If the geometry is given as Z-matrix, the default is to optimize the variables on which the Z-matrix depends. In case of \textit{xyz} input, always all 3N coordinates are optimized, even if the \textit{xyz} input depends on fewer variables. If Cartesian z-matrix input is used, optimization in full space is only enforced if automatic orientation is requested using the MASS, or CHARGE options on the ORIENT directive. See \textit{opt_space} in section \texttt{[46.2.2]} for details.

\texttt{SPACE=ZMAT | 3N} Specifies the coordinates to be used in the optimization. Z-matrix optimization is only possible if the geometry is given as Z-matrix.

\texttt{OPT3N | 3N} (logical). Same as \texttt{SPACE=3N}

\texttt{ZMAT} (logical). Same as \texttt{SPACE=ZMAT}
46.1.5 Options to specify the optimization coordinates

These options specify the coordinates in which the optimization takes place. The default is to use local normal coordinates. See opt_coord in section 46.2.2 for details.

COORD=NORMAL | NONORMAL | BMAT
NORMAL  (logical). Same as COORD=NORMAL.
NONORMAL (logical). Same as COORD=NONORMAL.
BMAT     (logical). Same as COORD=BMAT.

46.1.6 Options for numerical gradients

Numerical gradients can be computed with respect to variables on which the Z-matrix depends or with respect to Cartesian coordinates. In the latter case, it is most efficient to use symmetrical displacement coordinates. These do not change the symmetry of the molecule and the number of displacements is minimal. Alternatively (mainly for testing purpose) the gradients can be computed using symmetry unique Cartesian displacements or all 3N Cartesian displacements. In these cases the symmetry of the molecule can be reduced by the displacements and using such displacements is normally not recommended.

DISPLACE=ZMAT | SYMM | UNIQUE | CART
Displacement coordinates to be used for numerical gradient. The default is ZMAT if the geometry is given as a zmatrix which depends on variables, and SYMM (symmetrical displacement coordinates) otherwise. The use of UNIQUE or CART is not recommended.

SYMMETRY=AUTO | NOSYM
Symmetry to be used in wavefunction calculations of numerical gradients. This option is only relevant if DISPLACE=UNIQUE|CART. If AUTO is given, the maximum possible symmetry is used for each displacement. This implies that the energy is independent of the symmetry used. Note that this often not the case in MRCI or CASPT2 calculations. The option can also not be used in local correlation calculations.

AUTO     (logical). Same as SYMMETRY=AUTO
NOSYM    (logical). Same as SYMMETRY=NOSYM

RSTEP=rstep
Step length for distances in numerical gradient calculations (in bohr). The default is 0.01.

DSTEP=dstep
Step length for symmetrical displacements (in bohr). The default is 0.01.

STEP=astep
Step length for angles in numerical gradient calculations (in degree). The default is 1.

FOURPOINT (logical). Use 4-point formula for accurate numerical gradient.
NUMERICAL (logical). Force the use of numerical gradients, even if gradients are available.

In special cases the energy calculations may require several steps with different occupations and/or symmetries. In this case the FORCEINP directive must be given (see section 46.1.8).
46.1.7 Options for computing Hessians

By default, an approximate Hessian (model Hessian) is used. Optionally, a Hessian can be computed in the optimization or read from a previous Hessian or frequency calculation.

**NUMHESS=\textit{hstep}**
If given, a numerical Hessian is computed in each \textit{hstep}'th iteration. If \textit{hstep}=0 or not given, only an initial Hessian is computed.

**HESSREC=\textit{record}**
Read initial Hessian from the given record. If \textit{record} is not given or zero, the last computed Hessian is used.

**READHESS**
(logical). Same as HESSREC=0.

**HESSPROC=\textit{procname}**
specifies a procedure to be used for computing the Hessian. This procedure must be define a complete energy calculation (orbital optimization and correlation treatment). A different method can be used than for the optimized energy, but the basis must not be redefined in this procedure. For instance, an MP2 Hessian can be used for CCSD(T) optimizations, or a CASPT2 Hessian for MRCI optimizations. By default, the same procedure is used for the Hessian as for the optimized energy. Note: If a hessian procedure is used and two or more optimizations are done after each other in the same input, the complete energy calculation (including orbital optimization) must be defined before each optg command or in the optg procedure.

**HESSVAR=\textit{varname}**
Compute Hessian for variable \textit{varname}. This implies numerical calculation of the Hessian from energies. The default is to use the same variable as for the energy and gradient.

**HESSCENT**
Use central gradient differences for computing Hessian (only effective if gradients are available)

**HESSFORW**
Use forward gradient differences for computing Hessian (only effective if gradients are available). This effectively computes the Hessian at a slightly displaced geometry, but needs only half the number of displacements. This is the default.

**UPDATE=BFGS|IBFGS|CGRD|PMS|POWELL|MS|NONE**
Hessian update method to be used. See section 46.2.9 for details.

**MAXUPD=\textit{maxupd}**
Max number of Hessian updates. The count is reset to zero each time a Hessian is computed.

**NUMDIAG**
If true, replace diagonal elements of model hessian by diagonal numerical hessian (if available). This sometimes improves convergence, but since it may lead to symmetry breaking it is no the default.

Note that there are restrictions for computing Hessians for multireference methods (MCSCF, MRCI, ACPF,AQCC,RS2). For these methods the symmetry must not change by any displacements, since this could change the occupations and states and may lead to non-contiguous potential energy surfaces. One of the following three options can be used in these cases:

- Use no symmetry from the beginning (NOSYM).
- Use symmetric displacement coordinates. This is the default if the optimization is done in 3N cartesian coordinates. One can use OPTG,DISPLACE=SYMM to force the use of symmetrical displacements (this creates 3N cartesian coordinates if a Z-matrix is used in the geometry input).
• Use a Z-matrix with the restriction that no variable in the Z-matrix may change the symmetry. For example, \( \text{geometry} = \{ O; H1, O, r; H2, O, r, H1, \theta \} \) would work, but \( \text{geometry} = \{ O; H1, O, r1; H2, O, r2, H1, \theta \} \) would not work. In this case the program prints a warning message. If an incorrect Z-matrix is used and the symmetry changes, the program will crash.

### 46.1.8 Miscellaneous options:

- **VARSAVE**: Save Cartesian gradients in variables GRADX, GRADY, GRADZ.
- **NONUC**: Do not compute gradients at lattice points.
- **DEBUG**: Set debug print options.
- **PRINT=iprint**: Print option for optimization.
- **SAVEXYZ[=file]**: Save the optimized coordinates in an xyz-file. One file is written for each step. The filename is \( \text{file}_nn \).xyz, where \( nn \) is the iteration number. For the final geometry, \( \_nn \) is omitted. If filename is not given, \( \text{file} \) is taken to be the root name of the input, i.e. test.inp creates test_1.xyz in the first iteration and test.xyz for the converged geometry. By default, the xyz information is written to the log file in each step.
- **SAVEACT[=file]**: Save optimized variables in each step. The file name is \( \text{file}.act \). If \( \text{file} \) is not given the root name of the input is used. The file can be read later using the READVAR command or copied into new input.
- **SAVEGRD[=file]**: Write in each step the Cartesian coordinates and gradients. The file name is \( \text{file}.grd \). If file is not given, the root name of the input appended by .grd is used.
- **APPEND**: (logical). If given, existing SAVEACT and/or SAVEGRD files are appended.
- **REWIND**: (logical). If given, the SAVEACT and/or SAVEGRD files are rewound at each step, i.e. only the last geometry or gradient is saved, previous values are overwritten.
- **FORCEINP**: (logical) Disables the mechanism that freezes the occupations during geometry optimizations. If this option is given, the occupations and wave function definitions given in the input for the energy calculations are strictly obeyed.

### 46.2 Directives for OPTG

An alternative way to specify options is to use directives, as described in this section. In some cases this allows more detailed specifications than with the options on the OPTG command. In particular, directives ACTIVE or INACTICE can be used to define the optimization space in more detail.

#### 46.2.1 Selecting the optimization method (METHOD)

- **METHOD:.key:**

  \( \text{key} \) defines the optimization method.

  For minimization the following options are valid for \( \text{key} \):
RF  Rational Function method (default).

AH  Augmented Hessian method. This is similar to RF algorithm but uses a more sophisticated step restriction algorithm.

DIIS  Pulay’s Geometry DIIS method. As an additional option you may add the number of geometries to be used in GDIIS interpolation (default 5) and the interpolation type (i.e., the subspace in which the GDIIS interpolation is made.

METHOD, DIIS, number, type

*type* may be GRAD interpolation using the gradients (default), working good for rigid molecules, STEP interpolation using Quasi-Newton steps which could be advantageous in dealing with very floppy molecules, ENER interpolation using energies, which is an intermediate between the above two.

QSD  Quadratic steepest descent method of Sun and Ruedenberg.

SRMIN  Old version of QSD.

For transition state searches (invoked with the ROOT option, see section 46.2.11) key can be

RF  Rational Function method (default).

DIIS  Pulay’s Geometry DIIS method (see above).

QSD  Quadratic Steepest Descent Transition State search using the image Hessian method (see J. Sun and K. Ruedenberg, *J. Chem. Phys.* **101**, 2157 (1994)) The use of this option is recommended for transition state searches – especially in complicated cases. The optimization step is checked and the Hessian is recalculated when approaching a troublesome region of the PES. Thus this method is somewhat safer (and often faster) in reaching convergence than the RF or DIIS method. The Hessian recalculation safeguard may be turned off using the METHOD, QSD, NOHESS input card.

SRTRANS  Old version of QSD.

For reaction path following the input key is

QSDPATH  Quadratic Steepest Descent reaction path following. This method determines reaction paths (intrinsic reaction coordinates, IRCs) by following the exact steepest descent lines of subsequent quadratic approximations to the potential energy surface. The Hessian matrix is calculated numerically at the first optimization step and subsequently updated by Powell or BFGS update. If a given arc length of the steepest descent lines is exceeded, the Hessian is recalculated numerically (see OPTION section 46.2.16). For details see J. Sun and K. Ruedenberg, *J. Chem. Phys.* **99**, 5269 (1993) It is also possible to recalculate the Hessian after each $m$ steps using the NUMHES,$m$ command (see section 46.2.7). If the Hessian matrix is recalculated in every optimization step (NUMHES, 1) a algorithm different to the one with updated Hessians is used, which is very accurate. Using the PRINT, OPT card, this algorithm prints in every optimization step a reaction path point $r$ which is different from the point where the energy and the gradient is calculated but closer to the real reaction path (for further
details of the algorithm see J. Sun and K. Ruedenberg, J. Chem. Phys. 99, 5257 (1993)). For further input options of the QSD reaction path following see OPTION section. 46.2.16.

SRSTEEP Old Version of QSDPATH.

46.2.2 Optimization coordinates (COORD)

It is possible to use various coordinate types and algorithms for the optimization. This can be controlled by additional subcommands as described in this and the following subsections.

COORD,[opt_space],[opt_coord],[NOROT]

These options choose the optimization space and the coordinate system in which the optimization takes place.

opt_space defines the parameters to be optimized. By default, if the geometry input is given in Z-matrix format, all variables on which the Z-matrix depends are optimized. Subsets of the variables on which the Z-matrix depends can be chosen using the ACTIVE or INACTIVE subdirectives. If the Z-matrix depends on no variables or xyz input is used, all 3N cartesian coordinates are optimized.

opt_space can be one of the following:

ZMAT Optimize all variables on which the Z-matrix depends (default if the geometry is given as Z-matrix).

3N Optimize all 3N cartesian coordinates (default if the Z-matrix depends on no variables, or if xyz-input is used). Z-Matrix input coordinates will be destroyed if 3N is used.

opt_coord determines the coordinates in which the optimization takes place. By default, local normal coordinates are used. Optionally cartesian coordinates or natural internal coordinates can be used.

opt_coord can be one of the following:

NORMAL Optimization in local normal coordinates. This is default if the Model Hessian is used to approximate the Hessian.

NONORM Don’t use local normal coordinates.

BMAT[=filename] Use Pulay’s natural internal coordinates, see G. Fogarasi, X. Zhou, P. W. Taylor and P. Pulay J. Am. Chem. Soc. 114, 8191 (1992); P. Pulay, G. Fogarasi, F. Pang, J. E. Boggs J. Am. Chem. Soc. 101, 2550 (1979)). Optionally, the created coordinates as well as additional informations about this optimization are written to the specified file. These coordinates resemble in part the valence coordinates used by vibrational spectroscopist, and have the advantage of decreasing coupling between different modes. This often increases the speed of convergence. The use of this option is highly recommended, especially in minimization of large organic molecules with rings. Nevertheless you should keep in mind that these coordinates are constructed automatically, and there exist exotic bond structures which might not be treated properly (e.g. weakly bonded species as in transition state optimizations). In such a case, if the BMAT optimization converges slowly or leads to symmetry-breaking errors, you should try another optimization method and/or cartesian or Z-Matrix coordinates.
If the option [NOROT] is given, the cartesian coordinates are not transformed to minimize rotations.

### 46.2.3 Displacement coordinates (DISPLACE)

DISPLACE.displacement_type

see section [45.2.1] for details.

### 46.2.4 Defining active geometry parameters (ACTIVE)

ACTIVE.param;

Declares variable name param to be active in the optimization. By default, initially all variables on which the geometry depends are active; inclusion of an ACTIVE card makes all parameters inactive unless explicitly declared active (see also INACTIVE).

### 46.2.5 Defining inactive geometry parameters (INACTIVE)

INACTIVE.param;

Declares variable name param to be inactive in the optimization. If any ACTIVE card appears in the input, this card is ignored! (see also ACTIVE)

### 46.2.6 Hessian approximations (HESSIAN)

By default, the MOLPRO geometry optimization utilizes a force field approximation to the hessian (“Model Hessian”, see R. Lindh, A. Bernhardsson, G. Karlström and P. Malmqvist Chem. Phys. Lett. 241, 423 (1995)), which speeds up convergence significantly. The Model Hessian is parameterized for the elements up to the third row. Alternatively, the model Hessian of Schlegel can be used, or the Hessian can be computed numerically (see also section [46.2.7]).

HESSIAN.options

where options can be

- **MODEL**
  - Use Lindh’s Model Hessian in optimization (default).
- **MODEL=SCHLEGEL**
  - Use Schlegel’s Model Hessian.
- **MODEL=VDW**
  - Add vdW terms to Lindh’s Model Hessian.
- **SCHLEGEL**
  - same as **MODEL=SCHLEGEL**.
- **VDW**
  - same as **MODEL=VDW**.
- **NOMODEL**
  - Don’t use Model Hessian approximation to the hessian.
- **NUMERICAL=step**
  - Recompute Hessian after step iterations. This disables the use of a model hessian. If step=0, the Hessian is only computed in the first iteration. Default parameters are used for computing the numerical Hessian, unless modified using options as described for the NUMHESS directive, see Sect. [46.2.7] Any option valid for the NUMHESS directive may also follow the NUMERICAL option on the HESSIAN directive.
READ | RECORD | HESSREC=record  Read Hessian from given record. If record is not given or zero, the last computed hessian will be read. See section 46.2.7 for more details about numerical Hessians.

UPDATE=type  Method used for hessian update. See section 46.2.9 for possibilities and details.

MAXUPD=maxupd  Max number of hessian updates. The count is reset to zero each time a hessian is computed.

If the Model Hessian is disabled (NOMODEL) and no Hessian is read or computed, the initial hessian is assumed to be diagonal, with values 1 hartree*bohr**(-2) for all lengths, 1 hartree*radian**(-2) for all angles. Additional matrix elements of the hessian can be defined using the HESSELEM directive, see section 46.2.8.

In transition state searches the Hessian is evaluated numerically in the first iteration by default. Alternatively, if READ is specified, a previously computed hessian is used.

### 46.2.7 Numerical Hessian (NUMHESS)

NUMHESS.options

or

NUMHESS,hstep,options

If this directive is present a numerical Hessian is computed using finite differences. If analytical gradients are available, one can use forward gradient differences (needs one gradient calculation for each coordinate) or central differences (more accurate, needs two gradient calculations for each coordinate). For transition state optimizations it is usually sufficient to use forward differences. If analytical gradients are not available for the optimized method, the energy is differentiated twice. In this case only central differences are possible.

The following options can be given:

**HSTEP=hstep**  
*hstep*=1: Don’t calculate numerical hessian (default for minimization);  
*hstep*=0 Calculate numerical hessian only once at the start of the optimization (default for transition state searches).  
*hstep*=n Calculate numerical hessian after each n optimization steps. This is useful for difficult transition state optimizations (e.g. if the eigenvalue structure of the hessian changes during the optimization).

**FORWARD**  Use forward differences (default).

**CENTRAL**  Use the more accurate central differences.

**RSTEP=rstep**  Step length for distances (in bohr). The default is 0.01.

**ASTEP=astep**  Step length for angles (in degree). The default is 0.5 or 1 for angles below and above 90 degree, respectively.

**DSTEP=dstep**  Step length for symmetrical displacements (in bohr). The default is 0.01.

**VARIABLE=varname**  Use given variable for numerical calculation of the Hessian. Note that this disables the use of gradients, and Hessian evaluation can be very expensive.
PROCEDURE=\textit{procname} Procedure to be used for computing Hessian. This procedure must be define a complete energy calculation (orbital optimization and correlation treatment). A different method can be used than for the optimized energy. For instance, an MP2 hessian can be used for CCSD(T) optimizations, or a CASPT2 hessian for MRCI optimizations. By default, the same procedure is used for the hessian as for the optimized energy.

DISPLACE=\textit{type} \textit{type} can be one of the following:

\begin{itemize}
  \item \textbf{SYMM} Use symmetric displacement coordinates (default). This is the only recommended option.
  \item \textbf{CART} Use $3N$ cartesian displacements (not recommended). This requires many more energy calculations than necessary and does not preserve the molecular symmetry.
  \item \textbf{UNIQUE} Use symmetry-unique cartesian displacements (not recommended)
\end{itemize}

Note that the displacement type for gradient and hessian must be the same.

CALC=\textit{icalc} \textit{icalc}=0: Recalculate the complete Hessian matrix numerically after each $\textit{hstep}$ optimization steps (default).
\textit{icalc}=1 (currently disabled): Recalculate selected Hessian matrix elements if the relative deviation of this element before and after update (see \textit{UPDATE}, section 46.2.9) is larger than $\textit{thresh}$. If $\textit{thresh}$ is not specified, a default value of $\textit{thresh}=0.05$ (i.e. a maximum deviation of 5\%) is used.
\textit{icalc}=2 (currently disabled): Recalculate complete Hessian matrix if the RMS deviation of the Hessian matrix before and after update is larger than $\textit{thresh}$. If $\textit{thresh}$ is not specified a default value of $\textit{thresh}=0.5$ a.u. is used.

THRESH=\textit{thresh} Threshold for partial or dynamical update of hessian, see above

\subsection{46.2.8 Hessian elements (\texttt{HESSELEM})}

\texttt{HESSELEM},\textit{value}, \textit{active1},\textit{active2},\ldots

sets the starting value for hessian matrix element between active variables $\textit{active1}$, $\textit{active2}$ to $\textit{value}$. If $\textit{active2}$ is omitted it defaults to $\textit{active1}$ (diagonal element). As many \texttt{HESSELEM} directives as needed may be given.

\subsection{46.2.9 Hessian update (\texttt{UPDATE})}

\texttt{UPDATE},\texttt{[TYPE=]}\textit{type},\texttt{MAXUPD=}\textit{maxupd}

This directive chooses the update type and limits the number of points used for the hessian update to $\textit{maxupd}$. The default number of steps used in hessian update procedures is 5. If there are symmetry constraint in the coordinates of the optimization, the default number may be lower than five.

In minimizations \textit{type} may be

\begin{itemize}
  \item \textbf{BFGS} Use BFGS update of hessian (default).
\end{itemize}
IBFGS Use BFGS update of the inverse hessian.
CGRD Use Conjugate Gradient update (see also CUT, TRUST).
NONE Don’t do any update.

In transition state optimizations type may be

PMS Combined Powell/Murtagh-Sargent update of hessian (default).
POWELL Use Powell’s update of the hessian.
MS Use update procedure of Murtagh and Sargent.
NONE Don’t do any update.

### 46.2.10 Numerical gradients (NUMERICAL)

NUMERICAL,options.active1=step1, active2=step2 . . .

With this directive the gradients are computed by finite differences. stepi is the increment for the active geometry parameter activei. For active parameters which are not specified, the default values are used. By default, the increment is 0.01 bohr for bond distances and 0.5 or 1 degree for angles less than or greater than 90 degrees, respectively. These defaults can be modified by specifying RSTEP or ASTEP. DSTEP is the length of symmetrical displacements, which are used if the optimization is performed in 3N coordinates.

For each active variable, two energy calculations are necessary in each geometry optimization step – so numerical optimizations may be expensive! In optimizations of 3N coordinates symmetrical displacement coordinates are normally used to minimize the number of energy calculations. (see section 45.2.1).

For optimization of special energies see VARIABLE section 46.2.17.

The following options can be given:

RSTEP=rstep Step length for distances (in bohr). The default is 0.01.
ASTEP=astep Step length for angles (in degree). The default is 0.5 or 1 for angles below and above 90 degree, respectively.
DSTEP=dstep Step length for symmetrical displacements (in bohr). The default is 0.01.
CENTRAL Use central differences for gradient (default)
FORWARD Use forward differences (not recommended for gradient).
FOURPOINT Use four-point formula for very accurate numerical gradients.
PROCEDURE=procname Use given procedure for numerical calculation of the gradient. This procedure must define a complete energy calculation (orbital optimization and correlation treatment).
VARIABLE=varname Use given variable for numerical calculation of the gradient.
DISPLACE=type The displacement type. Note that the displacement type for gradient and hessian must be the same. type can be one of the following:

SYMM Use symmetric displacement coordinates (default). This is the only recommended option.
CART Use 3N cartesian displacements (not recommended). This requires many more energy calculations than necessary and does not preserve the molecular symmetry.

UNIQUE Use symmetry-unique cartesian displacements (not recommended)

46.2.11 Transition state (saddle point) optimization (ROOT)

ROOT,root

Specifies the eigenvector of the hessian to be followed.

root=1 specifies a minimization (default).
root=2 specifies a transition state (saddle point) optimization.

In the present implementation a saddle point search is possible with the rational function method (METHOD, RF), the geometry DIIS method (METHOD, DIIS) and the quadratic steepest descent method of Sun and Ruedenberg (METHOD, SRTRANS).

Note that convergence is usually much more difficult to achieve than for minimizations. In particular, a good starting geometry and a good approximation to the hessian is needed. The latter is achieved by evaluating the hessian numerically (see section 46.2.7) or using a precomputed hessian (see section 46.2.6).

46.2.12 Setting a maximum step size (STEP)

STEP,steplength,drmax,damax,drmax1,damax1

steplength is the initial step length in the scaled parameter space (default 0.3). In the AH-method this is dynamically adjusted, and can have a maximum value ahmax (see TRUST).

drmax is the initial max change of distances (in bohr, default 0.3). In the AH-method this is dynamically adjusted up to a maximum value of drmax1 (default 0.5 bohr).

damax is the initial max change of angles (in degree, default 2). In the AH-method this is dynamically adjusted up to a maximum value of damax1 (default 10 degrees).

46.2.13 Redefining the trust ratio (TRUST)

TRUST,ratio,ahmax

ratio determines the radius around the current minimum in which points are used to update the Hessian with the conjugate gradient method (default 0.5; see also UPDATE).

ahmax is the maximum step size allowed in the Augmented Hessian procedure. This refers to the scaled parameter space (default 0.5). The initial step size is stepmx (see STEP card).

46.2.14 Setting a cut parameter (CUT)

CUT,threshold

Specifies a threshold for ortho-normalization used in conjugate gradient update of hessian (default 1.d-3; see also UPDATE).
46.2.15 Line searching (LINESEARCH)

LINESEARCH,iflag,thrmin,thrmax

Interpolate the geometry of the stationary point (minimum or saddle point) by a quartic polynomial between the current and the previous geometry. If iflag=0 or no iflag is set, the next optimization step will be taken from the interpolated geometry using the interpolated energy and gradient. If iflag=1 the energy and gradient will be recalculated at the interpolated geometry before taking the new optimization step. Note though, that the additional effort of recalculating the energy and gradient is usually not met by the increase of the convergence rate of the optimization. thrmin and thrmax are min and max thresholds for the recalculation of the energy and the gradient in case iflag=1. I.e. the recalculation just takes place if the interpolated geometry isn’t too close to the actual geometry thrmin and isn’t too remote from the actual geometry thrmax. Default values are thrmin=0.001 and thrmax=0.05 in the scaled parameter space of the optimization.

46.2.16 Reaction path following options (OPTION)

OPTION, key=param;

where key can be

IDIR
If starting at a transition state (or near a transition state) determine where to take the first step. If IDIR=0 is chosen, the first step will be towards the transition state. This is the default. If IDIR=1 is given in the input the first optimization step will be along the ”transition vector” i.e. the hessian eigenvector to the smallest eigenvalue which points down towards the minimum. If using a larger IDIR parameter, the first step will be larger; if using a negative value, the first step will be in the opposite direction.

STPTOL
If using an updated hessian matrix, this parameter determines what update to take. If the step size between two subsequent points on which the steepest decent lines are puzzled together is smaller than stptol (i.e. if we are close to a minimum) the BFGS update is used, otherwise it is Powell update. The default value of stptol is 1.d−6. Note that the stepsize is also affected by the STEPMAX option.

SLMAX
This option is only valid with the old version of the reaction path following algorithm (i.e. METHOD, SRSTEEP). In this algorithm slmax determines the frequency of the recalculation of the numerical hessian. If the total step size of the last steps exceeds slmax the hessian will be recalculated, otherwise it will be updated. By default slmax is two times the maximum step size of the optimization step steplen (see STEP section 46.2.12). If you are using METHOD, QSD, the SLMAX option is obsolete and the NUMHES command (see above) should be used instead.

These options can also be given on the OPTG command line.

46.2.17 Optimizing energy variables (VARIABLE)

VARIABLE,name;
Defines a variable name which holds the energy value to be optimized in using finite differences. By default, this is ENERGY(1) as set by the most recent program. Other variables which can be used are

- \text{ENERGY}(i)\) holds last energy for state \(i\).
- \text{ENERGR}(i)\) holds last reference energy for state \(i\).
- \text{ENERGD}(i)\) holds last Davidson corrected energy for state \(i\).
- \text{ENERGP}(i)\) holds last Pople corrected energy for state \(i\).
- \text{ENERGC}\) holds CCSD (QCI, BCCD) energy in CCSD(T) [QCI(T), BCCD(T)] calculations (single state optimization).
- \text{ENERGT}(1)\) holds CCSD(T) energy in CCSD(T) calculations (single state)
- \text{ENERGT}(2)\) holds CCSD[T] energy in CCSD(T) calculations (single state).
- \text{ENERGT}(3)\) holds CCSD-T energy in CCSD(T) calculations (single state).

These variables are set automatically by the CI and/or CCSD programs. It is the user’s responsibility to use the correct variable name; an error exit occurs if the specified variable has not been defined by the last program or the user.

Note: The use of the \text{VARIABLE} option triggers \text{NUMERICAL}, so optimization can be very inefficient!

### 46.2.18 Printing options (PRINT)

\text{PRINT,code=level,…;}

Enables printing options. Usually level should be omitted or 0; values of level > 0 produce output useful only for debugging. code can be

- \text{HESSIAN}\) prints the updated hessian matrix. Note that its diagonal elements are printed anyway.
- \text{HISTORY}\) prints the complete set of previous geometries, gradients and energies.
- \text{GRADIENT}\) prints extended gradient information
- \text{OPT}\) prints detailed information about the optimization process (mainly for debugging).

Several print options can be specified with one \text{PRINT} command.

### 46.2.19 Conical Intersection optimization (CONICAL)

To optimize a conical intersection between two electronic states having the same spin, three vectors must be evaluated at SA-CPMCSF level:

1) Non-Adiabatic Derivative Coupling (DC).
2) Gradient of the lower state (LSG).
3) Gradient of the upper state (USG).
This requires three different CPMCSCF directives in the MULTI input:

- `CPMCSCF, NACM, S_i, S_j, ACCU=1.0d-7, record=record1.file`
- `CPMCSCF, GRAD, S_i, SPIN=Spin of state S_i, ACCU=1.0d-7, record=record2.file`
- `CPMCSCF, GRAD, S_j, SPIN=Spin of state S_j, ACCU=1.0d-7, record=record3.file`

where $S_i, S_j$ are the electronic states in the usual format `istate.istsym`, and `record[n].file` specifies the name and the file number where CPMCSCF solutions should be stored. Parameter `SPIN` is half of the value in the `WF` card used to define the electronic state.

Things to remember:

i) Specify always three different `record.file` on the CPMCSCF directives.

ii) Evaluate the CPMCSCF for USG always last.

iii) Skip the DC evaluation if the conical intersection involves states with different spin (e.g., a Singlet/Triplet crossing) because the coupling is then zero.

Three sets of `FORCE` commands (only two for Singlet/Triplet intersection) follow the MULTI input. They will be like:

```
FORCE
SAMC, record[n].file
CONICAL, record4.file[,NODC]
```

where `record.file` is one of the records containing CPMCSCF info and `record4.file` points to a free record used for internal storage by the CONICAL code. `record4.file` must be the same on all the CONICAL directives. Furthermore, the present implementation works properly only if `file=1` on the CONICAL directive. The optional keyword `NODC` must be used in case of different spins (e.g., S/T crossing) when DC is not needed.

The actual optimization is performed using `OPTG, STARTCMD=MULTI` The example below optimizes the conical intersection in LiH$_2$ (ground and excited states are both doublets).
This second example optimizes the singlet-triplet intersection in LiH$_2^+$ (ground state is Singlet, excited state is Triplet).
### Using the SLAPAF program for geometry optimization

It is optionally possible to use the SLAPAF program written by Roland Lindh for geometry optimizations. This is done by prepending the optimization method with 'SL'. The following methods are supported:

- **SLRF**: Use the rational function approximation;
- **SLNR**: Use the Newton-Raphson method;
- **SLC1**: Use the C1-DIIS method;
- **SLC2**: Use the C2-DIIS method.

When using DIIS methods (SLC1 or SLC2), the DIIS parameters are specified in the same way as in standard molpro optimizer.

There are some differences when using the SLAPAF program:

1. It is not possible to use Z-matrix coordinates in the optimization.
2. Instead, one can explicitly define internal coordinates to be varied or fixed.
3. Additional constraints can be imposed on the converged geometry in a flexible way.
46.3.1 Defining constraints

Constraints and internal coordinates (see below) can be linear combinations of bonds, angles etc. The latter, called here primitive internal coordinates, can be specified before the constraints definition, or directly inside. The general definition of a primitive coordinate is:

PRIMITIVE,[NAME=]symbolic name, explicit definition;

or

PRIM,[NAME=]symbolic name, explicit definition;

Here symbolic name is the name given to the primitive coordinate (if omitted, it will be generated automatically). This name is needed for further reference of this primitive coordinate.

explicit definition has the form:

type,atoms

type can be one of the following:

- **BOND**: Bond length, defined by 2 atoms.
- **ANGLE**: Bond angle, defined by 3 atoms (angle 1–2–3).
- **DIHEDRAL**: Dihedral angle, defined by 4 atoms (angle between the planes formed by atoms 1,2,3 and 2,3,4, respectively).
- **OUTOFPLANE**: Out-of-plane angle, defined by 4 atoms (angle between the plane formed by atoms 2,3,4 and the bond 1–4).
- **DISSOC**: A dissociation coordinate, defined by two groups of atoms (Not permitted with constraints).
- **CARTESIAN**: Cartesian coordinates of an atom.

For all types except DISSOC and CARTESIAN, atoms are given as:

ATOMS=[a1,a2,a3,...]

where the number of atoms required varies with type as specified above, and the atomic names a1,a2,a3,... can be either atomic tag names from the Z-matrix input, or integers corresponding to Z-matrix rows. Note that the square brackets are required here and do not indicate optional input.

For DISSOC the specification is as follows:

DISSOC, GROUP1=[a1,a2,...],GROUP2=[b1,b2,...];

The corresponding internal coordinate is the distance between the centres of mass of the two groups.

For CARTESIAN the definition is

CARTESIAN, I, atom;

where I can be one of X, Y, Z or 1,2,3 and atom can be a z-matrix atom name or an integer referring to the z-matrix row.

With this definition, the constraints are defined as

CONSTRAINT,[VALUE=]value,[unit],[[FACTOR=]fac,prim,[[FACTOR=]fac],prim,...;
where \textit{value} is the value imposed to the constraint, and \textit{prim} is either the name of the primitive defined before this constraint, or an explicit definition; and \textit{fac} is a factor of the corresponding primitive in the constraint. If \textit{fac} is omitted it is taken to be 1.

If \textit{value} is specified in Angstrom or Radian, \textit{unit} must be given.

Examples for H$_2$O in $C_s$ symmetry:

Constraining the bond angle to 100 degrees:

\begin{verbatim}
constraint,100,deg,angle,atoms=[h1,o,h2];
\end{verbatim}

which is equivalent to

\begin{verbatim}
primitive,a1,angle,atoms=[h1,o,h2];
constraint,100,a1;
\end{verbatim}

Keeping the two OH distances equal:

\begin{verbatim}
constraint,0,bond,atoms=[h1,o],-1.,bond,atoms=[h2,o];
\end{verbatim}

which is equivalent to

\begin{verbatim}
primitive,b1,bond,atoms=[h1,o];
primitive,b2,bond,atoms=[h2,o];
constraint,0,b1,-1.,b2;
\end{verbatim}

\subsection*{46.3.2 Defining internal coordinates}

By default SLAPAF optimizes in force-constant weighted normal coordinates that are determined automatically. However, the user can define his own coordinates. The definition of internal coordinates, similar to constraints, is based on primitive coordinates. The input is:

\begin{verbatim}
INTERNAL,[[NAME=]name],[[FACTOR=]fac],[[FACTOR=]fac],[prim],...;
\end{verbatim}

\begin{verbatim}
FIX,[[NAME=]name],[[FACTOR=]fac],[[FACTOR=]fac],[prim],...;
\end{verbatim}

Internal coordinates that are specified using \textit{INTERNAL} are varied and those using \textit{FIX} are fixed to their initial values.

An important point for the definition of internal coordinates is that their total number must be equal to the number of degrees of freedom of the molecule. Otherwise an error message is generated. Only symmetry independent coordinates need to be given.

\subsection*{46.3.3 Additional options for SLAPAF}

Some options can be passed to the SLAPAF program. Options are specified with \textit{SLOPT} sub-directive:

\begin{verbatim}
{opt;method=slnr;{slopt;opt1;opt2,par1,par2;opt3;...}}
\end{verbatim}

The available options are

\begin{description}
\item[CART] Use eigenvectors of the approximate Hessian, expressed in cartesian coordinates, as the definition of internal coordinates;
\item[NOMA] Don’t impose any restrictions on the step size;
\end{description}
UORD
Order the gradients and displacement vectors according to Schlegel prior to the update of the Hessian. Default is no reordering;

HWRS
Use force field weighted internal coordinates (default);

RS-P
Activate RS-P-RFO as default for transition state search; default is RS-I-RFO;

NOHW
Use unweighted internal coordinates;

PRBM
Print B-matrix;

RTHR, \( Thra, Thrb, Thrt \)
Thresholds for redundant coordinate selection for bonds, bends and torsions, respectively. Default 0.2, 0.2, 0.2

MODE, \( index \)
Hessian vector index for mode following when calculating transition states.

FIND
Enable unconstrained optimization for constrained cases, when looking for transition states (see MOLCAS manual).

GNRM, \( thr \)
Threshold for FIND, default 0.2 (see MOLCAS manual).

For more information, please consult the MOLCAS manual.

46.4 Examples

46.4.1 Simple HF optimization using Z-matrix

```plaintext
*** Allene geometry optimization using Z-Matrix
memory,1,m
basis=sto-3g

rcc=1.32 ang
rch=1.08 ang
acc=120 degree
Geometry={(C1 !Z-matrix input
   C2,c1,rcc
   Q1,c1,rcc,c2,45
   C3,c2,rcc,c1,180,q1,0
   h1,c1,rch,c2,acc,q1,0
   h2,c1,rch,c2,acc,h1,180
   h3,c3,rch,c2,acc,h1,90
   h4,c3,rch,c2,acc,h2,90)

hf
optg,saveact='allene.act',savexyz='allene.xyz' !default optimization using model hessian.
!Save optimized variables in file allene.act
!Save optimized geometry in xyz style in file allene.xyz
```

[http://www.molpro.net/info/current/examples/allene_optscf.com](http://www.molpro.net/info/current/examples/allene_optscf.com)
46.4.2 Optimization using natural internal coordinates (BMAT)

***, Allene geometry optimization using natural internal coordinates memory,1,m
basis=sto-3g
rcc=1.32 ang
rch=1.08 ang
acc=120 degree
symmetry,nosym
Geometry={C1; !Z-matrix input
        C2,c1,rcc
        Q1,c1,rcc,c2,45
        C3,c2,rcc,c1,180,q1,0
        h1,c1,rch,c2,acc,q1,0
        h2,c1,rch,c2,acc,h1,180
        h3,c3,rch,c2,acc,h1,90
        h4,c3,rch,c2,acc,h2,90}
hf;
optg !default optimization using model hessian
coord,bmat !use natural internal coordinates

http://www.molpro.net/info/current/examples/allene_opt_bmat.com

46.4.3 MP2 optimization using a procedure

***, Allene geometry optimization using Z-Matrix memory,2,m
basis=vdz
rcc=1.32 ang
rch=1.08 ang
acc=120 degree
Geometry={C1; !Z-matrix input
        C2,c1,rcc
        Q1,c1,rcc,c2,45
        C3,c2,rcc,c1,180,q1,0
        h1,c1,rch,c2,acc,q1,0
        h2,c1,rch,c2,acc,h1,180
        h3,c3,rch,c2,acc,h1,90
        h4,c3,rch,c2,acc,h2,90}

optg,procedure=runmp2 !use procedure optimp2
runmp2={hf;mp2} !procedure definition

http://www.molpro.net/info/current/examples/allene_optmp2.com
46.4.4 Optimization using geometry DIIS

***, CAFFEINE cartesian coordinates (XYZ format)
memory,1,m
basis=sto-3g
geomtyp=xyz
geometry=

CAFFEINE CARTESIAN COORDINATES
24
C   0.8423320060  -0.3654865620  0.0000000000
C  -0.2841017540  -1.1961236000  0.0000000000
N   2.0294818880  -1.1042264700  0.0000000000
N   0.0774743850  -2.5357317920  0.0000000000
N  -1.6472646000  -0.6177952290  0.0000000000
C  -1.4531962870  -2.3678913120  0.0000000000
C   0.6373131870  1.1735112670  0.0000000000
C  -1.7812691930  0.7688916330  0.0000000000
N  -0.6771444680  1.6306355000  0.0000000000
O   1.6106752160  1.9349693060  0.0000000000
O  -2.9202890400  1.2510058880  0.0000000000
C  -0.9202462430  3.1094501020  0.0000000000
C  -2.8623938560  -1.4824503660  0.0000000000
C   3.4552156930  -0.6811094280  0.0000000000
H   2.0878150460  -3.2451913360  0.0000000000
H  -1.49997252090  3.4222116470  -0.8897886280
H  -1.49997252090  3.4222116470  0.8897886280
H   0.0071905670  3.7148499490  0.0000000000
H  -3.4903070930  -1.2888938190  -0.8907763360
H  -3.4903070930  -1.2888938190  0.8907763360
H   -2.6289534570  -2.5638654230  0.0000000000
H    4.1360211370  -1.5529079440  0.0000000000
H   3.6817059520  -0.0685850980  0.8931597470
H   3.6817059520  -0.0685850980  -0.8931597470
}

hf
optg,savexyz=caffeine.xyz !save optimized geometry in file caffeine.xyz
coord,bmat !Optimization in natural internal coordinates
method,diis !Optimization method: Geometry DIIS

http: //www.molpro.net/info/current/examples/caffeine_opt_diis.com

46.4.5 Transition state of the HCN – HNC isomerization

The first example shows how to do a MP2 transition state optimization. The initial Hessian is taken from a previous HF frequency calculation.
GEOMETRY OPTIMIZATION (OPTG)

***, HCN <--> NHC Isomerization - Transition State Optimization and Frequencies

l1=1.18268242 ang
l2=1.40745082 ang
a1=55.05153416 degree

basis=3-21G

symmetry,nosym

geometry=

  C
  N,1,l1
  H,2,l2,1,a1

hf ! HF-SCF

frequencies,analytical ! Vibrational frequencies for HF-SCF (analytical Hessian)

mp2 ! MP2

optg,root=2,method=rf,readhess ! Transition State Search using Rational Function Optimizer and HF hessian

frequencies ! Vibrational frequencies for MP2 (numerical Hessian)

---

http://www.molpro.net/info/current/examples/hcn_mp2_ts.com

The second example shows how to do a CCSD(T) optimization with an MP2 hessian. Note that currently the CCSD(T) gradient is computed numerically using finite energy differences, and this can take long time for larger molecules. The calculation of the MP2 hessian finite differences of analytical gradients.

***, HCN <--> NHC Transition State Optimization and Frequencies

rcn=1.18 ang
rnh=1.40 ang
alpha=55 degree

basis=vtz

geometry=

  C
  N,1,rcn
  H,2,rnh,1,alpha

hf

ccsd(t)

optg,root=2,hessproc=runmp2 !Transition state optimization for ccsd(t) using mp2 hessian

frequencies !CCSD(T) frequencies (using numerical second derivatives)

runmp2=(hf;mp2) !procedure definition

---

http://www.molpro.net/info/current/examples/hcn_ccsd_ts.com

The last example shows how to do a MRCI+Q (MRCI with Davidson correction) optimization with an CASPT2 hessian. As for CCSD(T), the MRCI+Q gradient as computed numerically, while the CASPT2 hessian is obtained using finite differences of analytical CASPT2 gradients.
46.4.6 Reaction path of the HCN – HNC isomerization

The following input first optimizes the transition state, and then performs reaction path calculations in both directions. The results are plotted.
***, HCN <-+-> NHC Isomerization Reaction Path
memory,1,m
basis=3-21G

cnm=1.18282 ang ! Starting geometry is transition state
rnh=1.40745 ang
alpha=55.05 degree

symmetry,x ! Cs Symmetry
gemetry=
  C
  N,1,rcn
  H,2,rnh,1,alpha

int
rhf
optg,root=2,saveact=hcns ts,rewind ! Find and store the TS
(optg,method=qsdpath,dir=1, numhess=5,hesscentral,saveact=hcns_path) ! find IRC in positive direction
readvar,hcns ts.act ! Reset geometry to TS
(optg,method=qsdpath,dir=1,numhess=5,hesscentral,saveact=hcns_path,append) ! find IRC in negative direction
readvar,hcns_path.act

alpha=alpha*pi/180 ! convert angle to radian

table,irc,rcn,rnh,alpha,e_opt ! tabulate results

(plot,file='hcns_eopt.plot') ! plot energy profile as function of irc

{table,irc,rcn,rnh,alpha,e_opt ! plot distances and angle as function of irc
plot,file='hcns_dist.plot'}

http://www.molpro.net/info/current/examples/hcn_isomerization.com

This produces the plots
46.4.7 Optimizing counterpoise corrected energies

Geometry optimization of counterpoise corrected energies is possible by performing for the total system as well as for each individual fragment separate `FORCE` calculations. The gradients and energies are added using the `ADD` directive. This requires that `NOORIENT` has been specified in the geometry input, in order to avoid errors due to unintended rotation of the system. This default can be disabled using the `NOCHECK` option, see `ADD` above.

The way a counterpoise corrected geometry optimization works is shown in the following example. Note that the total counterpoise corrected energy must be optimized, not just the interaction energy, since the interaction energy depends on the monomer geometries and has a different minimum than the total energy. The interaction energy could be optimized, however, if the monomer geometries were frozen. In any case, the last calculation before calling `OPTG` must be the calculation of the total system at the current geometry (in the example below the dimer calculation), since otherwise the optimizer gets confused.
HF dimer MP2/CP optimization with relaxed monomers

basis=avtz
qthresh,energy=1.d-8

! INITIAL VALUES OF GEOMETRY VARIABLES

RFF= 5.3
R1= 1.76
R2 = 1.75
THETA1 = 7.0
THETA2 = 111

symmetry,x
orient,noorient
geometry=
  f1
  f2 f1 rff
  h1 f1 r1 f2 theta1
  h2 f2 r2 f1 theta2 h1 180.

label:

text, CALCULATION AT LARGE SEPARATION

rff_save=rff !save current rff distance
rff=1000 !dimer calculation at large separation

text, HF1

dummy,f2,h2; !second hf is now dummy
(hf;accu,16) !scf for first monomer
mp2; !mp2 for first monomer
ehf1inf=energy !save mp2 energy in variable
forces; !compute mp2 gradient for first monomer

text, HF2

dummy,f1,h1; !first hf is now dummy
(hf;accu,16) !scf for second monomer
mp2; !mp2 for second monomer
ehf2inf=energy !save mp2 energy in variable
forces; !compute mp2 gradient for second monomer
add,1 !add to previous gradient
einf=ehf1inf+ehf2inf !total energy of unrelaxed monomers

rff=rff_save !reset HF - HF distance to current value

text, CP calculation for HF1 MONOMER

dummy,f2,h2; !second hf is now dummy
(hf;accu,16) !scf for first monomer
mp2; !mp2 for first monomer
ehf1=energy !save mp2 energy in variable
forces; !compute mp2 gradient for first monomer
add,-1 !subtract from previous gradient

text, CP calculation for HF2 MONOMER

dummy,f1,h1; !first hf is now dummy
(hf;accu,16) !scf for second monomer
mp2; !mp2 for second monomer
ehf2=energy !save mp2 energy in variable
forces; !compute mp2 gradient for second monomer
add,-1 !subtract from previous gradient

text, DIMER CALCULATION

dummy !reset dummies
(hf;accu,16) !scf for dimer
mp2; !mp2 for dimer
edimer-energy !save mp2 energy in variable

...
The next example shows how the same calculations can be done using numerical gradients. In this case, first the total counter-poise corrected energy is formed and then optimized. Note that the `ADD` command does not work for numerical gradients.
HF dimer MP2/CP optimization with relaxed monomers

basis=avtz
gthresh,energy=1.d-8

! INITIAL VALUES OF GEOMETRY VARIABLES
RFF= 5.3
R1= 1.76
R2 = 1.75
THETA1 = 7.0
THETA2 = 111

symmetry,x
orient,noorient
group={f1
f2 f1 rff
h1 f1 r1 f2 theta1
h2 f2 r2 f1 theta2 h1 180.}

rff_save=rff !save current rff distance
rff=1000 !dimer calculation at large separation
text, HF1
dummy,f2,h2; !second hf is now dummy
(hf;accu,16) !scf for first monomer
mp2; !mp2 for first monomer
ehf1inf=energy !save mp2 energy in variable
text, HF2
dummy,f1,h1; !first hf is now dummy
(hf;accu,16) !scf for second monomer
mp2; !mp2 for second monomer
ehf2inf=energy !save mp2 energy in variable
einf=ehf1inf+ehf2inf !total energy of unrelaxed monomers
rff=rff_save !reset HF - HF distance to current value
text, CP calculation for HF1 MONOMER
dummy,f2,h2; !second hf is now dummy
(hf;accu,16) !scf for first monomer
mp2; !mp2 for first monomer
ehf1=energy !save mp2 energy in variable
text, CP calculation for HF2 MONOMER
dummy,f1,h1; !first hf is now dummy
(hf;accu,16) !scf for second monomer
mp2; !mp2 for second monomer
ehf2=energy !save mp2 energy in variable
text, DIMER CALCULATION
dummy !reset dummies
(hf;accu,16) !scf for dimer
mp2; !mp2 for dimer
edimer=energy !save mp2 energy in variable
etot=edimer-ehf2-ehf1+ehf1inf+ehf2inf !total BSSE corrected energy

optg,numerical,variable=etot,gradient=1.d-4,startcmd=label: !optimize geometry
text, compute optimized monomer energy
In the last example the monomer structures are kept fixed, and the interaction energy is optimized.

***, HF dimer MP2/CP optimization without monomer relaxation

```
basis=avtz
gthresh,energy=1.d-8

! INITIAL VALUES OF GEOMETRY VARIABLES
RFF   5.3
THETA1 = 7
THETA2 = 111

symmetry,x
orient,noorient
geometry={(f1 f2 f1 rff
   h1 f1 1.74764059 f2 theta1
   h2 f2 1.74764059 f1 theta2 h1 180.)} !using fixed HF distances of isolated HF

label:

text, CP calculation for HF1 MONOMER
dummy,f2,h2; !second hf is now dummy
(hf;accu,16) !scf for first monomer
mp2; !mp2 for first monomer
ehf1=energy !save mp2 energy in variable
forces; !compute mp2 gradient for first monomer
scale,-1 !multiply gradient by -1

text, CP calculation for HF2 MONOMER
dummy,f1,h1; !first hf is now dummy
(hf;accu,16) !scf for second monomer
mp2; !mp2 for second monomer
ehf2=energy !save mp2 energy in variable
forces; !compute mp2 gradient for first monomer
add,-1 !subtract from previous gradient

text, DIMER CALCULATION
dummy !reset dummies
(hf;accu,16) !scf for dimer
mp2; !mp2 for dimer
edimer=energy !save mp2 energy in variable
forces; !compute mp2 gradient for dimer
add,1 !add to previous gradient

optg,gradient=1.d-5,startcmd=label: !find next energy

text, optimized geometry parameters
show,rhf,rff,theta1,theta2

text, computed interaction energies
de=(edimer-ehf1-ehf2)*tocm !CPC corrected interaction energy with fixed monomers
```

[http://www.molpro.net/info/current/examples/hfdimer_cpcopt2.com](http://www.molpro.net/info/current/examples/hfdimer_cpcopt2.com)
Calculate harmonic vibrational frequencies and normal modes. For the calculation of anharmonic vibrational frequencies see sections 52 to 55. The hessian is calculated analytically or numerically by finite differences in 3N cartesian coordinates (Z-Matrix coordinates will be destroyed on entry). If analytic gradients are available these are differentiated once to build the hessian, otherwise the energy is differentiated twice. If for the wavefunction method dipole moments are available, the dipole derivatives and the IR intensities are also calculated. Note that numerical hessians cannot be computed when dummy atoms holding basis functions are present. To get reasonable results it is necessary to do a geometry optimization before using the frequency calculation.

47.1 Options

The following options are available:

ANALYTICAL

Use analytical second derivatives of the energy. At present, analytical second derivatives are only possible for closed shell Hartree-Fock (HF) and MCSCF wavefunctions without symmetry. It is not yet possible to calculate IR-intensities analytically. Note that, due to technical reasons, the analytical MCSCF second derivatives have to be computed in the MCSCF-program using e.g. multi; cpmcscf,hess (see MULTI) before they can be used in FREQUENCIES. If analytical MCSCF second derivatives have been computed using multi; cpmcscf,hess, FREQUENCIES will use them by default.

CENTRAL

Use central differences/high quality force constants (default).

NUMERICAL

Differentiate the energy twice, using central differences.

FORWARD

Use forward differences/low quality force constants (only effective if gradients are available).

SYMM=AUTO|NO

During the numerical calculation of the hessian, the symmetry of the molecule may be lowered. Giving SYMM=AUTO the program uses the maximum possible symmetry of the molecular wavefunction in each energy/gradient calculation, and this option therefore minimizes the computational effort. With SYMM=NO no symmetry is used during the frequency calculation (default). For single reference calculations like HF, MP2, CCSD, RCCSD the AUTO option can be safely used and is recommended. However, the AUTO option cannot be used for multireference methods (MCSCF/MRCI/ACPF/AQCC/RS2). If given, the option is disabled in these cases. For these methods frequency calculations are only possible without symmetry. Symmetry is turned off atomically if the state symmetry is 1. Note that this may fail if there are lower states in other symmetries. Use of RESTRICT, SELECT, REF, PROJECT, LOCAL, state-averaged MCSCF will lead on errors unless the calculation is performed in C1 symmetry In such cases the whole calculation must be done without symmetry.

AUTO

Same as SYMM=AUTO, see above.

NOAUTO|NOSYM

Same as SYMM=NO, see above.
HESSREC|SAVE=record  Save hessian to record. By default the hessian is saved on record 5300.2.

FREQREC=record  Save frequencies and normal modes to record (default 5400.2) This information is used, e.g., by the VSCF/VCI program.

TASKREC=record  Save task information in numerical hessian calculation to the given record. This information is required for a restart of a numerical hessian calculation. By default, the information is saved on record 5500.2.

READ  Read hessian from default hessian record.

READ|START=record  Use hessian from previously saved on record. If the hessian has been computed for the current method and geometry already, it is used by default.

RESTART  Attempt to restart a previous numerical frequency/hessian calculation using default task record.

RESTART=record  Attempt to restart a previous numerical frequency/hessian calculation using task record record.

LOW=value  Threshold for printing low frequencies in cm\(^{-1}\). If this option is given, frequencies below the given value are not printed. By default, all frequencies are printed.

STEP=value  Determines the step size of the numerical differentiation of the energy or the gradient. The default step size is 0.01 a.u.

MAXTASK=value  Stop the calculation if the number of tasks is exceeded (the calculation can be restarted later).

MAXCPU=value  Stop the calculation if the given CPU-time (in sec) exceeded (the calculation can be restarted later).

NEW  Recompute hessian, even if a hessian is already available.

PROJECT  Project rotations and translations out of the hessian (default).

NOPROJECT  Don’t project rotations and translations out of the hessian.

PRINT=value  Print option. If value is greater or equal to zero, the hessian and other information is printed (default −1).

DEBUG  Print Debug information, same as PRINT=1.

SCALE=value  Scaling factor for frequencies. The scaled frequencies are used to compute the ZPE and thermodynamic properties.

For compatibility with older MOLPRO versions many of the options can also be set using directives, as described in the following sections.

### 47.2 Printing options (PRINT)

PRINT.options  This directive can be used to control the output:

The following options can be given:

HESSIAN  Print the force constant matrix (hessian) i.e. the second derivative matrix of the energy and the mass weighted hessian matrix.
LOW

Print low vibrational frequencies (i.e., the 5 or 6 frequencies belonging to rotations and translations) and their normal modes (default; \texttt{LOW}=-1 suppresses the print).

\texttt{LOW=value}

Threshold for printing low vibrations in \text{cm}^{-1} (default 150). If a value \textgreater{} 0 is given, frequencies below this value are not printed.

### 47.3 Saving the hessian and other information (SAVE)

\texttt{SAVE.options}

The following \textit{options} can be given:

\texttt{hessian=record}

Save hessian to \textit{record} (same effect as option \texttt{HESSREC}). By default the hessian is saved on record 5300.2.

\texttt{FREQ=record}

Save frequencies and normal modes to \textit{record} (same effect as option \texttt{FREQREC}). By default the frequencies are saved on record 5400.2.

\texttt{TASK=record}

Save task information for possible restart of hessian calculation to \textit{record} (same effect as option \texttt{TASKREC}). By default the frequencies are saved on record 5500.2.

### 47.4 Restarting a hessian/Frequency calculation (START)

\texttt{START.options}

The following options can be given:

\texttt{HESSIAN=record}

Read hessian from \textit{record} \textit{record} (same effect as option \texttt{READHESS}).

\texttt{TASK=record}

Read task information from \textit{record} \textit{record} and restart numerical hessian calculation (same effect as option \texttt{RESTART}).

### 47.5 Coordinates for numerical hessian calculations (COORD)

\texttt{COORD.type}

\textit{type} can be one of the following:

\texttt{UNIQUE}

Use symmetry-unique displacements in the numerical calculation of the hessian (default).

\texttt{3N}

Don’t use symmetry-unique displacements (not recommended).

### 47.6 Stepsizes for numerical hessian calculations (STEP)

\texttt{[STEP,rstep]}

determines the step size of the numerical differentiation of the energy or the gradient. The default step size is \textit{rstep}=0.01 \text{a.u.}
47.7 **Numerical hessian using energy variables** (VARIABLE)

VARIABLE, name;

Defines a variable name which holds the energy value to be used for computing the hessian using finite differences. By default, this is ENERGY(1) as set by the most recent program. For other other variables which can be used see section 46.2.17. Note that numerical hessians cannot be computed when dummy atoms holding basis functions are present.

47.8 **Thermodynamical properties** (THERMO)

It is also possible to calculate the thermodynamical properties of the molecule. Since MOLPRO can only handle Abelian point groups it is necessary to give the point group of the molecule in the input file:

```
THERMO, [SYM=pointgroup], [TEMP=value], [PRESS=value], [TMIN=value, TMAX=value, TSTEP=value]
```

*pointgroup* has to be the Schoenflies Symbol (e.g. C3v for ammonia; linear molecules have to be C*v or D*h respectively). If no point group is given, the point group is determined automatically, but only Abelian groups (D2H and subgroups) are recognized. If the molecule has higher symmetry this may eventually cause deviations in the rotational entropy.

The temperature (in K), pressure (in atm) or a range of temperatures (in K) can be given as options.

If no temperature or pressure is specified the zero-point vibrational energy and the enthalpy \( H(T) - H(0) \) [kJ/mol], heat capacity \( C_v \) [J/mol K] and entropy \( S \) [J/mol K] are calculated for standard temperature and pressure \( T = 298.150 \) [K], \( p = 1 \) [atm]).

The FREQUENCIES program sets the variable ZPE containing the zero-point-energy of the harmonic vibrations in atomic units. If the THERMO option is used, the variables HTOTAL and GTOTAL, containing the enthalpy and the free enthalpy of the system in atomic units, are also set.
47.9 Examples

***, formaldehyde frequency calculation
memory, 8, m

basis = vdz
qthresh, energy = 1.d-8

geomtyp = xyz
symmetry, nosym
geometry={
  4
  FORMALDEHYDE
  C  0.0000000000 0.0000000000 -0.5265526741
  O  0.0000000000 0.0000000000 0.6555124750
  H  0.0000000000 -0.9325664988 -1.1133424527
  H  0.0000000000 0.9325664988 -1.1133424527
}
hf, accu, 14
optg; coord, 3n;

{frequencies, analytic
thermo, sym = c2v
print, thermo}

mp2
optg; coord, 3n
{frequencies
thermo, sym = c2v
print, thermo}

http://www.molpro.net/info/current/examples/form_freq.com

***, Phosphorous-pentafluoride Vibrational Frequencies
memory, 1, m
basis = 3-21G

geomtyp = xyz ! use cartesian coordinates xmol style
symmetry, nosym ! don’t use symmetry
geometry={
  6
  PF5
  P  0.00000 0.00000 0.00000
  F  0.00000 1.11100 -1.12400
  F  0.00000 -1.52800 -0.40100
  F  0.00000 0.41700 1.52500
  F -1.60400 0.00000 0.00000
  F  1.60400 0.00000 0.00000
}
rhf
optg ! optimize geometry

frequencies ! calculate vibrational frequencies
print, low ! print frequencies+modes of zero frequencies
thermo, sym = d3h ! calculate thermodynamical properties
temp, 200, 400, 50 ! temperature range 200 - 400 [K]

http://www.molpro.net/info/current/examples/pf5_freq.com
48 CHEMICAL SHIELDINGS, MAGNETIZABILITY, AND ROTATIONAL g-TENSOR

Bibliography:

All publications resulting from use of this program must acknowledge the above.

The command nmrshld invokes the calculation of NMR chemical shielding tensors at the level of (local) density-fitted HF (GIAO-DF-HF) or local density-fitted MP2 (GIAO-DF-LMP2). Note: Chemical shieldings at the level of MP2 are only implemented for DF-LMP2.

For the calculation of the chemical shielding tensor a preceding DF-HF, respectively, DF-LMP2 calculation is required. Symmetry has to be set to nosym. For the GIAO-DF-HF code one can use canonical orbitals from the DF-HF run or localized orbitals (recommended).

Example:

***,Chemical shielding tensors for water molecule
symmetry,nosym
GEOMETRY={ !geometry input
   h1;o,h1,r1;h2,o,r2,h1,theta}
r1=0.9583 ang
r2=0.9583 ang
theta=104.2
basis={ !specify basis
default,cc-pVDZ
set,mp2fit
default,vdz/mp2fit
set,jkfit
default,vdz/jkfit
}
df-hf,df_basis=jkfit
df-lmp2,df_basis=mp2fit
nmrshld;comp !invoke calculations of shieldings, print the components

The shielding calculation returns the chemical shielding tensors $\sigma$ and a summary of the chemical shifts (i.e. the arithmetic mean of the diagonal elements) for each nucleus in the order they were specified in the geometry input. The directive comp additionally prints the diamagnetic and paramagnetic contributions (for further information see R. Ditchfield, Mol. Phys. 27(4), 789 (1974)) for all shielding tensors.

Additionally, the calculation of magnetizabilities and rotational $g$ tensors has been implemented: the command magprop invokes the calculation of magnetizabilities and chemical shielding tensors. The directive comp can be specified. The command magnetiz invokes a pure magnetizability calculation. Note that a pure magnetizability calculation takes nearly as long as a chemical shielding calculation and hence does not provide any advantage in comparison to magprop. See also the input examples gly1_mag.com and h2o_mag.com.

If one is interested in the calculation of rotational $g$ tensors the molecule has to be aligned in the
principal axis system with the command `orient, mass`. Otherwise, the results are meaningless.
49 MINIMIZATION OF FUNCTIONS

The minimization of general functions of one or more variables can be carried out using the command:

\[
\text{MINIMIZE}, \text{func}, x_1[, x_2, x_3, \ldots]
\]

where \( \text{func} \) represents a function of up to 50 variables \( x_1, x_2, \ldots \). Two different optimization methods can be selected as described below which do or do not use numerical derivative information.

The optimization method, as well as finer control over \( \text{func} \), can be chosen using the \text{METHOD} directive

\[
\text{METHOD}, \text{key} [, \text{key1}=value, \text{key2}=value, \ldots]
\]

where \( \text{key} \) defines the optimization method. Valid options for \( \text{key} \) are:

- \text{BFGS} Broyden-Fletcher-Goldfarb-Shanno conjugate gradient method, which uses numerical gradients (default)
- \text{SIMPLEX} Downhill simplex method, which uses only function evaluations

Options to these methods, \( \text{key1}, \text{key2}, \ldots \), are:

- \text{VARSCALE}=\text{vscale} Optimization in space of scaled variables.
  \text{vscale}=0 no scaling (not recommended)
  \text{vscale}=1 optimization in the space of \( \ln(x) \)
  \text{vscale}=2 optimization in space of initial value scaling, e.g., \( x_1/x_{i1} \) (default)

- \text{THRESH}=\text{thresh} Required accuracy of either the gradient (BFGS) or parameters (SIMPLEX). The default is \( 1 \cdot 10^{-4} \) for BFGS and \( 1 \cdot 10^{-2} \) for SIMPLEX.
  Note that previously this pertained to the function value in the Simplex case.

- \text{VSTEP}=\text{epsd} Step size for numerical gradients (BFGS) or initial SIMPLEX vertices

- \text{PROC}=\text{procname} Specifies the procedure to be executed in each optimization step. This defines a complete function evaluation (if needed, numerical gradients will be evaluated using this procedure as well)

- \text{STARTCMD}=\text{command} Specifies a start command. In each optimization step all input beginning with \text{command} to the current \text{MINIMIZE} is processed.

Miscellaneous directives (separated by semicolons or line breaks)

- \text{MAXIT}, \text{maxit} maximum number of optimization cycles. The default is 30 for BFGS and 100 for SIMPLEX.
49.1 Examples

49.1.1 Geometry optimization

***, Simple geometry optimization

```plaintext
basis=vdz

geometry={
  O
  H 1 r
  H 1 r 2 theta}

r=1.8
theta=104

hf
mp2

{minimize,energy,r,theta}
---
```

http://www.molpro.net/info/current/examples/min_optgeo.com

49.1.2 Basis function optimizations

***, Optimization of 2 d functions

```plaintext
geometry={Ne}

dexp=[2.0,1.0]

basis={
  sp,Ne,vdz;c;
  d,Ne,dexp(1),dexp(2)
}

hf
mp2

eval=energy

minimize,eval,dexp(1),dexp(2)
---
```

http://www.molpro.net/info/current/examples/basisopt_simple.com
***, Optimization of 2 d functions

geometry={Ne}
dexp=[2.0,1.0]

{minimize,eval,dexp(1),dexp(2)
method,bfgs,varscale=1,thresh=1e-5,proc=optd}

proc optd

basis={
    sp,Ne,vdz;c;
d,Ne,dexp(1),dexp(2)
}

hf
mp2
eval=energy

endproc

http://www.molpro.net/info/current/examples/basisopt_proc.com

***, MP2 optimization of core-valence cc-pCVDZ functions

geometry={Ne}
sexp=20.
pexp=30.

{minimize,ecv,sexp,pexp
method,bfgs,varscale=1,thresh=1e-5,proc=myopt}

proc myopt

basis={
    spd,Ne,vdz;c;
    s,Ne,sexp
    p,Ne,pexp
}

hf
{mp2;core,1}
eval=energy

{mp2;core,0}
eall=energy

ecv=eall-eval

endproc

http://www.molpro.net/info/current/examples/basisopt_cv.com

50 INSTANTONS

Instantons can be located within the ring-polymer formalism using the INSTANTON command:
INSTANTON[, key1=value, key2=value, ...]
These instantons can be used to compute either the thermal reaction rate or the tunnelling splitting between degenerate potential wells. The behaviour can be controlled with the splitting option. It is a good idea to turn symmetry off (using nosym) during the calculation as the ring-polymer beads do not necessarily share the same symmetry operations as the transition state or well minima.

### 50.1 Thermal reaction rates

Quantum rate calculations proceed via an instanton which is equivalent to the transition state on the ring-polymer surface. These stationary points are computed using a quasi-Newton saddle-point search with Powell’s Hessian update. Because of the known symmetry of the final geometry (that the ring polymer folds back on itself), only half of the beads need be specified.

The geometry of the transition state should be specified with the geometry keyword, and the classical TST rate through this point is compared with the rate computed from the instanton. The action of the instanton, its fluctuations and rotations are printed to the output file. MOLPRO computes the tunnelling factor which is the ratio of these rates and the rate itself can be calculated if the reactant partition function is known. It is necessary to converge the results in the large-$N$ limit.

References for the ring-polymer instanton method are:


### 50.2 Tunnelling splittings

Instantons used to compute tunnelling splittings are local minima on the ring-polymer surface. They are located using the limited-memory Broyden-Fletcher-Goldfarb-Shanno (L-BFGS) method. All publications describing work using this method should quote at least one of these references:


The geometry of the well minimum should be specified with the geometry keyword. The action of the instanton, its fluctuations and the fluctuations about the well minimum are printed to the output file. MOLPRO computes the tunnelling-matrix element which can be used to construct the tunnelling-splitting pattern for a molecular cluster with two or more degenerate wells as described in the latter of the two references. It is necessary to converge the results in the limit that $\beta \to \infty$ and $\beta/N \to 0$.

References for the ring-polymer instanton method are:

50.3 Input file

An input file should be supplied in xyz format containing the Cartesian coordinates (in Ångstroms) of the beads used to initialize the instanton optimization. A rate calculation requires \( N/2 \) beads, whereas a tunnelling-splitting calculation requires \( N \). The first line contains the number of atoms in the system and the second has two numbers: \( N \), the number of beads, and \( T \), temperature in Kelvin (for the case of a rate calculation) or \( \beta \), the reciprocal temperature in atomic units (for the case of a tunnelling-splittings calculation). These two lines appear before the coordinates of each bead which are given one atom per line including the element symbol.

50.4 Procedures

A few procedures must be defined. beadpot defines the method for computing the potential energy of a single bead geometry. beadgrad gives the method for computing the gradient for a bead using the force command. beadfreq1, beadfreq2 and beadfreq3 define methods for computing frequencies of the transition state/well minimum, of the initial (pre-optimized) ring-polymer beads and of the final (optimized) beads. Because the procedure beadfreq1 is only called once directly after beadpot, it is not necessary to recalculate the wavefunction in this case. For the tunnelling-splitting calculations, beadfreq2 is not used as the L-BFGS optimization proceeds without a Hessian.

50.5 Options

SP\textsc{lit}TING runs the tunnelling splitting calculation instead of a rate calculation. The default is \textit{False}.

\textsc{in}\textsc{pu}T=\textit{filename} file containing initial instanton geometry in format described in section 50.3 The default is initial.xyz.

\textsc{ou}T\textsc{pu}T=\textit{filename} file containing final instanton geometry in format described in section 50.3 The default is final.xyz.

\textsc{re}\textsc{ac}t\textsc{an}t=\textit{value} value of potential (in \( E_h \)) of reactant states used to scale the instanton action in a rate calculation only. The default is \( 0 \).

\textsc{ma}x\textsc{it}=\textit{integer} maximum number of optimization cycles. The default is 50.

\textsc{gra}d\textsc{ient}=\textit{value} required accuracy of the optimized ring-polymer gradient. The default is \( 3 \cdot 10^{-4} \).

\textsc{ste}p\textsc{ma}x=\textit{value} maximum allowed step (in bohr) in the quasi-Newton instanton optimization. Attempted steps larger than this are scaled down. The default is \( 0 \cdot 3 \ a_0 \).

\textsc{m}sa\textsc{ve}=\textit{integer} number of gradients saved from previous iterations used in the L-BFGS optimization. The default is 3.

\textsc{re}\textsc{ad} Reads initial (pre-optimized) Hessian from file \$\textsc{t}mp\textsc{d}ir/instanton.hess, which is automatically created from the final geometry of the previous run, instead of calling beadfreq2. The default is \textit{False}.

\textsc{re}\textsc{ad} Uses a banded-matrix eigensolver in the quasi-Newton optimization. The default is \textit{False}.
50 INSTANTONS

50.6 Parallelization

The ring-polymer instanton approach is naturally parallelized by computing the energies and
gradients of each bead on separate processors. It is necessary to run MOLPRO with the --mppx
flag and it is recommended for the number of processors used to be a factor of the number of
beads.

50.7 Examples

Here we give an example for calculating the rate of the H + H₂ → H₂ + H reaction at 250 K
using MRCI. The MOLPRO input file is

```plaintext
***, H + H₂ instanton
if(NPROC_MPP.gt.1) then
  skipped
endif

proc beadpot={
  hf
casscf
mrci
}

proc beadgrad={
  beadpot
  force,numerical,dstep=1e-4
}

proc beadfreq1={
  frequencies
}

proc beadfreq2={
  beadpot
  frequencies,forward
}

proc beadfreq3={
  beadpot
  frequencies,print=0
}

nosym

geometry={!
  optimized geometry at transition state
  3
  MRCI/VDZ ENERGY=-1.64651538 ! comment line
  H -0.9401271688 0.0000000000 0.0000000000
  H 0.0033328462 0.0000000000 0.0000000000
  H 0.9467943226 0.0000000000 0.0000000000
}

mass,isotope,print
basis=vdz

instanton, input='instanton_initial.xyz', \\output='instanton_final.xyz', reactant=-1.66295138342, \\save='instanton_ts.dat', hessfile='instanton.hess'
!table,action,perm,rotratio,fluctratio,tunfac
text, $action $perm $rotratio $fluctratio $tunfac

http://www.molpro.net/info/current/examples/instanton.com
```
and an initial 16-bead half ring-polymer geometry is given in `instanton-initial.xyz`, which can be found in the examples directory.

An example calculation of the tunnelling splitting in the HO$_2$ cluster using UHF is provided by the input files

```plaintext
***, hydroperoxyl HO2 splitting instanton
if(NPROC_MPP.gt.1) then
  skipped
endif
FILE,2,ho2inst.wfu,new

proc beadpot=
  uhf

proc beadgrad=
  beadpot
  force

proc beadfreq1=
  frequencies

proc beadfreq3=
  beadpot
  frequencies

geometry=
  ! optimized geometry at well minimum
  3
  UHF-SCF002/VDZ ENERGY=-150.16631226 ! comment line
  H  0.904294157899999895  0.919502897200000113  0
  O  0.681281911699999965  -0.00702956160000003938  0
  O -0.683576069499999939  0.00706386439999998061  0

mass,isotope,print
basis=vdz

instanton, splitting, input='splitting_initial.xyz', \ \output='splitting_final.xyz', maxit=200
table,action,fluctratio,tunsplit*1e9

http://www.molpro.net/info/current/examples/splitting.com
```

where an initial 32-bead linear-polymer geometry is given in `splitting_initial.xyz`, which can be found in the examples directory.

In both examples, data is saved to a `.wfu` file. If another instanton calculation at a different temperature or with a different number of beads is run, some information can be recovered by using `frequencies,read=5300.2` in `beadfreq1`.
51  BASIS SET EXTRAPOLATION

Basis set extrapolation can be carried out for correlation consistent basis sets using

```plaintext
EXTRAPOLATE, BASIS=basislist, options
```

where basislist is a list of at least two basis sets separated by colons, e.g. AVTZ:AVQZ:AV5Z. Some extrapolation types need three or more basis sets, others only two. The default is to use \( n^{-3} \) extrapolation of the correlation energies, and in this case two subsequent basis sets and the corresponding energies are needed. The default is not to extrapolate the reference (HF) energies; the value obtained with the largest basis set is taken as reference energy for the CBS estimate. However, extrapolation of the reference is also possible by specifying the `METHOD_R` option.

The simplest way to perform extrapolations for standard methods like MP2 or CCSD(T) is to use, e.g.

```plaintext
***,H2O
memory,32,m
qthresh,energy=1.d-8
r = 0.9572 ang, theta = 104.52
geometry={O;
    H1,O,r;
    H2,O,r,H1,theta}

basis=avtz
hf
ccsd(t)
extrapolate,basis=avqz:av5z
table,basissets,energr,energy-energr,energy
head,basis,ehf,ecorr,etot
```

This will perform the first calculation with AVTZ basis, and then compute the estimated basis set limit using the AVQZ and AV5Z basis sets. The correlation energy obtained in the calculation that is performed immediately before the extrapolate command will be extrapolated (in this case the CCSD(T) energy), and the necessary sequence of calculations [here HF;CCSD(T)] will be automatically carried out.

The resulting energies are returned in variables ENERGR (reference energies), ENERGY (total energies), and ENERGD (Davidson corrected energy if available); the corresponding basis sets are returned in variable BASISSETS. The results can be printed, e.g., in a table as shown above, or used otherwise. The above input produces the table

<table>
<thead>
<tr>
<th>BASIS</th>
<th>EHF</th>
<th>ECORR</th>
<th>ETOT</th>
</tr>
</thead>
<tbody>
<tr>
<td>AVQZ</td>
<td>-76.06600082</td>
<td>-0.29758099</td>
<td>-76.36358181</td>
</tr>
<tr>
<td>AV5Z</td>
<td>-76.06732050</td>
<td>-0.30297495</td>
<td>-76.37029545</td>
</tr>
<tr>
<td>CBS</td>
<td>-76.06732050</td>
<td>-0.30863418</td>
<td>-76.37595468</td>
</tr>
</tbody>
</table>

The extrapolated total energy is also returned in variable ECBS (ECBSDL for Davidson corrected energy if available).

In order to extrapolate the HF energy as well (using exponential extrapolation), three energies are needed. One can modify the input as follows:

```plaintext
extrapolate,basis=avtz:avqz:av5z,method_r=ex1,npc=2
```

`method_r` determines the method for extrapolating the reference energy (in this case a single exponential); `npc=2` means that only the last two energies should be used to extrapolate the correlation energy (by default, a least square fit to all given energies is used). This yields
Rather than using the default procedure as above, one can also specify a procedure used to carry
out the energy calculation, e.g.

extrapolate,basis=avtz:avqz:av5z,proc=runccsd, method_r=ex1,npc=2}

procedure runccsd
hf
ccsd(t)
endproc

Alternatively, the energies can be provided via variables EREF, ECORR, ETOT etc. These must
be vectors, holding as many values as basis sets are given.

51.1 Options

The possible options and extrapolation methods are:

BASIS=basissets Specify as set of correlation consistent basis sets, separated by colons.
PROC=procname Specify a procedure to run the energy calculations
STARTCMD=command Start command for the energy calculations: the sequence of com-
mands from STARTCMD and the current EXTRAPOLATE is run. STARTCMD
must come before the extrapolate command in the input.
METHOD=key Specifies a keyword to define the extrapolation function, see section 51.2
METHOD_C=key Specifies a keyword to define the extrapolation function for the corre-
lation energy, see section 51.2
METHOD_R=key Specifies a keyword to define the extrapolation function for the refer-
ence energy, see section 51.2
VARIABLE=name Specifies a variable name; this variable should contain the energies to
be extrapolated.
ETOT=variable Provide the total energies in variable (a vector with the same number
of energies as basis sets are given) If only ETOT but not EREF is
given, the total energy is extrapolated.
EREF=variable Provide the reference energies to be extrapolated in variable (a vector
with the same number of energies as basis sets are given)
ECORR=variable Provide the correlation energies to be extrapolated in variable (a vector
with the same number of energies as basis sets are given)
ECORRD=variable Provide the Davidson corrected correlation energies to be extrapo-
lated in variable (a vector with the same number of energies as basis
sets are given). If both ECORR and ECORRD are given, both will be
extrapolated.
MINB=number First basis set to be used for extrapolation (default 1)
51 BASIS SET EXTRAPOLATION

\texttt{MAXB=number} \quad \text{Last basis set to be used for extrapolation (default number of basis sets)}

\texttt{NPR=number} \quad \text{If given, the last NPR values are used for extrapolating the reference energy. NPR must be smaller or equal to the number of basis sets.}

\texttt{NPC=number} \quad \text{If given, the last NPC values are used for extrapolating the reference energy. NPC must be smaller or equal to the number of basis sets.}

\texttt{XR=array} \quad \text{Provide a vector of exponents to be used for defining the extrapolation functional for the reference energy when using the }\texttt{LX}\text{ functional.}

\texttt{XC=array} \quad \text{Provide a vector of exponents to be used for defining the extrapolation functional for the correlation energy when using the }\texttt{LX}\text{ functional.}

\texttt{PR=array} \quad \text{Provide the constant }p\text{ to be used for defining the extrapolation functional for the reference energy.}

\texttt{PC=array} \quad \text{Provide the constant }p\text{ to be used for defining the extrapolation functional for the correlation energy.}

51.2 Extrapolation functionals

The extrapolation functional is chosen by a keyword with the \texttt{METHOD}, \texttt{METHOD_R}, and/or \texttt{METHOD_C} options. The default functional is \texttt{L3}. In the following, \(n\) is the cardinal number of the basis set (e.g., 2 forVDZ, 3 forVTZ etc), and \(x\) is an arbitrary number. \(p\) is a constant given either by the \texttt{PR} or \texttt{PC} options (default \(p = 0\)). \(x\) is a number or a vector given either by the \texttt{XR} or \texttt{XC} options (only for \texttt{LX}; \(nx\) is the number of elements provided in \(x\)). \(A, B, A_i\) are the fitting coefficients that are optioined by least-squares fits.

\texttt{Lx} \quad E_n = E_{CBS} + A \cdot (n + p)^{-x}

\texttt{LHx} \quad E_n = E_{CBS} + A \cdot (n + 1/2)^{-x}

\texttt{LX} \quad E_n = E_{CBS} + \sum_{i=1}^{nx} A_i \cdot (n + p)^{-x(i)}

\texttt{EX1} \quad E_n = E_{CBS} + A \cdot \exp(-C \cdot n)

\texttt{EX2} \quad E_n = E_{CBS} + A \cdot \exp(-(n - 1)) + B \cdot \exp(-(n - 1)^2)

\texttt{KM} \quad \text{Two-point formula for extrapolating the HF reference energy, as proposed by A. Karton and J. M. L. Martin, Theor. Chem. Acc. 115, 330 (2006): }E_{HF,n} = E_{HF,CBS} + A(n+1) \cdot \exp(-9 \sqrt{n}). \text{ Use } \texttt{METHOD_R=KM}\text{ for this.}

The following example shows various possibilities for extrapolation:
The second example shows extrapolations of MRCI energies. In this case both the MRCI and the MRCI+Q energies are extrapolated.
*** h2o
memory, 32, m

gthresh, energy=1.d-9
basis=avtz

r = 0.9572 ang, theta = 104.52
geometry=

 HF
multi
mrci
text, Compute energies, extrapolate reference energy using EX1 and correlation energy using L3;
text, The Davidson corrected energy is also extrapolated
extrapolate, basis=avtz:avqz:av5z, method_c=L3, method_r=EX1, npc=2

emc=energy-emc
ecorr_mrci=energy-emc
ecorr_mrciq=energy-emc
text, Extrapolate reference energy by EX1 and correlation energy by LH3
text, The Davidson corrected energy is also extrapolated
extrapolate, basis=avtz:avqz:av5z, ecorr=ecorr_mrci, ecorrd=ecorr_mrciq, method_c=LH3, eref=emc, met
51.3 Geometry optimization using extrapolated energies

Geometry optimizations are possible by using numerical gradients obtained from extrapolated energies. Analytical energy gradients cannot be used.

The following possibilities exist:

1.) If OPTG directly follows the EXTRAPOLATE command, the extrapolated energy is optimized automatically (only variable settings may occur between EXTRAPOLATE and OPTG).

Examples:

Extrapolating the energy for the last command:

```plaintext
genergy={o;h1,o,r;h2,o,r,h1,theta}
theta=102
r=0.96 ang
basis=vtz

hf
ccsd(t)
extrapolate,basis=vtz:vqz
optg
```

Extrapolating the energy computed in a procedure:

```plaintext
genergy={o;h1,o,r;h2,o,r,h1,theta}
theta=102
r=0.96 ang

proc ccsdt
hf
ccsd(t)
endproc
extrapolate,basis=vtz:vqz,proc=ccsdt

optg
```

Note that this is not possible if EXTRAPOLATE gets the input energies from variables.
2.) Using a procedure for the extrapolation:

By default, variable ECBS is optimized, but other variables (e.g. EBSD) can be specified using the VARIABLE option on the OPTG command.

```plaintext
geometry={o;h1,o,r;h2,o,r,h1,theta}
theta=102
r=0.96 ang
basis=vtz

proc cbs34
hf
ccsd(t)
extrapolate,basis=vtz:vqz
endproc

optg,variable=ecbs,proc=cbs34
```

http://www.molpro.net/info/current/examples/h2o_extrapol_opt3.com

```plaintext
geometry={o;h1,o,r;h2,o,r,h1,theta}
theta=102
r=0.96 ang

proc cbs34
basis=vtz
hf
ccsd(t)
eref(1)=energr
ecc(1)=energy

basis=vqz
hf
ccsd(t)
eref(2)=energr
ecc(2)=energy
extrapolate,basis=vtz:vqz,eref=eref,etot=ecc
endproc

optg,variable=ecbs,proc=cbs34
```

http://www.molpro.net/info/current/examples/h2o_extrapol_opt4.com

51.4 Harmonic vibrational frequencies using extrapolated energies

This is possible by defining the extrapolation in a procedure:
geometry={o;h1,o,r;h2,o,r,hl,theta}
theta=102
r=0.96 ang
basis=vtz

proc cbs34
  hf
  ccsd(t)
  extrapolate,basis=vtz:vqz
endproc

optg,variable=ecbs,proc=cbs34
freq,variable=ecbs,proc=cbs34

http://www.molpro.net/info/current/examples/h2o_extrapol_freq.com
The SURF program allows for the calculation of the potential energy surface around a reference structure as required for the calculation of anharmonic frequencies (see the VSCF and VCI programs). The reference structure is supposed to be a (local) minimum or a transition state of a double-minimum potential. The potential is represented by energy grid points rather than an analytical representation. Within the SURF program the potential energy surface is expanded in terms of normal coordinates, linear combination of normal coordinates or localized normal coordinates. Consequently, a harmonic frequency calculation needs to be performed first. The potential will then be represented by a multi-mode expansion, i.e. a hierarchical scheme given by

\[ V(q_1, \ldots, q_{3N-6}) = \sum_i V_i(q_i) + \sum_{i<j} V_{ij}(q_i, q_j) + \sum_{i<j<k} V_{ijk}(q_i, q_j, q_k) + \ldots \]  

with

\[ V_i(q_i) = V_i^0(q_i) - V(0) \]  
\[ V_{ij}(q_i, q_j) = V_{ij}^0(q_i, q_j) - \sum_{r \in \{i, j\}} V_r(q_r) - V(0) \]  
\[ V_{ijk}(q_i, q_j, q_k) = V_{ijk}^0(q_i, q_j, q_k) - \sum_{rs \in \{i, j, k\}} V_{rs}(q_r, q_s) - \sum_{r \in \{i, j, k\}} V_r(q_r) - V(0) \]  
\[ V_{ijkl}(q_i, q_j, q_k, q_l) = \ldots \]  

where \( q_i \) denotes the coordinates. This expansion needs to be terminated after an \( n \)-body contribution as controlled by the keyword NDIM. The SURF program is fully parallelized in a sense that the calculation of different grid points is send to different processors (embarrassingly parallel MPPX scheme). The START1D keyword is mandatory and defines the label where to jump in the input in order to do an electronic structure calculation which is terminated by the SURF command. This way the quality of the potential energy surface is defined. For example, the input for the calculation of a CCSD surface looks like:

```
label1
hf
ccsd
surf,START1D=label1
```

The SURF program is based on an iterative algorithm, i.e. grid points will be added automatically to the grid representation of the potential until a convergence threshold will be met. This guarantees a well-balanced description of the different terms in the expansion of the potential and simultaneously minimizes the number of \textit{ab initio} calculations for a representation of the potential. For further details see:


52.1 Options

The following options are available:

**NDIM** = \( n \)

The keyword **NDIM** = \( n \) terminates the expansion of the PES after the \( n \)-body term. Currently, at most 4-body terms can be included, but the default is set to 3. Please note, when you use **NDIM** = 4 as a keyword for the **SURF** program, you need to pass this information to the **VSCF** and **VCI** programs also. Otherwise these programs will neglect the 4-body terms.

**NGRID** = \( n \)

Based on a coarse grid of *ab initio* points a fine grid will be generated from automated interpolation techniques. The keyword **NGRID** = \( n \) determines the number of equidistant grid points in one dimension. **NGRID** = \( n \) has to be an even number. The default is currently set to 16. Note that the number of grid points also controls the extension of the \( n \)-dimensional potential energy surfaces (see keyword **SCALE**) and thus influences many internal thresholds which are optimized to the default value of **NGRID**. The number of grid points also determines the number of basis functions in the grid-based **VSCF** program. At present the maximum grid size is 36.

<table>
<thead>
<tr>
<th>Grid points</th>
<th>14</th>
<th>16</th>
<th>18</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface extension</td>
<td>4.30</td>
<td>4.69</td>
<td>5.05</td>
<td>5.39</td>
</tr>
</tbody>
</table>

**VAR1D** = *variable*

The **SURF** program reads the energy of electronic structure calculations from the internal **MOLPRO** variables, e.g. **ENERGY**, **EMP2**, ... . The internal variable is specified by the keyword **VAR1D**. Within the example shown above, **VAR1D** = **ENERGY** would read the CCSD energy, while **VAR1D** = **EMP2** would read the MP2 energy, which is a byproduct of the CCSD calculation. The default for the **VAR1D** keyword is the internal variable **ENERGY**.

**SYM** = *variable*

Symmetry within electronic structure calculations can be exploited by the keyword **SYM** = **Auto**. Usually this leads to significant time savings. By default this symmetry recognition is switched off as certain calculations may cause some trouble (e.g. local correlation methods). Symmetry in electronic structure calculations may not be mistaken by the symmetry of the mode-coupling terms (see keyword **MPG**).

**MPG** = \( n \)

Symmetry of the normal modes is recognized by the program automatically. Only Abelian point groups can be handled at the moment. Symmetry of the modes will be determined even if the **NOSYM** keyword is used in the electronic structure calculations. In certain cases numerical noise can be very high and thus prohibits a correct determination of the symmetry labels. Symmetry can be switched off by using **MPG** = 1.

**SCALE** = *value*

The extension of the potential energy surfaces is determined from Gauss-Hermite quadrature points. Using a fine grid **NGRID** = 16 the surface stretches out to the **NGRID**/2\(^{th}\) Gauss-Hermite point, i.e. 4.69, in each direction (see keyword **NGRID**). As these values are fairly large within the calculation of fundamental modes, a scaling factor, **SCALE** = \( f \), has been introduced. A default scaling of 0.75 is used. Increasing the size of the surfaces usually requires the calculation of
further ab initio points as the surface interpolation is more stable for surfaces of limited size.

**THRFIT=value**

The iterative algorithm for generating potential energy surfaces is based on a successive increase of interpolation points. The iterations are terminated once the interpolation of two subsequent iteration steps became stable. The convergence threshold can be changed by the keyword THRFIT=$f$. There is currently just one control variable for the different 1D, 2D, 3D, and 4D iterations. The 4 thresholds are different but depend on each other. Consequently, changing the default value (THRFIT=4.0d-2) will change all thresholds simultaneously which keeps the calculation balanced.

**FIT1D=$n$**

The maximum order of the polynomials used for fitting within the iterative interpolation scheme can be controlled by the keywords FIT1D, FIT2D, FIT3D, FIT4D. The default is given by 8. However in certain cases higher values may be necessary, but require an appropriate number of coarse grid points, which can be controlled by MIN1D etc.

**MIN1D=$n$**

The minimum number of coarse grid points can be controlled by the keywords MIN1D, MIN2D, MIN3D, MIN4D. These 4 keywords determine the minimum number of ab initio calculations in one dimension for each 1D, 2D, 3D and 4D surface. The defaults are currently MIN1D=4, MIN2D=4, MIN3D=4, MIN4D=4. Presently, values larger than 24 are not supported.

**MAX1D=$n$**

The maximum number of coarse grid points can be controlled by the keywords MAX1D, MAX2D, MAX3D, MAX4D. These 4 keywords determine the maximum number of ab initio calculations in one dimension for each 1D, 2D, 3D and 4D surface. The defaults are currently MAX1D=24, MAX2D=16, MAX3D=10, MAX4D=8. Presently, values larger than 24 are not supported.

**EXT12D=value**

Outer regions of the potential energy surfaces may be determined by extrapolation rather than interpolation schemes. By default extrapolation is switched off, i.e. EXT12D=1.0 and EXT34D=1.0. However, an extrapolation of 10% in case of the 1D and 2D contributions to the potential (EXT12D=0.9) and of 20% in case of the 3D and 4D terms (EXT34D=0.8) may be useful as it usually stabilizes the fitting procedure.

**SKIP3D=value**

As the number of 3D and 4D surfaces can increase very rapidly, there exists the possibility to neglect unimportant 3D and 4D surfaces by the keywords SKIP3D and SKIP4D. The criterion for the prescreening of the 3D surfaces is based on the 2D terms and likewise for the 4D terms the 3D surfaces are used. The neglect of 3D surfaces automatically leads to the neglect of 4D surfaces, as the latter depend on the previous ones. By default prescreening is switched on, but can be switched off by SKIP3D=0.0 and SKIP4D=0.0.

**VRC=$n$**

Once the keyword VRC=1 is provided, the SURF program will also compute the vibrational-rotational coupling surfaces and thus increases the number of degrees of freedom to 3N-3. Vibrational-rotational coupling surfaces can only be used within the PESTRANS program (see below), but will be neglected in any VSCF or VCI calculations.
BATCH3D=$n$

After calculating a number of grid points within the iterative interpolation scheme the convergence of the individual surfaces will be checked and, if provided by the keyword DUMP, dumped to disk. This leads typically to 3-5 iterations and thus the same number of restart points within the calculation of the 1D, 2D, ... surfaces. As the number of 3D and 4D terms can be very large this is not sufficient in these cases. Therefore, the lists of 3D and 4D terms is cut into batches which will be processed subsequently. BATCH3D and BATCH4D control the number of 3D and 4D surfaces within each batch. By default BATCH3D is set to 30 times the number of processors and BATCH4D to 10 times the number of processors. Accordingly the number of restart points is increased. Smaller values for BATCH3D and BATCH4D, e.g. BATCH3D=20, increase the number of restart points on cost of the efficiency of the parallelization.

SADDLE=$n$

Standard SURF calculations expect the reference structure to be a (local) minimum on the PES, i.e. SADDLE=0 (default). Alternatively, one may start the PES generation from a transition state, which is recommended for the calculation of double-minimum potentials. This situation is not recognized automatically and thus requires the keyword SADDLE=1.

TYPE=variable

TYPE=QFF calls a macro, which modifies the parameters of the SURF program in order to compute a quartic force field in the most efficient manner. This implies a reduction of the size of the coupling surfaces and a limitation of the maximum number of points for the nD-terms. It should be used for VPT2 calculations. TYPE=ZPVE calls a macro, which changes the defaults for several parameters of the SURF, VSCF and VCI programs. It is meant for the quick and efficient calculation of zero point vibrational energies on cost of some accuracy. For example, the expansion of the potential will be truncated after the 2D terms. As a consequence the output of course is reduced to the presentation of the vibrational ground state only. TYPE=FULL (default) performs a standard calculation as needed for VSCF or VCI calculations.

USEMRCC=$n$

Once the Mrcc program of M. Kallay is used for determining individual grid points, the option USEMRCC=1 needs to be set, which is needed to ensure proper communication between MOLPRO and Mrcc. Default: USEMRCC=0.

DELLOG=$n$

For large molecules or in the case of modelling the 3D and 4D terms, the .log-file may become huge. First of all the .log-file can be directed to scratch within the electronic structure program, i.e. logfile, scratch. The option DELLOG=1 always truncates the .log-file in a way that it contains only the very last energy calculation. Default: DELLOG=0.

INFO=$n$

INFO=1 provides a list of the values of all relevant program parameters (options). Default: INFO=0.

PLOT=$n$

PLOT=$n$ plots all nD surfaces and a corresponding GNUPLOT script in a separate subdirectory (plots1) in the home-directory in order to allow for visualization of the computed nD surfaces. E.g. the command "gnuplot plotV1D.gnu" in the plots1 directory produces .eps files for all 1D surfaces. Default: PLOT=0.
The following example shows the input of a calculation which computes energy and dipole surfaces at the MP2/cc-pVTZ level and subsequently determines the anharmonic frequencies at the VSCF and VCI levels. Hartree-Fock calculations will not be restarted and the .log-file is directed to the scratch directory as defined by the $TMPDIR$ variable.

```
memory,20,m
orient,mass
geometry={
  3
  Water
  O  0.0675762564  0.0000000000  -1.3259214590
  H  -0.4362118830  -0.7612267436  -1.7014971211
  H  -0.4362118830   0.7612267436  -1.7014971211
}
mass,iso
basis=vdz
logfile,scratch
hf
mp2
optg
frequencies,symm=auto
label1
{hf
  start,atden}
{mp2
  cphf,1}
{surf,start1D=label1,sym=auto
  intensity,dipole=2}
vscf,combi=1
vci,combi=1
```

## 52.2 Multi-level calculations

**VMULT.options**

The level of the electronic structure calculations can be changed for the different $i$-body terms in the expansion of the potential. As a consequence, the keywords START2D, START3D, VAR2D and VAR3D exist in full analogy to the keywords START1D and VAR1D in standard calculations (see above). The number always represents the level of the expansion term. Such calculations are termed multi-level calculations. There does not exist a corresponding set of keywords for the 4-body terms. 4-body terms will always use the variables specified for the 3-body terms.

**MULTI=n**

The keywords START1D, START2D, START3D in combination with the commands VAR1D, VAR2D and VAR3D allow for the calculation of multi-level potential energy surfaces. This would imply in principle that the 1D term of the potential needs to be computed at all three levels and the 2D term at two computational levels. As certain low level results are byproducts of more sophisticated methods (e.g. the HF energy is a byproduct of an MP2 calculation or the MP2 energy is a byproduct of a CCSD(T) calculation) the computational overhead can be avoided by the MULTI option.

**MULTI=1:** This is the default and most expensive choice. The 1D potential will be computed at all 3 levels of theory. Likewise, the 2D
potential will be calculated at 2 levels explicitly. An example would be:

1D: CCSD(T)/cc-pVTZ  
2D: MP4(SDQ)/cc-pVTZ  
3D: MP2/cc-pVDZ  

{SURF,Start1D=label1  
VMULT,Start2D=label1,Start3D=label3,Multi=1}  

**MULTI=2:** All information is provided by the preceding calculations and thus no part of the potential has to be computed twice. Examples:

1D: CCSD(T)/cc-pVTZ  
2D: CCSD(T)/cc-pVTZ  
3D: MP2/cc-pVTZ  

{SURF,Start1D=label1  
VMULT,Start2D=label1,Start3D=label1  
VMULT,Var3D=EMP2,Multi=2}  

MULTI=3: The 2D potential provides all information for the 3D part while there is no connection between 1D and 2D. Consequently, the 1D contributions need to be computed twice (at the 1D and 2D levels) while all other terms will be computed just once. Examples:

1D: CCSD(T)/cc-pVTZ  
2D: MP4(SDQ)/cc-pVTZ  
3D: MP4(SDQ)/cc-pVTZ  

{SURF,Start1D=label1  
VMULT,Start2D=label1,Start3D=label2  
VMULT,Var2D=EMP2,Var3D=EMP2,Multi=3}  

MULTI=4: The 1D calculation provides all information for the 2D potential but does not so for the 3D part. Hence, the 1D contribution and the 2D contributions need to be computed twice. Examples:

1D: CCSD(T)/cc-pVTZ  
2D: CCSD(T)/cc-pVTZ  
3D: MP4(SDQ)/cc-pVTZ  

{SURF,Start1D=label1  
VMULT,Start2D=label1,Start3D=label2,Multi=4}
In 2D and 4D calculations (i.e. NDIM=2, 4) the VMULT command can be used as well. In 4D calculations the last level must always be identical to the 3D level. In 2D the meaning of MULTI=1 and MULTI=3 is the same. Likewise, MULTI=2 and MULTI=4 are the same in case of 2D calculations.

**START2D=label**

START2D and START3D define labels in the input stream in order to compute the 2D and 3D terms at different levels of electronic structure theory than the 1D terms. The use of the START2D and START3D commands usually requests the use of GOTO commands in the input.

**VAR2D=variable**

The keywords VAR2D and VAR3D are defined in full analogy to the VAR1D option. They specify the internal variable (e.g. ENERGY, EMP2, CCSD, ...) to be read out for a given grid point.

The following example shows a 1D:CCSD(T)/cc-pVTZ; 2D:MP4(SDQ)/cc-pVTZ and 3D:MP2/cc-pVTZ multi-level calculation. As the MP2 energy is a byproduct of the CCSD(T) and MP4(SDQ) calculations only the 1D grid points will be computed twice (at the CCSD(T) and MP4(SDQ) levels). The 1D and 2D energies will be obtained from the internal variable ENERGY while the 3D energies make use of the EMP2 variable.
Special options for Intensities

INTENSITY.options

The INTENSITY.directive of the SURF program provides the option to alter the electronic structure methods for calculating the dipole surfaces. It also allows to define the \( \text{VARDIP}_n[D,X,Y,Z] \) variables separately. \( n \) describes the dimension of the coupling surface and can be chosen to be 1 - 4.

Dipole surfaces can be computed for all those methods for which analytical gradients are available in MOLPRO. For all methods except Hartree-Fock this requires the keyword \( \text{CPHF},1 \) after the keyword for the electronic structure method. In multi-level schemes for which the variables \( \text{VAR1D, VAR2D and VAR3D} \) are set individually, the \( \text{VARDIP}_n[D,X,Y,Z] \) variables have to be set accordingly. Symmetry is currently only implemented for the 1D, 2D and 3D dipole surfaces. For 4D terms symmetry will automatically switched off at the moment. The determination of dipole surfaces beyond Hartree-Fock quality effectively doubles the computation time for surface calculations.

\begin{align*}
\text{DIPOLE} &= n \\
\text{NDIMDIP} &= n \\
\text{VARDIP1DX} &= \text{variable} \\
\text{VARDIP1DY} &= \text{variable} \\
\text{VARDIP1DZ} &= \text{variable} \\
\text{POLAR} &= n
\end{align*}

- **DIPOLE**\( n \) Allows to switch between the different dipole surface calculations. \( \text{DIPOLE}=0 \) switches of all dipole calculations. \( \text{DIPOLE}=1 \) (this is the default) computes the dipole surfaces at the Hartree Fock level of theory, and therefore does not increase the computation time of electronic structure theory. \( \text{DIPOLE}=2 \) switches on the dipole surfaces at the full level of theory therefore \( \text{CPHF},1 \) is required, this effectively doubles the computation time for surface calculations.

- **NDIMDIP**\( n \) This denotes the term after which the \( n \)-body expansion of the dipole surfaces is truncated. The default is set to 3. Note that \( \text{NDIMDIP} \) has to be lower or equal to \( \text{NDIM} \).

- **VARDIP1DX**=variable Variable which is used for the \( x \) direction of the dipole moment for 1D surfaces.

- **VARDIP1DY**=variable Variable which is used for the \( y \) direction of the dipole moment for 1D surfaces.

- **VARDIP1DZ**=variable Variable which is used for the \( z \) direction of the dipole moment for 1D surfaces.

- **POLAR**\( n \) By default (POLAR=0) Raman intensities will not be computed. POLAR=1 switches the calculation of polarizability tensor surfaces on. Note that currently only Hartree-Fock polarizabilities are supported, which requires the POLAR1 keyword in the Hartree-Fock program.
NDIMPOL\(=n\) This variable denotes the term after which the \(n\)-body expansion of the polarizability tensor surfaces is truncated. The default is set to 2. Note that NDIMPOL has to be lower or equal to NDIM and must be smaller than 4.

VARPOL1DXX=\(\text{variable}\) Variable which is used for the \(xx\) component of the polarizability tensor for 1D surfaces.

VARPOL1DYY=\(\text{variable}\) Variable which is used for the \(yy\) component of the polarizability tensor for 1D surfaces.

VARPOL1DZZ=\(\text{variable}\) Variable which is used for the \(zz\) component of the polarizability tensor for 1D surfaces.

VARPOL1DXY=\(\text{variable}\) Variable which is used for the \(xy\) component of the polarizability tensor for 1D surfaces.

VARPOL1DXZ=\(\text{variable}\) Variable which is used for the \(xz\) component of the polarizability tensor for 1D surfaces.

VARPOL1DYZ=\(\text{variable}\) Variable which is used for the \(yz\) component of the polarizability tensor for 1D surfaces.

The higher order terms VARDIP\(n\)D[X,Y,Z] and VARPOL\(n\)D[XX,...,YZ] can be defined the same way. An example for a calculation, which provides both, infrared and Raman intensities, is given below.

```
label1
{hf
  start,atden
  polari}

{surf,start1D=label1,ndim=3,info=1
  intensity,polar=1,ndimpol=3
  scalnm,auto=on }

vscf,polar=1,ndimpol=3,info=1
vci,version=4,polar=1,ndimpol=3,info=1
```

### 52.4 Error correction schemes

**ALTER,\(options\)**

The ALTER directive of the SURF program allows to provide error correction schemes for individual single point calculations. For example, in case that the Hartree Fock calculation for a certain grid point did not converge and the ORBITAL directive in the subsequent electron correlation calculation uses the IGNORE_ERROR option, an alternative calculation scheme can be provided, e.g. MCSCF in contrast to RHF. In the case of multi level calculations the ALT2D and ALT3D options can be set according to the START2D and START3D options. Note that the energy variable has to be the same in the original method and the alternative.

ALT1D=\(\text{label}\) Alternative procedure to calculate the 1D single points.

ALT2D=\(\text{label}\) Alternative procedure to calculate the 2D single points.

ALT3D=\(\text{label}\) Alternative procedure to calculate the 3D single points.

Note that DFT calculations often still converge when RHF calculations already fail to do so.
52.5 Restart capabilities

**DISK.options**

As SURF calculations are very demanding it is highly recommended to dump the grid representation of the potential to disk. This allows for convenient restarts for subsequent vibrational structure calculations. In contrast to previous Molpro releases, the current version supports only restarts from external ASCII-files - due to many new options. Note, that restarts can also be performed for incomplete potentials. An open-access database of high-level potential files is available at http://pes-database.theochem.uni-stuttgart.de/surfaces. Potential files have their own version number and start with version 3.0 for the current Molpro release. Older potential file versions may not support the full capabilities of the current Molpro release.

**WHERE=value**  
In combination with the keywords DUMP and EXTERN for an external restart file, the keyword WHERE specifies the path for the external ASCII file. Two options are available, WHERE=home and WHERE=scr. As the external files can be huge for SURF calculations, they will be stored on the scratch disk given by the MOLPRO variable $TMPDIR by default.

**DUMP=file name**  
The potential can be dumped into an external ASCII-file which can be used for restarting. Its name must be provided as the argument of the DUMP keyword, e.g. DUMP=`formaldehyde.pot`. The ASCII-file provides the interface to other programs and offers the possibility for controlled storage and modification of the computed potentials. Dipole and polarizability surfaces will also be dumped if available.

**EXTERN=file name**  
In principle, SURF calculations should be restartable at any point of a truncated calculation. However, since only fully converged difference potentials will be stored in the ASCII file (DUMP), this is not the case. As a consequence, SURF calculations can be restarted from dump-files once a batch of surfaces has been dumped. Since the generation of the 2D or 3D surfaces usually requires about 2 to 3 batches, there are about 6-10 restart points for surface calculation including 3D potentials (see also the keywords BATCH3D and BATCH4D of the SURF program). Restarting from the ASCII dump-file is possible for any type of VMULT calculation. Harmonic frequencies should not be recalculated for restarts.

**SAVE=record**  
Once a complete surface has been generated, a record can be specified, where to dump the potential in the temporary binary files. Once this keyword is not provided explicitly, the potential will be dumped in record 5600.2

52.6 Linear combinations of normal coordinates

**LINCOMB.options**

The LINCOMB directive allows for the calculation of linear combinations of normal coordinates for the expansion of the potential. This is realized by 2x2 Jacobi rotations. At most 3N-6/2 rotations can be provided in the input. Using an angle of 45° between the degenerate modes of non-Abelian molecules avoids symmetry breaking in the subsequent VSCF and VCI calculations.
NM1=$n$, NM2=$m$ Denotes the normal coordinates to be rotated.

ANGLE=$value$ Rotation angle in degree.

LOCAL=$value$ LOCAL=1 localizes the normal coordinates of the CH-stretchings. Note that this destroys symmetry of these modes. Usually localization has strong impact on subsequent VSCF calculations. LOCAL=2 localizes the normal coordinates of a molecular cluster to the contributing entities. This localization scheme localizes within the individual irreps, which usually leads to a very faint localization. Switching symmetry off by MPG=1 in the SURF program leads to a much stronger localization. LOCAL=3 is a combination of LOCAL=1 and LOCAL=2.

52.7 Scaling of individual coordinates

SCALNM, options

The SCALE option of the SURF program enables a modification of the extension of all difference potentials by a common factor. In contrast to that the SCALNM directive allows for the scaling with respect to the individual normal coordinates. This is the recommended choice for potentials dominated by quartic rather than quadratic terms. At most 3N-6 individual scale factors and shift parameters can be provided. In particular the AUTO option was found to be very helpful in practical applications.

MODE=$n$ Denotes the normal coordinate to be scaled or shifted.

SFAC=$value$ Scaling factor for mode MODE. The default is 1.0.

SHIFT=$n$ Allows to shift the potential with respect to the specified coordinate by $n$ or -$n$ grid points, respectively. Default: SHIFT=0.

AUTO=on / off AUTO=on switches on an automatic scaling procedure of the potential in order to determine meaningful elongations and SHIFT values with respect to all coordinates, i.e. for each normal mode an optimized scaling parameter SFAC and SHIFT parameter will be determined. Usually this results in an increased number of 1D grid points. The AUTO keyword intrinsically depends on the thresholds and parameters, which can be controlled by the keywords THRSHIFT, ITMAX, LEVMAX, DENSMAX, and DENSMIN.

ITMAX=$n$ Specifies the maximum number of iterations within the automatic scaling of the potentials (see Keyword AUTO).

THRSHIFT=$value$ Threshold controlling the automated shifting of potentials as obtained from the state densities on the lhs and rhs of the potentials. The default is given as THRSHIFT=0.05.

LEVMAX=$n$ Maximum number of vibrational states to be included for controlling the automated scaling and shifting procedure. The default is set to 5.

DENSMAX=$value$ Threshold for the maximum vibrational density on the edges of the potential needed for the automated upscaling of the potentials (see keyword AUTO).

DENSMIN=$value$ Threshold for the minimum vibrational density on the edges of the potential needed for the automated downscaling of the potentials (see keyword AUTO).
52.8 Deleting individual surfaces

DELETE, surface labels

The DELETE directive allows to eliminate individual surfaces within the multi-mode expansion of the potential. Unlike the SKIP3D and SKIP4D keywords, this directive can only be used once a calculation is restarted from a completed potential energy surface calculation. This directive is meant for studying the impact of individual surfaces or to eliminate troublesome surfaces, which failed to converge in the iterative fitting procedure.

- \texttt{DELETE},i \text{ deletes the 2D surface } ij
- \texttt{DELETE},i,j,k \text{ deletes the 3D surface } ijk
- \texttt{DELETE},i,j,k,l \text{ deletes the 4D surface } ijk\ell

52.9 Modeling of high-order \textit{n}-body terms

REPAR, options

Within the framework of multi-level calculations (see the directive VMULT), 3D and 4D terms can be modeled. The modeling scheme is based on a reparametrization of the semiempirical AM1 method. Consequently, in the input stream the energy variable to be read in must refer to a semiempirical calculation. After the 2D terms the program optimizes the semiempirical parameters in order to represent the 1D and 2D surfaces best.

- \texttt{RMS1D=value} \text{ The keywords RMS1D and RMS2D specify the threshold for terminating the 1D and 2D iterations in the local optimization of the semiempirical parameters. The defaults are given by RMS1D=1.d-6 and RMS2D=1.d-6.}
- \texttt{ITMAX1D=n} \text{ The maximum number of iterations in the local optimization of the semiempirical parameters can be controlled by ITMAX1D and ITMAX2D. The defaults are ITMAX1D=100 and ITMAX2D=150.}

The following example shows the input for a surface calculation in which the 3D terms will be modeled.

```plaintext
memory, 20, m
orient, mass
geometry={
  3
  Water
  O 0.0675762564 0.0000000000 -1.3259214590
  H -0.4362118830 -0.7612267436 -1.7014971211
  H -0.4362118830 0.7612267436 -1.7014971211
}
hf
mp2
optg
freq
label1
abinitio
basis=vdz
int
rhf
```
52.10 Quality Check

The **CHECK** directive of the **SURF** program allows for a quality check of a completed surface. This routine simply computes the exact *ab initio* energies at randomly selected grid points and compares these values with the interpolated ones, which will be used subsequently for the determination of the wavefunction. This program is fully parallelized.

- **LEVEL=** *n*  Denotes the level to be checked, i.e. 1 corresponds to 1D, etc. Note, levels below *n* will not be checked automatically.
- **POINTS=** *value*  Determines the number of grid points in one dimension to be checked. The default is set to 4.

52.11 Grid Computing

The **GRIDCOMP** directive of the **SURF** program allows to interface **MOLPRO** with a grid computing client such as **SEGL**. It is also possible to use the grid computing interface without any grid computing client by using the two scripts (**CREATE** and **COLLECT**) being supplied in the directory "**src/vscf**". The charge of the molecule as well as some other general commands are transferred to the individual grid point command files, which are printed out in the subdirectory **POINTS**. If there are any doubts whether the specified command is transferred to the single point or not, the command should be given within the definition of the electronic structure calculations.

- **MEMORY=** *n*  Denotes the amount of memory (in MW) which is needed in each single point calculation. The default is given by 100 MW.
- **MAXFILE=** *n*  Defines the maximum number of files produced in a single run of the grid computing interface. Default: **MAXFILE=100000**.
- **FREEZE=** *n*  Determines to which permanent file some relevant orbital information has been saved. This is necessary when using the i explicitly correlated or local methods. Default: **FREEZE=0**.
- **FRNAME=** *value*  The name of the permanent file, which should be used in each single point.
To generate a potential energy surface with the grid computing interface, follow these steps:

- Run a Molpro calculation on the master control file (see the example above) to generate the control files for the individual single points.

- Calculate the energies for all generated control files in the POINTS subdirectory.

- Collect the results and start with point 1 until no more new .com files are produced.

The results of the point calculations should be collected as listed below:

```
grep -h '*** 1D Surf ilev=1' *.out >> results1Dilev-1
grep -h '*** 1D Surf ilev=2' *.out >> results1Dilev-2
grep -h '*** 1D Surf ilev=3' *.out >> results1Dilev-3
grep -h '*** 2D Surf ilev=2' *.out >> results2Dilev-2
grep -h '*** 2D Surf ilev=3' *.out >> results2Dilev-3
```
To reduce the calculation time of the first step, the restart procedure can be used.

52.12 Recommendations

It is recommended to

- use the ORIENT,MASS keyword in order to rotate the molecule into standard orientation. This is necessary for a full exploitation of symmetry within the generation of the potential energy surface.

- use the MASS,ISO keyword to use the most available isotopes.

- use multi-level schemes in combination with symmetry and a parallelized MOLPRO version (MPPX) in order to speed up the calculations. Explicitly correlated methods are preferable over conventional approaches.

- reduce the quality of the normal coordinates. If you do not require extremely high accuracy, it is sufficient to compute the normal coordinates (i.e. the harmonic frequencies) at the DFT level rather than the CCSD(T) level. This saves a lot of computer time and the deviations are usually not larger than 1 or 2 wavenumbers in the subsequent VSCF and VCI calculations.

52.13 Standard Problems

- Problem: The SURF calculation crashes with an error message like

```
?ERROR IN VIRTORB: INCORRECT NUMBER OF ORB...
ERROR EXIT
CURRENT STACK: MAIN
```

Solution: The program has problems in the symmetry conversion when restarting a Hartree-Fock calculation from the reference calculation at the equilibrium geometry. You need to start the Hartree-Fock calculations independently by using the keywords start, atden.

- Problem: In parallel calculations (MPPX) the CPU-time of a SURF calculation differs considerably from the real-time (wallclock time).

Solution: There may be two reasons for this: (1) Usually a SURF calculation spends a significant amount of the total time in the Hartree-Fock program and the 2-electron integrals program. As the integrals are stored on disk, 2 processes on the same machine may write on disk at the same time and thus the calculation time depends to some extend on the disk controller. It is more efficient to stripe several disks and to use several controllers. This problem can be circumvented by distributing the job over several machines, but limiting the number of processors for each machine to 1. (2) The integrals program buffers the integrals. Parallel jobs may require too much memory (factor of 2 plus the
shared memory) and thus the integrals buffering will be inefficient. Try to reduce the memory as much as you can. It might be advantageous to separate the memory demanding VCI calculation from the SURF calculation.
53 PES TRANSFORMATIONS

Once a potential energy surface (PES) has been generated by the SURF program, it can be transformed to different representations. The first possibility is a representation by polynomials, i.e. the POLY program. The representation by grid points may be altered by the VGRID program, which includes a grid to grid transformation. Finally the PESTRANS program offers a transformation of the PES for vibrational structure calculations of isotopologues or Franck-Condon factors.

53.1 Polynomial representations (POLY)

POLY, options

The POLY program allows for the transformation of the potential energy surface and property surfaces from a grid representation to a polynomial representation. Once a polynomial representation has been chosen, the corresponding VSCF, VCI or VMP2 programs need to be selected (see below). The POLY program is fully parallelized in terms of the MPPX scheme. An example for the use of the POLY program can be found in chapter 55.1.3.

The following options are available:

NDIM=n The keyword NDIM=n terminates the transformation after the nD terms within the n-mode expansion of the surfaces. The default is set to 3. The transformation of the 4D terms can be very time consuming.

NDIMDIP=n Term after which the n-body expansions of the dipole surfaces are truncated. The default is set to 3. Note that NDIMDIP has to be lower or equal than NDIM.

NDIMPOL=n Term after which the n-body expansions of the polarizability tensor surfaces are truncated. The default is 0. NDIMPOL has to be lower or equal than NDIM and must be smaller than 4.

NGRID=n Once the value of the NGRID=n keyword for controlling the number of grid points has been changed in the SURF program, this information will be passed to the POLY program automatically.

AUTOPOL=n AUTOPOL=1 (default) determines the optimal parameters for PMAX and PSUM in an iterative procedure. In combination with AUTOPOL=1 the PMAX and PSUM keywords specify the maximum values within the automated determination of these parameters.

PMAX=n This keyword controls the order of the polynomial to be determined in the fitting procedure. The default is set to 8. The definition of this keyword changes in combination with the AUTOPOL keyword (see above).

PSUM=n In multidimensional fitting the maximum order of the polynomial is not given by PMAX times the dimension, but rather by PSUM. The default is set to 24. This reduces the computational cost for fitting tremendously. However, for accurate calculations PMAX=12 and PSUM=30 are recommended. The definition of this keyword changes in combination with AUTOPOL keyword (see above).
Once polynomials have been generated, the expansion of the potential can be restricted to the harmonic approximation or a semi-quartic force field, i.e. TYPE=HARM or TYPE=QFF.

In case that dipole surfaces have been computed, they need to be transformed to a polynomial representation as well. This can be accomplished by DIPOLE=1 and will be set by default, if dipole surfaces are available. DIPOLE=0 excludes existing dipole surfaces from the transformation.

Once set to one this keyword switches the transformation of the polarizability tensor surfaces on. The default is POLAR=0.

The Watson correction term, i.e. VAM=1, is absorbed in the potential by default. Once the polynomials to be generated should exclude this correction, this needs to be specified by VAM=0. Any other values, i.e. 2 or 3, will be ignored.

In order to delete troublesome 2D, 3D or 4D surfaces from the multimode expansion of the potential, the DELAUTO keyword sets all coefficients of the polynomial expansion of these surfaces to zero. The threshold passed to the DELAUTO keyword corresponds to the $\chi^2$ value of the least squares fitting procedure. It acts on both, the energy and the dipole surfaces. The default is set to 9.99, i.e. all surfaces with $\chi^2$ values below this threshold will not be affected.

By default, SOLVER=1, an LU decomposition will be used within the fitting procedure. Alternatively, a Cholesky decomposition is available, which sometimes leads to more stable solutions (SOLVER=2).

For the calculation of vibrationally averaged rotational constants $\mu$-tensor surfaces will be generated and transformed to polynomials up to 2nd order (default). The order can be changed by the integer passed to the NVARC keyword. This transformation can also be extended within the VSCF program.

Once vibrational-rotational coupling surfaces have been computed in the SURF program, these couplings can be considered (VRC=1) or excluded (VRC=0, default) in the POLY program.

The coefficients of the polynomial representation can be printed. In order to identify quartic potentials, it is recommended to use SHOW=1. Higher values will lead to a very long output file.

This keyword controls the record, from which the potential shall be read. The default is 5600.2. This keyword usually is only needed within the calculation of vibronic spectra.

Specification of the record, where to dump the polynomials. The default is 5750.2. This keyword usually is only needed within the calculation of vibronic spectra.

INFO=1 provides a list of the values of all relevant program parameters (options).

53.1.1 Plotting of 3D surfaces

LEVELCURVES.options
The **LEVELCURVES** directive within the **POLY** program allows to plot isosurfaces for the sum of the corresponding 1D, 2D, and 3D surfaces. This enables the visual control of the potential including the 3D terms. Datafiles for the gnuplot program and associated input files will be provided in individual subdirectories.

The following *options* are available:

**ENERGY=*

If this keyword isn’t used, the energy value for the isosurface will be determined by the program automatically. The value determined this way is the lowest energy of the outer surfaces of the 3D cube. If a specific value is provided for **ENERGY**, the corresponding 3D level surface will be plotted.

**ESTEP=*

Once several isosurfaces shall be plotted for a given 3D potential, the energy difference between two isosurfaces can be specified by **ESTEP=value**. The first isosurface, that will be plotted, corresponds to the level energy of the stepwidth itself. In all subsequent isosurfaces the energy will be increased by the value of the stepwidth **ESTEP**, until the final energy as defined by the **ENERGY** keyword is obtained. As a consequence, a series of isosurfaces will be produced, which is different for each 3D potential.

**DUMP=path**

**DUMP=path** provides the path of the subdirectory, in which the datafiles for the isosurfaces will be dumped.

**MODE=n**

In order to restrict the generation of isosurfaces to individual triples of modes, the **MODE** keyword can be used. For example, **LEVELCURVES, MODE=5, MODE=3, MODE=2** generates the isosurface for the 3D potential $V_{532}$. The ordering of the modes is insignificant. Once isosurfaces for different triples shall be plotted, the directive **LEVELCURVES** needs to be provided several times.

### 53.2 Grid to grid transformations (**VGRID**)  
**VGRID, options**

For certain applications a finer grid may be needed than generated by the **SURF** program. In order to avoid the recalculation of the entire PES the **VGRID** program offers the possibility of a grid to grid transformation. The transformation of polarizability tensor surfaces is not yet supported.

The following *options* are available:

**NGRID=n**

This keyword provides the number of grid points as generated by the **SURF** program, i.e. this is the *old* number of grid points.

**NEWGRID=n**

Determines the number of grid points to be used in all subsequent programs. Note that in the subsequent programs the variable **NGRID** controls the number of grid points. The keyword **NEWGRID** exists only within the **VGRID** program.

**NDIM=n**

Specifies the maximum order of the PES expansion, which shall be transformed. Default: **NDIM=3**.
DIPOLE=$n$

In case that dipole surfaces have been computed, these may be transformed to a finer or coarser grid as well. This transformation can be switched off by DIPOLE=0.

NDIMDIP=$n$

 Specifies the maximum order of the dipole surfaces, which shall be transformed. $n$ must be equal or smaller than the corresponding value of NDIM.

INFO=$n$

INFO=1 provides a list of the values of all relevant program parameters (options).

53.3 Transformation of the coordinate system (PESTRANS)

PESTRANS, options

The PESTRANS program allows to change the coordinate system being used within the representation of the potential by a Duschinsky-like transformation. This allows for the transformation of PESs as needed for the calculation of the vibrational spectra of isotopologues or Franck-Condon factors including Duschinsky rotations. For further details see:


The following options are available:

ECKART=$n$

By default the Eckart transformation matrix needed within the PESTRANS program will be computed explicitly. ECKART=0 replaces the Eckart transformation matrix by a unit matrix.

UMAT=$n$

As needed for Franck-Condon calculations, UMAT=1 defines the linear combinations of the displacement vectors due to Duschinsky rotations, which influences the selection of states in subsequent VCI calculations. The default, UMAT=0, switches off this feature.

VRC=$n$

Once vibrational-rotational coupling surfaces have been computed in the SURF program, these couplings can be considered (VRC=1) or excluded (VRC=0, default) in the PESTRANS program. The inclusion of these terms usually increases the accuracy of the transformation.

CUT=$n$

CUT=0 (default) transforms all surfaces as requested by the input. CUT=1 neglects the generation of vibrational-rotational coupling surfaces for the new potential. CUT=2 neglects rotational-rotational coupling surfaces within the transformation and thus also for the new potential.

THRQ=value

Elements in the displacement vectors below this threshold (default THRQ=$10^{-8}$) will be neglected within the transformation.

THRMATS=value

Threshold controlling the analysis of the S-matrix indicating the accuracy of the transformation (default: THRMTS=0.3).

Most keywords and directives of the SURF program can also be used in the PESTRANS program (i.e. NDIM, SCALE, INFO, INTENSITY, SCALNM, DISK, LINCOMB), while specific ones had to be excluded (i.e. NGRID, etc.).
53.3.1 Definition of atomic masses

**MASS, options**

Once the PESTRANS program will be used for the calculation of isotopologues, the atomic masses of the individual atoms can be specified by this directive. Note, the use of the MASS directive here differs from that in the electronic structure code as it requests the running number of the atoms in the geometry definition.

**MASS,n,value**  The n-th atom is supposed to have the mass value.

53.3.2 Reading of 2nd Hessian

**DISK, options**

Within Franck-Condon calculations information about the geometry and the Hessian of the 2nd system (belonging to the 2nd electronic state) is needed. This can be realized by the DISK directive, which thus differs from the directive of the same name within the SURF program. The options of this directive are the same as for the directive of the SURF program.

**EXTERN= file name**  Specifies the name of the ASCII restart file (see the SURF program) belonging to the 2nd system, which includes the 2nd coordinate system.

The following example shows a calculation for water including vibrational-rotational coupling surfaces, the corresponding VSCF and VCI calculations a subsequent transformation of the potential to doubly deuterated water.

```plaintext
memory,100,m
qthresh,optgrad=1.d-7,twoint=1.d-14,prefac=1.d-16
geometry={
  O ,, 0.0000000000 , 0.0000000000 , 0.1241819425
  H ,, 0.0000000000 , -1.4320403835 , -0.9855926792
  H ,, 0.0000000000 , 1.4320403835 , -0.9855926792
}
basis=vtz-f12
hf
optg
ccsd(t)-f12
freq,symm=auto
label1
{hf
  start,atden}
ccsd(t)-f12
{surf,start1D=label1,sym=auto,vrc=1,ndim=4
  scalnm,auto=on
  disk,where=home,dump='h2o.pot'}
vscf
vci
poly,vam=0,vrc=1,ndim=4
```
{pestrans,vrc=1,ndim=4
 mass,2,2.0141017778d0
 mass,3,2.0141017778d0
 scalnm,auto=on
 disk,where=home,dump='d2o.pot'}
vscf
vci
54 VIBRATIONAL SCF PROGRAMS

54.1 The VSCF program (VSCF)

VSCF, options

The VSCF program is exclusively based on the Watson Hamiltonian

\[ \hat{H} = \frac{1}{2} \sum_{\alpha\beta} (\hat{J}_\alpha - \hat{\pi}_\alpha) \mu_{\alpha\beta} (\hat{J}_\beta - \hat{\pi}_\beta) - \frac{1}{8} \sum_\alpha \mu_{\alpha\alpha} - \frac{1}{2} \sum_i \frac{\partial^2}{\partial q_i^2} + V(q_1, \ldots, q_{3N-6}) \]  \hspace{1cm} (65)

in which the potential energy surfaces, \( V(q_1, \ldots, q_{3N-6}) \), are provided by the SURF module. The Watson correction term and the 0D term of the vibrational angular momentum terms are by default \( VAM=2 \) included. Within the grid-based version of the program the one-dimensional Schrödinger equation is solved by the DVR procedure of Hamilton and Light. Note that, the number of basis functions (distributed Gaussians) is determined by the grid points of the potential and cannot be increased without changing the PES grid representation. In contrast to that the number of basis functions can be modified without restrictions in the polynomial based version. In all cases the basis is fixed to distributed Gaussians (DG). As VSCF calculations are extremely fast, these calculations cannot be restarted. For details see:


The anharmonic frequencies and intensities calculated by the VSCF program can be used to plot an IR spectrum, using the PUT command (see subsection 10.3) with the style IRSPEC.

The following options are available:

- **TYPE=variable**
  - VSCF solutions can be obtained using a potential in grid representation, i.e. TYPE=GRID, or in a polynomial representation, TYPE=POLY. In the latter case the POLY program needs to be called prior to the VSCF program in order to transform the potential.

- **SADDLE=n**
  - By default, i.e. SADDLE=0, the VSCF program assumes, that the reference point of the potential belongs to a local minimum. Once the PES calculation has been started from a transition state, this information must be provided to VSCF program by using SADDLE=1. Currently, the VSCF program can only handle symmetrical double-minimum potentials.

- **VAM=n**
  - The 0D terms of the vibrational angular momentum terms, i.e. \( \frac{1}{2} \sum_{\alpha\beta} \hat{\pi}_\alpha \mu_{\alpha\beta} \hat{\pi}_\beta \), and the Watson correction term are by default \( VAM=2 \) included.
    - \( VAM=1 \) adds the Watson correction term (see eq. 65) as a pseudo-potential like contribution to the fine grid of the potential.
    - \( VAM=2 \) allows for the calculation of the integrals of the VAM operator using the approximation that the \( \mu \) tensor is given as the inverse of the moment of inertia tensor at equilibrium geometry.
    - When using \( VAM=4 \) the expansion of the effective moment of inertia tensor will be truncated after the 1D terms (rather than the 0D term in case of \( VAM=2 \)). Note that values higher than 2 are only active for
non-linear molecules. VAM=5 truncates the series after the 2D term. In almost all cases VAM=2 is fully sufficient. Vibrational angular momentum terms are accounted for in a perturbational manner and do not affect the wavefunction.

**MUPLOT=n**
Plots all $\mu$-tensor surfaces up to $nD$ and a corresponding GNUPlot script in a separate subdirectory (plots). This option works only in combination with TYPE=POLY. The VAM option has to be set accordingly.

**COMBI=n**
By default the VSCF program calculates the fundamental modes of the molecule only. However, choosing COMBI=n allows for the calculation of the vibrational overtones and combination bands. The value of $n$ controls the excitation level, i.e. the number of states to be computed increases very rapidly for large values of $n$. Therefore, by default the upper limit is set to 5000 cm$^{-1}$, but this cutoff can be changed by the option UBOUND. See also the VIBSTATE program (section 54.3) for even more possibilities of defining vibrational states.

**USERMODE=n**
Once vibrational states have been defined with the VIBSTATE program (section 54.3), the VSCF program can be forced to compute just these states by the option USERMODE=1. Note that the vibrational ground state will always be computed and needs not to be specified explicitly.

**UBOUND=n**
Once overtones and combination bands shall be computed, the upper energy limit is controlled by the keyword UBOUND, i.e. states, for which the harmonic estimate is larger than $n$, will not be computed. the default is set to $n=5000$ cm$^{-1}$.

**SOLVER=n**
For solving the one-dimensional Schrödinger equation within a grid representation two different algorithms can be used. The default, i.e. SOLVER=1, calls the discrete variable representation (DVR) as proposed by Hamilton and Light. Alternatively, the collocation algorithm of Young and Peet can be used (SOLVER=2).

**GUESS=n**
The initial guess for the VSCF programs is by default generated from the uncoupled one-dimensional potentials, i.e. GUESS=1. Alternatively, one may start within the calculation of excited vibrational states from the solution of the vibrational ground state, GUESS=2.

**BASIS=n**
BASIS=1 (default) defines a mode-specific basis of distributed Gaussians, which is the recommended choice. However, for certain applications a mode-independent basis (BASIS=2) can be used as well. Very often this leads to worse results for torsional modes. BASIS=3 distributes the Gaussians in a way, that the overlap integral between two functions is always the same (controlled by THRBSOVLIP). This guarantees that an increasing number of basis functions will always lead to an improvement.

**THRBSOVLIP=value**
Overlap between two Gaussian basis functions, once BASIS=3 has been chosen. The default is 0.75.

**ORTHO=n**
Determines the type of orthogonalization within the VSCF program. ORTHO=1 invokes a symmetrical orthogonalization, ORTHO=2 a canonical one and ORTHO=3 uses a canonical one together with an elimination of linear dependencies (see also keyword THRINDEP. The default is ORTHO=1.
THRLINDEP=value  
Threshold for eliminating linear dependencies in the VSCF procedure (see keyword BASIS=3). The default is THRLINDEP=1e-8.

THERMO=n  
THERMO=1 allows for the improved calculation of thermodynamical quantities (compare the THERMO keyword in combination with a harmonic frequency calculation). However, the approach used here is an approximation: While the harmonic approximation is still retained in the equation for the partition functions, the actual values of the frequencies entering into these functions are the anharmonic values derived from the VSCF calculation. Default: THERMO=0.

DIPOLE=n  
DIPOLE=1 allows for the calculation of infrared intensities. Calculation of infrared intensities requires the calculation of dipole surfaces within the SURF program. By default the intensities will be computed on the basis of Hartree-Fock dipole surfaces.

POLAR=n  
POLAR=1 allows to compute Raman intensities in addition to infrared intensities, but of course requires polarizability tensor surfaces from the SURF program. By default Raman intensities are switched off.

NDIM=n  
The expansion of the potential in the VSCF calculation can differ from the expansion in the SURF calculation. However, only values less or equal to the one used in the surface calculation can be used.

NDIMDIP=n  
Term after which the n-body expansions of the dipole surfaces are truncated. The default is set to 3. Note that NDIMDIP has to be lower or equal to NDIM.

NDIMPOL=n  
Term after which the n-body expansions of the polarizability tensor surfaces are truncated. The default is set to 0. Note that NDIMPOL has to be lower or equal to NDIM and must be smaller than 4.

NBAS=n  
The number of basis functions (distributed Gaussians) to be used for solving the VSCF equations can be controlled by NBAS=n. The default is NBAS=20. This option is only active once a polynomial representation of the potential has been chosen, see the option TYPE=POLY and the POLY program.

NVARC=n  
By default the expansion of the µ-tensor for calculating the vibrationally averaged rotational constants is truncated after the 2nd order terms, i.e. NVARC=2. This may be altered by the NVARC keyword.

PRINT=n  
This option provides an extended output. PRINT=1 prints the vibrationally averaged rotational constants for all computed states and the associated vibration-rotation constants α. PRINT=2 prints the effective 1D polynomials in case that the potential is represented in terms of polynomials, see the option TYPE=POLY and the POLY program. In addition the generalized VSCF property integrals, i.e. ⟨VSCF |qₖ| VSCF⟩ are printed. These integrals allow for the calculation of arbitrary vibrationally averaged properties once the property surfaces are available. Default: PRINT=0.

STARTSURF=record  
Surface information shall be read from the specified record. This must correspond to the record, to which the potential has been dumped in the SURF program. This option is only of importance within the calculation of vibronic spectra.

START=record  
Polynomial and other information shall be read from the specified record. This must be the same record, to which the polynomials have
been dumped in the POLY program. This option is only of importance within the calculation of vibronic spectra.

**SAVE=record**

This specifies the record, where to dump the VSCF information. Usually this is the same record as specified in the \texttt{START} option. Note that the VSCF information is currently stored in the same record as the polynomial information.

**INFO=n**

INFO=1 provides a list of the values of all relevant program parameters (options).

The following input example for a grid based calculation of anharmonic frequencies and intensities on the VSCF level (1) optimizes the geometry of water, (2) computes the harmonic frequencies,(3) generates a potential energy surface around the equilibrium structure and (4) computes the nuclear wave function and the infrared intensities at the VSCF level. Vibrational angular momentum terms (VAM) are included. Note, that it is recommended to perform a VCI calculation after a VSCF calculation. The details of the VCI input are described in the next chapter.

```plaintext
memory,20,m
basis=vdz
orient,mass
geometry={
    3
    Water
    O 0.0675762564 0.0000000000 -1.3259214590
    H -0.4362118830 -0.7612267436 -1.7014971211
    H -0.4362118830 0.7612267436 -1.7014971211
}

mass,iso

hf
mp2
optg !(1) optimizes the geometry
frequencies,symm=auto !(2) compute harmonic frequencies

label1
{hf
start,atden}
{mp2
cphf,1} lc

{(surf,startId=label1,sym=auto
intensity,dipole=2)
vscf !(4) do a VSCF calculation
put,irspec,irspec.gnu !writes a gnuplot file to plot an IR !spectrum of the VSCF calculation
}
```

### 54.2 The VMCSCF program (VMCSCF)

**VMCSCF.options**

The VMCSCF program is still under development and has not yet been fully optimized with respect to speed and efficiency. It is strongly recommended to run a VSCF calculation prior to the VMCSCF calculation and thus to use VSCF modals as an initial guess. By default configuration-selective VMCSCF calculations will be performed. The polynomial based VMCSCF calculation is significantly faster than the grid-based version and should be used whenever possible. For details see:


The following *options* are available:

- **NACT=** $n$
  - Is the number of active modals for each mode. The smallest meaningful value for NACT is 3, which is the current default. Configurations will only be generated within this space. Note that there is no equivalent in the VMCSF program to the closed and core orbitals in electronic structure theory.

- **NVIRT=** $n$
  - Is the number of modals on top of the number of active modals. The default is NVIRT=3. The virtual modals are needed for the modal rotations. Modals above the virtual modals are entirely neglected.

- **ROT=** $n$
  - Specifies, if only active-virtual modal rotations shall be considered (ROT=0, default) or if active-active modal rotations shall be considered as well (ROT=1). Formally one would need active-active modal rotations for configuration-selective VMCSF calculations, but the effects are usually extremely small.

- **CALCANGLE=** $n$
  - The procedure how to determine the rotational angles between the modals within the Jacobi rotations can be specified by this keyword. CALCANGLE=1 uses the standard quadratic procedure, which is the current default. CALCANGLE=2 uses a cubic equation instead. CALCANGLE=3 switches to a full numerical determination of the rotational angle.

- **USERMODE=** $n$
  - Once vibrational states have been defined with the VIBSTATE program (section 54.3), the VMCSF program can be forced to compute just these states by the option USERMODE=1. Note that the vibrational ground state will always be computed and needs not to be specified explicitly.

- **VERSION=** $n$
  - By default configuration-selective VMCSF calculations will be performed (VERSION=3). Note that the selection is always performed prior to the VMCSF iterations but not within them. The selection of configurations can be switched off by (VERSION=4).

- **CITYPE=** $n$
  - Defines the maximum number of simultaneous excitations within the configurations generated from modals of the active space, i.e. Singles, Doubles, Triples, ... The maximum excitation level is limited to CITYPE=6, the default is set to 4.

- **REF=** $n$
  - REF=0 specifies ground-state based VMCSF calculations, i.e. the initial guess of the VMCSF calculation is given by the VSCF wave function of the vibrational ground state. In contrast to that, REF=1 allows for a state-specific initial guess (default).

- **GSMODALS=** $n$
  - By default all VMCSF calculations are based on state-specific VSCF modals, GSMODALS=0. GSMODALS=1 uses the modals of the VSCF ground-state for all VMCSF calculations.
MAXMAC = \( n \)  
Controls the maximum number of macroiterations of the VMCSCF program. The default is 25.

THRMAC = \( \text{value} \)  
Controls the convergence threshold for the macroiterations of the VMCSCF program. The default is 1.d-2.

MAXMIC = \( n \)  
Controls the maximum number of microiterations of the VMCSCF program. The default is 50.

THRMIC = \( \text{value} \)  
Controls the convergence threshold for the microiterations of the VMCSCF program. The default is 1.d-5.

PRINT = \( n \)  
Provides additional information within the VMCSCF iterations, once a value larger than 0 (default) is used.

SAVE = \( \text{record} \)  
Specifies the record and file, on which the VMCSCF wave function shall be stored. The default is 5950.2.

SAVEVSCF = \( n \)  
Once set to 1, this option allows to store the VMCSCF modals in the record of the VSCF modals (which will be overwritten). This allows for VCI calculations with VMCSCF modals.

Besides these VMCSCF specific keywords, a number of option can be used, which are identical with those provided for the VCI program. These keywords are NDIM, VAM, TYPE, NBAS, DIPOL, NDIMDIP, COMBI, INFO, MPG, DIAG, CONT, THRSEL, THRCF, ANALYZE.

### 54.2.1 Explicit definition of active spaces

**NACT, options**

Within the VMCSCF program the active space can be specified in a general manner (keyword NACT), which means that the same number of active modals for each mode will be used. Alternatively, one may use the NACT directive. This allows to specify active spaces for the individual modes. Typically such definition refer to just one vibrational state and thus the program should be used within the USERMODE mode.

**MODE (n) = m**  
The number of active modals for mode \( n \) is set to \( m \). This always includes the vibrational ground state. In order to resolve Fermi resonances, one would need to choose \( m \) at least to be 3, which corresponds to the modals 0, 1 and 2.

### 54.3 The VIBSTATE program (VIBSTATE)

**VIBSTATE, options**

The VIBSTATE program allows to specify the occupation number vectors for individual vibrational states to be calculated in the following vibrational SCF and vibration correlation programs. Within the input stream, the VIBSTATE program needs to be called prior to the first call of the VSCF program. Note that, the VIBSTATE program needs only to be called, if a limited number of states shall be computed. On the contrary, the COMBI keyword within the VSCF and VCI programs generate large lists of vibrational states, which may result in significant computational effort. The VIBSTATE program necessarily requests the VSTATE directive to be called as described below. If only those vibrational states shall be computed, which are defined by the VIBSTATE program, all subsequent programs need to call the USERMODE option.
54.3.1 Definition of vibrational states

VSTATE options

This directive specifies the occupation number vector of the vibrational state to be calculated.

\textbf{MODE}(n) = m

The \textit{n}th mode of the molecule is supposed to have the quantum number \textit{m}. If several modes are excited, the option can be repeated accordingly, e.g. \textit{VSTATE,MODE(1)=3,MODE(3)=2,MODE(6)=2. All other modes are not excited and thus have the quantum number 0.}
55 VIBRATION CORRELATION PROGRAMS

55.1 The VCI program (VCI)

The VCI program (VCI) calculations account for vibration correlation effects and use potential energy surfaces as generated from the SURF program and a basis of VSCF modals. All VCI calculations will be performed state-specific, i.e. for each vibrational mode an individual VCI calculation will be performed. As VCI calculations may require substantial computer resources, these calculations can be rather expensive. Currently, two different VCI programs (configuration selective and conventional) are available (see below). Moreover, VCI calculations can be performed using the grid-based version of the program or within a polynomial representation. The latter is significantly faster and is thus recommended. The different versions of the configuration selection VCI program and the underlying configuration selection scheme are described in detail in:


The anharmonic frequencies and intensities calculated by the VCI program can be used to plot an IR spectrum, using the PUT command (see subsection 10.3) with the style IRSPEC.

55.1.1 Options

The following options are available:

- **TYPE=variable** VCI solutions can be obtained using a potential in grid representation, i.e. TYPE=GRID (default), or in a polynomial representation, TYPE=POLY. In the latter case the POLY program needs to be called prior to the VSCF and VCI programs in order to transform the potential.

- **SADDLE=n** By default, i.e. SADDLE=0, the VCI program assumes, that the reference point of the potential belongs to a local minimum. Once the PES calculation has been started from a transition state, this information must be provided to VCI program by using SADDLE=1. Currently, the VCI program can only handle symmetrical double-minimum potentials.

- **VERSION=n** Both, the grid-based and the polynomial-based versions of the VCI programs offer 2 different kinds of VCI implementations: VERSION=3 (which is the default) is a configuration selective and most efficient VCI program. VERSION=4 is a conventional VCI program without configuration selection. It is thus computationally extremely demanding.

- **CITYPE=n** CITYPE defines the maximum number of simultaneous excitations, i.e. Singles, Doubles, Triples, ... and thus determines the kind of calculations, i.e. VCISD, VCISDT, ... The default is CITYPE=4 (VCISDTQ), which appears to be a fair compromise between accuracy and computational speed. The maximum excitation level is currently limited to CITYPE=6.
LEVEX = \( n \)  
LEVEX determines the level of excitation within one mode, i.e. \( 0 \rightarrow 1, \ 0 \rightarrow 2, \ 0 \rightarrow 3, \ldots \). The default is \( \text{LEVEX}=5 \), which was found to be sufficient for many applications.

CIMAX = \( \text{value} \)  
CIMAX is the maximum excitation level corresponding to \text{CITYPE} and \text{LEVEX}. In principle, a triple configuration \((1^42^33^4)\) would contribute to the VCI space. However, \( \text{CIMAX}=7 \) restricts this to \((1^42^3), (1^32^33^4), (1^32^32^3), \ldots \). The default is \( \text{CIMAX}=9 \), which needs to be extended for certain applications.

THRSEL = \( \text{value} \)  
THRSEL controls the determination of the iterative configuration selection scheme. By default the wavefunction is considered to be converged once energy changes drop below \( \text{THRSEL}=0.05 \text{ cm}^{-1} \).

THRCF = \( \text{value} \)  
THRCF is the threshold for selecting individual configurations. The default is given by \( \text{THRCF}=10^{-9} \).

CONT = \( n \)  
Within the evaluation of the VCI integrals contraction schemes are used to reduce the computational effort. In the polynomial based VCI program values 0, 1 and 2 are supported, while in the grid based version only the options 0 and 1 exist. Memory demands and CPU speed-ups increase with increasing values. The default is set to 1. On machines with limited memory a value of 0 is recommended for this keyword.

VAM = \( n \)  
VAM = 0: switches off all vibrational angular momentum terms and the Watson correction term.
VAM = 1: adds the Watson correction term (see eq. 65) as a pseudo-potential like contribution to the fine grid of the potential.
VAM = 2: (default) the 0D terms of the vibrational angular momentum terms, i.e. \( \frac{1}{2} \sum \alpha \beta \hat{\pi}_{\alpha \mu} \hat{a}_{\alpha \beta} \hat{a}_{\beta} \), and the Watson correction term are included. The VAM-terms will be added to the diagonal elements of the VCI-matrix only. This approximations works rather well for many applications.
VAM = 3: again, the \( \mu \) tensor is given as the inverse of the moment of inertia tensor at equilibrium geometry, but is added to all elements of the VCI matrix.
VAM = 4: extends the constant \( \mu \)-tensor (0D) by 1D terms and is added to all elements of the VCI matrix. A prescreening technique is used for the 1D terms, in which the convergence of the VAM operator will be checked for each VCI matrix element.
VAM = 5: includes 0D, 1D and 2D terms of the \( \mu \)-tensor, which are added to all elements of the VCI matrix. Prescreening is used for the 1D and 2D terms.
VAM = 6: includes 0D and 1D terms of the \( \mu \)-tensor without prescreening.
VAM = 7: includes 0D, 1D and 2D terms of the \( \mu \)-tensor, which are added to all elements of the VCI matrix. Prescreening is used for the 2D terms only.
VAM = 8: includes 0D, 1D and 2D terms of the \( \mu \)-tensor without any prescreening.
Note that the 1D and 2D corrections increase the computational cost considerably and are only available for non-linear molecules.

COMBI = \( n \)  
By default the \text{VSCF} program calculates the fundamental modes of the molecule only. However, choosing \( \text{COMBI}=n \) allows for the calcu-
tion of the vibrational overtones and combination bands. The value of $n$ controls the excitation level, i.e. the number of states to be computed increases very rapidly for large values of $n$. Therefore, by default the upper limit is set to 5000 cm$^{-1}$, but this cutoff can be changed by the option UBOUND.

**USERMODE=$n$**

Once vibrational states have been defined with the VIBSTATE program (section [54.3]), the VCI program can be forced to compute just these states by the option USERMODE=1. Note that the vibrational ground state will always be computed and needs not to be specified explicitly.

**UBOUND=$n$**

Once overtones and combination bands shall be computed, the upper energy limit is controlled by the keyword UBOUND, i.e. states, for which the harmonic estimate is larger than $n$, will not be computed. the default is set to $n=5000$ cm$^{-1}$.

**BASIS=$n$**

BASIS=1 (default) defines a mode-specific basis of distributed Gaussians, which is the recommended choice. However, for certain applications a mode-independent basis (BASIS=2) can be used as well. Very often this leads to worse results for torsional modes. BASIS=3 distributes the Gaussians in a way, that the overlap integral between two functions is always the same (controlled by THRBASOVLP). This guarantees that an increasing number of basis functions will always lead to an improvement.

**THRBASOVLP=value**

Overlap between two Gaussian basis functions, once BASIS=3 has been chosen. The default is 0.75.

**THERMO=$n$**

THERMO=1 allows for the improved calculation of thermodynamical quantities (compare the THERMO keyword in combination with a harmonic frequency calculation). However, the approach used here is an approximation: While the harmonic approximation is still retained in the equation for the partition functions, the actual values of the frequencies entering into these functions are the anharmonic values derived from the VCI calculation. Default: THERMO=0.

**DIPOLE=$n$**

DIPOLE=1 (default) allows for the calculation of infrared intensities. Calculation of infrared intensities requires the calculation of dipole surfaces within the SURF program. By default the intensities will be computed on the basis of Hartree-Fock dipole surfaces.

**POLAR=$n$**

POLAR=1 allows to compute Raman intensities in addition to infrared intensities, but of course requires polarizability tensor surfaces from the SURF program. By default Raman intensities are switched off.

**NDIM=$n$**

The expansion of the potential in the VCI calculation can differ from the expansion in the SURF calculation. However, only values less or equal to the one used in the surface calculation can be used. Default: NDIM=3.

**NDIMDIP=$n$**

Term after which the $n$-body expansions of the dipole surfaces are truncated. The default is set to 3. Note that NDIMDIP has to be lower or equal to NDIM.

**NDIMPOL=$n$**

Term after which the $n$-body expansions of the polarizability tensor surfaces are truncated. The default is set to 0. Note that NDIMPOL has to be lower or equal to NDIM and must be smaller than 4.
MPG=n  By default the symmetry of the molecule will be recognized automatically within the VCI calculations. MPG=1 switches symmetry off.

NBAS=n  The number of basis functions (distributed Gaussians) to be used for obtaining the VCI solutions can be controlled by NBAS=value. The number of basis functions must be identical to the number used in the VSCF program. The default is NBAS=20. This option is only active once a polynomial representation of the potential has been chosen, see the option TYPE=POLY and the POLY program.

REFERENCE=n  This keyword specifies the reference for the definition of the configurations. By default, REFERENCE=0 the reference for all state-specific calculations is the vibrational ground-state configuration. This leads to a violation of the Brillouin condition, but often to also to faster convergence. REFERENCE=1 uses the VSCF configuration as reference for generating all excited configurations. This is the proper way of doing it, but usually requests higher excitation levels.

GSMODALS=n  By default all VCI calculations will be done state-specifically, GSMODALS=0, i.e. the modals refer to the individual VSCF solutions. GSMODALS=1 uses the modals of the VSCF ground-state for all VCI calculations. This still requests an individual VCI calculation for each vibrational state (in contrast to just one VCI calculations from which all solutions will be retrieved) and thus the final VCI wave functions may not be strictly orthogonal to each other once the VCI space is incomplete.

DIAG=n  In the polynomial configuration selective VCI program different diagonalization schemes can be used. DIAG=CON specifies a conventional non-iterative diagonalization as used in the grid-based versions. DIAG=JAC is the default and uses a Jacobi-Davidson scheme. DIAG=HJD denotes a disk-based Jacobi-Davidson algorithm.

ANALYZE=value  In case of resonances or strongly mixed states in general (i.e. low VCI coefficients) a multi-state analysis can be performed, which prints major contributions of the VCI-vectors for all states in a certain window around the state of interest. Typically a window between 10 and 20% (i.e. ANALYZE=0.1 or ANALYZE=0.2) provides all the information needed. As this analyses requires a conventional diagonalization (see DIAG), the CPU time may increase significantly.

NVARC=n  By default the expansion of the $\mu$-tensor for calculating vibrationally averaged rotational constants is truncated after the 2nd order terms, i.e. NVARC=2. This may be altered by the NVARC keyword.

PRINT=n  This option provides an extended output. PRINT=1 prints the vibrationally averaged rotational constants for all computed states and the associated vibration-rotation constants $\alpha$. PRINT=2 prints the effective 1D polynomials in case that the potential is represented in terms of polynomials, see the option TYPE=POLY and the POLY program. In addition the generalized VSCF property integrals, i.e. $\langle VSCF | q_i VSCF \rangle$ are printed. These integrals allow for the calculation of arbitrary vibrationally averaged properties once the property surfaces are available. Default: PRINT=0.

START=record  This card specifies the record from where to read the VSCF information. As the VSCF information usually is stored in the same record as
the polynomials, it is usually defined in the POLY program. This option is only of importance within the calculation of vibronic spectra.

**SAVE=record**

This keyword specifies the record where to dump the VCI information. This option is only of importance within the calculation of vibronic spectra.

**EXPORT=variable**

If variable is set to FCON, important VCI information will be passed to the Franck-Condon calculation. Within Franck-Condon calculations this option has to be used.

**INFO=n**

INFO=1 provides a list of the values of all relevant program parameters (options).

### 55.1.2 Explicit definition of the correlation space

**LEVEX, options**

Within the VCI program the correlation space can be specified in a general manner (keyword LEVEX), which means that the same number of modals for each mode will be used. Alternatively, one may use the LEVEX directive. This allows to specify the correlation spaces for the individual modes.

**MODE(n)=m**

The number of correlating modals for mode $n$ is set to $m$.

### 55.1.3 Examples

The following input example for a grid based calculation of anharmonic frequencies and intensities (1) optimizes the geometry of water, (2) computes the harmonic frequencies, (3) generates a potential energy surface around the equilibrium structure, (4) computes the vibrational wave function and the infrared intensities at the VSCF level, and finally (5) a VCI calculation will be performed. Vibrational angular momentum terms (VAM) are included even for the non-diagonal elements of the VCI matrix.

```plaintext
memory, 20, m
basis=vdz
orient, mass
geometry={
  3
  Water
  O  0.0675762564  0.0000000000  -1.3259214590
  H -0.4362118830 -0.7612267436  -1.7014971211
  H -0.4362118830  0.7612267436  -1.7014971211
}
mass, iso
hf
mp2
optg !(1) optimizes the geometry
frequencies, symm=auto !(2) compute harmonic frequencies
label1
{hf
start, atden}
{mp2
```
The following input example for a polynomial based calculation of anharmonic frequencies and intensities (1) optimizes the geometry of water, (2) computes the harmonic frequencies, (3) generates a potential energy surface around the equilibrium structure, (4) converts the potential energy surface into a polynomial representation (5) computes the nuclear wave function and the infrared intensities at the VSCF level, and finally (6) performs a VCI calculation. Vibrational angular momentum terms (VAM) are included even for the non-diagonal elements of the VCI matrix.

```
memory,20,m
basis=vdz
orient,mass
gateway=
3
Water
O 0.0675762564 0.0000000000 -1.3259214590
H -0.4362118830 -0.7612267436 -1.7014971211
H -0.4362118830 0.7612267436 -1.7014971211
}
mass,iso
hf
mp2
optg !(1) optimizes the geometry
frequencies,symm=auto !(2) compute harmonic frequencies
label1
{hf
start,atden}
{mp2
chf,1}
{srf,start1D=labell,sym=auto (3) generate potential energy surface
intensity,dipole=2}
vscf !(4) do a VSCF calculation
vci,vam=3 !(5) do a VCI calculation
put,irspec,irspec.gnu !(6) writes a gnuplot file to plot an IR
!spectrum of the last VCI calculation
```

55.2 The vibrational MP2 program (VMP2)

VMP2_options

The VMP2 program allows to perform 2nd order vibrational Møller-Plesset calculations. The program has been implemented in a grid-based and a polynomial-based version. Most of the keywords as described for the VCI program are also valid for the VMP2 program, i.e. TYPE, CICTYPE, LEVEL, CIMAX, NGRID, NDIM, NBAS, VAM, COMBI, THERMO, DIPOLE, MPG and INFO.
memory,20,m
basis=vdz
orient,mass
gemoty=xzy
geometry={
  "Water"
  O 0.0675762564 0.0000000000 -1.3259214590
  H -0.4362118830 -0.7612267436 -1.7014971211
  H -0.4362118830 0.7612267436 -1.7014971211
}
hf
mp2
optg
{frequencies,symmm=auto
print,low=50}
label1
{hf
start,atden}
{mp2
cphf,1}
{surf,start1D=label1,sym=auto
intensity,dipole=2}
poly,pmp=1,dipole=1,show=1
vscf,type=poly,pmp=2,dipole=1
vmp2,type=poly,pmp=3,dipole=1

http://www.molpro.net/info/current/examples/vmp2.com

55.3 The vibrational multi-reference CI program (VMRCI)

VMRCI, options

The vibrational multi-reference CI program requests a preceding VMCSCF calculation and accounts for correlation effects on top of those considered in the VMCSCF run. Note, in all VMRCI calculations, configurations being considered within the active space of the underlying VMCSCF calculation, will be relaxed. Configurations to be generated for the VMRCI correlation space refer to all reference configurations and thus the VMRCI correlation space increases significantly faster than the VCI space. Once parameters have been altered with respect to the defaults in the VMCSCF program, e.g. NGRID, the same settings must be used within the VMRCI program. Further details are described in:


55.3.1 Options

The following options are available:

VSCFMODALS=n Instead of using VMCSCF modals (default), VSCF modals will be used (once a VSCF calculation has been performed prior to the VM-CSCF calculation), i.e. VSCFMODALS=1.
Most of the keywords as described for the VCI program are also valid for the VMRCI program, i.e. TYPE, CTYPE, LEVEX, CIMAX, NDIM, NBAS, DIAG, VAM, COMBI, DIPOLE, CONT, ANALYZE, MPG and INFO.

55.3.2 Explicit definition of the correlation space

LEVEX, options

Within the VMRCI program the correlation space can be specified in a general manner (keyword LEVEX), which means that the same number of modals for each mode will be used. Alternatively, one may use the LEVEX directive. This allows to specify the correlation spaces for the individual modes.

\[ \text{MODE}(n) = m \quad \text{The number of correlating modals for mode } n \text{ is set to } m. \]
56 VIBRATIONAL PERTURBATION THEORY (VPT2)

VPT2.options

The VPT2 program is based on force constants, which are retrieved from the polynomial coefficients as generated by the POLY program. Therefore, each VPT2 calculation requests a call of the POLY program prior to the VPT2 call. As the VPT2 program relies on a quartic force field (QFF), one may use the option TYPE=QFF in the SURF program. This will lead to tremendous time savings as the size of the potential energy surface is significantly reduced. However, this is an option and the force constants can be retrieved from any potential provided by the SURF program. Note, the option QFF=1 in the POLY program has no impact on VPT2 calculations, but on VSCF and VCI calculations. The current VPT2 implementation is limited to asymmetric top molecules. For further details see:


56.1 Options

The following options are available:

PRINT=n

PRINT=0 (default) prints the anharmonic vibrational frequencies and the most important vibrational constants.

PRINT=1 prints in addition the force constants as retrieved from the polynomial coefficients.

PRINT=2 prints the force constants and an analysis of the detected resonances.

INFO=n

INFO=1 provides a list of the values of all relevant program parameters.

56.1.1 Example

The following example shows an input for water, for which a semi-quartic force field will be generated at the MP2/cc-pVDZ level.

```
memory,20,m
basis=vdz
orient,mass
goal,geometry={
    3
    Water
    O  0.0675762564  0.0000000000  -1.3259214590
    H  -0.4362118830 -0.7612267436  -1.7014971211
    H  -0.4362118830  0.7612267436  -1.7014971211
}
mass,iso
hf
mp2
optg
```

{(1) optimizes the geometry}
frequencies,symm=auto
 label1
 {hf
  start,atden}
 mp2

 surf,start1D=label1,type=qff,sym=auto
 poly,vam=0
 vpt2

 !(2) compute harmonic frequencies
 !(3) generate a QFF
 !(4) transform the PES to polynomials
 !(5) do a VPT2 calculation
The \texttt{FCON} program allows for the calculation of Franck-Condon factors based on potential energy surfaces obtained from the \texttt{SURF} program and vibrational wavefunctions as provided by the \texttt{VSCF} or \texttt{VCI} programs. Duschinsky effects may or may not be included. These can either be applied to the vibrational wavefunction (of the vibrational ground state) or the potential by using the \texttt{PESTRANS} program. The latter possibility is the recommended one as it is significantly faster. The \texttt{FCON} program including Duschinsky rotations can only be used with analytical representations of the potential energy surfaces. A prescreening of the Franck-Condon factors without Duschinsky effects at the \texttt{VSCF} level is used to reduce the computational effort for correlated levels, e.g. \texttt{VCI}. Note that, Franck-Condon factors at the uncorrelated \texttt{VSCF} level including Duschinsky effects are usually of fairly poor quality. As the calculation of Franck-Condon factors often involves very high quantum numbers for the vibrational states of the final electronic state, very high excitation levels must be enabled in the \texttt{VCI} calculations, i.e. see keyword \texttt{LEVEX}. As a consequence, the \texttt{SCALE} parameter in \texttt{SURF} calculations needs to be modified in most applications.

\subsection{Options}

The following \textit{options} are available:

\begin{itemize}
\item \texttt{WF=type} \hspace{1cm} Defines the type of the wavefunction. \texttt{WF=VSCF} specifies state-specific \texttt{VSCF} wavefunctions for both levels, while \texttt{WF=VCI} denotes state-specific \texttt{VCI} wavefunctions. Alternatively, one may use \texttt{WF=VSCFG} for ground-state based \texttt{VSCF} wavefunctions and \texttt{WF=VCIG} for ground-state based \texttt{VCI} wavefunctions. The default is \texttt{WF=VCI}.
\item \texttt{THRPRINT=value} \hspace{1cm} This keyword defines the smallest value of a Franck-Condon factor to be printed in the output. The default is set to 1.0d-99, i.e. this threshold usually is inactive.
\item \texttt{THRFCFSPEC=value} \hspace{1cm} This threshold controls, if a Franck-Condon factor will be considered within the plotting of the spectrum. See the \texttt{PUT} command and the \texttt{IRSPEC} style. The default is 1.0d-6.
\item \texttt{THRFCF=value} \hspace{1cm} The sum of all Franck-Condon factors is 1.0d0 by definition. However, this value is hard to reach by sum over states approaches. Therefore, it can be lowered by this keyword.
\item \texttt{THRDELTA=value} \hspace{1cm} The $\delta$-criterion is a threshold, which allows for the prescreening of overlap integrals within the evaluation of the Franck-Condon factors prior to their evaluation. The default is set to 1.0d-8.
\item \texttt{THRSKIPBAS=value} \hspace{1cm} Basis functions in the outer regions of the potentials may be skipped within the calculation of Franck-Condon factors. In particular within the approach of Doktorov, the CPU time depends strongly on the number of basis functions. This keyword allows to skip such basis functions and is given as the overlap integral of the modal. The default is 0.999999d0.
\item \texttt{THRSEL=value} \hspace{1cm} This threshold controls, if a Franck-Condon factor shall be selected and thus be considered in all subsequent calculations or not. The default is 1.0d-5.
\end{itemize}
Within the calculation of Franck-Condon factors based on VCI wavefunctions, the leading VCI coefficient should be largest in order to correspond to the state of interest. The default is set to 0.01d0, which of course means that this keyword essentially is inactive.

This threshold controls the sum of the selected Franck-Condon factors, which must formally be 1.0d0. The default is set to 0.999999d0. MAXSEL=n determines the maximum number of Franck-Condon factors to be selected. By default n is set to 100.

This option switches the selection of Franck-Condon factors based on VSCF calculation on (SEL=1) or off (SEL=0, default).

This keyword controls the Duschinsky transformation. DUSCH=0 entirely neglects the Duschinsky transformation - including the shift-vector. DUSCH=1 switches the Duschinsky transformation on and the algorithm of Doktorov will be used. Note that this option is only limited to 3-atomic systems. DUSCH=3 neglects the Duschinsky rotation, but includes the shift-vector. This is the default option as the Duschinsky rotation can be passed to the PESTRANS program, which is much more efficient.

ECKART=n ECKART=1 (default) determines the Eckart transformation matrix as described in the literature. ECKART=0 approximates the Eckart transformation matrix by a unit matrix, which is meaningless unless for debugging purposes or for some very special tests.

Some of the keywords as described for the VCI program are also valid for the FCON program, i.e. CITYPE, LEVEX, CIMAX, DIPOLE, NDM, NBAS, NGRID, BASIS and INFO.

### 57.1.1 Information Handling

**DISK.options**

As the Franck-Condon program requests the information of two sets of potentials and wave functions, the information handling is controlled by an extra directive. All the record provided here must refer to the defaults or the explicitly given records in the preceding POLY, VSCF and VCI calculations.

**SURF1=record** Specifies the record from where to read the potential information for the final PES.

**SURF2=record** Specifies the record from where to read the potential information for the initial PES.

**VSCF1=record** Specifies the record from where to read the VSCF information for the final wave function.

**VSCF2=record** Specifies the record from where to read the VSCF information for the initial wave function.

**VCI1=record** Specifies the record from where to read the VCI information for the final wave function.

**VCI2=record** Specifies the record from where to read the VCI information for the initial wave function.
The following example shows the input for a calculation of Franck-Condon factors at the VCI level. The selection of important Franck-Condon factors will be done at the VSCF level without Duschinsky rotation.

```
memory,20,m
basis=vdz
orient,mass
group={
  Water
  O 0.0675762564 0.0000000000 -1.3259214590
  H -0.4362118830 -0.7612267436 -1.7014971211
  H -0.4362118830 0.7612267436 -1.7014971211
}
labell

hf
{
  surf,start1D=labell,sym=auto
  ! reads the PES of the final electronic
  disk,where=home,extern='final.pot'
  ! state from 'final.pot'
}
poly
vscf,type=poly ! saves VSCF wavefunction in record 5750.2
vci,type=poly,export=fcon ! saves VCI wavefunction in record 5800.2
{
  surf,start1D=labell,sym=auto
  ! reads the PES of the initial electronic
  disk,where=home,save=5601.2,extern='initial.pot'
  ! state from 'initial.pot'
}
poly
vscf,type=poly,save=5751.2
vci,type=poly,save=5751.2
{
  fcon,wf=vscfg,sel=1
  ! selection of the FCFs based on a VSCF calc.
  disk,surf1=5600.2,surf2=5601.2
}
poly
vscf,type=poly,save=5751.2,save=5750.2
vci,type=poly,export=fcon,save=5800.2
{
  pestrans,umat=1
  ! rotate the PES of initial.pot in the
  ! coordinates of final.pot
  disk,where=home,save=5601.2,extern='final.pot'
  ! U-matrix for the VCI program, the extern file
  ! provides the hessian of the other system
}
poly
vscf,type=poly,save=5750.2,save=5751.2
vci,type=poly,export=fcon,save=5800.2
{
  fcon
  ! calculate the selected FCFs
  disk,surf1=5600.2,surf2=5601.2
  ! disk directive is not necessary here,
  disk,vscf1=5750.2,vscf2=5751.2
  ! but one can see the standard values this way
  disk,vci1=5800.2,vci2=5801.2
  ! 1 correspond to the final state;
  ! 2 correspond to the initial state
}
put,irspec,h2o_pe.gnu
! generate a GNU file with the PE spectrum
```

The COSMO model is invoked by the COSMO card:

```
COSMO[\text{option}_1=value_1, \text{option}_2=value_2, \ldots]
```

where option can be

- **NPPA**: size of the underlying basis grid. The value must satisfy: \( value = 10 \times 3^k \times 4^l + 2 \) (default = 1082; type integer).

- **NSPA**: number of segments for non hydrogen atoms. The value must satisfy: \( values = 10 \times 3^k \times 4^l + 2 \) (default = 92; type integer).

- **CAVITY**: the intersection seams of the molecular surface are closed (1) or open (0) (default = 1; type integer).

- **EPSILON**: dielectric permittivity (default = -1.d0, which means \( \varepsilon = \infty \); type real)

- **DISEX**: distance criteria for the A-matrix setup. Short range interactions (segment centre distances \( \leq \text{DISEX} \times \text{mean atomic diameter} \)) are calculated using the underlying basis grid. Long range interactions are calculated via the segment centres (default = 10.d0; type float).

- **ROUTF**: factor used for outer cavity construction. The radii of the outer cavity are defined as: \( r^\text{out}_i = r_i + \text{ROUTF} \times \text{RSOLV} \) (default = 0.85d0; type float)

- **PHSRAN**: phase offset of coordinate randomization (default = 0.d0; type float)

- **AMPRAN**: amplitude factor of coordinate randomization (default = 1.0d-5; type float)

- **RSOLV**: additional radius for cavity construction (default = -1d0, the optimized H radius is used; type float).

- **MAXNPS**: maximal number of surface segments (default = -1, will be estimated; type integer).

It is recommended to change the default values for problematic cases only.

By default the program uses optimized radii if existent and 1.17 \times \text{vdW radius} else. The optimized radii [Å] are: H=1.30, C=2.00, N=1.83, O=1.72, F=1.72, S=2.16, Cl=2.05, Br=2.16, I=2.32. Own proposals can be given directly subsequent to the cosmo card:

```
RAD, symbol, radius
```

where the radius has to be given in Å.

Example:

```
cosmo
rad, O, 1.72
rad, H, 1.3
```

Output file:

The COSMO output file will be written after every converged SCF calculation. The segment charges and potentials are corrected by the outlying charge correction. For the total charges and energies corrected and uncorrected values are given. The normal output file contains uncorrected values only. It is recommended to use the corrected values from the output file.

Optimizations:

It is recommended to use optimizer that operates with gradients exclusively. Line search techniques that use energies tends to fail, because of the energy discontinuities which may occur due to a reorganization of the segments after a geometry step. For the same reasons numerical gradients are not recommended.
58.1 BASIC THEORY

COSMO is a continuum solvation model, in which the solvent is represented as a dielectric continuum of permittivity $\varepsilon$. The solute molecule is placed in a cavity inside the continuum. The response of the continuum due to the charge distribution of the solute is described by the generation of a screening charge distribution on the cavity surface. This charge distribution can be calculated by solving the boundary equation of vanishing electrostatic potential on the surface of a conductor. After a discretization of the cavity surface into sufficiently small segments, the vector of the screening charges on the surface segments is

$$q^* = -A^{-1}\Phi$$

where $\Phi$ is the vector of the potential due to the solute charge distribution on the segments, and $A$ is the interaction matrix of the screening charges on the segments. This solution is exact for an electric conductor. For finite dielectrics the true dielectric screening charges can be approximated very well by scaling the charge density of a conductor with $f(\varepsilon)$.

$$q = f(\varepsilon)q^*; \quad f(\varepsilon) = (\varepsilon - 1)/(\varepsilon + 0.5)$$

In every SCF step the screening charges $q$ have to be generated from the potential $\Phi$, and then added to the Hamiltonian as external point charges. The total energy of the system is

$$E_{\text{tot}} = E_0 + E_{\text{die}}; \quad E_{\text{die}} = \frac{1}{2}\Phi q$$

where $E_0$ is the bare self-energy of the system and $E_{\text{die}}$ the dielectric energy.

Cavity construction:
First a surface of mutually excluding spheres of radius $R_i + rsolv$ is constructed, where the $R_i$ are the radii of the atoms, defined as element specific radii and $rsolv$ is some radius representing a typical maximum curvature of a solvent molecular surface. $rsolv$ should not be misinterpreted as a mean solvent radius, nor modified for different solvents. Every atomic sphere is represented by an underlying basis grid of $nppa$ points per full atom. Basis grid points which intersect a sphere of a different atom are neglected. In a second step the remainder of the basis grid points are projected to the surface defined by the radii $R_i$. As a third step of the cavity construction the remaining basis grid points are gathered to segments, which are the areas of constant screening charges in the numerical solution. Finally, the intersection seams between the atoms are filled with additional segments.
Now the $A$-matrix can be set up. The matrix elements will be calculated from the basis grid points of the segments for close and medium segment distances (governed by the disex value), or using the segment centres for large segment distances.

Outlying charge correction:
The non vanishing electron density outside the cavity causes an error that can be corrected by the outlying charge correction. This correction uses the potential on the so called outer surface (defined by the radii $R_i + rsolv \times routf$) to estimate a correction term for the screening charges and the energies (A. Klamt and V. Jonas, J. Chem. Phys., 105, 9972-9981(1996)). The correction will be performed once at the end of a converged SCF calculation. All corrected values can be found in the COSMO output file.
QM/MM INTERFACES

The MOLPRO program package can be used in combination with other software to perform hybrid Quantum Mechanics/Molecular Mechanics (QM/MM) calculations. Through the use of point charges, electrostatic embedding can be used for both energy and gradient runs. In particular, lattices of point charges can be included in an external file, gradients with respect to charge positions can be computed, as described in section 10.5. Gradients with respect to QM nuclear positions can be computed (and include the effect of the MM charges) as usual using the FORCE command (section 45).

Although MOLPRO itself does not offer any interface to force field programs, the coupling is supplied by other commercial and non-commercial software. The following is a list of QM/MM software which allow the use of MOLPRO.

59.1 Chemshell

The Chemshell computational chemistry environment (http://www.chemshell.org) offers an interface to many well known force field software (CHARMM, GROMOS, GULP,...). The program supports several geometry optimization algorithms; a molecular dynamics driver for NVE, NVT and NPT ensembles; Monte Carlo; and many other utilities.

The Chemshell Manual can be found at the following website:
http://www.cse.scitech.ac.uk/ccg/software/chemshell/manual/

Instructions on the use of Molpro are available therein. Also concerning the Chemshell environment, a free Graphical User Interface (GUI) has been released. The CCP1GUI facilitates the input for hybrid calculations, allows visualisation of molecular structures and includes molecule editing tools:
http://www.cse.scitech.ac.uk/ccg/software/ccp1gui/

PERIODIC-BOUNDARY CONDITIONS

Periodic-boundary conditions are indicated by use of the PBC command. It can take the following options and directive

- **LATT\_TYPE**  The shape of the unit cell. CUBIC: cubic unit cell, HEXAG: hexagonal unit cell, PARAP: a parallelepiped shaped cell
- **BOXSIZE**  For cubic unit cells this specifies the length of the side of the cube in Angstroms.
- **HEXWIDTH, HEXHEIGHT**  For hexagonal unit cells this specifies the width and height of the cell in Angstroms.
- **VEC**  A directive which should be followed by 3 numbers to specify a lattice vector. When specifying lattice vectors like this, there are usually 3 instances of such a directive and the vectors will be checked that they conform to the specified LATT\_TYPE. This is the only way to specify lattice vectors for LATT\_TYPE=PARAP. The program will not error if less than 3 vectors have been given, as in principle 1 or 2 dimensional periodicity could be desired, although this has not been implemented.

To define parallelepiped lattice vectors, something like the following would be used

```
{PBC,LATT\_TYPE='PARAP'
  VEC,1.0,0.0,0.0
  VEC,0.0,1.5,1.5
  VEC,0.0,0.0,1.5
}
```
61  MANY-BODY EXPANSION

61.1  Compilation

To run MBE for large systems, the default maximum number of atoms must be increased. This can be done via configure. The maximum number that can be entered here is 1000. To increase this further the configure script must be modified. The default number of records should also be increased. This should typically be about 4 times the number of monomers in the system, as multipoles, polarizabilities and density-fitting information are held separate records for each monomer. To compile for parallel execution the MPPX parallel mode should be chosen.

61.2  Units

All lengths in the input file should be given in Angstroms.

61.3  Incremental Monte-Carlo

- $L_{\text{MAX},M}$  Angular momentum of multipoles to be used
- $L_{\text{MAX},P}$  Angular momentum of polarizabilities to be used
- PRINT  Level of information to output
- IMCDUMP  At end of a calculation dump various levels of information: $>=$ 1 dumps properties and one-body energies, $>=$ 2 dumps all two-body energies, $>=$ 3 all three-body energies
- MAXLEV  Maximum level of MBE. Default is to include dimers (=2). For IMC maximum is trimers. For a manybody analysis can go up to 5.
- CUTOFF  Distance within which to do QM calculations. For 3 body calculations, all dimer separations must be within this distance.
- THRDENOV  Distance within which to calculate the overlap for damping. By default the same as CUTOFF.
- MC  Do a Monte-Carlo simulation if 1 (Default 0)
- MCMAX  Maximum number of MC steps to perform
- MCTEMP  Temperature of a MC simulation
- NPT  Do a NPT simulation
- PRESSURE  Pressure for a NPT MC simulation
- PRFREQ  How often to print output during a MC simulation
- RESFREQ  How often to save restart information (may not work!)
- ENG_PROC  Name of energy procedure for all levels (if the same is to be used for all)
- ENG_PROC1  Name of energy procedure for monomers
- ENG_PROC2  Name of energy procedure for dimers
- ENG_PROC3  Name of energy procedure for trimers
- PROP_PROC  Name of property procedure
- RESTART  If we are doing a restart (may not work)
- DAMPING  Use damping (Tang-Toennies with empirical factor of 1.94 by default)
- DAMPFAC  Empirical factor to use in damping function
- DF_SET  Density-fitting set to use in damping. Density damping is only switched on if this is specified
• **DF_CON**  Optional specification of **CONTEXT** for **DF_SET**, e.g. **JKFIT** or **MP2FIT**. **JKFIT** by default
• **DFMAXL**  Optional specification of maximum angular momentum functions to use in **DF_SET**
• **DENREC**  Location where density has been stored for calculating distributed multipoles
• **GEOMLOC**  Location where geometry output from MC should be stored
• **ANALYSE**  Only do analysis and no calculation
• **RDF_TYPES**  Type of RDFs to calculate
• **RDF_VOL**  Volume for non-periodic RDF
• **RDF_NBIN**  Number of bins for RDF
• **RDF_DBIN**  Width of bin
• **RDF_EQ**  Number of equilibration steps to ignore when calculating RDF
• **MANYBODY**  Just do a many-body analysis. =1 does normal many-body analysis and =2 does full counterpoise corrected.
• **SCALTYPE**  Scale box before starting calculation. =A for side of box in Angstroms, =B for side of box in Bohr, =N for number density, =D for density in kg/m³
• **SCALE**  Size of scaled box in whatever type has been specified in **SCALTYPE**
• **DTRANS**  Initial size of translational move in Angstrom
• **DROT**  Initial size of rotational move in degrees
• **DSTR**  Initial size of bond stretch in Angstrom
• **DBEND**  Initial size of bond angle bend in degrees
• **DBOX**  Initial size of box move in Angstroms (for NPT simulations)
• **DINTRA**  Bias for intramolecular moves (this plus **DRIGID** will be equal to one. **DINTRA** takes priority, if both specified)
• **DRIGID**  Bias for rigid-body moves (this plus **DINTRA** will be equal to one. **DINTRA** takes priority, if both specified)
• **DVOL**  Bias for volume moves versus molecular moves in NPT simulations
• **TARGINT**  Acceptance/rejection ratio target for intramolecular moves
• **TARTRIG**  Acceptance/rejection ratio target for rigid-body moves
• **TARGVOL**  Acceptance/rejection ratio target for volume moves in NPT simulations
• **MONFILE**  File to specify connectivity of system which overrides automatic connectivity subroutine. Should not be used with MC simulations, but OK for energy.
• **CHGFILE**  File to specify if any of the monomers are charged.
• **ANISODISP**  Are we using anisotropic dispersion integrals
• **DISPFILE**  File to specify dispersion coefficients or integrals, bohr for isotropic and anisotropic
• **INDMETH**  Method to use for self-consistent induction calculation. =0 don’t iterate, =1 iterate and use Ewald only on first iteration for PBC, =2 iterate and use Ewald at every step for PBC, =3 use Lanczos algorithm which uses Ewald on first iteration only.
• **ITNUM**  Starting value for the iteration number.
• **NBODY**  Include n-body energy (default =1)
• **CLASSICAL**  Include classical energies (default =1)
• **SWITCH**  Use a switching function. =0 no switching, =1 quintic splines switching, (=2 GAP switching)
61.4 EWALD directive

- **GAMMA** Exponent of screening gaussian in Ewald summation
- **KCUT** Cutoff radius for radius of k-vectors
- **RCUT** Cutoff radius for real-space ewald
- **LCUT** Cutoff for angular momentum in multipolar Ewald. Higher-order terms probably convergent in real-space radius
- **EPS** Permittivity to use for surface term in Ewald

61.5 Examples

61.5.1 Obtaining TDHF and UCHF dispersion coefficients

The example below demonstrates how to get T. Korona’s CC-SAPT program to output TDHF and UCHF dispersion coefficients. The UCHF coefficients are the relevant ones for an MP2 calculation. This example gives dispersion coefficients for water-water, ammonia-ammonia and water-ammonia. To use them in a calculation all of the integrals listed in the output for a given interaction should be put into a file in exactly the format they are output, i.e. four indices and an integral. This can then be read by the MBE program.
memory,100,m
if(NPROC_MPP.gt.1) then
  skipped
end if

qthresh,energy=1.d-10
! don't use symmetry - can mess things up
symmetry,nosym
geometry={
  H
  O 1 R
  H 2 R 1 A
}
R=0.966443838 Angstrom
A=103.84335748 Degree

gexpec,nspmlt3
ileden=0
iledenp=0

! first call just sets up CCSAPT program
dispgg=15
set,CC_NORM_MAX=50
basis=sto-3g
hf;maxit,0
(ccsd,check=0
polari,nspmlt3
orbital,ignore_error=1;maxit,3
cprop,ccsapt=3)

! now calculate the dispersion integrals for water

basis=avdz
hf;save,scfa
tdhf=tdhfa
tdhfdisp=tdhfdispa
(ccsd,check=0
polari,nspmlt3
orbital,ignore_error=1;maxit,3
cprop,ccsapt=5,dispcoef=dispgg,dispomega=0.3)

! calculate dispersion integrals for ammonia and mixed coefficient for NH3-H2O

symmetry,nosym
geometry={
  N
  X1 N RX
  H1 N RNH X1 DUMB
  H2 N RNH X1 DUMB H1 DIHE 0
  H3 N RNH X1 DUMB H1 -DIHE 0
}
RX= 1.02 Angstrom
RNH= 1.02071411 Angstrom
DIHE= 120. Degree
DUMB= 112.48619220 Degree
ileden=0
iledenp=0
gexpec,nspmlt3
dispgg=15
set,CC_NORM_MAX=50
basis=sto-3g
hf;maxit,0
(ccsd,check=0
polari,nspmlt3
orbital,ignore_error=1;maxit,3
cprop,ccsapt=3)

basis=avdz
There are testjobs already present which show how to calculate dispersion coefficients using CC-SAPT. These should be modified to use the spherical harmonic multipole operators on the EXPEC and POLARI cards to produce the required integrals.

### 61.5.2 Many-body analysis of water hexamer

This example performs a many-body analysis of the water hexamer up to 3-body contributions. The routines go up to a maximum of 5-body contributions. By specifying MANYBODY=2 a full counterpoise corrected many-body analysis would be done.

```molpro
PROC mbeeng
  {df-hf;start,atden}
  {df-lmp2,interact=1 enepart}
ENDPROC

! input ensemble geometry
memory,20,m
symmetry,nosym
orient,noorient
geomtyp=xyz
geometry=

18

DF-LMP2/AVDZ ENERGY=-457.63602408
O  -2.1233226309  -1.7688858791 0.1524109399
H  -2.4367986815  -2.2103390376 0.9513842141
H  -1.2045230633  -2.0982518768 0.0330050109
O  2.5947061994  -0.9537736740 0.1422730545
H  2.4193021370  -2.0982518768 0.9513842141
H  3.1418238405  -1.0061708640 0.9356521604
O  -2.5946186870  0.9534257806 -0.1546242536
H  -3.1315700574  1.0016502753 -0.9551345770
H  -2.4201260402  0.0065436988 -0.0322861934
O  2.1219816165  1.7703156035 0.1450981681
H  1.2027719526  2.0987725437 -0.0263944582
H  2.4388614383  2.2190153349 -0.9386745371
O  -0.4725613825  2.7226532886 0.1512286611
H  -0.7014891628  3.2160843341 0.9484803611
H  -1.2168653397  2.091678132  0.0293211623
O  0.4703934181  -2.7233099281 -0.1463373783
H  0.6968166194  -3.2213522313 -0.9414479081
H  1.2152177361  -2.0918266148 -0.0304245102
}

basis,avdz
{mbe,manybody=1,maxlev=3}
```

http://www.molpro.net/info/current/examples/water6_mbe.com

### 61.5.3 Two-body-plus-polarization treatment of water hexamer

This demonstrates a many-body evaluation of the energy of the cluster using the long-range model for well-separated dimers and the polarization model for many-body (beyond two-body) effects. Two procedures are defined, one for the energy and one for the properties. Properties up to quadrupoles (LMAX_M=2, LMAX_P=2) are used. MBEENG and MBEPROP are the default names for these procedures and hence do not need to be specified on the input line. MAXLEV=2 indicates that up to dimers should be calculated using MBEENG and within CUTOFF=4.5 (in Angstroms). Isotropic dispersion coefficients of Wormer et al. are used by default for water.
61.5.4 Three-body-plus-polarization treatment of water hexamer

Same as previous but with MAXLEV=3 so that trimers are also calculated using MBEENG. Note that SWITCH=0 has been used as no 3-body switching function has been implemented and ‘unswitched’ 3-body energies should not be mixed with ‘switched’ 2-body ones.

http://www.molpro.net/info/current/examples/water6_mbe2.com
PROC mbeeng  !default procedure name
hf
ENDPROC

PROC mbeprop  !default procedure name
hf
polarizability,nspmlt2
ENDPROC

! input ensemble geometry
memory,10,m
symmetry,nosym
orient,noorient
geomtyp=xyz
geometry={
  Water hexamer
  18
  O -2.123226309 -1.7688858791 0.1524109399 0.1524109399
  H -2.4367986815 -2.2103390376 0.9513842141
  H -1.2045230633 -2.0982518768 0.0330050109
  O 2.5947061994 -0.9537736740 0.1422730545
  H 2.4193021370 0.0068583194 0.026664332
  H 3.1418238405 -1.0061708640 0.9356521604
  O -2.5946186870 0.9534257806 -0.1546242536
  H -3.1315700574 1.0016502753 -0.9551345770
  H -2.4201260402 -0.0065436988 -0.0322861934
  O 2.1219816165 1.7703156035 -0.1450981681
  H 1.2027719526 2.0987725437 -0.0263944582
  H 2.438614383 2.2190153349 -0.9386745371
  O -0.4725613825 2.7226532886 0.151228661
  H -0.7014891628 3.2160843341 0.9484803611
  H -1.2168655397 2.0916787132 0.0293211623
  O 0.4703934181 -2.7233099281 -0.1463373783
  H 0.6968166194 -3.2213522313 -0.9414479081
  H 1.2152177361 -2.0918266148 -0.0304245102
} basis,avdz
{mbe,maxlev=3,cutoff=4.5,lmax_m=2,lmax_p=2,switch=0}

http://www.molpro.net/info/current/examples/water6_mbe3.com

61.5.5 Specifying isotropic dispersion coefficients

Similar to the example in Subsection 61.5.3 but here we are specifying the isotropic dispersion coefficients which should be used. The DISPFILE variable specifies the file where these should be found. It should be a list of the relevant interactions and the \( C_6, C_8 \) and \( C_{10} \) coefficients. For example

\[
\text{OH}_2:\text{OH}_2 \quad 46.0 \quad 800.0 \quad 10000.0
\]

where molecules should be listed by elements of decreasing atomic mass. If a charged species is being used, the charge should be included in parentheses, e.g. \( F(-1) \). The file may contain interactions not relevant to the system under consideration, so a library of dispersion coefficients may be built up. The input file is
PROC mbeeng !default procedure name
hf
ENDPROC

PROC mbeprop !default procedure name
hf
polarizability, nspmlt2
ENDPROC

! input ensemble geometry
memory, 10, m
symmetry, nosym
orient, noorient
geomtyp=xyz
geometry=

Water hexamer
O   -2.1233226309   -1.7688858791   0.1524109399
H   -2.4367986815   -2.2103390376   0.9513842141
H   -1.2045230633   -2.0982518768   0.0330050109
O    2.5947061994   -0.9537736740   0.1422730545
H    2.4193021370    0.0068583194   0.026664332
H    3.1418238405   -1.0061708640   0.9356521604
O   -2.5946186870    0.9534257806  -0.1546242536
H   -3.1315700574    1.0016502753  -0.9551345770
H   -2.4201260402   -0.0065436988   -0.0322861934
O    2.1219816165    1.7703156035  -0.1450981681
H    1.2027719526    2.0987725437  -0.0263944582
H    2.4388614383    2.2190153349  -0.9367453711
O   -0.4725613825    2.7226532886   0.1512286611
H   -0.7014891628    3.2160843341   0.9484803611
H   -1.2168653397    2.0916787132   0.0293211623
O    0.4703934181   -2.7233099281  -0.1463373783
H    0.6968166194   -3.2213522313  -0.9414479081
H    1.2152177361   -2.0918266148  -0.0304245102
}
basis, avdz
{mbe, maxlev=2, cutoff=4.5, mc=0, lmax_m=2, lmax_p=2, anisodisp=0, dispfile='disp_iso.inp'}

http://www.molpro.net/info/current/examples/water6_iso.com

and the required dispersion file is:

OH2:OH2 40.196 496.889 8263.5

http://www.molpro.net/info/current/examples/disp_iso.inp

61.5.6 Specifying anisotropic dispersion coefficients

Again this is controlled by the DISPFILE variable, but the file now has a different format. For each type of interaction three filenames should be specified. The first should contain the dispersion integrals and the second two the reference geometries at which they were calculated, e.g.

OH2:OH2 h2oh2odisp.dat h2o.xyz h2o.xyz

The geometries should be given in standard XYZ format. The input file is:
PROC mbeeng !default procedure name
hf
ENDPROC

PROC mbeprop !default procedure name
hf
polarizability, nspmlt2
ENDPROC

! input ensemble geometry
memory, 10, m
symmetry, nosym
orient, noorient
geomtyp=xyz
genometry={
    Water hexamer
    O -2.1233226309 -1.7688858791 0.1524109399
    H -2.4367986815 -2.2103390376 0.9513842141
    H -1.2045230633 -2.0982518768 0.0330050109
    O 2.5947061994 -0.9537736740 0.1422730545
    H 2.4193021370 0.0068583194 0.0266664332
    H 3.1418238405 -1.0061708640 0.9356521604
    O -2.5946186870 0.9534257806 -0.1546242536
    H -3.1315700574 1.0016502753 -0.9551345770
    H -2.4201260402 -0.0065436988 -0.0322861934
    O 2.1219816165 1.7703156035 -0.1450981681
    H 1.2027719526 2.0987725437 -0.0263944582
    H 2.4388614383 2.2190153349 -0.9386745371
    O -0.4725613825 2.7226532886 0.1512286611
    H -0.7014891628 3.2160843341 0.9484803611
    H -1.2168653397 2.0916787132 0.0293211263
    O 0.4703934181 -2.7233099281 -0.1463373783
    H 0.6968166194 -3.2213522313 -0.9414479081
    H 1.2152177361 -2.0918266148 -0.0304245102
}
basis, avdz
{mbe, maxlev=2, cutoff=4.5, mc=0, lmax_m=2, lmax_p=2, anisodisp=1, dispfile='disp.inp'}
http://www.molpro.net/info/current/examples/water6_aniso.com

The additional files that are required are: disp.inp, h2o_tip.xyz and h2o_tip_uchf.disp, which can be found in the examples directory.

61.5.7 Using MP2 properties

As the example in Subsection 61.5.3 but using MP2 properties. We have now also specified different procedures for monomer and dimer energies. This is important for correlated energies as the specifying the correct number of core orbitals is important. The examples require auxiliary files disp.inp, h2o_tip.xyz and h2o_tip_uchf.disp, which can be found in the examples directory.
PROC mbeeng1
core,1
  {df-hf;start,atden}
  {df-lmp2,interact=1
   pipek,delete=1
   enepart}
ENDPROC

PROC mbeeng2
core,2
  {df-hf;start,atden}
  {df-lmp2,interact=1
   pipek,delete=1
   enepart}
ENDPROC

PROC mbeprop
core,0
  {hf;start,atden
   polarizability,NSPMLT2}
  {mp2;dm,11000.2}
ENDPROC

! input ensemble geometry
memory,10,m
symmetry,nosym
orient,noorient
geomtyp=xyz
gallery=

Water hexamer

18
O     -2.1233226309   -1.7688858791    0.1524109399
H     -2.4367986815   -2.2103390376    0.9513842141
H     -1.2045230633   -2.0982518768    0.0330050109
O      2.5947061994   -0.9537736740    0.1422730545
H      2.4193021370    0.0068583194    0.0266664332
H      3.1418238405   -1.0061708640    0.9356521604
O     -2.5946186870    0.9534257806   -0.1546245363
H     -3.1315700574    1.0016502753   -0.9551345770
H     -2.4201260402   -0.0065436988   -0.0322861934
O      2.1219816165    1.7703156035   -0.1450981681
H      1.2027719526    2.0987725437   -0.0263944582
H      2.4388614383    2.2190153349   -0.9386745371
H     -0.4725613825    2.7226532886    0.1512286611
O     -0.7014891628    3.2168043341    0.9484803611
H     -1.2168653397    2.0916787132    0.0293211623
O      0.4703934181   -2.7233099281   -0.1463373783
H      0.6968166194   -3.2213522313   -0.9414479081
H     1.2152177361   -2.0918266148    0.0304245102
}
basis,avdz
  (mbe,maxlev=2,cutoff=4.5,mc=0,lmax_m=2,lmax_p=2,eng_proc1=’MBEENG1’,eng_proc2=’MBEENG2’,anisodisp=1,dispfile=’disp.inp’)

http://www.molpro.net/info/current/examples/water6_mp2.com

A second example is provided which produces more verbose output.
61.5.8 Mixed water–ammonia cluster

A mixed cluster of 10 water molecules and two ammonia molecules. There is now anisotropic dispersion information listed for multiple interactions. The dispersion file disp_h2o_nh3.inp specifies monomer reference geometries (h2o.xyz and nh3.xyz) and UCHF dispersion coefficients in h2o_nh3_uchf.dat, h2o_uchf.dat, and nh3_uchf.dat. The geometry is specified in water10_ammonia2.xyz.
The input file is below, and all other auxiliary files can be found in the examples directory.

```
memory,40,m

PROC MBEENG1
core,1
{df-hf;start,atden}
{df-lmp2,interact=1
pipek,delete=1
enepart}
ENDPROC

PROC MBEENG2
core,2
{df-hf;start,atden}
{df-lmp2,interact=1
pipek,delete=1
enepart}
ENDPROC

PROC MBEPROP
core,0
{hf;start,atden
polarizability,nspmlt3}
{mp2;dm,11000.2}
ENDPROC

symmetry,nosym
geomtyp=xyz
geom=water_ammonia_12.xyz
basis,avdz
{mbf,maxlev=2,cutoff=4.5,lmax_m=3,lmax_p=3,damping=1,df_set='CC-PVTZ(D/P)',dispfile='disp.inp',eng_proc1='MBEENG1',eng_proc2='MBEENG2',switch=0}
```

http://www.molpro.net/info/current/examples/water10_ammonia2.com

61.5.9 Single calculation on 64 water molecules in periodic boundary conditions

The PBC command specifies that periodic boundary conditions should be invoked. The ewald directive is also present so that periodic electrostatic and induction energies are included. Without this directive everything would simply be done in the minimum image convention. Damping is used and since a fitting set has been specified using DF_SET, damping will be done using density overlap of monomers. The required auxiliary files for this example are:

- dispersion files: `disp.inp`, `h2o_tip.xyz` and `h2o_tip_uchf.disp`
- geometry: `water64.xyz`

all available in the examples directory. The input file is below.
Embedding methods allow a system to be divided into two smaller subsystems, each of which can be treated using a different level of theory. For example, in WF-in-DFT embedding, a WF-level (e.g. HF, MP2, CCSD(T), CASSCF, etc.) calculation is performed on one subsystem, while a DFT-level calculation is performed on the other subsystem. The interactions between the two subsystems are calculated at the DFT level. The primary advantage of WF-in-DFT embedding is that it facilitates the application of an accurate, systematically improvable WF method to regions where such accuracy is required, while a more efficient DFT method is applied to the remainder of the system. The overall strategy for WF-in-DFT embedding is described as follows:

(1) A DFT calculation is performed on the full system.

(2) The system is partitioned into two subsystems, labeled the active subsystem and the frozen subsystem.

(3) The interaction potential between the two subsystems is calculated at the DFT level.
A WF-level calculation is performed on the electrons in the active subsystem, embedded in the DFT-level interaction potential produced by the electrons in the frozen subsystem.

Note: WF-in-DFT embedding is not implemented with symmetry.

It is possible to replace the WF-level calculation on subsystem A with a DFT-level calculation, which corresponds to DFT-in-DFT embedding. Because the interaction potential between the subsystems is calculated at the DFT level, the result of a DFT-in-DFT embedding calculation is numerically identical to the results of a DFT calculation on the full system. Confirming that the DFT-in-DFT energy is numerically equivalent to the energy of a DFT calculation on the full system can thus be a useful sanity check. Similarly, it is possible to replace the DFT-level calculation with a HF-level calculation, which corresponds to WF-in-HF embedding.

Molpro implements the numerically exact projection-based WF-in-DFT embedding method for open and closed shell systems developed in the following papers:


All publications resulting from the use of this method must acknowledge the above.

### 62.1 Getting Started

The DFT embedding program is called by the `EMBED,PROJ` directive. When using this directive, the user must specify which MOs are associated with the active subsystem. This can be most directly accomplished through the `ORBS` option:

- **ORBS=[orbital1, orbital2, orbital3...]**
  
  where `orbital1` is an integer indicating that MO number `orbital1` is associated with the active subsystem. The minimum input to run using the `ORBS` array is:
  
  ```
  {ks}
  {embed,proj,orbs=[orbital1]}
  {hf}
  {ccsd(t)}
  ```

  The KS calculation is performed on the full system. The `EMBED,PROJ` directive indicates the beginning of an embedding calculation in which subsystem A corresponds to the single MO `orbital1`. The HF and CCSD(T) calculations are performed on subsystem A, embedded in a subsystem interaction potential calculated at the KS level.

  Alternatively to setting the `ORBS` array, the user can instead specify the `ATOMS` card:

- **ATOMS,atom1,atom2,atom3...**
  
  where `atom1` is the name of an atom from the geometry specification. Any MO having a Mulliken population greater than `CHARGE_THRESHOLD` (see subsection 62.1) on one of the listed atoms is associated with subsystem A. The minimum input to run using the `ATOMS` card is:
  
  ```
  {ks}
  {embed,proj;atoms,atom1}
  {hf}
  {ccsd(t)}
  ```
CASSCF calculations can be used as the WF method, but some care must be taken for the specification of the active space. In particular, the OCC, CLOSED, and FROZEN cards must be specified, and they must correspond to the number of OCC, CLOSED, and FROZEN orbitals within the active subsystem:

\[
\begin{align*}
\{ & \text{ks} \\
\{ & \text{embed,proj;atoms,atom1,atom2,...} \\
\{ & \text{hf} \\
\{ & \text{Multi} \\
\text{OCC} \\
\text{CLOSED} \\
\text{FROZEN} \\
\end{align*}
\]

### 62.2 Options

#### 62.2.1 EMBED,PROJ Options

The following options may be specified on the EMBED,PROJ command line:

- **ORBS=\{orbital1,orbital2,orbital3...\}**
  
The ORBS option is described in the section Getting Started (62.1).

- **ATOMS,atom1,atom2,atom3...**
  
The ATOMS option is described in the section Getting Started (62.1).

- **MU=value (default 1.d6)**
  
The value of the coefficient for the level shift used in the projection-based embedding calculations. The projection-based embedding method is in principle numerically exact in the limit of infinite \(\text{MU}\), but in practice very large values of \(\text{MU}\) will lead to machine-precision errors. Typically, changing \(\text{MU}\) by 1-2 orders of magnitude relative to the default value should have only negligible impact on the energy.

- **CHARGE\_THRESHOLD=value (default 0.4)**
  
  This option is only relevant if the \text{ATOMS} card is present. Any MO having a Mulliken population on an atom specified by the \text{ATOMS} card that is greater than \(\text{CHARGE\_THRESHOLD}\) is associated with the active subsystem.

- **N\_ORBITALS=value (default none)**
  
  If the \text{ATOMS} card is present, as an alternative to defining \text{CHARGE\_THRESHOLD}, one can instead define \text{N\_ORBITALS}. In this case, the \text{N\_ORBITALS} MOs with the largest summed Mulliken population on the atoms specified by the \text{ATOMS} card are associated with the active system. This can be particularly useful for ensuring that the number of MOs in the active subsystem remains constant when calculating the potential energy surface of a reaction.

- **ORBITAL, [record], local**
  
  This card specifies the orbital record from which MOs corresponding to a HF-level or DFT-level calculation on the full system are read. These MOs should be localized prior to use by the embedding calculation, as shown in the following example:

  \[
  \begin{align*}
  \{ & \text{ks;orbital,2200.2} \\
  \{ & \text{locali,pipek;orbital,2200.2;save,2300.2} \\
  \{ & \text{embed,proj;atoms,atom1;orbital,2300.2,local} \\
  \{ & \text{hf} \\
  \{ & \text{ccsd(t)} \\
  \end{align*}
  \]

  If this card is not present, the last calculated HF or DFT MOs are localized using the Pipek-Mezey algorithm and then employed by the embedding calculation. Thus the preceding example is equivalent to:
{ks}
{embed,proj;atoms,atom1}
{hf}
{ccsd(t)}

• PRINT=value (default 0)
Level of output. The value print=0 gives standard output. The value print=1 prints the atoms and molecular orbitals in the active region as well as the active and frozen electrons. The value print=2 prints the same output as print=1 along with the localized molecular orbital composition.

• DIRECTA
The DIRECTA option controls whether the calculation on the active subsystem is performed in integral-direct mode. By default, the calculation on the active subsystem is performed in integral-direct mode only if the DIRECT or GDIRECT directives have been used globally (see section 14.3). Setting DIRECTA=1 causes all calculations on the active subsystem to be performed in integral-direct mode, while setting DIRECTA=0 causes all calculations on the active subsystem to be performed without integral-direct mode, even if the DIRECT or GDIRECT directives have been previously used globally. Setting DIRECTA=0 is necessary when the calculation on the full system is performed using integral-direct mode and the calculation on the active subsystem is performed using a method for which integral-direct mode is not supported, such as CCSD(T). In this case, it is also necessary to use the FDIRECT directive instead of the DIRECT or GDIRECT directives, which forces Molpro to ignore potential method conflicts when enabling integral-direct mode.

An example of this process is provided below:
FDIRECT
{ks}
{embed,proj,directa=0;atoms,atom1,atom2,...} 
DIRECT=.false.
{hf}
{ccsd(t)}

• REMOVE
The EMBED,PROJ command modifies the core Hamiltonian and orbital occupation such that subsequent calculations are performed only on the active subsystem. The EMBED,PROJ,REMOVE command is required to revert to full system calculations after the EMBED,PROJ command. An example is provided below:
{ks}
{embed,proj;atoms,atom1,atom2,...}
{hf}
{ccsd(t)}
{embed,proj,remove}

• SAVE_ORBITALS
The SAVE_ORBITALS command is used in conjunction with REMOVE. If this card is present, orbitals that are generated on the active subsystem are not deleted when calling REMOVE. By default, REMOVE will delete all records and orbitals that were saved by the embedding code. To use the EMBED,PROJ code in input file loops, the SAVE_ORBITALS card must not be present.

62.2.2 SCF Options in Regards to WF-in-DFT Embedding

The following options may be specified in the SCF directive in regards to WF-in-DFT embedding.

• HF_COR=value (default 1)
This option refers to the calculation of the first-order correction to the energy, described in the following paper:
The value \( \text{HF.COR}=1 \) causes the first-order correction to be calculated and automatically added to the energy. The value \( \text{HF.COR}=0 \) stops the first-order correction from being calculated.

\{ks\}
\{embed,proj;atoms,atom1,atom2,...\}
\{hf,hf_cor=0\}
\{ccsd(t)\}

### 62.3 Corrections to the non-additive exchange-correlation

Often the largest source of error in a WF-in-DFT calculation, relative to a WF calculation on the full system, results from evaluation of the exchange-correlation contributions to the embedding potential at the DFT level. This error can be largely removed by evaluating the exchange-correlation contributions to the embedding potential using MP2 theory. It is thus possible to calculate an MP2-level correction to the WF-in-DFT energies, as described in the following paper:


The MP2 correction can be invoked by running the \texttt{EMBED,PROJ,MP2\_CORR} command:

- \texttt{EMBED,PROJ,MP2\_CORR}
  \{ks\}
  \{embed,proj;atoms,atom1,atom2,...\}
  \{hf\}
  \{ccsd(t)\}
  \{embed,proj,mp2\_corr\}

By default, the program will calculate the MP2 correction using LMP2; however, any local method can be used. The program will search for a procedure named \texttt{PROC\_MP2\_CORR} and will use any location correlation method specified there. For example, including the following procedure at the top of the input file:

\texttt{PROC MP2\_CORR}
\{df-imp2,THRBP=1;orbital,5300.2\} ! Must be 5300.2
\ENDPROC

will calculate the MP2 correction with all pairs correlated using density fitting. Similarly,

\texttt{PROC MP2\_CORR}
\{df-lccsd,THRBP=0.99,throsv=1.d-4;orbital,5300.2\} ! Must be 5300.2
\ENDPROC

will calculate the MP2 correction using the orbital-specific virtual LCCSD method.
62.4 Improved efficiency using basis set truncation

By default, the calculation on the active subsystem is performed using all basis functions employed by the calculation on the full system. The computational cost of a high-level WF calculation on even a small active subsystem can thus be prohibitively high if the full system is sufficiently large. This cost can be greatly reduced by performing the calculation on the active subsystem using only the basis functions that are most important for representation of the MOs associated with the active subsystem. Two methods are implemented to facilitate truncation of the active subsystem basis set, and these methods are described in the subsections below.

62.4.1 Atom-based method

In the atom-based method for truncating the active subsystem basis set, only basis functions that are centered on atoms near the active subsystem are included in the active subsystem basis set. This method is described more detail in:


This method can be invoked using the BATOMS card:

- BATOMS, atom1, atom2, atom3...
  where atomi is the name of an atom from the geometry specification, and the atoms are listed in the order in which they appear in the geometry specification. The calculation on the active subsystem is performed using only basis functions centered on atoms listed by the BATOMS card.
  The minimum input to run using the BATOMS card is:
  \{ks\}
  \{embed, proj; atoms, atom1; batsoms, atom1\}
  \{hf\}
  \{ccsd(t)\}

Alternatively to using the BATOMS card, the user can instead specify the BASECUT option:

- BASECUT=value
  \{ks\}
  \{embed, proj, basecut=value; atoms, atom1\}
  \{hf\}
  \{ccsd(t)\}
  where value is a distance in Angstroms. The calculation on the active subsystem is performed using only basis functions centered on atoms within a distance BASECUT of an atom specified by the ATOMS card.

When employing basis set truncation, the embedding potential produced by the MOs in the frozen subsystem is only partially calculated using the numerically exact projection-based embedding method described in section 62. For MOs that have negligible Mulliken population on the basis functions that are employed in the calculation on the active subsystem, the non-additive kinetic energy contribution to embedding potential is calculated using the approximate Thomas-Fermi (TF) functional. Specifically, the TF functional is used for any MO in the frozen subsystem for which the sum of the absolute Mulliken populations on the atoms included by the BATOMS card or BASECUT option is less than the option \(\tau\) (default = 0.1). For closed-shell MOs, \(\tau\) should typically be in the range 0.0-2.0. Setting \(\tau\) to a value that is too close to zero can cause numerical artifacts that prevent convergence of the energy with respect to the value of the MU option (see subsection 62.1); as a result, it is recommended to perform all calculations with multiple values of MU to ensure that these numerical artifacts are not present.
62.4.2 Density threshold method

The density threshold truncation method is an alternative to the atom-based truncation method described in section 62.4.1. Its primary advantage is that it requires just one parameter to be adjusted for all types of molecular system and functions that are important in the long range are automatically kept. At its low truncation limit it produces the full basis embedding answer or at high truncation its limit is a result constructed from just the functions on the active embedding region. Application of this method involves slightly different input options:

- **AOTRUNC**
  The AOTRUNC option invokes the use of the density threshold method, and must always be be given when this method is used.

- **DENKEEP=value (default 0.0)**
  The DENKEEP option is the minimum gross Mulliken population that each basis function is compared against. Environment functions with a greater gross populations than this value are grouped (according to angular momentum partners i.e. px, with py and pz) and are kept. Environment functions lower than DENKEEP are grouped and discarded from the post embedding calculation. Setting DENKEEP=0.0 is equivalent to the case in which the basis set is not truncated as all functions have a gross population greater than 0. For accurate type-in-type energies, DENKEEP should typically be no more than 0.001, although convergence with respect to this parameter slightly varies according to the system and degree of delocalisation.

For example:

\{
  ks;orbital,2100.2
\}
\{
  ibba,bonds=1;orbital,2100.2;save,2300.2
\}
\{
  embed,proj,AOTRUNC,DENKEEP=0.001;orbital,2300.2,local
\}
\{hf\}
\{ccsd(t)\}

- **STOREAO**
  Enables the retention of selected functions along a geometry scan. This can be useful for basis set consistency for a dissociation reaction, which naturally would have fewer functions retained for a given threshold as the active and environment are separated. It is recommended that the calculations always go from associated to dissociated in order to benefit from this routine.

When using this method, the following should be taken into consideration:

1. The accuracy of this truncation method is sensitive to the size of the basis set. For this reason, it is recommended to use at least a triple-zeta basis set.
2. It is recommended to use Knizia’s IBO localization method, which reduces the orbital tails.
3. For accurate HF-in-HF and DFT-in-DFT results, it is recommended to use a value for DENKEEP of less than 0.0001. This is especially important when embedding across covalent bonds.
4. The geometry must be in Cartesian coordinates.

All publications resulting from the use of this method must acknowledge the following:


62.5 Examples

62.5.1 Projection-Based Embedding

This example performs a HF-in-HF and CCSD(T)-in-HF calculation on methanol. The HF-in-HF energy is numerically identical to the HF energy of the full system. By replacing the initial HF calculation on the full system with a DFT calculation, it is possible to perform HF-in-DFT and CCSD(T)-in-DFT calculations.
62.5.2 Embedded Multiconfigurational Calculations

This example performs an MCSCF-in-DFT calculation on butene.
!butene
memory,10,m
symmetry,nosym ! Embedding is not implemented with symmetry

{gthresh,grid=1e-12,orbital=1e-8,coeff=1e-7}

geometry={
  C1,, 0.835432384 , 0.049538050 , -1.305177530
  C2,, -0.187431703 , -1.125601622 , 1.070665830
  C3,, -0.143380420 , 0.687719249 , 3.341106035
  H1,, -2.118667450 , -1.789600571 , 0.735591607
  H2,, 0.942690000 , -2.802115823 , 1.537268881
  H3,, -0.860542916 , -0.240216354 , 5.042940132
  H4,, -1.309266799 , 2.354788168 , 2.978399494
  H5,, 1.778149207 , 1.339614495 , 3.742333311
  C4,, -0.440429873 , 0.344384131 , -3.450328416
  H6,, 2.782544497 , 0.715697009 , -1.20678342
  H7,, -0.434433198 , -1.089606640 , -4.914726597
  H8,, -1.545390643 , 2.035286250 , -3.818951212
} !Geometry is in Bohr

basis=6-31g*

! Step 1: Perform DFT on full system.
! Level shift added for improved convergence for this system.
! The system is a butene where the double bond is twisted by 90 degrees.
{rks,b-lyp,shifta=-0.3}

! Step 2: Call embedding code and specify the atoms corresponding to the twisted double bond.
{embed,proj;atoms,C1,C4,H6,H7,H8}

! Step 3: Generate initial orbitals for MCSCF.
{rhf}

! Step 4: Perform MCSCF calculation.
! When performing an embedded MCSCF calculation, always specify the active space.
{mcscf;
  config,csf;
  OCC,9;
  closed,7;
  frozen,2;}

! Step 5: Add dynamic correlation
{mrci}

! Step 6: Remove the projection operator from the core if additional calculations are given in the input after embedding.
{embed,proj,remove}

http://www.molpro.net/info/current/examples/embed_mrci.com

### 62.5.3 Atom-Based Truncation

This example performs an RCCSD(T)-in-B3LYP calculation on a water hexamer. The basis set used by the calculation on the active subsystem is truncated using the atom-based method.
!water hexamer
memory,10,m
symmetry,nosym ! Embedding is not implemented with symmetry

\{gthresh,grid=1e-12,orbital=1e-8,coeff=1e-7\}

Geometry=

\begin{align*}
\text{O1}, & \quad 30.135084563, -74.799706380, 1.048420054 \\
\text{H1}, & \quad 28.921313473, -75.753640128, 0.078612607 \\
\text{H2}, & \quad 31.789161840, -75.151195440, 0.241884944 \\
\text{O2}, & \quad 34.670994180, -75.109054547, -1.258935544 \\
\text{H3}, & \quad 36.151405626, -75.595470051, -0.256813780 \\
\text{H4}, & \quad 34.965413510, -73.329310483, -1.617038645 \\
\text{O3}, & \quad 39.016608376, -75.723971428, 1.713981595 \\
\text{H5}, & \quad 40.543885030, -76.445468862, 1.027066149 \\
\text{H6}, & \quad 39.369987161, -73.909078458, 1.857033863 \\
\text{O4}, & \quad 39.375845312, -70.481115268, 1.713981595 \\
\text{H7}, & \quad 37.857450371, -69.945566884, 0.797653397 \\
\text{H8}, & \quad 37.857450371, -69.945566884, 0.797653397 \\
\text{O5}, & \quad 30.452369580, -69.704059885, 1.057490739 \\
\text{O6}, & \quad 31.04659973, -71.541440596, 1.112103824 \\
\text{O7}, & \quad 33.76531785, -69.444222543, -0.300466454 \\
\end{align*}

!Geometry is in Bohr basis,VDZ

\begin{itemize}
\item \textbf{Step 1:} Perform a B3LYP calculation on the full system.
\{rks,B3LYP\}
\item \textbf{Step 2:} Perform orbital localization.
\{local,pipek;save,3101.2\}
\item \textbf{Step 3:} Call embedding code to generate the embedding potential.
\{embed,proj,mu=1.d6,tau=0.1,basecut=3.5;atoms,O1,H1,H2;orbital,3101.2,local\}
\item \textbf{Step 4:} Perform a HF-in-B3LYP calculation.
\{hf;noenest\}
\item \textbf{Step 5:} Perform an RCCSD(T)-in-B3LYP calculation.
\{rccsd(t)\}
\item \textbf{Step 6:} Remove the projection operator from the core if additional calculations
\ are given in the input after embedding.
\{embed,proj,remove\}
\end{itemize}

\url{http://www.molpro.net/info/current/examples/embed_trunc.com}

\subsection*{62.5.4 Density Threshold Truncation}

This example performs a CCSD(T)-in-B3LYP calculation on a water dimer, using the density-threshold method with a DENKEEP of 0.001.
!water dimer
!memory,150,m

{gthresh,orbital=1e-8,coeff=1e-7}

geometry=
O1,, 2.872302451 , -0.739837226 , 2.587473481
H11,, 1.114872273 , -1.362093804 , 2.841067168
H12,, 3.830013761 , -1.316171569 , 4.018958028
O2,, 1.378439935 , 3.695314083 , -0.113721828
H21,, 2.070708975 , 2.651580550 , 1.227452707
H22,, 2.064068477 , 2.891071211 , -1.605148488
} !Geometry is in Bohr

Basis,avtz

! Step 1: Perform a HF calculation on the full system
{hf}

! Step 2: Perform orbital localization.
{locali,pipek;save,3100.2}

! Step 3: Call embedding code to generate the embedding potential
! using truncation with the density threshold method.
{embed,proj,N_orbitals=5,Aotrunc,DENKEEP=0.0001;atoms,O1,H11,H12;orbital,3100.2,local}

! Step 4: Perform a HF-in-HF calculation
{hf;noenest;wf,10}

! Step 5: Perform a CCSD(T)-in-HF calculation
{ccsd(t);wf,10}

! Step 6: Remove the projection operator from the core if additional calculations
! are given in the input after embedding
{embed,proj,remove}

http://www.molpro.net/info/current/examples/embed_trunc2.com

62.5.5 Open Shell System

This example performs a RCCSD(T)-in-LDA calculation on the methoxy radical.
Methoxy Radical
memory,8,M
zsymel=nosym  Embedding is not implemented with symmetry

(gthresh,grid=1e-12,orbital=1e-8,coeff=1e-7)

Geometry=
O1,, 2.328578323 , -0.516253350 , -0.241152468
H1,, -3.930899693 , 0.818199944 , 0.136592671
C1,, -2.292181882 , -0.433746123 , -0.018359872
H2,, -2.391620554 , -1.802771746 , 1.530291417
C2,, 0.160581025 , 1.056429748 , 0.096479104
H3,, 0.284618712 , 2.116540479 , 1.878957579
H4,, 0.248705545 , 2.426749515 , -1.444737877
H5,, -2.407046505 , -1.464278195 , -1.802909809
! Geometry is in Bohr

basis,6-31g

! Step 1: Perform a DFT calculation on the full system.
(ks,lda;wf,25,1,1)

! Step 2: Perform orbital localization.
(locali,pipek;save,3100.2)

! Step 3: Call embedding code to generate the embedding potential.
{embed,proj,mu=1d5;atoms,O1}

! Step 4: Now call HF, but this time only subsystem A will be calculated.
! This corresponds to a HF-in-LDA calculation.
{hf}

! Step 5: Now call CCSD(T). This will perform a RCCSD(T)-in-LDA calculation
{rccsd(t)}

! Step 6: Remove the projection operator from the core if addition calculations
! are given in the input after embedding.
{embed,proj,remove}

http://www.molpro.net/info/current/examples/embed_open.com

63  THE TDHF AND TDKS PROGRAMS

Real-time electronic dynamics using time-dependent Hartree-Fock and time-dependent Kohn-Sham theories can be performed using the commands TDHF and TDKS respectively, which have to be preceded by a HF and KS command. Unrestricted versions are available through TDUHF and TDUKS and should be preceded by UHF and UKS runs respectively. All methods require symmetry to be switched off. For details on the theory and methods see H. Eshuis, G. G. Balint-Kurti and F. R. Manby, J. Chem. Phys. 128, 114113 (2008), and references therein. The commands take several options:

command, t=, dt=, ns=, ng=, grsize=, print=;
PULSE, options

The total propagation time (in au) is set by $t$; $dt$ sets the timestep and $ns$ the number of steps, where two of the three have to be provided. $ng$ sets the number of grid points in one dimension (default = 0) and grsize the grid size in bohr (default = 10 bohr). Setting $ng > 2$ switches on the calculation of quantum currents (see below). The option $print$ determines the level of output (0=normal output, 1=object linear
in matrices, 2=matrices as well, > 2 debug). The subcommand PULSE determines the envelope used, and takes several options depending on the envelope selected. Possibilities are:

NONE: no pulse, no options
STEP, \( e_x, e_y, e_z, \text{length} \)
a DC-field of strength \( e_q \) is applied in the \( q \)th direction for a total time \( \text{length} \) (in au)
DC, \( e_x, e_y, e_z, \alpha \)
a DC-field of strength \( e_q \) is applied in the \( q \)th direction. The field is switched on exponentially with a rate determined by \( \alpha \).
TRAP, \( e_x, e_y, e_z, \omega, \alpha \)
an oscillating field of strength \( e_q \) is applied in the \( q \)th direction. The field oscillates with angular frequency \( \omega \). The envelope reaches \( e_q \) in one period of the field, stays constant for \( \alpha \) periods and then decays to zero in one period.
CW, \( e_x, e_y, e_z, \omega \)
an oscillating field of strength \( e_q \) is applied in the \( q \)th direction. The field oscillates with angular frequency \( \omega \). No envelope present.
CWSIN, \( e_x, e_y, e_z, \omega, \alpha \)
an oscillating field of strength \( e_q \) is applied in the \( q \)th direction. The field oscillates with angular frequency \( \omega \) and is switched on using a \( \sin^2 \) envelope, where \( \alpha \) determines how fast the field is switched on.
CWGAUSS, \( e_x, e_y, e_z, \omega, \alpha \)
like CWSIN, but with a Gaussian envelope

The finite pulses TRAP and STEP produce an absorption spectrum obtained from the time-dependent dipole moment sampled after the field is switched off. It is located in \((\text{input}).\text{spec}\), or in molpro.spec when running interactively, and contains 4 columns, which contain energy (eV) and the absorption in the \( x, y, z \) direction respectively.

All runs produce a file \((\text{input}).\text{dat}\) (or molpro.dat) which contains time-dependent properties, like the components of the field, components of the dipole moment, total energy, orbital occupation numbers, orbital energies and total number of electrons. The Molpro output file specifies the order of the data in the file. For very long runs the size of the file is restricted by printing only every twentieth set of data.

In case of an unrestricted run three files are produced: \((\text{input}).\text{dat}\), \((\text{input})a.\text{dat}\), \((\text{input})b.\text{dat}\). The first file contains the generic data about the field, total energy, dipole moments and the expectation value of the total spin operator. The other two files contain the orbital energies and occupation numbers for the \( \alpha \) and \( \beta \) electrons respectively.

TDKS and TDUKS use the options provided by the KS and UKS commands. At the moment TDKS/TDUKS suffers from numerical instabilities when using strong fields. Divergence of the energy is observed, possibly due to the use of quadrature for the evaluation of the potential.

Quantum currents will be calculated when choosing \( ng > 2 \). A cubic grid will be computed of size \( grsize \) with a total of \( ng^3 \) gridpoints. The imaginary part of the density will be summed at every timestep and after the dynamics the total current will be evaluated at every gridpoint. The user can extract the required data from this array by printing out parts of it, or by integrating over point, but this requires actual coding, as this has not been implemented sufficiently neat. It is also straightforward to evaluate the currents at every timestep or at selected timesteps. This is not done automatically, because it slows down the dynamics considerably.

64 ORBITAL MERGING

Orbitals can be manipulated using the MERGE facility. For instance, this allows the construction of molecular orbitals from atomic orbitals, to merge and orthogonalize different orbital sets, or to perform \( 2 \times 2 \) rotations between individual orbitals. Other orbital manipulations can be performed using the LOCALI program (see section 18) or the MATROP program (section 65).
The merge program is called using

```
MERGE [namout.file]
```

All subcommands described in the following sections may be abbreviated by three characters. `namout.file` specifies the output data set (see also `SAVE` command). If `namout.file` is omitted and no `SAVE` card is present, the new orbitals are not saved. All output orbitals must be supplied via `ORBITAL` and `ADD`, `MOVE`, `EXTRA`, or `PROJECT` directives before they can be saved.

### 64.1 Defining the input orbitals (ORBITAL)

```
ORBITAL,namin.file.specifications
```

Reads an input orbital set from a dump record. `specifications` can be used to select specific orbital sets, as described in section 4.11. Subsets of these orbitals can be added to the output set by the `ADD`, `MOVE`, or `EXTRA` commands.

### 64.2 Moving orbitals to the output set (MOVE)

```
MOVE,orb1.sym1,orb2.sym2,orb3.sym3,ioff,fac,istart,iend
```

Moves orbitals `orb1.sym1` to `orb2.sym2` from the input set to the first vector of symmetry `sym3` in the output set which is undefined so far. The first `orb3-1` vectors in the output set are skipped regardless of whether they have been defined before or not. If `sym2 > sym1`, `sym3` will run from `sym1` to `sym2` and the input for `sym3` has no effect. If `orb1.sym1` is negative, `abs(orb1)` is the maximum number of orbitals to be moved, starting with orbital `1.sym1` to `orb2.sym2`. If `orb2.sym2` is negative, `abs(orb2)` is the maximum number of vectors to be moved, starting at `orb1.isym1` to the last orbital in symmetry `sym2`.

Orbitals from the input set which have already been moved or added to the output set are generally skipped. If `orb1` and `orb2` are zero, the whole input set is moved to the output set. In this case the input and output dimensions must be identical. If `orb1` is nonzero but `orb2` is zero, `orb2` is set to the last orbital in symmetry `sym2`. If `sym2=0`, `sym2` is set to `sym1`. `ioff` is an offset in the output vector, relative to the global offset set by `OFFSET` directive. `fac` has no effect for move. The elements `istart` to `iend` of the input vector are moved. If `istart=0` and `iend=0`, the whole input vector is moved.

The usage of the `MOVE` directive is most easily understood by looking at the examples given below. See also `ADD` and `EXTRA` commands.

### 64.3 Adding orbitals to the output set (ADD)

```
ADD,orb1.sym1,orb2.sym2,orb3.sym3,ioff,fac,istart,iend
```

This adds orbitals `orb1.sym1` to `orb2.sym2` to the output vectors, starting at `orb3(sym3)`. The input vectors are scaled by the factor `fac`. If `fac=0`, `fac` is set to 1.0. For other details see `MOVE` command. Note, however, that the output vectors which have already been defined are not skipped as for `MOVE`.

See also `MOVE` and `EXTRA` commands.

### 64.4 Defining extra symmetries (EXTRA)

```
EXTRA,exsym,orb1.sym1,orb2.sym2,orb3.sym3,ioff,fac,istart,iend
```

Works exactly as `MOVE`, but only input vectors with extra symmetry `exsym` are considered. If `orb1.sym1` and `orb2.sym2` are zero, all input vectors are moved to the output set ordered according to increasing extra symmetries.

Examples:
EXTRA, 1, -4.1 will move the next 4 orbitals in symmetry 1 which have extra symmetry 1. Orbitals which have been moved before are skipped.

EXTRA, 2, 1.1 will move all orbitals of symmetry 1 which have extra symmetry 2. Orbitals which have been moved before are skipped.

EXTRA will move all orbitals (all symmetries) and order them according to extra symmetries.

EXTRA, 3, 1.1, 0.8 Will move all orbitals which have extra symmetry 3 in all symmetries. Orbitals which have been moved before are skipped.

See also ADD and MOVE commands.

64.5 Defining offsets in the output set (OFFSET)

OFFSET, iоф1, iоф2, ..., iоф8;

Sets offsets in the output vector for symmetries 1 to 8. In subsequent MOVE or ADD commands, the input vectors are moved to the locations $iоф1 + i$ in the output vectors. The offset for individual ADD or MOVE commands can be modified by the parameter $iоф$ on these cards. This card should immediately follow the orbital directive to which it applies. Generally, this card is only needed if the dimensions of input and output vectors are not identical.

If the dimensions of the input orbital sets are smaller than the current basis dimension, the offsets are determined automatically in the following way: each time an orbital set is read in, the previous input orbital dimensions are added to the offsets. Hence, this works correctly if the orbital sets are given in the correct order and if the individual dimensions add up to the current total dimension. If this is not the case, the offsets should be specified on an OFFSET card which must follow the orbital directive.

64.6 Projecting orbitals (PROJECT)

PROJECT, namin.file

This command will read vectors from record namin.file. These vectors must have the same dimension as those of the current calculation. All orbitals defined so far by the ORBITAL, MOVE, and ADD directives are projected out of the input set. The projected orbitals are then orthonormalized and moved to the undefined output vectors. This should always yield a complete set of vectors.

64.7 Symmetric orthonormalization (ORTH)

ORTH, n1, n2, ..., n8

Symmetrically orthonormalizes the first $n_i$ vectors in each symmetry $i$. These vectors must be supplied before by ORBITAL and MOVE or ADD directives.

64.8 Schmidt orthonormalization (SCHMIDT)

SCHMIDT, n1, n2, ..., n8

Schmidt orthonormalizes the first $n_i$ vectors in each symmetry $i$. These vectors must be supplied before by ORBITAL and MOVE or ADD directives.

64.9 Rotating orbitals (ROTATE)

ROTATE, iorb1.sym, iorb2, angle

Will perform $2 \times 2$ rotation of orbitals $iorb1$ and $iorb2$ in symmetry $sym$ by the specified angle (in degree). $angle=0$ means to swap the orbitals (equivalent to $angle=90$). These vectors must be supplied before by ORBITAL and MOVE or ADD directives.
**64.10 Initialization of a new output set (INIT)**

`INIT,namout.file`

Will initialize a new output set. All previous vectors in the output set are lost unless they have been saved by a `SAVE` directive!

**64.11 Saving the merged orbitals**

`SAVE,namout.file`

Saves the current output set to record `namout.file`. The current output set must be complete and will be Schmidt orthonormalized before it is saved. If the `SAVE` directive is not supplied, the output vectors will be saved after all valid commands have been processed to the record specified on the `MERGE` card.

**64.12 Printing options (PRINT)**

`PRINT,iprint,ideb`

Specifies print options.

- `iprint = 0`:
  - no print
- `iprint ≥ 1`:
  - orthonormalized orbitals specified on `ORTH` card are printed.
- `iprint ≥ 2`:
  - orbitals are also printed before this orthonormalization.
- `iprint ≥ 3`:
  - all final vectors are printed.
- `ideb ≠ 0`:
  - the overlap matrices are printed at various stages.

**64.13 Examples**

**64.13.1 H₂F**

This example merges the orbitals of H₂ and F
This example merges the SCF orbitals of N and O to get a full valence space for NO. In the simplest case the atomic calculations are performed in the individual separate basis sets, but using the same symmetry ($\text{C}_2\text{v}$) as the molecular calculation.
One can also do the atomic calculations in the total basis set, using dummy cards. In this case the procedure is more complicated, since the union of the two orbital spaces is over-complete. The calculation can be done as follows:

a) SCF for the total molecule, orbitals saved to 2100.2

b) SCF for the N atom with dummy basis on the O atom, orbitals saved on 2110.2

c) SCF for the O atom with dummy basis on the N atom, orbitals saved on 2120.2

d) Merge the atomic SCF orbitals. Finally, obtain the virtual orbitals by projecting the merge orbitals out of the SCF orbitals for NO.

http://www.molpro.net/info/current/examples/no_merge1.com
http://www.molpro.net/info/current/examples/no_merge2.com

65 MATRIX OPERATIONS

MATROP:

MATROP performs simple matrix manipulations for matrices whose dimensions are those of the one particle basis set. To do so, first required matrices are loaded into memory using the LOAD command. To each matrix an internal name (an arbitrary user defined string) is assigned, by which it is referenced in further commands. After performing operations, the resulting matrices can be saved to a dump record using the SAVE directive. Numbers, e.g. traces or individual matrix elements, can be saved in variables. code may be one of the following:

http://www.molpro.net/info/current/examples/no_merge2.com
LOAD
Loads a matrix from a file
SAVE
Saves a matrix to a file
ADD
Adds matrices
TRACE
Forms the trace of a matrix or of the product of two matrices
MULT
Multiplies two matrices
TRAN
Transforms a matrix
DMO
Transforms density into MO basis
NATORB
Computes natural orbitals
DIAG
Diagonalizes a matrix
OPRD
Forms an outer product of two vectors
DENS
Forms a closed-shell density matrix
FOCK
Computes a closed-shell fock matrix
COUL
Computes a coulomb operator
EXCH
Computes an exchange operator
PRINT
Prints a matrix
PRID
Prints diagonal elements of a matrix
PRIO
Prints orbitals
PRIC
Prints the transpose of a matrix in scientific notation
ELEM
Assigns a matrix element to a variable
READ
Reads a square matrix from input
WRITE
Writes a square matrix to a file
SET
Assigns a value to a variable
ADDVEC
Adds a multiple of a column of one matrix to a column of a second matrix

Note that the file name appearing in above commands is converted to lower case on unix machines.

See the following subsections for explanations.

65.1 Calling the matrix facility (MATROP)

The program is called by the input card MATROP without further specifications.

MATROP

It can be followed by the following commands in any order, with the restriction that a maximum of 50 matrices can be handled. The first entry in each command line is a command keyword, followed by the name of the result matrix. If the specified result matrix result already exists, it is overwritten, otherwise a new matrix is created. All matrices needed in the operations must must have been loaded or defined before, unless otherwise stated.

If a backquote (') is appended to a name, the matrix is transposed.

65.2 Loading matrices (LOAD)

All matrices which are needed in any of the subsequent commands must first be loaded into memory using the LOAD command. Depending on the matrix type, the LOAD command has slightly different options. In all forms of LOAD name is an arbitrary string (up to 16 characters long) by which the loaded matrix is denoted in subsequent commands.
65.2.1 Loading orbitals

LOAD, name, ORB [record] [specifications]

loads an orbital coefficient matrix from the given dump record. If the record is not specified, the last dump record is used. Specific orbitals sets can be selected using the optional specifications, as explained in section 4.11. The keyword ORB needs not to be given if name=ORB.

65.2.2 Loading density matrices

LOAD, name, DEN [record] [specifications]

loads a density matrix from the given dump record. If the record is not given, the last dump record is used. Specific densities sets can be selected using the optional specifications, as explained in section 4.11. The keyword DEN needs not to be given if name=DEN.

Example,
load, trdm, dens, 6000.2, stateb=1.1, statek=3.2

loads a transition density matrix that has previously been saved on record 6000.2. The bra state is the first state in symmetry 1, and ket is the third state in symmetry 2.

An equivalent input would be
load, trdm, dens, 6000.2, stateb=1, statek=3, symb=1, symk=2

65.2.3 Loading the AO overlap matrix S

LOAD, name, S

loads the overlap matrix in the AO basis. The keyword S needs not to be given if name=S.

65.2.4 Loading S$^{-1/2}$

LOAD, name, SMH

loads S$^{-1/2}$, where S is the overlap matrix in the AO basis. The keyword SMH needs not to be given if name=SMH.

65.2.5 Loading the one-electron hamiltonian

LOAD, name, H0

LOAD, name, H01

loads the one-electron hamiltonian in the AO basis. H01 differs from H0 by the addition of perturbations, if present (see sections 38.5.1, 38.5.2). The keyword H0 (H01) needs not to be given if name=H0 (H01). The nuclear energy associated to H0 or H01 is internally stored.

65.2.6 Loading the kinetic or potential energy operators

LOAD, name, EKIN

LOAD, name, EPOT

loads the individual parts of the one-electron hamiltonian in the AO basis. EPOT is summed for all atoms. The nuclear energy is associated to EPOT and internally stored. The keyword EKIN (EPOT) needs not to be given if name=EKIN (EPOT).
65.2.7 Loading one-electron property operators

\[ \text{LOAD}, \text{name}, \text{OPER}, \text{opname}, [\text{isym}], x, y, z \]

loads one-electron operator opname, where opname is a keyword specifying the operator (a component must be given). See section 6.13 for valid keys. isym is the total symmetry of the operator (default 1), and x, y, z is the origin of the operator. If the operator is not available yet in the operator record, it is automatically computed. The nuclear value is associated internally to name and also stored in variable OPNUC (this variable is overwritten for each operator which is loaded, but can be copied to another variable using the SET command. Note that the electronic part of dipole and quadrupole operators are multiplied by -1.

65.2.8 Loading matrices from plain records

\[ \text{LOAD}, \text{name}, \text{TRIANG}, \text{record}, [\text{isym}] \]
\[ \text{LOAD}, \text{name}, \text{SQUARE}, \text{record}, [\text{isym}] \]

Loads a triangular or square matrix from a plain record (not a dump record or operator record). If isym is not given, 1 is assumed.

65.3 Saving matrices (SAVE)

\[ \text{SAVE}, \text{name}, \text{record}, [\text{type}] \]

At present, type can be DENSITY, ORBITALS, FOCK, H0, ORBEN, OPER, TRIANG, SQUARE, or VECTOR. If type is not given but known from LOAD or another command, this is assumed. Orbitals, density matrices, fock matrices, and orbital energies are saved to a dump record (the same one should normally be used for all these quantities). If type is H0, the one-electron hamiltonian is overwitten by the current matrix and the nuclear energy is modified according to the value associated to name. The nuclear energy is also stored in the variable ENUC. All other matrices can be saved in triangular or square form to plain records using the TRIANG and SQUARE options, respectively (for triangular storage, the matrix is symmetrized before being stored). Eigenvectors can be saved in plain records using the VECTOR option. Only one matrix or vector can be stored in each plain record.

One-electron operators can be stored in the operator record using

\[ \text{SAVE}, \text{name}, \text{OPER}, [\text{PARITY}=\text{np}], [\text{NUC}=	ext{opnuc}], [\text{CENTRE}=\text{icen}], [\text{COORD}=[x,y,z]] \]

The user-defined operator name can then be used on subsequent EXPEC or GEXPEC cards. np = 1, 0, \(-1\) for symmetric, square, antisymmetric operators, respectively (default 1). If CENTRE is specified, the operator is assumed to have its origin at the given centre, where icen refers to the row number of the z-matrix input. The coordinates can also be specified explicitly using COORD. By default, the coordinates of the last read operator are assumed, or otherwise zero.

If NATURAL orbitals are generated and saved in a dump record, the occupation numbers are automatically stored as well. This is convenient for later use, e.g., in MOLDEN.

65.4 Adding matrices (ADD)

\[ \text{ADD}, \text{result}, [\text{fac1}], \text{mat1}, [\text{fac2}], \text{mat2}, \ldots \]

calculates result = fac1 \cdot mat1 + fac2 \cdot mat2 + \ldots

The strings result, mat1, mat2 are internal names specifying the matrices. mat1, mat2 must exist, otherwise an error occurs. If result does not exist, it is created.

The factors fac1, fac2 are optional (may be variables). If not given, one is assumed.

The nuclear values associated to the individual matrices are added accordingly and the result is associated to result.
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65.5 Trace of a matrix or the product of two matrices (TRACE)

TRACE, variable, mat1, [factor]
Computes variable = factor*\text{tr}(mat1).

TRACE, variable, mat1, mat2, [factor], [facnuc]
Computes variable = factor*\text{tr}(mat1 \cdot mat2) + facnuc*opnuc.

The result of the trace operation is stored in the MOLPRO variable variable, which can be used in subsequent operations.

If factor is not given, one is assumed. If facnuc is given, the nuclear contribution multiplied by facnuc is added. It is assumed that either mat1 or mat2 has a nuclear contribution. The default for facnuc is zero.

65.6 Setting variables (SET)

SET, variable, value
Assigns value to MOLPRO variable variable, where value can be an expression involving any number of variables or numbers. Indexing of variable is not possible, however.

65.7 Multiplying matrices (MULT)

MULT, result, mat1, mat2, [fac1], [fac2]
calculates result = fac2 * result + fac1 * mat1 \cdot mat2

The strings result, mat1, mat2 are the internal names of the matrices. If fac1 is not given, fac1=1 is assumed. If fac2 is not given, fac2=0 is assumed. If a backquote (’) is appended to mat1 or mat2 the corresponding matrix is transposed before the operation. If a backquote is appended to result, the resulting matrix is transposed.

65.8 Transforming operators (TRAN)

TRAN, result, Op, C
calculates result = C(T)*Op*C. The strings result, C, and Op are the internal names of the matrices. If a backquote (’) is appended to C or Op the corresponding matrix is transposed before the operation. Thus, TRAN, result, Op, C’
computes result = C*Op*C(T).

65.9 Transforming density matrices into the MO basis (DMO)

DMO, result, D, C
calculates result = C(T)*S*D*S*C. The strings result, C, and D are internal names.

65.10 Diagonalizing a matrix (DIAG)

DIAG, eigvec, eigval, matrix [, iprint]
Diagonalizes matrix. The eigenvectors and eigenvalues are stored internally with associated names eigvec and eigval, respectively (arbitrary strings of up to 16 characters). The if iprint.gt.0, the eigenvalues are printed. If iprint.gt.1, also the eigenvectors are printed.
65.11 Generating natural orbitals (NATORB)

\[ \text{NATORB, name, dens, thresh} \]

computes natural orbitals for density matrix \( \text{dens} \). Orbitals with occupation numbers greater or equal to \( \text{thresh} \) (default 1.d-4) are printed.

65.12 Forming an outer product of two vectors (OPRD)

\[ \text{OPRD, result, matrix, orb1, orb2, factor} \]

Takes the column vectors \( v1 \) and \( v2 \) from \( \text{matrix} \) and adds their outer product to \( \text{result} \). \( v1 \) and \( v2 \) must be given in the form \( icol.isym \), e.g., 3.2 means the third vector in symmetry 2. The result is \( \text{result}(a,b) = \text{result}(a,b) + \text{factor} \times v1(a) \times v2(b) \)

If \( \text{result} \) has not been used before, it is zeroed before performing the operation.

65.13 Combining matrix columns (ADDVEC)

\[ \text{ADDVEC, result, orbr, source, orbs, factor} \]

Takes the column vector \( \text{orbs} \) from \( \text{source} \) and adds it to column \( \text{orbr} \) of \( \text{result} \). \( v1 \) and \( v2 \) must be given in the form \( icol.isym \), e.g., 3.2 means the third vector in symmetry 2.

65.14 Forming a closed-shell density matrix (DENS)

\[ \text{DENS, density, orbitals, iocc1, iocc2 ...} \]

Forms a closed-shell density matrix \( \text{density} \) from the given \( \text{orbitals} \). The number of occupied orbitals in each symmetry \( i \) must be provided in \( \text{iocc}i \).

65.15 Computing a fock matrix (FOCK)

\[ \text{FOCK, f, d} \]

computes a closed shell fock matrix using density \( d \). The result is stored in \( f \).

65.16 Computing a coulomb operator (COUL)

\[ \text{COUL, J, d} \]

computes a coulumb operator \( J(d) \) using density \( d \).

65.17 Computing an exchange operator (EXCH)

\[ \text{EXCH, K, d} \]

computes an exchange operator \( K(d) \) using density \( d \).

65.18 Printing matrices (PRINT)

\[ \text{PRINT, name, [ncol(1), ncol(2), ...]} \]

prints matrix \( \text{name} \). \( \text{ncol(isym)} \) is the number of columns to be printed for row symmetry \( isym \) (if not given, all columns are printed). For printing orbitals one can also use \text{ORB}.
65.19  Printing diagonal elements of a matrix (PRID)

PRID, name prints the diagonal elements of matrix name.

65.20  Printing orbitals (PRIO)

PRIO, name, n1, n2, n3, ..., n8

prints orbitals name. The first ni orbitals are printed in symmetry i. If ni = 0, all orbitals of that symmetry are printed.

65.21  Printing a matrix transpose in scientific notation (PRIC)

PRIC, name, [ncol(1), ncol(2), ...]

prints the transpose of matrix name in scientific notation (comma delimited). ncol(isym) is the number of columns to be printed for row symmetry isym (if not given, all columns are printed). For printing orbitals one can also use ORB.

65.22  Assigning matrix elements to a variable (ELEM)

ELEM, name, matrix, col, row

assigns elements (col, row) of matrix to variable name. col and row must be given in the form number.isym, where number is the row or column number in symmetry isym. The product of the row and column symmetries must agree with the matrix symmetry.

65.23  Setting a matrix element to a variable (POKE)

POKE, name, matrix, col, row

sets elements (col, row) of matrix to variable name. col and row must be given in the form number.isym, where number is the row or column number in symmetry isym. The product of the row and column symmetries must agree with the matrix symmetry.

65.24  Reading a matrix from the input file (READ)

READ, name, [[TYPE=type], [[SUBTYPE=subtype], [[SYM=symmetry]], [FILE=file]

{ values }

Reads a square matrix (symmetry 1) from input or an ASCII file. The values can be in free format, but their total number must be correct. Comment lines starting with '#', '*', or '!' are skipped. If the data are given in input, the data block must be enclosed either by curly brackets or the first line must be BEGIN_DATA and the last line END_DATA. If a filename is specified as option, the data are read from this file. In this case, the BEGIN_DATA, END_DATA lines in the file are optional, and no data block must follow.

For compatibility with older versions, the data can also be included in the input using the INCLUDE command (see section 3.1). In this case, the include file must contain the BEGIN_DATA and END_DATA lines (this is automatically the case if the file has been written using the MATROP, WRITE directive).

type is a string which can be used to assign a matrix type. If appropriate, this should be any of the ones used in the LOAD command. In addition, SUBTYPE can be specified if necessary. This describes, e.g., the type of orbitals or density matrices (e.g., for natural orbitals TYPE=ORB and SUBTYPE=NATURAL). The matrix symmetry needs to be given only if it is not equal to 1.
65.25 Writing a matrix to an ASCII file (WRITE)

WRITE.name,[filename [status]]

Writes a matrix to an ASCII file. If filename is not given the matrix is written to the output file, otherwise to the specified file (filename is converted to lower case). If filename=PUNCH it is written to the current punch file.

If status=NEW, ERASE or em REWIND, a new file is written, otherwise as existing file is appended.

65.26 Examples

The following example shows various uses of the MATROP commands.

```plaintext
*** h2o matrop examples
geometry={o;h1,o,r;h2,o,r,h1,theta} !Z-matrix geometry input
r=1 ang !bond length
theta=104 !bond angle
hf
{multi
natorb
canonical}
{matrop
load,D_ao,DEN,2140.2 !load mcscf density matrix
load,Cnat,ORB,2140.2,natural !load mcscf natural orbitals
load,Ccan,ORB,2140.2,canonical !load mcscf canonical orbitals
load,Dscf,DEN,2100.2 !load scf density matrix
load,S !load overlap matrix
prio,Cnat,4,1,2 !prints occupied casscf orbitals
elem,d11,Dscf,1.1,1.1 !print element D(1,1)
elem,d21,Dscf,2.1,1.1 !print element D(2,1)
elem,d12,Dscf,1.1,2.1 !print element D(1,2)
tran,S_mo,s,Cnat !transform s into MO basis (same as above)
print,S_mo !print result - should be unit matrix
trace,Nel,D_ao,S !form trace(DS) = number of electrons
mult,SC,S,Cnat !form SC=S*Cnat
tran,D_nat,D_ao,SC !transform density to natural MO (could also be done using dmo)
prio,D_nat !print diagonal elements (occupation numbers)
dmo,D_can,D_ao,Ccan !transform D_ao to canonical MO basis. Same as above simplification
add,D_neg,-1,D_can !multiply d_can by -1
diag,U,EIG,D_neg !diagonalizes density D_can
mult,Cnati,Ccan,U !transforms canonical orbitals to natural orbitals
prio,Cnati,4,1,2 !prints new natural orbitals
natorb,Cnat2,D_ao !make natural orbitals using MCSCF density D_ao directly
prio,Cnat2,4,1,2 !prints new natural orbitals (should be the same as above simplification)
add,diffden,D_ao,-1,Dscf !form mcscf-scf difference density
natorb,C_diff,diffden !make natural orbitals for difference density
write,diffden,denfile !write difference density to ASCII file denfile
save,C_diff,2500.2 !store natural orbitals for difference density in dump record
```

http://www.molpro.net/info/current/examples/matrop.com
This second example adds a quadrupole field to $H_0$. The result is exactly the same as using the QUAD command. $H_0$ is overwritten by the modified one-electron matrix, and the nuclear energy is automatically changed appropriately. The subsequent SCF calculations use the modified one-electron operator.

Note that it is usually recommended to add fields with the DIP, QUAD, or FIELD commands.

```
http://www.molpro.net/info/current/examples/matropfield.com
```

### 65.27 Exercise: SCF program

Write a closed-shell SCF program for $\text{H}_2\text{O}$ using MATROP!

**Hints:**

First generate a starting orbital guess by finding the eigenvectors of $h_0$. Store the orbitals in a record. Basis and geometry are defined in the usual way before the first call to MATROP.

Then use a MOLPRO DO loop and call MATROP for each iteration. Save the current energy in a variable (note that the nuclear energy is stored in variable ENUC). Also, compute the dipole moment in each iteration. At the end of the iteration perform a convergence test on the energy change using the IF command. This must be done outside MATROP just before the ENDDO. At this stage, you can also store the iteration numbers, energies, and dipole moments in arrays, and print these after reaching convergence using TABLE. For the following geometry and basis set

```
geometry={o;h1,o,r;h2,o,r,h1,theta} !Z-matrix geometry input
```
the result could look as follows:

SCF has converged in 24 iterations

<table>
<thead>
<tr>
<th>ITER</th>
<th>E</th>
<th>DIP</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>-68.92227207</td>
<td>2.17407361</td>
</tr>
<tr>
<td>2.0</td>
<td>-71.31376891</td>
<td>-5.06209922</td>
</tr>
<tr>
<td>3.0</td>
<td>-73.73536433</td>
<td>2.10199751</td>
</tr>
<tr>
<td>4.0</td>
<td>-74.64753557</td>
<td>-1.79658706</td>
</tr>
<tr>
<td>5.0</td>
<td>-75.41652680</td>
<td>1.43669203</td>
</tr>
<tr>
<td>6.0</td>
<td>-75.77903293</td>
<td>0.17616098</td>
</tr>
<tr>
<td>7.0</td>
<td>-75.93094231</td>
<td>1.05644998</td>
</tr>
<tr>
<td>8.0</td>
<td>-75.98812258</td>
<td>0.63401784</td>
</tr>
<tr>
<td>9.0</td>
<td>-76.00939154</td>
<td>0.91637513</td>
</tr>
<tr>
<td>10.0</td>
<td>-76.01708679</td>
<td>0.76319435</td>
</tr>
<tr>
<td>11.0</td>
<td>-76.01988143</td>
<td>0.86107911</td>
</tr>
<tr>
<td>12.0</td>
<td>-76.02088864</td>
<td>0.80513445</td>
</tr>
<tr>
<td>13.0</td>
<td>-76.02125263</td>
<td>0.83990621</td>
</tr>
<tr>
<td>14.0</td>
<td>-76.02138387</td>
<td>0.81956198</td>
</tr>
<tr>
<td>15.0</td>
<td>-76.02143124</td>
<td>0.83202128</td>
</tr>
<tr>
<td>16.0</td>
<td>-76.02144833</td>
<td>0.82464809</td>
</tr>
<tr>
<td>17.0</td>
<td>-76.02145450</td>
<td>0.82912805</td>
</tr>
<tr>
<td>18.0</td>
<td>-76.02145672</td>
<td>0.82646089</td>
</tr>
<tr>
<td>19.0</td>
<td>-76.02145752</td>
<td>0.82807428</td>
</tr>
<tr>
<td>20.0</td>
<td>-76.02145781</td>
<td>0.82711046</td>
</tr>
<tr>
<td>21.0</td>
<td>-76.02145792</td>
<td>0.82769196</td>
</tr>
<tr>
<td>22.0</td>
<td>-76.02145796</td>
<td>0.82734386</td>
</tr>
<tr>
<td>23.0</td>
<td>-76.02145797</td>
<td>0.82755355</td>
</tr>
<tr>
<td>24.0</td>
<td>-76.02145797</td>
<td>0.82742787</td>
</tr>
</tbody>
</table>

It does not converge terribly fast, but it works!
66 Post-processing of output and databases

66.1 Output

MOLPRO produces an output file that is in XML format with appropriate mark-up for all important results. This file, which has a .xml suffix, is normally filtered into a plain-text file (.out suffix) with all of the mark-up removed, for more convenient browsing. The XML file conforms strictly to a well-defined schema, and the the schema definition file molpro-output.xsd can be found in the main MOLPRO source or installation tree in the directory lib/schema. The principal elements of marked-up output are

- **jobstep**: The results from one job step.
- **molecule**: A container for data on a single molecule.
- **cml:molecule**: Molecular geometry in the Chemical Markup Language (CML) format.
- **property**: A computed property, for example an energy or dipole moment.
- **table**: The output of MOLPRO's TABLE command in XHTML format.
- **basisSet**: A self-contained description of the orbital basis set.
- **orbitals**: A set of orbitals.
- **vibrations**: Harmonic normal vibrational modes.
- **variables**: MOLPRO's internal variables.
- **platform**: Information about the computing system on which a job was run.

Not all of these elements are produced by default in the regular job transcript .xml file; some of them can result from using the PUT,XML to make a separate dump file.

molpro-output is understood by several post-processing programs, including Jmol (http://www.jmol.org) and its derivative molproView (http://www.molpro.net/molproView).

66.2 Databases

A facility is provided to store and interrogate sets of molecules, together with information about how they are to be combined in balanced chemical equations. This collection of information is referred to as a **database**, and can be generated completely manually, or partially by running appropriate MOLPRO calculations. Analysis of the database can give a summary of the energy changes associated with each described reaction, and two or more similar databases can be compared reaction by reaction, to give a statistical analysis of the differences between them.

All of the files associated with the database facility can be found in the directory database in the main MOLPRO source or installation tree.

66.2.1 Description and specification of databases

A database is an XML file conforming to the molpro-database schema, and consists one or more occurrences of each of the following two principal elements.

- **molecule**: Information about a single molecular species in the molpro-output XML format. This will usually be the result of PUT,XML in a MOLPRO calculation, but can also be constructed directly from an external data source. The important quantities that are used are the geometry and energy, together with metadata such as the method and basis set, and other quantities such as spin and symmetry that might be useful for constructing a new MOLPRO job for the molecule.
reaction A list of species specifications that point uniquely to one of the molecule nodes, together with information on how the species appears stoichiometrically in the reaction, and whether it is a special point such as a transition state. species specifications can also be given without either of these tags, allowing additional geometries, for example along a reaction coordinate or potential surface cut, to be included.

Normally, the molecule nodes will be in separate self-contained files that are then referenced in the main database file through the syntax of XInclude. There are three reasons for this. Firstly, these files can be produced directly by a Molpro calculation, with the rest of the database being constructed by hand. Secondly, they allow the possibility that the molecule files be replaced in the future by, for example, running all the molecule calculations again using a different method; in that case, the rest of the database, i.e. the reaction specifications, does not need to change. This supports the possibility of having several databases that have the same structure – specification of reactions – but different numerical data, and therefore being capable of numerical comparison. Thirdly, several databases can coexist in the same directory, and share some of the same molecule files. An example of this is a supplementary database that consists of a subset of the reactions contained in the main database.

The following is an example of a complete database of four reactions involving the species O, H₂, H₂O, H₂O₂ and CH₂O. Note that the association between the species and the molpro-output:molecule nodes is achieved through the use of InChI tags, which PUT, XML will produce provided that OpenBabel (http://openbabel.org) is installed on the system. An alternative is through syntax such as

{PUT,XML,file.xml; index,73}

and the use of <species index="73"> in the database file. Note that sometimes different species have the same InChI, and so the use of index is necessary to resolve ambiguities.
<?xml version="1.0"?>
<database xmlns="http://www.molpro.net/schema/molpro-database"
  xmlns:xi="http://www.w3.org/2001/XInclude">
  <xi:include href="h2o.xml" />
  <xi:include href="h2o2.xml"/>
  <xi:include href="h2.xml"/>  
  <xi:include href="o2.xml"/>
  <xi:include href="co.xml"/>
  <xi:include href="h2co.xml"/>
  <xi:include href="h2cots.xml"/>
  <xi:include href="o.xml"/>
  <reaction title="insertion of O into H2">
    <species InChI="InChI=1S/H2O/h1H2" count="1"/>
    <species InChI="InChI=1S/O" count="-1"/>
    <species InChI="InChI=1S/2H2/h2*1H" count="-1"/>
  </reaction>
  <reaction title="H2O formation">
    <species InChI="InChI=1S/H2O/h1H2" count="1"/>
    <species InChI="InChI=1S/O2/c1-2" count="-0.5"/>
    <species InChI="InChI=1S/2H2/h2*1H" count="-1"/>
  </reaction>
  <reaction title="H2O2 formation">
    <species InChI="InChI=1S/H2O2/c1-2/h1-2H" count="1"/>
    <species InChI="InChI=1S/O2/c1-2" count="-1"/>
    <species InChI="InChI=1S/2H2/h2*1H" count="-1"/>
  </reaction>
  <reaction title="Formaldehyde dissociation">
    <species InChI="InChI=1S/CH2O/c1-2/h1H2" count="-1"/>
    <species InChI="InChI=1S/CO/c1-2" count="1"/>
    <species InChI="InChI=1S/2H2/h2*1H" count="1"/>
    <species InChI="InChI=1S/CHO.H/c1-2;/h1H;" transitionState="true"/>
  </reaction>
</database>

http://www.molpro.net/info/current/examples/../../database/sets/examples/reactions/reactions.xml

For full specification of the possible structure of a database, see the schema file lib/schema/molpro-database.xsd.

The directory database/utilities contains several Python scripts that manipulate databases. For convenience, they can be run through the script

```
molpro --database script-name arguments ...
```

so long as Python (version 3 preferred) is installed on the system. You need the lxml and requests package included in your Python installation:

```
ip install lxml requests
```

(or pip3 if you are using Python 3).

The script validate checks whether a database conforms to the schema, for example

```
cd Molpro # assuming below that we are in Molpro source tree, but works from anywhere
bin/molpro --database validate \
  database/sets/examples/reactions/reactions.xml
```

66.2.2 Computation of new database data

The script clone takes an existing database, for which the file name should be provided as an argument, and generates a set of Molpro jobs that will run the same method on each of the molecules, with the
end result that a new database is created. If the database master file is the only one in the directory that
declares itself to belong to the molpro-database schema, then you can just give the directory name
as the argument to this and other scripts instead. In addition, if the database master file has the suffix
.xml, the suffix does not need to be specified. For the above example, this could be

cd Molpro  # assuming below that we are in Molpro source tree, but works from anywhere
bin/molpro --database clone \
database/sets/examples/reactions

This will create a new directory reactions.d with the following contents.

original/ reactions.xml runall/
procedures.molpro run/

reactions.d/original:
co.xml  h2co.xml  h2o.xml  o.xml
h2.xml  h2cots.xml  h2o2.xml  o2.xml

reactions.d/run:
co.molpro  h2co.molpro  h2o.molpro  o.molpro
h2.molpro  h2cots.molpro  h2o2.molpro  o2.molpro

reactions.d/runall:
reactions.molpro

The file procedures.molpro contains a procedure that will be run on every molecule, and it should
be edited to use the desired methods. Then the calculations can be run, either via each of the individual
MOLPRO input files in run/, or the single input file reactions.molpro in the directory runall. Once these jobs have completed, then the directory contains a complete database with the original reaction scheme but new data.

66.2.3 Analysis of databases

cd Molpro
bin/molpro --database analyse \
database/sets/examples/reactions/reactions.xml

will analyse the database, and report the energy change for each described reaction. If two or more
databases are given as arguments, the analysis will be done on each, and also on the difference between
the first database and the second and any subsequent, including a statistical summary. For the example
given above, one might say

cd Molpro/reactions.d
../bin/molpro --database analyse original .

analyse has a number of options that are described by running

molpro --database analyse --help

66.2.4 Library of databases

The directory database/sets contains several standard databases. Within each one is a description
of its origin, contents and purpose. The scripts described above can take these databases as inputs, for
dexample database/sets/examples/reactions/reactions.xml; as a shortcut, one could simply instead use examples/reactions which will find the system database irrespective of the current working directory.
67 PHYSICAL CONSTANTS

The values of fundamental physical constants are revised periodically by CODATA. Molpro uses the values from the latest revision. Some previous values are available, see the lib/include/codata/ directory. To use these system include files, simply add for instance:

```
include,codata/molpro2006
```

to use the values from Molpro 2006.

A Installation Guide

MOLPRO is distributed to licensees on a self-service basis using the world-wide web. Those entitled to the code should obtain it from [https://www.molpro.net/download](https://www.molpro.net/download) supplying the username and password given to them. The web pages contain both source code and binaries, although not everyone is entitled to source code, and binaries are not available for every platform.

Execution of MOLPRO, whether a supplied binary or built from source, requires a valid licence key. Note that the key consists of two components, namely a list of comma-separated key=value pairs, and a password string, and these are separated by ‘&’. In most cases the licence key will be automatically downloaded from the website when building or installing the software.

A.1 Installation of pre-built binaries

Binaries are given as self-extracting tar archives which are installed by running them on the command line. There are binaries tuned for several architectures. These also support parallel execution. The parallel binaries are built using GA with MPI.

The tar archives are fully relocatable, the location can be changed when running the script interactively, the default is /usr/local.

If the script finds a licence key which has been cached in $HOME/.molpro/token from a previous install then that key will be installed with the software. If the script cannot find a key or automatically download it from the molpro website then the script will prompt that this part of the install has failed. All files of Molpro are installed, but the user must then manually install the key with the library files in a file named .token, e.g.:

```
/usr/local/molpro-mpptype-arch/lib/.token
```

Other configuration options as described in section A.2.5 may also be specified in the script file:

```
/usr/local/bin/molpro
```

A.2 Installation from source files

A.2.1 Overview

There are usually four distinct stages in installing MOLPRO from source files:

- **Configuration**: A shell script that allows specification of configuration options is run, and creates a configuration file that drives subsequent installation steps.
- **Compilation**: The program is compiled and linked, and other miscellaneous utilities and files, including the default options file, are built. The essential resulting components are
  1. The molpro shell script which launches the main executable. In serial case one can directly run the main executable.
2. The molpro.exe executable, which is the main program. For parallel computation, multiple copies of molpro.exe are started by a single instance of molpro shell script using the appropriate system utility, e.g., mpirun.


**Validation**
A suite of self-checking test jobs is run to provide assurance that the code as built will run correctly.

**Installation**
The program can be run directly from the source tree in which it is built, but it is usually recommended to run the procedure that installs the essential components in standard system directories.

### A.2.2 Prerequisites

The following are required or strongly recommended for installation from source code.

1. A Fortran 2003 compiler. On HPC systems the latest vendor-supplied compiler should be used. The program is regularly tested with recent versions of GNU and Intel Fortran compilers.

2. GNU make, freely available from http://www.fsf.org and mirrors. GNU make must be used; most system-standard makes do not work. In order to avoid the use of a wrong make, it may be useful to set an alias, e.g., alias make='gmake -s'. A recent version of GNU make is required, 3.80 or above.

3. Libxml2 library and header files.

4. About 10GB disk space (strongly system-dependent; more with large-blocksize file systems, and where binary files are large) during compilation. Typically 100Mb is needed for the finally installed program. Large calculations will require larger amounts of disk space.

5. One or more large scratch file systems, each containing a directory that users may write on. There are parts of the program in which demanding I/O is performed simultaneously on two different files, and it is therefore helpful to provide at least two filesystems on different physical disks if other solutions, such as striping, are not available. The directory names should be stored in the environment variables $TMPDIR, $TMPDIR2, $TMPDIR3, ... These variables should be set before the program is installed (preferably in .profile or .cshrc), since at some stages the installation procedures will check for them (cf. section A.2.5).

6. If the program is to be built for parallel execution then the Global Arrays toolkit or the MPI-2 library is needed. For building MOLPRO with the Global Arrays toolkit, we recommend the latest stable version (although earlier versions may also work). This is available from http://www.emsl.pnl.gov/docs/global and should be installed prior to compiling MOLPRO. For building MOLPRO with the MPI-2 library, we recommend to use the built-in MPI-2 library, which may have advantages of optimization on some platforms. If there is no built-in one on the platform, a fresh MPI-2 library (e.g.: MPICH2, see http://www.mpich.org/) should be installed prior to compiling MOLPRO. Many MPI-2 libraries, including Intel MPI, Bull MPI, MPICH2, and Open MPI, have been tested, and others untested could also work.

7. The source distribution of MOLPRO, which consists of a compressed tar archive with a file name of the form molpro.2015.1.tar.gz. The archive can be unpacked using gunzip and tar.

**Fedora packages** To build using GNU compilers one should ensure the following packages are installed (via dnf):

- gcc-c++ provides GNU C and C++ compiler,
- gcc-gfortran provides GNU Fortran compiler,
- libxml2-devel provides libxml2 library & headers,
- make provides GNU make.
Optionally one can choose to install:

- blas-devel provides a BLAS library,
- lapack-devel provides a LAPACK library,

which will be used instead of compiling the equivalent MOLPRO routines.

**openSUSE packages** To build using GNU compilers one should ensure the following packages are installed (via YaST):

- gcc-c++ provides GNU C and C++ compiler,
- gcc-fortran provides GNU Fortran compiler,
- libxml2-devel provides libxml2 library & headers,
- make provides GNU make.

Optionally one can choose to install:

- blas provides a BLAS library,
- lapack provides a LAPACK library,

which will be used instead of compiling the equivalent MOLPRO routines.

**Ubuntu packages** To build using GNU compilers one should ensure the following packages are installed via (apt-get):

- build-essential provides GNU C++ compiler,
- curl provides curl for downloading patches,
- gfortran provides GNU Fortran compiler,
- libxml2-dev provides libxml2 library & headers,
- openssh-server provides ssh access to localhost.

Optionally one can choose to install:

- libblas-dev provides a BLAS library,
- liblapack-dev provides a LAPACK library,

which will be used instead of compiling the equivalent MOLPRO routines. Set up password-less ssh by running the following commands and not entering a password when prompted:

```
ssh-keygen -t rsa
cat ~/.ssh/id_rsa.pub >> ~/.ssh/authorized_keys
```

This must be done for each user account which will be running MOLPRO.

**Mac OSX** It is recommended to install and manage the additional compilers and utilities needed for building and running MOLPRO using the Homebrew system. Visit [http://brew.sh](http://brew.sh) and copy the installation command into a terminal window. On an empty system, you will be prompted to install command line tools; do this first. Then accept all prompts from the Homebrew installation script.

The following will install all utilities that might be needed for building and running MOLPRO either as a developer or installer.
brew unlink mpich2 # not needed if mpich has not been installed
brew install molpro/ga/ga Caskroom/cask/xquartz homebrew/x11/grace \
    open-babel doxygen automake wget \
    Caskroom/cask/java homebrew/science/jmol

Assuming /usr/local/bin is in your path,

./configure CXX=mpicxx FC=mpif90 --enable-mpp=/usr/local/lib

will configure MOLPRO.

A.2.3 Configuration

Once the distribution has been unpacked, change to the Molpro directory that has been created. Having changed to the Molpro directory, you should check that the directory containing the Fortran compiler you want to use is in your PATH. Then run the command

./configure

which creates the file CONFIG. This file contains machine-dependent parameters, such as compiler options. Normally CONFIG will not need changing, but you should at least examine it, and change any configuration parameters which you deem necessary. Any changes made to CONFIG will be lost next time ./configure is invoked, so it is best to supply as many of these as possible via the command line.

The configure procedure may be given command line options, and, some commonly used options include:

1. In the case of building for parallel execution, the option --enable-mpp must be given on the command line. This enables both mpp and mppx parallelism; for the distinction between these two parallelism modes, please refer to the user manual, section 2. The option --enable-mpp must be set to the location of the Global Arrays library directory or the MPI-2 library include directory. For the case of using the Global Arrays toolkit, one example can be

./configure --enable-mpp=/usr/local/ga-install/lib

If using a Global Arrays build with an MPI library the appropriate MPI executable should appear first in PATH when more than one is available.

Queries regarding Global Arrays installations should be sent directly to the Global Arrays team, any Molpro related queries will assume a fully functional Global Arrays suite with all internal tests run successfully.

For the case of using the MPI-2 library, one example can be

./configure --enable-mpp=/usr/local/mpich2-install/include

and the directory should contain file mpi.h. Please ensure the built-in or freshly built MPI-2 library fully supports MPI-2 standard and works properly.

For desktop or single node installations, there are a series of options prefixed with auto which build any prerequisites, and can be passed to --enable-mpp, eg.

./configure --enable-mpp=auto-ga-mpich

2. For good performance it is important to use appropriate BLAS libraries; in particular, a fast implementation of the matrix multiplication dgemm is very important for MOLPRO. Therefore you should use a system tuned BLAS library whenever available.

MOLPRO will automatically detect the most appropriate BLAS library in many cases. In certain cases, in particular when the BLAS library is installed in a non-default location, configure should be directed to the appropriate directory with:

./configure --with-blas-path=/path/to/lib/dir

3. The Molpro installation directory can be given with --prefix.
A.2.4 Compilation and linking

After configuration, the remainder of the installation is accomplished using the GNU `make` command. Remember that the default `make` on many systems will not work, and that it is essential to use GNU `make` (cf. section A.2.2). Everything needed to make a functioning program together with all ancillary files is carried out by default simply by issuing the command

```
made
```

in the MOLPRO base directory. Most of the standard options for GNU `make` can be used safely; in particular, `-j` can be used to speed up compilation on a parallel machine. The program can then be accessed by making sure the `bin/` directory is included in the PATH and issuing the command `molpro`. If MPI library is used for building Global Arrays or building MOLPRO directly, please be aware that some MPI libraries use mpd daemons to launch parallel jobs. In this case, mpd daemons must already be running before `make`.

A.2.5 Adjusting the default environment for MOLPRO

The default running options for MOLPRO are stored in the script `bin/molpro`. After program installation, either using binary or from source files, this file should be reviewed and adjusted, if necessary, to make system wide changes.

A.2.6 Tuning

MOLPRO can be tuned for a particular system by running in the root directory the command

```
made tuning
```

This job automatically determines a number of tuning parameters and appends these to the file `bin/molpro`. Using these parameters, MOLPRO will select the best BLAS routines depending on the problem size. This job should run on an empty system. It may typically take 10 minutes, depending on the processor speed, and you should wait for completion of this run before doing the next steps.

A.2.7 Testing

At this stage, it is essential to check that the program has compiled correctly. The makefile target `test` (i.e., command `make test`) will do this using the full suite of test jobs, and although this takes a significantly long time, it should always be done when porting for the first time. A much faster test, which checks the main routes through the program, can be done using `make quicktest`. For parallel installation, it is highly desirable to perform this validation with more than one running process. This can be done conveniently through the `make` command line as, for example,

```
made MOLPRO_OPTIONS=-n2 test
```

If any test jobs fail, the cause must be investigated. If, after due efforts to fix problems of a local origin, the problem cannot be resolved, the developers of MOLPRO would appreciate receiving a report. There is a web-based mechanism at [https://www.molpro.net/bugzilla](https://www.molpro.net/bugzilla) at which as many details as possible should be filled in. It may also be helpful to attach a copy of the CONFIG file along with the failing output. Please note that the purpose of such bug reports is to help the developers improve the code, and not for providing advice on installation or running.

A.2.8 Installing the program for production

Although the program can be used in situ, it is usually convenient to copy only those files needed at runtime into appropriate installation directories as specified at configuration time (see section A.2.3) and stored in the file `CONFIG`. To install the program in this way, do

```
made install
```
The complete source tree can then be archived and deleted. The overall effect of this is to create a shell script in the INSTBIN directory. The name should relate to the architecture, type of build, integer etc. Symbolic links relating to the type of build are then made, and finally providing that INSTBIN/molpro is not a file, a symbolic link is created to the new script. In some cases it is preferable to create a localized script in INSTBIN/molpro which will not be over written. The overall effect of this cascade of links is to provide, in the normal case, the commands molpro and one or both of molpros (serial) and molprop (parallel) for normal use, with the long names remaining available for explicit selection of particular variants.

For normal single-variant installations, none of the above has to be worried about, and the molpro command will be available from directory INSTBIN.

During the install process the key from $HOME/.molpro/token is copied to PREFIX/.token so that the key will work for all users of the installed version.

A.2.9 Installation of documentation

The documentation is available on the web at [http://www.molpro.net/info/users.](http://www.molpro.net/info/users) It is also included with the source code. The PDF user's manual is found in the directory Molpro/doc/manual.pdf, with the HTML version in the directory Molpro/doc/manual/index.html. After make install the documentation is installed in the doc subdirectory of PREFIX specified in CONFIG file generated by the configure command. Numerous example input files are included in the manual, and can alternatively be seen in the directory Molpro/examples.

A.2.10 Simple building for single workstations Linux or Mac OS X

The following instructions are quick instructions for installing MOLPRO on a single-workstation Linux or Mac OS X system. The instructions assume GNU compilers have been installed (details of getting GNU compilers for common Linux distributions are contained in the prerequisites section), but these can be substituted with alternative compilers. For serial MOLPRO:

```
./configure CXX=g++ FC=gfortran
make
```

For parallel MOLPRO one can use:

```
./configure CXX=g++ FC=gfortran --enable-mpp=/path/to/ga-install/lib
make
```

if Global Arrays has already been built. There is a simpler option, providing the curl utility is installed, and the machine is connected to the internet:

```
./configure CXX=g++ FC=gfortran --enable-mpp=auto-ga-mpich
make
```

which will automatically download and install MPICH and Global Arrays.

A.2.11 Installation on a Cygwin system

On a Windows machine Cygwin should be installed. In addition to the default package list one should also install the packages listed in table 23. If undertaking development work table 24 contains a list of potentially useful packages.

With the above steps, configure can be run and the Molpro built in the normal way.
### B Recent Changes

#### B.1 New features of MOLPRO2015.1

Molpro 2015 contains many improvements, bug-fixes and new features. Only the most important ones are listed in the following.

**B.1.1 Projector-based wavefunction-in-DFT embedding**


**B.1.2 Intrinsic bond-orbital analysis and orbital localization (IBO).**

IBOs provide a reliable and efficient way to generate localized orbitals and to analyze wavefunctions, see G. Knizia, J. Chem. Theory Comput. 9, 4834 (2013)

**B.1.3 Interface to NBO6**

Molpro 2015 supports NBO6 Natural Bond Orbital Analysis (NBO6) via an interface. NBO6 must be licensed separately.

**B.1.4 Beyond LMP2 treatment of intermolecular pairs in local coupled cluster methods**

Usually close (and weak) pairs are treated only at the LMP2 level in LCCSD(T) calculations. This not satisfying since LMP2 often treats van der Waals interactions poorly, hence compromising the high accuracy of the actual LCCSD(T) calculation. Fortunately, close pairs can now be treated in an inexpensive way at a level beyond LMP2, ranging from local direct RPA via ring CCD to LCCD[S]-R−6. This is described in O. Masur, D. Usvyat and M. Schütz, J. Chem. Phys., 139, 164116 (2013); M. Schütz, O. Masur and D. Usvyat, J. Chem. Phys., 140, 244107 (2014).
B.1.5 Distinctable Cluster Approximation (DCSD and DCSD-F12)

This approximation yields improved results at the cost of CCSD. In particular, DCSD equilibrium structures are as accurate as for CCSD(T), see

D. Kats and F. R. Manby, J. Chem. Phys. 139, 021102 (2013);
D. Kats, J. Chem. Phys. 141i, 061101 (2014);

B.1.6 Analytical Energy Gradients

Analytical gradients are now available for DCSD. Analytical gradients for CCSD(T), as well as for MP2-F12, CCSD(T)-F12, and DCSD-F12 are under development and will be made available free of charge at a later stage.

B.1.7 Orbital Relaxed Properties and Analytical Nuclear Gradients for Excited States

Orbital relaxed properties, and analytical nuclear gradients for excited states are now available for local CC2 response and local ADC(2). This allows for geometry optimizations of excited states of large chromophores at these levels of theory. Furthermore, also local ADC(2) transition moments at the level of strict ADC(2) (which require second-order ground state singles and doubles) are available. For further reference see

K. Ledermüller, D. Kats and M. Schütz, J. Chem. Phys. 139, 084111 (2013);

B.1.8 PNO-LMP2 and PNO-LMP2-F12

New parallel linear scaling PNO-LMP2 and PNO-LMP2-F12 programs as described in


are available in version 2015. PNO-LCCSD(T) is currently under development and will be made freely available to licensees of Molpro 2015 at a later stage.

B.1.9 Magnetizability and Rotational g-Tensor at DF-LMP2 Level using GIAOs

The program for NMR chemical shifts has been extended to include also magnetizability and rotational g-tensor. This is described in


B.1.10 Faster Density Fitting Integral Routines

DFT and F12 methods with density fitting are significantly speeded up using improved integration routines written by G. Knizia.

B.1.11 Vibrational Perturbation Theory: VPT2

A VPT2 program based on a semi-quartic force field (QFF) has been implemented, which allows for low-cost evaluations of anharmonic vibrational frequencies and associated vibrational constants. The determination of the QFF does not require analytical gradients (see the SURF program) and can thus be used in combination with any electronic structure method.
B.1.12 Vibrational multi-reference methods: VMCSFC, VMRCI


B.1.13 Anharmonic Franck-Condon factors: FCON

A Franck-Condon program based on anharmonic vibrational wavefunctions has been implemented. Franck-Condon factors can either be computed by rotating the vibrational wavefunction or by transforming the potential energy surface in order to account for Duschinsky effects. This program, which allows for the accurate calculation of photoelectron spectra (absorption and fluorescence) relies on the newly developed transformation program SURFTRANS [P. Meier and G. Rauhut, J. Chem. Phys. (2015)].

B.1.14 Transformation of multi-dimensional potential energy surfaces: PESTRANS

Multi-dimensional potential energy surfaces spanned in terms of normal coordinates - as computed with the SURF program - can now be rotated or transformed into an arbitrary set of normal coordinates. This allows for the efficient calculation of Franck-Condon factors or the calculation of vibrational spectra of isotopologues from just one potential energy surface [P. Meier, D. Oschetzki, R. Berger and G. Rauhut, J. Chem. Phys. 140, 184111 (2014)].

B.1.15 Localized normal coordinates

Within the SURF program, multi-dimensional potential energy surfaces can now alternatively be spanned in terms of localized normal coordinates. Three localization schemes are offered: (a) localization of the CH-stretching modes only and (b) localization of all normal coordinates to the subunits in molecular cluster calculations or (c) both. All localization schemes are symmetry sensitive.

B.1.16 Calculation of arbitrary vibrational states: VIBSTATE

In the old Molpro release the calculation of vibrational states was limited to fundamentals, first vibrational overtones and simple combination bands. The new VIBSTATE program allows to specify arbitrary vibrational states, but the user must take care, that the parameters in the SURF program and the vibrational correlation programs are adjusted accordingly.

B.1.17 Raman scattering activities

Raman scattering activities can now be computed within all vibrational SCF and vibration correlation programs. As polarizabilities can only be determined at the Hartree-Fock level, the accuracy is currently still limited.

B.1.18 Reaction databases

A facility is provided to store and interrogate sets of molecules, together with information about how they are to be combined in balanced chemical equations. This database can be generated manually, or partially by running appropriate MOLPRO calculations. Analysis of the database can give a summary of the energy changes associated with each described reaction, and two or more similar databases can be compared reaction by reaction, to give a statistical analysis of the differences between them. Several common databases are included.
B.1.19 New density-fitting DFT-SAPT program

A new DFT-SAPT program has been implemented in Molpro which can be used in conjunction with monomer-centered (MCBS), monomer-centered plus (MC+BS) or dimer-centered (DCBS) basis sets. Even in DCBS mode fairly large complexes with about 800 electrons can be studied with this program, see A. Heßelmann and T. Korona. J. Chem. Phys. 141, 094107 (2014).

B.2 New features of MOLPRO2012.1


The new features of MOLPRO version 2012.1 include the following.

B.2.1 Quasi-variational coupled-cluster theory


B.2.2 A new internally contracted MRCI code: MRCIC

A new internally contracted MRCI code [see K. R. Shamasundar, G. Knizia, and H.-J. Werner, A new internally contracted multi-reference configuration interaction (MRCI) method, J. Chem. Phys. 135, 054101 (2011)] is now available. As compared to the old MRCI code it has the following advantages: (i) inactive orbitals (correlated in MRCI but closed-shell in the reference function) are treated explicitly, i.e., no density matrices and coupling coefficients need to be computed that involve these orbitals. Thus, in principle any number of inactive orbitals can be correlated, without the previously existing limitation to 32 correlated orbitals. Furthermore, additional configuration spaces are internally contracted (as in the RS2C code), resulting in a much improved efficiency, particularly for cases with many inactive orbitals. Currently, the method is implemented only for single-state calculations, but an extension to multi-state cases is under development and will be provided in the near future.

B.2.3 Explicitly correlated multireference theories: RS2-F12, MRCI-F12


B.2.4 Extended multi-state CASPT2

Extended multistate CASPT2 (XMS-CASPT2) [see T. Shiozaki, W. Győrffy, P. Celani, and H.-J. Werner, *Communication: The extended multi-state CASPT2 method: Energy and nuclear gradients*, J. Chem. Phys. 135, 081106 (2011)] provides a better description of near degenerate situations and avoided crossings. Currently this option is available only with the RS2 code, not for RS2C.

B.2.5 Density fitted CASSCF and CASPT2


B.2.6 Extensions of explicitly correlated coupled-cluster methods


Further basis sets of K. A. Peterson and J.G. Hill for explicitly correlated methods have been included. In particular these include the aug-cc-pVnZ-PP/OpRl and aug-cc-pwCVnZ-PP/OpRl sets for the group 11 and 12 transition metals. A full set of F12 basis sets for the p-block elements Ga-Rn will be added in the very near future. For recent work on molecules containing transition metals see D. H. Bross, J. G. Hill, H.-J. Werner, and Kirk A. Peterson, *Explicitly correlated composite thermochemistry of transition metal species*, J. Chem. Phys. 139, 094302 (2013).

B.2.7 Density fitted local coupled-cluster methods: DF-LCCSD(T), DF-LUCCSD(T), DF-LRPA

The local coupled cluster methods have been further improved. See H.-J. Werner and M. Schütz, *An efficient local coupled-cluster method for accurate thermochemistry of large systems*, J. Chem. Phys. 135, 144116 (2011) for a description of the current implementation. An open-shell implementation [DF-LUCCSD(T)] is now also available (Y. Liu and H.-J. Werner, to be published.) Furthermore, the direct random phase approximation (RPA) has been implemented as a local method and using density fitting. Direct RPA can be considered as a CCD method reduced to only ring diagrams. In contrast tp MP2 it also contains higher-order diagrams which e.g. cover Axilrod-Teller terms in intermolecular calculations. It is therefore especially attractive to replace in LCC calculations the LMP2 method for weak pairs by LRPA. This is now possible in our LCC code (O. Masur and M. Schütz, to be published.)

B.2.8 Local coupled-cluster methods with orbital-specific virtual orbitals: OSV-LCCSD(T)

B.2.9 Explicitly correlated local MP2 and CC methods: DF-LMP2-F12, DF-LCCSD(T)-F12


B.2.10 Improved DFT with density fitting

The efficiency of density functional theory has been much improved. In particular, the density fitting (DF-RKS, DF-UKS) codes for analytical energy gradients are now very much faster, due to a new integral code (adaptive integral core, AIC) written by G. Knizia. Some benchmarks can be found in H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, and M. Schütz, *Molpro – a general purpose quantum chemistry program package*, WIRES Comput. Mol. Sci. 2, 242 (2012).

B.2.11 Additional density functionals

A large number of additional density functionals has been added, including PBE0, PBEREV, M05, M05-2X, M06, M06-2X, M06-HF, M08-HX, M08-SO, M11-L, SOGGA, SOGGA11, SOGGA11-X. (M11 is currently not available, but will likely be added in the near future).

B.2.12 Additional gradient theories: CCSD, DF-MP2, DF-CASSCF, DF-RS2

New analytical gradient codes are now available for DF-MP2, DF-CASSCF, DF-RS2 (including MS and XMS options, also without density fitting), and for CCSD.

B.2.13 Local methods for excited states

First-order properties of excited states via time-dependent Local CC2 linear response theory and ADC(2) are now also available for triplet states. This is described in K. Freundorfer, D. Kats, T. Korona, and M. Schütz, *Local CC2 response method for triplet states based on Laplace transform: Excitation energies and first-order properties*, J. Chem. Phys. 133, 244110 (2010);

B.2.14 NMR shielding tensors at DF-LMP2 level using GIAOs

An efficient method for calculating NMR shielding tensors at the local MP2 level has been implemented. Gauge including atomic orbitals (GIAOs) are used to eliminate the gauge origin dependence. Density fitting is employed to factorize the relevant electron repulsion integrals and their derivatives w.r. to the magnetic field. So far, the method has been already applied to systems with more than 2500 contracted basis functions and 300 correlated electrons. Relevant publications are S. Loibl, F. R. Manby, and M. Schütz, *Density fitted, local Hartree-Fock treatment of NMR chemical shifts using London atomic orbitals*, Mol. Phys., 108, 477 (2010), and S. Loibl and M. Schütz, *NMR shielding tensors for density fitted local second-order Møller-Plesset perturbation theory using gauge including atomic orbitals*, J. Chem. Phys., 137, 084107 (2012).
B.2.15 SAPT(CCSD)

Symmetry-adapted perturbation theory of intermolecular interactions with monomers described in the CCSD level.

B.2.16 Improved SCF algorithms for high-spin open-shell systems

For open-shell systems, RHF and RKS now use a two-step diagonalization process by default: Here the beta orbitals are found by a second diagonalization in the subspace of occupied alpha orbitals. This process usually leads to more stable convergence in difficult cases, compared to the standard diagonalization of a single open-shell Fock matrix (the latter behavior is recovered by \{rhf,algo=0\}). An additional section with suggestions for dealing with difficult cases has been added to be manual under “The SCF program”. Additionally, various limitations of the SCF program have been lifted. In particular, \{rhf; maxit,1\} now always works, and just calculates a Fock matrix and energy from the input orbitals, without updating said orbitals.

B.2.17 FCIQMC: Stochastic Full CI

The FCIQMC program exists through an interface to the NECI codebase, which is actively developed in the group of A. Alavi, and has been integrated into the MOLPRO code. The FCIQMC method is a recently introduced stochastic method which can calculate in principle FCI-quality energies for small to medium-sized molecules. See G. H. Booth, A. J. W. Thom, and A. Alavi, J. Chem. Phys. 131, 054106 (2009); D. M. Cleland, G. H. Booth, and A. Alavi, J. Chem. Phys. 134, 024112 (2011); G. H. Booth, D. M. Cleland, A. J. W. Thom, and A. Alavi, J. Chem. Phys. 135, 084104 (2011).

B.2.18 Ab Initio Multiple Spawning Dynamics

The AIMS module implements the Ab Initio Multiple Spawning method to perform dynamics calculations on multiple electronic states. It can also be used quite generally for first principles molecular dynamics on a single electronic surface, provided that nuclear gradients are available. Currently, non-adiabatic dynamics is limited to CASSCF wavefunctions; however, MS-CASPT2 non-adiabatic dynamics (with an implementation of analytical MS-CASPT2 non-adiabatic couplings) will be provided in the very near future. See M. Ben-Nun and T. J. Martinez, Chem. Phys. Lett. 298, 57 (1998); B. G. Levine, J. D. Coe, A. M. Virshup and T. J. Martinez, Chem. Phys. 347, 3 (2008); T. Mori, W. J. Glover, M. S. Schuurman and T. J. Martinez, J. Phys. Chem. A 116, 2808 (2012).

B.2.19 Updated def2 basis sets

The partially augmented Turbomole basis sets def2-SVPD, def2-TZVPD, and def2-QZVPPD (Rapporto, Furche: J. Chem. Phys. 133, 134105 (2010)) have been added to the library. Additionally, the recently developed dhf- variants of the def2- basis sets have been included (dhf-SVP, dhf-TZVPP, ...). Weigend, Baldes: J. Chem. Phys. 133, 174102 (2010)); these are reoptimized versions for the more modern MDF effective core potentials (most elements used MDF ECPs already in def2- and are unchanged). Short names like TZVPP (without prefix) now refer to dhf- basis sets.

B.2.20 Parallel builds merged

The MPP and MPPX builds of Molpro have been merged and the decision to run in MPP or MPPX mode made a run-time option. To build parallel Molpro the \-mpp flag to configure should be used; the \-mppx flag is no longer required or valid. When running parallel Molpro, the \--mpp option (default) can be used to specify MPP mode, and the \--mppx option for MPPX mode.
B.2.21 Auto-build options for parallel configuration

New options for configuring parallel Molpro to run on a single node or workstation have been implemented. These options (see manual) are prefixed with -auto, and in conjunction with -mpp configure will download, build and install a variety of different prerequisites for parallel Molpro.

B.3 New features of MOLPRO2010.1

The functionality is essentially the same as in 2009.1, but many bug fixes and small improvements have been added. Please note the following major changes, in particular of the default RI basis sets in explicitly correlated methods as described below.

B.3.1 AIC density fitting integral program

A faster integral program for density fitting, written by Gerald Knizia, has been added. In particular this speeds up the integral evaluation in F12 calculations by up to a factor of about 10 (depending on the basis set). This program is now used by default, but can be disabled by setting
dfit,aic=0
in the beginning of the input.

B.3.2 Pair specific geminal exponents in explicitly correlated methods

Different exponents for the Slater-type geminals can be used for valence-valence, core-valence, and core-core pairs. See manual for details.

B.3.3 Change of defaults in explicitly correlated methods

For explicitly correlated F12 calculations that use the VnZ-F12 orbital basis sets (OBS), it is now the default to use the corresponding VnZ-F12/OPTRI basis sets to construct the complementary auxiliary orbital basis (CABS). In case that CABS is not used (e.g., in LMP2-F12), the OBS and OPTRI sets are merged automatically. This yields exactly the same results as would be obtained with the CABS approach. In order to use the default RI sets of 2009.1, please specify option RI_BASIS=JKFIT on the command line, or
explicit,ri_basis=jkfit
For compatibility reasons, it is still the default to use the JKFIT sets as RI basis for the AVnZ orbital basis sets. In order to use the corresponding OPTRI sets (where available) please specify option RI_BASIS=OPTRI.

B.3.4 New basis sets in the Molpro library

A number of new basis sets have been added to the Molpro library since version 2009.1. The references for these sets can be found in the headers of the respective libmol files.

Li, Be, Na, Mg: a) New official versions of the correlation consistent basis sets for these elements have been added, both non-relativistic and those contracted for Douglas-Kroll relativistic calculations. Specifically these are:
cc-pVnZ (n=D-5) cc-pwCVnZ (n=D-5) aug-cc-pVnZ (n=D-5) aug-cc-pwCVnZ (n=D-5)
and the above with a -DK extension. The older cc-pVnZ basis sets for these elements can still be accessed via the keywords vdz-old, etc.
b) New basis sets, including RI and MP2 auxiliary sets, have been added for F12 explicit correlation calculations:

\[
\begin{align*}
{\text{cc-pVnZ-F12 (n=D-Q)}} & \quad {\text{cc-pCVnZ-F12 (n=D-Q)}} \\
\end{align*}
\]

The optimized CABS auxiliary sets have the same name but with a /OptRI context

For MP2 and CCSD auxiliary sets, the cc-pVnZ/MP2FIT sets of H"attig can be used, but a new cc-pV5Z/MP2FIT set has been added that is optimal for the new cc-pV5Z basis set; new aug-cc-pVnZ/MP2FIT (n=D-5) sets have been added as well. The original cc-pV5Z/MP2FIT sets of H"attig have been renamed v5z-old/mp2fit.

Cu-Zn, Y-Cd, Hf-Hg:

a) While the aug-cc-pVnZ-PP (n=D-5) and cc-pwCVnZ-PP (n=D-5) sets were already available, the combination aug-cc-pwCVnZ-PP was not yet defined. These have now been added for these elements.

b) Triple-zeta DK sets have been included now for all of these elements. Unless otherwise noted, these were optimized for 2nd-order DKH. In the cases of Hf-Hg, sets contracted for 3rd-order DKH are also now included:

\[
\begin{align*}
{\text{cc-pVTZ-DK}} & \quad {\text{cc-pwCVTZ-DK}} & \quad {\text{aug-cc-pVTZ-DK}} & \quad {\text{aug-cc-pwCVTZ-DK}} \\
\end{align*}
\]

and the above with -DK replaced by -DK3 for DKH3 calculations in the case of Hf-Hg.

H-He, B-Ne, Al-Ar, Ga-Kr:

a) A variety of DK contracted basis sets have been added for these elements:

\[
\begin{align*}
{\text{aug-cc-pVnZ-DK (n=D-5)}} & \quad {\text{cc-pCVnZ-DK (n=D-5)}} & \quad {\text{cc-pwCVnZ-DK (n=D-5)}} & \quad {\text{aug-cc-pCVnZ-DK (n=D-5)}} \\
\end{align*}
\]

b) Official cc-pCV6Z and aug-cc-pCV6Z are now also available for Al-Ar

c) For explicitly correlated calculations, the core-valence sets have been added:

\[
\begin{align*}
{\text{cc-pCVnZ-F12 (n=D-Q)}} & \quad {\text{for B-Ne, Al-Ar cc-pCVnZ-F12/OptRI (n=D-Q)}} \\
\end{align*}
\]

for B-Ne, Al-Ar

d) cc-pVnZ-F12/OptRI (n=D-Q) as also been added for He

Turbomole def2 basis sets:

The complete Turbomole def2 basis set family has been added to the Molpro basis library (for all elements H to Rn, except Lanthanides). The def2-orbital basis sets can now be accessed as SV(P), SVP, TZVP, TZVPP, QZVP and QZVPP. In this nomenclature SVP, TZVPP, and QZVPP correspond to valence double-zeta (VDZ), valence triple-zeta (VTZ) and valence quadruple-zeta (VQZ) basis sets, respectively.

Auxiliary density fitting basis sets for all elements are available as well (e.g., TZVPP/JFIT, TZVPP/JKFIT, TZVPP/MP2FIT) and are chosen automatically in density-fitted calculations. Supposedly, the JKFIT sets are universal and also applicable in combination with the AVnZ basis sets. Initial results indicate that they also work well with the cc-pVnZ-PP and aug-cc-pVnZ-PP series of basis sets.

The orbital basis sets can also be accessed in singly and doubly augmented versions (carrying A or DA prefixes, respectively, e.g., ASVP, DASVP), and the auxiliary fitting sets in singly augmented versions (e.g., ATZVPP/MP2FIT). The old Turbomole basis sets have been renamed; if required, they can be accessed with a def1-prefix (e.g., def1-SVP, def1-TZVPP, etc.).

B.3.5 Improved support for MPI implementation of parallelism

The ppidd harness that manages interprocess communication has been improved. The performance of the implementation based on pure MPI, as an alternative to use of the Global Arrays toolkit, is considerably improved, through the use of dedicated helper processes that service one-sided remote memory accesses.
B.3.6 Change of the order of states and the defaults for computing the Davidson correction in multi-state MRCI

The previous way to compute the Davidson correction in multi-state MRCI could lead to non-continuous cluster corrected energies. This is now avoided by ordering the MRCI eigenstates according to increasing energy (previously they were ordered according to maximum overlap with the reference wavefunctions). Furthermore, additional options for computing the Davidson correction in multi-state calculations are added (for details see manual). The old behavior can be recovered using options SWAP, ROTREF=-1.

B.3.7 IPEA shift for CASPT2

A variant of the IPEA shift of G. Ghigo, B. O. Roos, and P.A. Malmqvist, Chem. Phys. Lett. 396, 142 (2004) has been added. The implementation is not exactly identical to the one in MOLCAS, since in our program the singly external configurations are not (RS2) or only partially (RS2C) contracted. The shift is invoked by giving option IPEA=shift on the RS2 or RS2C commands; the recommended value for shift is 0.25. For details of the implementation see manual.

B.3.8 Karton-Martin extrapolation of HF energies

The two-point formula for extrapolating the HF reference energy, as proposed by A. Karton and J. M. L. Martin, Theor. Chem. Acc. 115, 330 (2006) has been added: \( E_{\text{HF},n} = E_{\text{HF,CBS}} + A(n+1) \cdot \exp(-9\sqrt{n}) \). Use METHOD_R=KM for this.

B.4 New features of MOLPRO2009.1

B.4.1 Basis set updates

Correlation consistent basis sets for Li, Be, Na, and Mg have been updated to their official versions as reported in Prascher et al., Theor. Chem. Acc. (2010). These now also include core-valence, diffuse augmented, and Douglas-Kroll relativistically contracted versions. The previous sets are still available but have been renamed vdz-old, vtz-old, etc.

B.4.2 Explicitly correlated calculations

Due to new findings, the default behavior of the F12 programs was changed in the following points:

1. For open-shell systems the default wave function ansatz for was modified. This affects RMP2-F12 and open-shell CCSD-F12 calculations. The new default generally improves open-shell treatments and leads to more consistent behavior. The previous behavior can be restored by explicit,extgen=0
   (for more details see manual).
2. The procedure for the construction of complementary auxiliary basis sets (CABS) and the thresholds were changed. This affects all non-local F12 calculations. The previous behavior can be restored by explicit,ortho_cabs=0,thrcabs=1-7,thrcabs_rel=1e-8
3. In numeric frequency calculations, the freezing of auxiliary basis sets was improved. This can affect calculations where many redundant functions are deleted.
4. Pair energies for the explicitly correlated methods can be printed using print,pairs
   If inner-shell orbitals are correlated, the cc, cv, and vv contributions to the correlation energies are also printed.
B.4.3 Improvements to the Hartree-Fock program

The atomic density guess in Hartree-Fock has been improved and extended. Guess basis sets are now available for most atoms and for all pseudopotentials. Most pseudopotentials have been linked to the appropriate basis sets, so that it is sufficient to specify, e.g.

```
basis=vtz-pp
```

which will select the correlation consistent triple zeta basis sets and the associated (small core) pseudopotential. Similarly, it is mostly sufficient to specify the basis set for other pseudopotential/basis set combinations.

If the wavefunction symmetry is not given in the Hartree-Fock input and not known from a previous calculation, the HF program attempts to determine it automatically from the aufbau principle (previously, symmetry 1 was assumed in all cases). For example,

```
geometry={n};
{hf;wf,spin=3}
```

automatically finds that the wavefunction symmetry is 8.

B.4.4 Changes to geometry input

1. Rationalisation of options for molecular geometry. It is now illegal to specify symmetry and orientation options (eg x;noorient;angstrom) inside a geometry block, which now contains just the geometry specification (Z-matrix or XYZ). Options have to be specified using the new ORIENT and SYMMETRY commands, and/or existing commands such ANGSTROM. This change will, unfortunately, render many inputs incompatible with 2008.1 and earlier versions of Molpro, but has been introduced to allow correct and clean parsing of geometries containing, for example, yttrium atoms, which previously conflicted with the Y symmetry option.

2. Simplification of geometry input. The program now detects automatically whether the geometry is specified as a Z-matrix, or using cartesian coordinates, and so there is no need any more to set the geomtyp variable. The standard XYZ format is still accepted for cartesian coordinates, but the first two lines (number of atoms, and a comment) can be omitted if desired.

B.4.5 MPI-2 parallel implementation

The program now can be built from the source files with the Global Arrays toolkit or the MPI-2 library for parallel execution.

B.5 New features of MOLPRO2008.1

The new features of MOLPRO version 2008.1 include the following.

1. Efficient closed-shell and open-shell MP2-F12 and CCSD(T)-F12 methods which dramatically improve the basis set convergence, as described in J. Chem. Phys. 126, 164102 (2007); ibid. 127, 221106 (2007); ibid. 128, 154103 (2008).

2. Natural bond order (NBO) and natural population analysis (NPA) as described in Mol. Phys. 105, 2753 (2007) and references therein.


6. Enhanced connections to other programs, including graphical display of output and 3-dimensional structures.

7. Support for latest operating systems and compilers, including Mac OS X.

B.6 New features of MOLPRO2006.1

Features and enhancements in MOLPRO version 2006.1 most notably included efficient density fitting methods, explicitly correlated methods, local coupled cluster methods, and several new gradient programs: following:

1. More consistent input language and input pre-checking.
2. More flexible basis input, allowing to handle multiple basis sets
3. New more efficient density functional implementation, additional density functionals.
4. Low-order scaling local coupled cluster methods with perturbative treatment of triples excitations (LCCSD(T) and variants like LQCISD(T))
5. Efficient density fitting (DF) programs for Hartree-Fock (DF-HF), Density functional Kohn-Sham theory (DF-KS), Second-order Møller-Plesset perturbation theory (DF-MP2), as well as for all local methods (DF-LMP2, DF-LMP4, DF-LQCISD(T), DF-LCCSD(T))
6. Analytical QCISD(T) gradients
7. Analytical MRPT2 (CASPT2) and MS-CASPT2 gradients, using state averaged MCSCF reference functions
9. Explicitly correlated methods with density fitting: DF-MP2-R12/2A', DF-MP2-F12/2A' as well as the local variants DF-LMP2-R12/2*A(loc) and DF-LMP2-F12/2*A(loc).
10. Coupling of multi-reference perturbation theory and configuration interaction (CIPT2)
11. DFT-SAPT
12. Transition moments and transition Hamiltonian between CASCCF and MRCI wavefunctions with different orbitals.
15. Improved procedures for geometry optimization and numerical Hessian calculations, including constrained optimization.
16. Improved facilities to treat large lattices of point charges for QM/MM calculations, including lattice gradients (see section [59]).
17. An interface to the MRCC program of M. Kallay, allowing coupled-cluster calculations with arbitrary excitation level.
19. Additional parallel codes, e.g. DF-HF, DF-KS, DF-LCCSD(T) (partly, including triples).
20. Additional output formats for tables (XHTML, LATEX, Maple, Mathematica, Matlab) and comma-separated variables), orbitals and basis sets (XML), and an optional well-formed XML output stream with important results marked up.
B.7 New features of MOLPRO2002.6

Relative to version 2002.1, there are the following changes and additions:

1. Support for IA-64 Linux systems (HP and NEC) and HP-UX 11.22 for IA-64 (Itanium2).
2. Support for NEC-SX systems.
3. Support for IBM-power4 systems.
4. Modified handling of Molpro system variables. The \texttt{SET} command has changed (see sections 8 and 8.4).
5. The total charge of the molecule can be specified in a variable \texttt{CHARGE} or on the \texttt{WF} card (see section 4.9).
6. Improved numerical geometry optimization using symmetrical displacement coordinates (see sections 45.2 and 46).
7. Improved numerical frequency calculations using the symmetry (\texttt{AUTO} option (see section 47)

B.8 New features of MOLPRO2002

Relative to version 2000.1, there are the following principal changes and additions:

1. Modules direct and local are now included in the base version. This means that integral-direct procedures as described in
   M. Schütz, R. Lindh, and H.-J. Werner, Mol. Phys. 96, 719 (1999),
   linear-scaling local MP2, as described in
   as well as LMP2 gradients as described in
   are now available without special license. The linear scaling LCCSD(T) methods as described in
   will be made available at a later stage.
3. Additional and more flexible options for computing numerical gradients and performing geometry optimizations.
4. A large number of additional density functionals have been added, together with support for the automated functional implementer described in Comp. Phys. Commun. \textbf{136} 310–318 (2001).
5. Multipole moments of arbitrary order can be computed.
6. Further modules have been parallelized, in particular the CCSD(T) and direct LMP2 codes. The parallel running procedures have been improved. The parallel version is available as an optional module.
7. The basis set library has been extended.
8. Some subtle changes in the basis set input: it is not possible any more that several one-line basis input cards with definitions for individual atoms follow each other. Each new basis card supercedes previous ones. Either all specifications must be given on one \texttt{BASIS} card, or a basis input block must be used. \texttt{BASIS,NAME} is now entirely equivalent to \texttt{BASIS=NAME}, i.e. a global default basis set is defined and the variable \texttt{BASIS} is set in both cases.
9. Pseudopotential energy calculations can now be performed with up to $i$-functions, gradients with up to $h$-functions.

10. Many internal changes have been made to make MOLPRO more modular and stable. Support has been added for recent operating systems on Compaq, HP, SGI, SUN, and Linux. The patching system has been improved.

### B.9 Features that were new in MOLPRO2000

Relative to version 98.1, there are the following principal changes and additions:

1. There was a fundamental error in the derivation of the spin-restricted open-shell coupled-cluster equations in J. Chem. Phys. 99, 5129 (1993) that is also reflected in the RCCSD code in MOLPRO version 98.1 and earlier. This error has now been corrected, and an erratum has been published in J. Chem. Phys. 112, 3106 (2000). Fortunately, the numerical implications of the error were small, and it is not anticipated that any computed properties will have been significantly in error.

2. There was a programming error in the transformation of gradients from Cartesian to internal coordinates, which in some cases resulted in slow convergence of geometry optimizations. The error is now fixed.

3. Vibrational frequencies formerly by default used average atomic masses, rather than those of the most common isotopes, which is now the default behaviour.

4. MCSCF second derivatives (author Riccardo Tarroni) added (preliminary version, only without symmetry). Frequency and geometry optimization programs are modified so that they can use the analytic Hessian.


6. EOM-CCSD for excited states (author Tatiana Korona).

7. QCISD dipole moments as true analytical energy derivatives (author Guntram Rauhut).


9. Improved handling of basis and geometry records. 98.1 and 99.1 dump files can be restarted, but in case of problems with restarting old files, add \texttt{RESTART,NOGEOM} immediately after the file card. Also, if there are unjustified messages coming up in very large cases about "ORBITALS CORRESPOND TO DIFFERENT GEOMETRY" try \texttt{ORBITAL,record,NOCHECK}. (This can happen for cases with more than 100 atoms, since the old version was limited to 100).

10. Reorganization and generalization of basis input. Increased basis library.

11. Counterpoise geometry optimizations.

12. Improved running procedures for MPP machines. Parallel direct scf and scf gradients are working. These features are only available with the MPP module, which is not yet being distributed.

13. Important bugfixes for DFT grids, CCSD with paging, finite field calculations without core orbitals, spin-orbit coupling.

14. Many other internal changes.

As an additional service to the MOLPRO community, an electronic mailing list has been set up to provide a forum for open discussion on all aspects of installing and using MOLPRO. The mailing list is intended as the primary means of disseminating hints and tips on how to use Molpro effectively. It is not a means of raising queries directly with the authors of the program. For clearly demonstrable program errors, reports should continue to be sent to molpro@molpro.net; however, ‘how-to’ questions sent there will merely be redirected to this mailing list.
In order to subscribe to the list, send mail to molpro-user-request@molpro.net containing the text `subscribe;` for help, send mail containing the text `help.`

Messages can be sent to the list (molpro-user@molpro.net), but this can be done only by subscribers. Previous postings can be viewed in the archive at http://www.molpro.net/molpro-user/archive irrespective of whether or not you subscribe to the list. Experienced Molpro users are encouraged to post responses to queries raised. Please do contribute to make this resource mutually useful.

## B.10 Facilities that were new in MOLPRO98

**MOLPRO98** has the full functionality of **MOLPRO96**, but in order to make the code more modular and easier to use and maintain, a number of structural changes have been made. In particular, the number of different records has been significantly reduced. The information for a given wavefunction type, like orbitals, density matrices, fock matrices, occupation numbers and other information, is now stored in a single dump record. Even different orbital types, e.g., canonical, natural, or localized orbitals, are stored in the same record, and the user can subsequently access individual sets by keywords on the **ORBITAL** directive. New facilities allow the use of starting orbitals computed with different basis sets and/or different symmetries for SCF or MCSCF calculations. The default starting guess for SCF calculations has been much improved, which is most useful in calculations for large molecules. The use of special procedures for computing non-adiabatic couplings or diabatization of orbitals has been significantly simplified. We hope that these changes make the program easier to use and reduce the probability of input errors. However, in order to use the new facilities efficiently, even experienced **MOLPRO** users should read the sections **RECORDS** and **SELECTING ORBITALS AND DENSITY MATRICES** in the manual. It is likely that standard **MOLPRO96** inputs still work, but changes may be required in more special cases involving particular records for orbitals, density matrices, or operators.

All one-electron operators needed to compute expectation values and transition quantities are now stored in a single record. Operators for which expectation values are requested can be selected globally for all programs of a given run using the global **GEXPEC** directive, or for a specific program using the **EXPEC** directive. All operators are computed automatically when needed, and the user does not have to give input for this any more. See section **ONE-ELECTRON OPERATORS AND EXPECTATION VALUES** of the manual for details.

Due to the changed structure of dump and operator records, the utility program **MATROP** has a new input syntax. **MOLPRO96** inputs for **MATROP** do not work any more.

In addition to these organizational changes, a number of new programs have been added. Analytic energy gradients can now be evaluated for MP2 and DFT wavefunctions, and harmonic vibrational frequencies, intensities, and thermodynamic quantities can be computed automatically using finite differences of analytical gradients. Geometry optimization has been further improved, and new facilities for reaction path following have been added.

An interface to the graphics program **MOLDEN** has been added, which allows to visualize molecular structures, orbitals, electron densities, or vibrations.

Integral-direct calculations, in which the two-electron integrals in the AO basis are never stored on disk but always recomputed when needed, are now available for all kinds of wavefunctions, with the exception of perturbative triple excitations in MP4 and CCSD(T) calculations. This allows the use of significantly larger basis sets than was possible before. The direct option can be selected globally using the **GDIRECT** command, or for a specific program using the **DIRECT** directive. See section **INTEGRAL DIRECT METHODS** in the manual for details. Note that the **DIRECT** module is optional and not part of the basic **MOLPRO** distribution.

**Local** electron correlation methods have been further improved. In combination with the integral-direct modules, which implement efficient prescreening techniques, the scaling of the computational cost with molecular size is dramatically reduced, approaching now quadratic or even linear scaling for MP2 and higher correlation methods. This makes possible to perform correlated calculations for much larger molecules than were previously feasible. However, since these methods are subject of active current research and still under intense development, we decided not to include them in the current **MOLPRO** release. They will be optionally available in one of the next releases.
C Density functional descriptions

C.1 B86: Xαβγ

Divergence free semiempirical gradient-corrected exchange energy functional. $\lambda = \gamma$ in ref. (66)

$$g = -\frac{c(\rho(s))^{4/3}(1 + \beta(\chi(s))^2)}{1 + \lambda(\chi(s))^2},$$

(66)

$$G = -\frac{c(\rho(s))^{4/3}(1 + \beta(\chi(s))^2)}{1 + \lambda(\chi(s))^2},$$

(67)

$$c = \frac{3}{8}\sqrt[3]{3\sqrt[3]{3}2\sqrt[3]{\pi} - 1},$$

(68)

$$\beta = 0.0076,$$

(69)

$$\lambda = 0.004.$$}

C.2 B86MGC: Xαβγ with Modified Gradient Correction

B86 with modified gradient correction for large density gradients.

$$g = -c(\rho(s))^{4/3} - \frac{\beta(\chi(s))^2(\rho(s))^{4/3}}{(1 + \lambda(\chi(s))^2)^{4/5}},$$

(71)

$$G = -c(\rho(s))^{4/3} - \frac{\beta(\chi(s))^2(\rho(s))^{4/3}}{(1 + \lambda(\chi(s))^2)^{4/5}},$$

(72)

$$c = \frac{3}{8}\sqrt[3]{3\sqrt[3]{3}2\sqrt[3]{\pi} - 1},$$

(73)

$$\beta = 0.00375,$$

(74)

$$\lambda = 0.007.$$}

C.3 B86R: Xαβγ Re-optimised

Re-optimised $\beta$ of B86 used in part 3 of Becke’s 1997 paper.

$$g = -\frac{c(\rho(s))^{4/3}(1 + \beta(\chi(s))^2)}{1 + \lambda(\chi(s))^2},$$

(76)

$$G = -\frac{c(\rho(s))^{4/3}(1 + \beta(\chi(s))^2)}{1 + \lambda(\chi(s))^2},$$

(77)

$$c = \frac{3}{8}\sqrt[3]{3\sqrt[3]{3}2\sqrt[3]{\pi} - 1},$$

(78)

$$\beta = 0.00787,$$

(79)

$$\lambda = 0.004.$$}
C.4  **B88**: Becke 1988 Exchange Functional

\[ G = - (\rho(s))^{4/3} \left( c + \frac{\beta(\chi(s))^2}{1 + 6\beta \chi(s) \text{arsinh}(\chi(s))} \right), \]  
\[ g = - (\rho(s))^{4/3} \left( c + \frac{\beta(\chi(s))^2}{1 + 6\beta \chi(s) \text{arsinh}(\chi(s))} \right), \]  
\[ c = 3/8 \sqrt[4/3]{\pi^2} \sqrt[3]{c}, \]  
\[ \beta = 0.0042. \]  

C.5  **B88C**: Becke 1988 Correlation Functional

Correlation functional depending on B86MGC exchange functional with empirical atomic parameters, \( t \) and \( u \). The exchange functional that is used in conjunction with B88C should replace B88MGC here.

\[ f = -0.8 \rho(a) \rho(b) q^2 \left( 1 - \frac{\ln(1 + q)}{q} \right), \]  
\[ q = t(x + y), \]  
\[ x = 0.5 \left( c \sqrt[4/3]{\rho(a)} + \frac{\beta(\chi(a))^2 \sqrt[4/3]{\rho(a)}}{(1 + \lambda (\chi(a))^2)^{4/5}} \right)^{-1}, \]  
\[ y = 0.5 \left( c \sqrt[4/3]{\rho(b)} + \frac{\beta(\chi(b))^2 \sqrt[4/3]{\rho(b)}}{(1 + \lambda (\chi(b))^2)^{4/5}} \right)^{-1}, \]  
\[ t = 0.63, \]  
\[ g = -0.01 \rho(s) dz^4 \left( 1 - 2 \frac{\ln(1 + 1/2z)}{z} \right), \]  
\[ z = 2ur, \]  
\[ r = 0.5 \rho(s) \left( c (\rho(s))^{4/3} + \frac{\beta(\chi(s))^2 (\rho(s))^{4/3}}{(1 + \lambda (\chi(s))^2)^{4/5}} \right)^{-1}, \]
\( u = 0.96, \) 

\( d = \tau (s) \)
\( - \frac{1}{4} \frac{\sigma (ss)}{\rho (s)}, \)  

\( G = -0.01 \rho (s) dz^2 \left( 1 - 2 \frac{\ln (1 + 1/2z)}{z} \right), \) 

\( c = \frac{3}{8} \sqrt{34^{2\beta} \sqrt{\pi^{-1}}}, \) 

\( \beta = 0.00375, \) 

\( \lambda = 0.007. \)  

C.6 \textbf{B95: Becke 1995 Correlation Functional}

\( \tau \) dependent Dynamical correlation functional.

\( T = [0.031091, 0.015545, 0.016887], \) 

\( U = [0.21370, 0.20548, 0.11125], \) 

\( V = [7.5957, 14.1189, 10.357], \) 

\( W = [3.5876, 6.1977, 3.6231], \) 

\( X = [1.6382, 3.3662, 0.88026], \) 

\( Y = [0.49294, 0.62517, 0.49671], \) 

\( P = [1, 1, 1], \) 

\( f = \frac{E}{1 + l ((\chi (a))^2 + (\chi (b))^2)}, \) 

\( g = \frac{F \varepsilon (\rho (s), 0)}{H (1 + \nu (\chi (s))^2)^2}, \) 

\( G = \frac{F \varepsilon (\rho (s), 0)}{H (1 + \nu (\chi (s))^2)^2}, \) 

\( E = \varepsilon (\rho (a), \rho (b)) \)
\( - \varepsilon (\rho (a), 0) \)
\( - \varepsilon (\rho (b), 0), \) 

\( l = 0.0031, \)
\[ F = \tau(s) - \frac{1}{4} \frac{\sigma^{(ss)}}{\rho(s)}, \]  

\[ H = 3/56 6^{2/3} (\pi^2)^{2/3} (\rho(s))^{5/3}, \]  

\[ \nu = 0.038, \]  

\[ \epsilon(\alpha, \beta) = (\alpha + \beta) \left( e(r(\alpha, \beta), T_1, U_1, V_1, W_1, X_1, Y_1, P_1) \right. \]  

\[ + \left. (r(\alpha, \beta), T_2, U_2, V_2, W_2, X_2, Y_2, P_2) \right) \right) \omega(\xi(\alpha, \beta)) \left( 1 - (\xi(\alpha, \beta))^4 \right) \]  

\[ r(\alpha, \beta) = 1/4 \sqrt[3]{\frac{\pi}{\alpha + \beta}}, \]  

\[ \zeta(\alpha, \beta) = \frac{\alpha - \beta}{\alpha + \beta}, \]  

\[ \omega(z) = \frac{(1 + z)^{4/3} + (1 - z)^{4/3} - 2}{2 \sqrt[3]{2} - 2}, \]  

\[ e(r,t,u,v,w,x,y,p) = -2t(1 + \epsilon) \ln \left( \frac{1}{1/2 (\sqrt{\frac{1}{\tau} + \frac{1}{\omega} + \frac{1}{w} + \frac{1}{x} + \frac{1}{y} + \frac{1}{p}) \right)}, \]  

\[ c = 1.709921. \]  

\[ C \ DENSITY FUNCTIONAL DESCRIPTIONS \]  

**C.7 B97DF: Density functional part of B97**

This functional needs to be mixed with 0.1943*exact exchange.

\[ T = [0.031091, 0.015545, 0.016887], \]  

\[ U = [0.21370, 0.20548, 0.11125], \]  

\[ V = [7.5957, 14.1189, 10.357], \]  

\[ W = [3.5876, 6.1977, 3.6231], \]
\[ X = [1.6382, 3.3662, 0.88026], \]  
\[ Y = [0.49294, 0.62517, 0.49671], \]  
\[ P = [1, 1, 1], \]  
\[ A = [0.9454, 0.7471], \]  
\[ B = [0.1737, 2.3487], \]
\[ C = [0.8094, 0.5073, 0.7481], \]  
\[ \lambda = [0.006, 0.2, 0.004], \]  
\[ d = \frac{1}{2} (\chi (a))^2 \]
\[ + \frac{1}{2} (\chi (b))^2, \]
\[ f = (\varepsilon (\rho (a), \rho (b))) \]
\[ - \varepsilon (\rho (a), 0) \]
\[ - \varepsilon (\rho (b), 0) \] \( A_0 \)  
\[ + A_2 (\eta (d, \lambda_2))^2 \]  
\[ \eta (\theta, \mu) \]
\[ = \frac{\mu \theta}{1 + \mu \theta^3} \]
\[ g = \varepsilon (\rho (s), 0) \] \( B_0 \)  
\[ + B_2 (\eta ((\chi (s))^2, \lambda_2))^2 \]  
\[ - \frac{3}{8} \sqrt{3} \frac{2}{3} \pi^{-1} (\rho (s))^{4/3} (C_0 \]  
\[ + C_2 (\eta ((\chi (s))^2, \lambda_3))^2 \)  
\[ G = \varepsilon (\rho (s), 0) \] \( B_0 \)  
\[ + B_2 (\eta ((\chi (s))^2, \lambda_2))^2 \]  
\[ - \frac{3}{8} \sqrt{3} \frac{2}{3} \pi^{-1} (\rho (s))^{4/3} (C_0 \]
\[ + C_2 (\eta ((\chi (s))^2, \lambda_3))^2 \)  
\[ \varepsilon (\alpha, \beta) \]
\[ = (\alpha \]
\[ + \beta \left( e (r (\alpha, \beta), T_1, U_1, V_1, W_1, X_1, Y_1, P_1) \]  
\[ - e (r (\alpha, \beta), T_3, U_3, V_3, W_3, X_3, Y_3, P_3) \] \( \omega (\zeta (\alpha, \beta)) (1 - (\zeta (\alpha, \beta))^4) \]  
\[ + e (r (\alpha, \beta), T_2, U_2, V_2, W_2, X_2, Y_2, P_2) \]  
\[ - e (r (\alpha, \beta), T_1, U_1, V_1, W_1, X_1, Y_1, P_1) \] \( \omega (\zeta (\alpha, \beta)) (\zeta (\alpha, \beta))^4 \) \) \).
\( r(\alpha, \beta) \)
\[
= \frac{1}{4} \sqrt[3]{\frac{2}{\pi}} \frac{1}{\sqrt[3]{(\alpha + \beta)}},
\]
\( (137) \)

\( \zeta(\alpha, \beta) \)
\[
= \frac{\alpha - \beta}{\alpha + \beta},
\]
\( (138) \)

\( \omega(z) \)
\[
= \frac{(1 + z)^{4/3} + (1 - z)^{4/3} - 2}{2 \sqrt{2} - 2},
\]
\( (139) \)

\( e(r, t, u, v, w, x, y, p) \)
\[
= -2t \left( 1 + \frac{1}{2} \ln \left( \frac{1}{t(v\sqrt{r + w} + x^{3/2} + y + r + p + 1)} \right) \right),
\]
\( (140) \)

\( c = 1.709921. \)
\( (141) \)

**C.8 B97RDF: Density functional part of B97 Re-parameterized by Hamprecht et al**

Re-parameterization of the B97 functional in a self-consistent procedure by Hamprecht et al. This functional needs to be mixed with 0.21*exact exchange.

\( T = [0.031091, 0.015545, 0.016887], \)
\( (142) \)

\( U = [0.21370, 0.20548, 0.11125], \)
\( (143) \)

\( V = [7.5957, 14.1189, 10.357], \)
\( (144) \)

\( W = [3.5876, 6.1977, 3.6231], \)
\( (145) \)

\( X = [1.6382, 3.3662, 0.88026], \)
\( (146) \)

\( Y = [0.49294, 0.62517, 0.49671], \)
\( (147) \)

\( P = [1, 1, 1], \)
\( (148) \)

\( A = [0.955689, 0.788552, -5.47869], \)
\( (149) \)

\( B = [0.0820011, 2.71681, -2.87103], \)
\( (150) \)

\( C = [0.789518, 0.573805, 0.660975], \)
\( (151) \)

\( \lambda = [0.006, 0.2, 0.004], \)
\( (152) \)
\[d = \frac{1}{2} \left( \chi (a) \right)^2 + \frac{1}{2} \left( \chi (b) \right)^2, \quad (153)\]

\[f = (\varepsilon (\rho (a), \rho (b)) - \varepsilon (\rho (a), 0) - \varepsilon (\rho (b), 0)) (A_0 + A_2 (\eta (d, \lambda_1))^2), \quad (154)\]

\[\eta (\theta, \mu) = \frac{\mu \theta}{1 + \mu \theta}, \quad (155)\]

\[g = \varepsilon (\rho (s), 0) (B_0 + B_1 \eta ((\chi (s))^2, \lambda_2) + B_1 \eta ((\chi (s))^2, \lambda_2) ) (156)\]

\[G = \varepsilon (\rho (s), 0) (B_0 + B_1 \eta ((\chi (s))^2, \lambda_2)) (157)\]

\[\varepsilon (\alpha, \beta) = (\alpha + \beta) \left( \varepsilon (r (\alpha, \beta), T_1, U_1, V_1, W_1, X_1, Y_1, P_1) \right) \quad (158)\]

\[r (\alpha, \beta) = \frac{1}{4} \sqrt{\frac{3}{4}} \frac{1}{\sqrt{\pi (\alpha + \beta)}}, \quad (159)\]

\[\zeta (\alpha, \beta) = \frac{\alpha - \beta}{\alpha + \beta}, \quad (160)\]

\[\omega (z) = \frac{(1 + z)^{4/3} + (1 - z)^{4/3} - 2}{2 \sqrt{2} - 2}, \quad (161)\]
\[ e(r,t,u,v,w,x,y,p) = -2t \left( 1 + ur \right) \ln \left( \frac{1 + 1/2}{v \sqrt{r + wr + xr^{3/2} + yr^{3/2} + 1}} \right), \]  
\[ c = 1.709921. \]  

\section*{C.9 \ BR: Becke-Roussel Exchange Functional}


\[ K = \frac{1}{2} \sum \rho_s U_s, \]  
\[ U_s = -\left( 1 - e^{-x} - xe^{-x/2} / b, \right. \]  
\[ b = \frac{x^3 e^{-x}}{8\pi \rho_s} \]  

and \( x \) is defined by the nonlinear equation

\[ \frac{x e^{-2x^3}}{x - 2} = \frac{2\pi^{2/3} \rho_s^{5/3}}{3 Q_s}, \]  

where

\[ Q_s = (u_s - 2\gamma D_s)/6, \]  
\[ D_s = \tau_s - \frac{\sigma_{ss}}{4\rho_s} \]  

and

\[ \gamma = 1. \]  

\section*{C.10 \ BRUEG: Becke-Roussel Exchange Functional — Uniform Electron Gas Limit}


As for \( \text{BR} \) but with \( \gamma = 0.8. \)
C.11 BW: Becke-Wigner Exchange-Correlation Functional


\[ \alpha = -3/8 \sqrt{3/2} \sqrt{\pi}^{-1}, \]  

(171)

\[ g = \alpha (\rho (s))^{4/3} \left( \frac{\beta}{1 + 6\beta \chi (s) \text{arcsinh} (\chi (s))} \right)^{4/3} \]  

(172)

\[ G = \alpha (\rho (s))^{4/3} \left( \frac{\beta}{1 + 6\beta \chi (s) \text{arcsinh} (\chi (s))} \right)^{4/3} \]  

(173)

\[ f = -4c \rho (a) \rho (b) \rho^{-1} \left( 1 + \frac{d}{\sqrt{\rho}} \right)^{-1}, \]  

(174)

\[ \beta = 0.0042, \]  

(175)

\[ c = 0.04918, \]  

(176)

\[ d = 0.349. \]  

(177)

C.12 CS1: Colle-Salvetti correlation functional


CS1 is formally identical to CS2, except for a reformulation in which the terms involving \( \nu \) are eliminated by integration by parts. This makes the functional more economical to evaluate. In the limit of exact quadrature, CS1 and CS2 are identical, but small numerical differences appear with finite integration grids.

C.13 CS2: Colle-Salvetti correlation functional


CS2 is defined through

\[ K = -a \left( \frac{\rho + 2h \rho^{-5/3} [\rho_{\alpha} t_{\alpha} + \rho_{\beta} t_{\beta} - \rho t_{W}] e^{-c \rho^{-1/3}}}{1 + d \rho^{-1/3}} \right) \]  

(178)

where

\[ t_{\alpha} = \frac{\alpha}{2} - \frac{\nu_{\alpha}}{8} \]  

(179)

\[ t_{\beta} = \frac{\beta}{2} - \frac{\nu_{\beta}}{8} \]  

(180)

\[ t_{W} = \frac{1}{8} \sigma \left( \frac{1}{2} - \frac{v}{2} \right) \]  

(181)

and the constants are \( a = 0.04918, b = 0.132, c = 0.2533, d = 0.349. \)
C.14 DIRAC: Slater-Dirac Exchange Energy

Automatically generated Slater-Dirac exchange.

\[ g = -c (\rho(s))^{4/3}, \]  
\[ c = 3/8 \sqrt{2/3} 4^{2/3} \sqrt{\pi}^{-1}. \]  

C.15 ECERF: Short-range LDA correlation functional

Local-density approximation of correlation energy for short-range interelectronic interaction \( \text{erf}(\mu r_{21})/r_{12} \),

\[ e^{\text{SR}}_c(r_s, \xi, \mu) = e^{\text{PW92}}_c(r_s, \xi) - \frac{[\phi_2(\xi)]^3 Q \left( \frac{\mu r_s}{\phi_2(\xi)} \right) + a_1 \mu^3 + a_2 \mu^4 + a_3 \mu^5 + a_4 \mu^6 + a_5 \mu^8}{(1 + b_0^2 \mu^2)^4}, \]  
\[ \text{where} \]  
\[ Q(x) = \frac{2 \ln(2) - 2}{\pi^2} \ln \left( \frac{1 + ax + b x^2 + c x^3}{1 + ax + dx^2} \right), \]  
\[ \text{with} \ a = 5.84605, \ c = 3.91744, \ d = 3.44851, \ \text{and} \ b = d - 3 \pi a/(4 \ln(2) - 4). \ \text{The parameters} \ a_i(r_s, \xi) \ \text{are given by} \]  
\[ a_1 = 4 b_0^6 C_3 + b_0^8 C_5, \]  
\[ a_2 = 4 b_0^6 C_2 + b_0^8 C_4 + 6 b_0^8 e^{\text{PW92}}_c, \]  
\[ a_3 = b_0^8 C_3, \]  
\[ a_4 = b_0^8 C_2 + 4 b_0^8 e^{\text{PW92}}_c, \]  
\[ a_5 = b_0^8 e^{\text{PW92}}_c, \]  
\[ \text{with} \]  
\[ C_2 = -\frac{3(1 - \xi^2) g_c(0, r_s, \xi = 0)}{8 r_s^3} \]  
\[ C_3 = -(1 - \xi^2) g(0, r_s, \xi = 0) \]  
\[ C_4 = -\frac{9 c_4(r_s, \xi)}{64 r_s^3} \]  
\[ C_5 = -\frac{9 c_5(r_s, \xi)}{40 \sqrt{2\pi} r_s^3} \]  
\[ c_4(r_s, \xi) = \left( \frac{1 + \xi}{2} \right)^2 g'' \left( 0, r_s \left( \frac{2}{1 + \xi} \right)^{1/3}, \xi = 1 \right) + \left( \frac{1 - \xi}{2} \right)^2 \times \]  
\[ g'' \left( 0, r_s \left( \frac{2}{1 - \xi} \right)^{1/3}, \xi = 1 \right) + (1 - \xi^2) D_2(r_s) - \frac{\phi(\xi)}{5 \alpha^2 r_s^2}, \]  
\[ c_5(r_s, \xi) = \left( \frac{1 + \xi}{2} \right)^2 g'' \left( 0, r_s \left( \frac{2}{1 + \xi} \right)^{1/3}, \xi = 1 \right) + \left( \frac{1 - \xi}{2} \right)^2 \times \]  
\[ g'' \left( 0, r_s \left( \frac{2}{1 - \xi} \right)^{1/3}, \xi = 1 \right) + (1 - \xi^2) D_3(r_s), \]  
\[ (186) \]
and

\[ b_0(r_s) = 0.784949 r_s \]  

\[ g''(0, r_s, \zeta = 1) = \frac{2^{5/3}}{5 \alpha^2 r_s^2} \frac{1 - 0.02267 r_s}{(1 + 0.4319 r_s + 0.04 r_s^2)} \]  

\[ D_2(r_s) = \frac{e^{-0.547 r_s}}{r_s^2} \left( -0.388 r_s + 0.676 r_s^2 \right) \]  

\[ D_3(r_s) = \frac{e^{-0.31 r_s}}{r_s^3} \left( -4.95 r_s + r_s^2 \right). \]  

Finally, \( \varepsilon_{c}^{\text{PW92}}(r_s, \zeta) \) is the Perdew-Wang parametrization of the correlation energy of the standard uniform electron gas [J.P. Perdew and Y. Wang, Phys. Rev. B 45, 13244 (1992)], and

\[ g(0, r_s, \zeta = 0) = \frac{1}{2} (1 - Br_s + Cr_s^2 + Dr_s^3 + Er_s^4) e^{-dr_s}, \]  

is the on-top pair-distribution function of the standard jellium model [P. Gori-Giorgi and J.P. Perdew, Phys. Rev. B 64, 155102 (2001)], where \( B = -0.0207, C = 0.08193, D = -0.01277, E = 0.001859, d = 0.7524 \). The correlation part of the on-top pair-distribution function is \( g_c(0, r_s, \zeta = 0) = g_c(0, r_s, \zeta = 0) - \frac{1}{2} \).

### C.16 ECERFPBE: Range-Separated Correlation Functional


### C.17 EXACT: Exact Exchange Functional

Hartree-Fock exact exchange functional can be used to construct hybrid exchange-correlation functional.

### C.18 EXERF: Short-range LDA correlation functional

Local-density approximation of exchange energy for short-range interelectronic interaction \( \text{erf}(\mu r_{12})/r_{12} \). A. Savin, in Recent Developments and Applications of Modern Density Functional Theory, edited by J.M. Seminario (Elsevier, Amsterdam, 1996).

\[ \varepsilon_{c}^{\text{SR}}(r_s, \zeta, \mu) = \frac{3}{4\pi} \frac{\phi_4(\zeta)}{\alpha r_s} - \frac{1}{2} (1+ \zeta)^{4/3} f_4 \left( r_s, \mu (1+ \zeta)^{-1/3} \right) + \frac{1}{2} (1- \zeta)^{4/3} f_4 \left( r_s, \mu (1- \zeta)^{-1/3} \right) \]  

with

\[ \phi_4(\zeta) = \frac{1}{2} \left[ (1+ \zeta)^{4/3} + (1- \zeta)^{4/3} \right], \]  

\[ f_4(r_s, \mu) = \frac{-\mu}{\pi} \left[ (2y - 4y^3) e^{-1/4y^2} - 3y + 4y^3 + \sqrt{\pi} \text{erf} \left( \frac{1}{2y} \right) \right], \quad y = \frac{\mu \alpha r_s}{2}, \]  

and \( \alpha = (4/9 \pi)^{1/3} \).
C.19 EXERFPBE: Range-Separated Exchange Functional


C.20 G96: Gill’s 1996 Gradient Corrected Exchange Functional

\[ \alpha = -\frac{3}{8} \sqrt{\frac{3}{4}} \sqrt[3]{\pi}^{-1}, \]  
\[ g = (\rho(s))^{4/3} \left( \alpha - \frac{1}{137} (\chi(s))^{3/2} \right), \]  
\[ G = (\rho(s))^{4/3} \left( \alpha - \frac{1}{137} (\chi(s))^{3/2} \right). \]

C.21 HCTH120: Handy least squares fitted functional

\[ T = [0.031091, 0.015545, 0.016887], \]  
\[ U = [0.21370, 0.20548, 0.11125], \]  
\[ V = [7.5957, 14.1189, 10.357], \]  
\[ W = [3.5876, 6.1977, 3.6231], \]  
\[ X = [1.6382, 3.3662, 0.88026], \]  
\[ Y = [0.49294, 0.62517, 0.49671], \]  
\[ P = [1, 1, 1], \]  
\[ A = [0.51473, 6.9298, -24.707, 23.110, -11.323], \]  
\[ B = [0.48951, -0.2607, 0.4329, -1.9925, 2.4853], \]  
\[ C = [1.09163, -0.7472, 5.0783, -4.1075, 1.1717], \]  
\[ \lambda = [0.006, 0.2, 0.004], \]  
\[ d = \frac{1}{2} (\chi(a))^2 + \frac{1}{2} (\chi(b))^2, \]
\[ f = (e(\rho(a),\rho(b)) - e(\rho(a),0) - e(\rho(b),0)) (A_0 + A_1 \eta(d,\lambda_1)) + A_2 (\eta(d,\lambda_1))^2 + A_3 (\eta(d,\lambda_1))^3 + A_4 (\eta(d,\lambda_1))^4, \]

\[ \eta(\theta,\mu) = \frac{\mu \theta}{1 + \mu \theta}, \]

\[ g = e(\rho(s),0) (B_0 + B_1 \eta((\chi(s))^2,\lambda_2)) + B_2 (\eta((\chi(s))^2,\lambda_2))^2 + B_3 (\eta((\chi(s))^2,\lambda_3))^3 + B_4 (\eta((\chi(s))^2,\lambda_3))^4) - 3/8 \sqrt{34^{2/3} \sqrt{\pi}} (\rho(s))^{4/3} (C_0 + C_1 \eta((\chi(s))^2,\lambda_3)) + C_2 (\eta((\chi(s))^2,\lambda_1))^2 + C_3 (\eta((\chi(s))^2,\lambda_1))^3 + C_4 (\eta((\chi(s))^2,\lambda_1))^4), \]

\[ \epsilon(\alpha,\beta) = (\alpha + \beta) \left( e(r(\alpha,\beta),T_1,U_1,V_1,W_1,X_1,Y_1,P_1) - e(r(\alpha,\beta),T_2,U_2,V_2,W_2,X_2,Y_2,P_2) \right) + e(r(\alpha,\beta),T_1,U_1,V_1,W_1,X_1,Y_1,P_1) \omega(\zeta(\alpha,\beta))(1 - (\zeta(\alpha,\beta))^4) \]

\[ r(\alpha,\beta) = 1/4 \sqrt{34^{2/3} \sqrt{\pi}} (\alpha + \beta)^{1/3}, \]

\[ \zeta(\alpha,\beta) = \frac{\alpha - \beta}{\alpha + \beta}, \]

\[ \omega(z) = \frac{(1+z)^{4/3} + (1-z)^{4/3} - 2}{2 \sqrt{2} - 2}, \]
\[ e(r,t,u,v,w,x,y,p) = -2t (1 + ur) \ln \left( \frac{1}{t(\sqrt{r + wr + xr^{3/2} + yr^{3/2}})} \right), \]
\[ c = 1.709921. \]

C.22 HCTH147: Handy least squares fitted functional

\[ T = [0.031091, 0.015545, 0.016887], \]
\[ U = [0.21370, 0.20548, 0.11125], \]
\[ V = [7.5957, 14.1189, 10.357], \]
\[ W = [3.5876, 6.1977, 3.6231], \]
\[ X = [1.6382, 3.3662, 0.88026], \]
\[ Y = [0.49294, 0.62517, 0.49671], \]
\[ P = [1, 1, 1], \]
\[ A = [0.542352, 7.01464, -28.3822, 35.0329, -20.4284], \]
\[ B = [0.562576, -0.0171436, -1.30636, 1.05747, 0.885429], \]
\[ C = [1.09025, -0.799194, 5.57212, -5.86760, 3.04544], \]
\[ \lambda = [0.006, 0.2, 0.004], \]
\[ d = \frac{1}{2} (\chi(a))^2 + 1/2 (\chi(b))^2, \]
\[ f = (\varepsilon (\rho(a), \rho(b)) - \varepsilon (\rho(a), 0) - \varepsilon (\rho(b), 0)) (A_0 + A_1 \eta (d, \lambda_1)) + A_2 (\eta (d, \lambda_1))^2 + A_3 (\eta (d, \lambda_1))^3 + A_4 (\eta (d, \lambda_1))^4), \]
\[
\eta(\theta, \mu) = \frac{\mu \theta}{1 + \mu \theta}, \tag{232}
\]

\[
g = \varepsilon(\rho(s), 0) \left( B_0 \right. \tag{233}
+ B_1 \eta \left( (\chi(s))^2, \lambda_2 \right) \]
\[
+ B_2 \left( \eta \left( (\chi(s))^2, \lambda_3 \right) \right)^2 \]
\[
+ B_3 \left( \eta \left( (\chi(s))^2, \lambda_3 \right) \right)^3 \]
\[
+ B_4 \left( \eta \left( (\chi(s))^2, \lambda_3 \right) \right)^4 \]
\[
- 3/8 \sqrt{34}^{2/3} \sqrt{\pi^{-1}} (\rho(s))^{4/3} \left( C_0 \right. \tag{234}
+ C_1 \eta \left( (\chi(s))^2, \lambda_3 \right) \]
\[
+ C_2 \left( \eta \left( (\chi(s))^2, \lambda_3 \right) \right)^2 \]
\[
+ C_3 \left( \eta \left( (\chi(s))^2, \lambda_3 \right) \right)^3 \]
\[
+ C_4 \left( \eta \left( (\chi(s))^2, \lambda_3 \right) \right)^4 \right). \]

\[
\varepsilon(\alpha, \beta) = (\alpha \tag{235}
+ \beta) \left( e(r(\alpha, \beta), T_1, U_1, W_1, X_1, Y_1, P_1) \right. \]
\[
+ e(r(\alpha, \beta), T_3, U_3, W_3, X_3, Y_3, P_3) \omega(\zeta(\alpha, \beta)) \left( 1 - (\zeta(\alpha, \beta))^4 \right) \]
\[
+ e(r(\alpha, \beta), T_2, U_2, W_2, X_2, Y_2, P_2) \right. \tag{236}
\[
- e(r(\alpha, \beta), T_1, U_1, W_1, X_1, Y_1, P_1) \omega(\zeta(\alpha, \beta)) (\zeta(\alpha, \beta))^4 \right) \],

\[
r(\alpha, \beta) = 1/4 \sqrt{34}^{2/3} \sqrt{\frac{1}{\pi (\alpha + \beta)}}, \tag{237}
\]

\[
\zeta(\alpha, \beta) = \frac{\alpha - \beta}{\alpha + \beta}, \tag{238}
\]

\[
\omega(z) = \frac{(1 + z)^{4/3} + (1 - z)^{4/3} - 2}{2 \sqrt{2} - 2}, \tag{239}
\]

\[
e(r,t,u,v,w,x,y,p) = \tag{240}
\]
\[
-2t(1 \tag{241}
+ ur)\ln \left( \frac{1 \tag{242}
+ 1/2 \frac{1}{r\sqrt{r + wr + xr^{3/2} + yr^{3/2}}} \right) \right); \tag{243}
\]

\[
c = 1.709921. \tag{244}
\]
C.23 HCTH93: Handy least squares fitted functional

\[ T = [0.031091, 0.015545, 0.016887], \quad (240) \]
\[ U = [0.21370, 0.20548, 0.11125], \quad (241) \]
\[ V = [7.5957, 14.1189, 10.357], \quad (242) \]
\[ W = [3.5876, 6.1977, 3.6231], \quad (243) \]
\[ X = [1.6382, 3.3662, 0.88026], \quad (244) \]
\[ Y = [0.49294, 0.62517, 0.49671], \quad (245) \]
\[ P = [1, 1, 1], \quad (246) \]
\[ A = [0.72997, 3.35287, -11.543, 8.08564, -4.7857], \quad (247) \]
\[ B = [0.222601, -0.0338622, -0.012517, -0.802496, 1.55396], \quad (248) \]
\[ C = [1.0932, -0.744056, 5.5992, -6.78549, 4.49357], \quad (249) \]
\[ \lambda = [0.006, 0.2, 0.004], \quad (250) \]
\[ d = \frac{1}{2} (\chi(a))^2 \]
\[ + \frac{1}{2} (\chi(b))^2, \quad (251) \]
\[ f = (\varepsilon(\rho(a), \rho(b)) \]
\[ - \varepsilon(\rho(a), 0) \]
\[ - \varepsilon(\rho(b), 0)) (A_0 \]
\[ + A_2 (\eta(d, \lambda_1))^2 \]
\[ + A_3 (\eta(d, \lambda_1))^3 \]
\[ + A_4 (\eta(d, \lambda_1))^4), \quad (252) \]
\[ \eta(\theta, \mu) \]
\[ = \frac{\mu \theta}{1 + \mu \theta}, \quad (253) \]
\( g = \epsilon ( \rho ( s ) , 0 ) ( B_0 + B_1 \eta ( ( \chi ( s ) )^2 , \lambda_2 ) ) + B_2 ( \eta ( ( \chi ( s ) )^2 , \lambda_2 ) )^2 \\
+ B_3 ( \eta ( ( \chi ( s ) )^2 , \lambda_2 ) )^3 \\
+ B_4 ( \eta ( ( \chi ( s ) )^2 , \lambda_2 ) )^4 \\
- \frac{3}{8} \sqrt{\frac{4}{3}} \sqrt[3]{\frac{1}{\pi}} ( \rho ( s ) )^{4/3} ( C_0 + C_1 \eta ( ( \chi ( s ) )^2 , \lambda_3 ) ) \\
+ C_2 ( \eta ( ( \chi ( s ) )^2 , \lambda_3 ) )^2 \\
+ C_3 ( \eta ( ( \chi ( s ) )^2 , \lambda_3 ) )^3 \\
+ C_4 ( \eta ( ( \chi ( s ) )^2 , \lambda_3 ) )^4 . \)

\( \epsilon ( \alpha , \beta ) = ( \alpha + \beta ) e ( r ( \alpha , \beta ) , T_1 , U_1 , V_1 , W_1 , X_1 , Y_1 , P_1 ) \\
+ ( e ( r ( \alpha , \beta ) , T_2 , U_2 , V_2 , W_2 , X_2 , Y_2 , P_2 ) + ( e ( r ( \alpha , \beta ) , T_1 , U_1 , V_1 , W_1 , X_1 , Y_1 , P_1 ) ) \omega ( \zeta ( \alpha , \beta ) ) ( \zeta ( \alpha , \beta ) )^4 ) \).

\( r ( \alpha , \beta ) = \frac{1}{4} \sqrt{\frac{4}{3}} \sqrt[3]{\frac{1}{\pi ( \alpha + \beta )}} . \)

\( \zeta ( \alpha , \beta ) = \frac{\alpha - \beta}{\alpha + \beta} . \)

\( \omega ( z ) = \frac{(1 + z)^{4/3} + (1 - z)^{4/3} - 2}{2 \sqrt{2} - 2} . \)

\( e ( r , u , v , w , x , y , p ) = -2r ( 1 + ur ) \ln \left( 1 + \frac{1}{1/2 \left( v \sqrt{r + wr + xr^{3/2} + yr^{3/2}} + 1 \right)} \right) . \)

\( c = 1.709921 . \)

**C.24 HJSWPBEX: Meta GGA Correlation Functional**

C.25 LTA: Local $\tau$ Approximation

LSDA exchange functional with density represented as a function of $\tau$.

\begin{align}
g & = 1/2 E(2 \tau(s)), \quad (261) \\
E(\alpha) & \\
& = 1/9 c^{4/5} \sqrt[4/5]{\frac{\alpha \sqrt{3}}{(\pi^2)^2/3}}, \quad (262) \\
c & = -3/4 \sqrt{3} \sqrt{\pi}, \quad (263) \\
G & = 1/2 E(2 \tau(s)). \quad (264)
\end{align}

C.26 LYP: Lee, Yang and Parr Correlation Functional


\begin{align}
f & = -4 A \rho(a) \rho(b) \left(1 + \frac{d}{\sqrt{\rho}}\right)^{-1} \rho^{-1} \quad (265) \\
& - AB \omega \left( \rho(a) \rho(b) \left(82^{2/3} c f \left((\rho(a))^{8/3} \right) \right) \right. \\
& \left. + \left(\frac{47}{18} \right) \right) - \left(\frac{5}{2} \right) \sigma(b) \right) \\
& - \left(1/9 \right) \left(\delta \right) \\
& - \left(2/3 \rho^2 \sigma \right) + \left(2/3 \rho^2 \right) \\
& + \left(2/3 \rho^2 \right) \\
\omega & = e^{-\frac{c}{3\sqrt{\rho}}} \rho^{-1/3} \left(1 + \frac{d}{\sqrt{\rho}}\right)^{-1} \quad (266)
\end{align}
\[ \delta = \frac{c}{\sqrt[3]{\rho}} + d \frac{1}{\sqrt[3]{\rho}} \left( 1 + \frac{d}{\sqrt[3]{\rho}} \right)^{-1}, \]  
\[ cf = 3/103 (\pi^2)^{2/3}, \]  
\[ A = 0.04918, \]  
\[ B = 0.132, \]  
\[ c = 0.2533, \]  
\[ d = 0.349. \]  

C.27 M05.2XC: M05-2X Meta-GGA Correlation Functional

\[ T = [0.031091, 0.015545, 0.016887], \]  
\[ U = [0.21370, 0.20548, 0.11125], \]  
\[ V = [7.5957, 14.1189, 10.357], \]  
\[ W = [3.5876, 6.1977, 3.6231], \]  
\[ X = [1.6382, 3.3662, 0.88026], \]  
\[ Y = [0.49294, 0.62517, 0.49671], \]  
\[ P = [1, 1, 1], \]  

\[ \epsilon(\alpha, \beta) \]  
\[ = (\alpha + \beta) \left( \epsilon(r(\alpha, \beta), T_1, U_1, V_1, W_1, X_1, Y_1, P_1) \right. \]  
\[ - \epsilon(r(\alpha, \beta), T_3, U_3, V_3, W_3, X_3, Y_3, P_3) \omega(\zeta(\alpha, \beta)) (1 - (\zeta(\alpha, \beta))^4) \right. \]  
\[ + (c^e r(\alpha, \beta), T_2, U_2, V_2, W_2, X_2, Y_2, P_2) \]  
\[ - \epsilon(r(\alpha, \beta), T_1, U_1, V_1, W_1, X_1, Y_1, P_1) \omega(\zeta(\alpha, \beta)) (\zeta(\alpha, \beta))^4 \right) \right), \]  

\[ r(\alpha, \beta) \]  
\[ = 1/4 \sqrt[3]{34^{2/3}} \sqrt{\frac{1}{\pi(\alpha + \beta)}}, \]  

\[ \zeta(\alpha, \beta) \]  
\[ = \frac{\alpha - \beta}{\alpha + \beta}. \]
\( \omega(z) = \frac{(1 + z)^{4/3} + (1 - z)^{4/3} - 2}{2 \sqrt{2} - 2} \),
\( e(r,t,u,v,w,x,y,p) = -2t (1 + ur) \ln \left( 1 + \frac{1}{\sqrt{v} + \sqrt{w} + \sqrt{x} + \sqrt{y} + 1} \right) \),
c = 1.709921,
\( \tau_{sMFM} = \frac{1}{2} \tau(s) \),
\( ds = 2 \tau_{sMFM} - \frac{1}{4} \frac{\sigma(ss)}{\rho(s)} \),
\( Gab(chia, chib) = \sum_{i=0}^{n} c_{Cab} \left( \frac{y_{Cab}(chia^2 + chib^2)}{1 + y_{Cab}(chia^2 + chib^2)} \right)^i \),
\( Gss(chis) = \sum_{i=0}^{n} c_{Css} \left( \frac{y_{Css}chis^2}{1 + y_{Css}chis^2} \right)^i \),
n = 4,
\( c_{Cab} = [1.0, 1.09297, -3.79171, 2.82810, -10.58909] \),
\( c_{Css} = [1.0, -3.05430, 7.61854, 1.47665, -11.92365] \),
y_{Cab} = 0.0031,
y_{Css} = 0.06,
\( f = (\epsilon(\rho(a), \rho(b)) - \epsilon(\rho(a), 0) - \epsilon(\rho(b), 0)) Gab(\chi(a), \chi(b)) \),
g = \frac{1}{2} \frac{\epsilon(\rho(s), 0) Gss(\chi(s)) ds}{\tau_{sMFM}} \),
\( G = \frac{1}{2} \frac{\epsilon(\rho(s), 0) Gss(\chi(s)) ds}{\tau_{sMFM}} \).
C.28 M052XX: M05-2X Meta-GGA Exchange Functional

\[ g = -\frac{3}{4} \sqrt[6]{\sqrt{\pi^2}} \left( \frac{4/3}{\pi} F(S) F_s(ws) \right) \]

\[ G = -\frac{3}{4} \sqrt[6]{\sqrt{\pi^2}} \left( \frac{4/3}{\pi} F(S) F_s(ws) \right) \]

\[ S = \frac{1}{12} \frac{\chi(s) 6^{2/3}}{\sqrt{\pi^2}} \]

\[ F(S) = 1 + R - R \left( 1 + \frac{\mu S^2}{R} \right)^{-1} \]

\[ R = 0.804, \]

\[ \mu = 1/3 \delta \pi^2, \]

\[ \delta = 0.066725, \]

\[ n = 11, \]

\[ A = [1.0, \]

\[ -0.56833, \]

\[ -1.30057, 5.50070, 9.06402, \]

\[ -32.21075, \]

\[ -23.73298, 70.22996, 29.88614, \]

\[ -60.25778, \]

\[ -13.22205, 15.23694], \]

\[ F_s(ws) = \sum_{i=0}^{n} A_i ws^i, \]

\[ ws = \frac{ts - 1}{ts + 1}, \]

\[ ts = \frac{t slepta}{\text{tausMFM}}, \]

\[ t slepta = 3/106^{2/3} \left( \pi^2 \right)^{2/3} (\rho(s))^{5/3}, \]

\[ \text{tausMFM} = 1/2 \tau(s). \]
C.29  M05C: M05 Meta-GGA Correlation Functional

\[ T = [0.031091, 0.015545, 0.016887], \quad (312) \]
\[ U = [0.21370, 0.20548, 0.11125], \quad (313) \]
\[ V = [7.5957, 14.1189, 10.357], \quad (314) \]
\[ W = [3.5876, 6.1977, 3.6231], \quad (315) \]
\[ X = [1.6382, 3.3662, 0.88026], \quad (316) \]
\[ Y = [0.49294, 0.62517, 0.49671], \quad (317) \]
\[ P = [1, 1, 1], \quad (318) \]
\[ \epsilon(\alpha, \beta) = (\alpha + \beta) \left( e(\alpha, \beta, T_1, U_1, V_1, W_1, X_1, Y_1, P_1) \right) \]
\[ - e(\alpha, \beta, T_3, U_3, V_3, W_3, X_3, Y_3, P_3) \omega(\zeta(\alpha, \beta)) (1 - (\zeta(\alpha, \beta))^4) \]
\[ + (e(\alpha, \beta, T_3, U_3, V_3, W_3, X_3, Y_3, P_3)) \omega(\zeta(\alpha, \beta)) (\zeta(\alpha, \beta))^4 \], \quad (319) \]
\[ r(\alpha, \beta) = \frac{1}{4} \sqrt{3} \sqrt{\frac{1}{\pi (\alpha + \beta)^3}} \quad (320) \]
\[ \zeta(\alpha, \beta) = \frac{\alpha - \beta}{\alpha + \beta}, \quad (321) \]
\[ \omega(z) = \frac{(1 + z)^{4/3} + (1 - z)^{4/3} - 2}{2 \sqrt{2} - 2}, \quad (322) \]
\[ e(r, t, u, v, w, x, y, p) = -2t (1 + ur) \ln \left( 1 + \frac{1}{t (v \sqrt{r + wr + x^p + yr^{p+1})}} \right), \quad (323) \]
\[ c = 1.709921, \quad (324) \]
\[ \tau_{sMFM} = 1/2 \tau(s), \quad (325) \]
\[ ds = 2 \, \text{tausMFM} - \frac{1}{4} \frac{\sigma^{(ss)}}{\rho(s)^\frac{1}{4}}, \]  

\[(326)\]

\[ Gab(chia, chib) \]
\[ = \sum_{i=0}^{n} c_{Cab_i} \left( \frac{y_{Cab} (chia^2 + chib^2)}{1 + y_{Cab} (chia^2 + chib^2)} \right)^i, \]

\[(327)\]

\[ Gss(chis) \]
\[ = \sum_{i=0}^{n} c_{Css_i} \left( \frac{y_{Css} chis^2}{1 + y_{Css} chis^2} \right)^i, \]

\[(328)\]

\[ n = 4, \]

\[(329)\]

c_{Cab} = [1.0, 3.78569, -14.15261, -7.46589, 17.94491],

c_{Css} = [1.0, 3.77344, -26.04463, 30.69913, -9.22695],

\[ y_{Cab} = 0.0031, \]

\[(330)\]

\[ y_{Css} = 0.06, \]

\[(331)\]

\[ f = (\varepsilon(\rho(a), \rho(b)) \] 
\[ - \varepsilon(\rho(a), 0) \] 
\[ - \varepsilon(\rho(b), 0)) Gab(\chi(a), \chi(b)), \]

\[(332)\]

\[ g = \frac{1}{2} \frac{\varepsilon(\rho(s), 0) Gss(\chi(s)) ds}{\text{tausMFM}}, \]

\[(333)\]

\[ G = \frac{1}{2} \frac{\varepsilon(\rho(s), 0) Gss(\chi(s)) ds}{\text{tausMFM}}. \]

\[(334)\]

\[ C.30 \ M05X: \ M05 \text{ Meta-GGA Exchange Functional} \]

\[ g = -3/4 \sqrt[3]{6\sqrt{\pi}} \frac{(\rho(s))^{4/3} F(S) F_s(w_s)}{\pi}, \]

\[(335)\]

\[ G = -3/4 \sqrt[3]{6\sqrt{\pi}} \frac{(\rho(s))^{4/3} F(S) F_s(w_s)}{\pi}, \]

\[(336)\]

\[ S = 1/12 \frac{\chi(s) 6^{2/3}}{\sqrt{\pi^2}}, \]

\[(337)\]

\[ F(S) \]
\[ = 1 + R \] 
\[ - R \left( 1 + \frac{\mu S^2}{R} \right)^{-1}, \]

\[(338)\]
\( R = 0.804, \) 
\( \mu = 1/3 \delta \pi^2, \) 
\( \delta = 0.066725, \) 
\( n = 11, \) 
\( A = [1.0, 0.08151,\) 
\( -0.43956,\) 
\( -3.22422, 2.01819, 8.79431,\) 
\( -0.00295, 9.82029,\) 
\( -4.82351,\) 
\( -48.17574, 3.64802, 34.02248], \)

\[ Fs(ws) = \sum_{i=0}^{n} A_i ws^i, \]

\[ ws = \frac{ts - 1}{ts + 1}, \]

\[ ts = \frac{ts_{lsda}}{tausMFM}, \]

\[ ts_{lsda} = 3/106^{3/3} (\pi^2)^{2/3} (\rho(s))^{5/3}, \]

\[ tausMFM = 1/2 \tau(s). \]

**C.31 M062XC: M06-2X Meta-GGA Correlation Functional**

\[ T = [0.031091, 0.015545, 0.016887], \]

\[ U = [0.21370, 0.20548, 0.11125], \]

\[ V = [7.5957, 14.1189, 10.357], \]

\[ W = [3.5876, 6.1977, 3.6231], \]

\[ X = [1.6382, 3.3662, 0.88026], \]

\[ Y = [0.49294, 0.62517, 0.49671], \]

\[ P = [1, 1, 1], \]

\[ \epsilon(\alpha, \beta) = \langle \alpha \]

\[ + \beta \rangle \left( \epsilon(r(\alpha, \beta), T_1, U_1, V_1, W_1, X_1, Y_1, P_1) \right.\]

\[ - \epsilon(r(\alpha, \beta), T_3, U_3, V_3, W_3, X_3, Y_3, P_3) \omega(\zeta(\alpha, \beta)) (1 - (\zeta(\alpha, \beta))^4) \]

\[ + \epsilon(r(\alpha, \beta), T_2, U_2, V_2, W_2, X_2, Y_2, P_2) \]

\[ - \epsilon(r(\alpha, \beta), T_1, U_1, V_1, W_1, X_1, Y_1, P_1) \omega(\zeta(\alpha, \beta)) (\zeta(\alpha, \beta))^4 \right), \]
\( r(\alpha, \beta) \)
\[ = \frac{1}{4} \sqrt[3]{\frac{8}{3^2}} \sqrt{\frac{1}{\pi (\alpha + \beta)}}, \]  
(359)
\( \zeta(\alpha, \beta) \)
\[ = \frac{\alpha - \beta}{\alpha + \beta}, \]  
(360)
\( \omega(z) \)
\[ = \frac{(1 + z)^{4/3} + (1 - z)^{4/3} - 2}{2 \sqrt{2} - 2}, \]  
(361)
\( e(r, t, u, w, x, y, p) \)
\[ = -2t (1 + ur) \ln \left( \frac{1}{1 + \frac{1}{2} (\sqrt{r} + wr + x^{3/2} + yp^{1})} \right), \]  
(362)
\( c = 1.709921, \)  
(363)
\( Gab(chia, chib) \)
\[ = \sum_{i=0}^{n} c_{Gab} \left( \frac{y_{Cab} (chia^2 + chib^2)}{1 + y_{Cab} (chia^2 + chib^2)} \right)^i, \]  
(364)
\( Gss(chis) \)
\[ = \sum_{i=0}^{n} c_{Cssj} \left( \frac{y_{Css} chis^2}{1 + y_{Css} chis^2} \right)^i, \]  
(365)
\( n = 4, \)  
(366)
\( c_{Cab} = [0.8833596, 33.57972, -70.43548, 49.78271, -18.52891], \)  
(367)
\( c_{Css} = [0.3097855, -5.528642, 13.47420, -32.13623, 28.46742], \)  
(368)
\( y_{Cab} = 0.0031, \)  
(369)
\( y_{Css} = 0.06, \)  
(370)
\( x = \sqrt{(\chi(a))^2 + (\chi(b))^2}, \)  
(371)
\( taua_{MFM} = 1/2 \tau(a), \)  
(372)
\( taua_{MFM} = 1/2 \tau(a), \)  
(373)
\text{taubMFM} = 1/2 \tau (b), \quad (374)

zs = 2^{\tau\text{ausMFM}} (\rho(s))^{3/3} - cf, \quad (375)

z = 2^{\tau\text{ausMFM}} (\rho(a))^{3/3} + 2^{\text{taubMFM}} (\rho(b))^{3/3} - 2cf, \quad (376)

cf = 3/5 6^{3/3} (\pi^2)^{2/3}, \quad (377)

ds = 1 - \frac{(\chi(s))^2}{4zs + 4cf}, \quad (378)

h(x, z, d0, d1, d2, d3, d4, d5, \alpha)
\quad d0
\quad = \frac{\lambda(x, z, \alpha)}{\lambda(x, z, \alpha)^2}
\quad + \frac{d1}{\lambda(x, z, \alpha)^2} + \frac{d2z}{\lambda(x, z, \alpha)^2}
\quad + \frac{d3}{\lambda(x, z, \alpha)^3} + \frac{d4}{\lambda(x, z, \alpha)^3} + \frac{d5}{\lambda(x, z, \alpha)^3}, \quad (379)

\lambda(x, z, \alpha)
\quad = 1 + \alpha (x^2 + z), \quad (380)

dCab = [0.1166404, -0.09120847, -0.06726189, 0.00006720580, 0.0008448011, 0.0], \quad (381)

dCss = [0.6902145, 0.09847204, 0.2214797, -0.001968264, -0.006775479, 0.0], \quad (382)

aCab = 0.003050, \quad (383)

aCss = 0.005151, \quad (384)

f = (\varepsilon(\rho(a), \rho(b)) \quad (385)
\quad - \varepsilon(\rho(a), 0) \quad - \varepsilon(\rho(b), 0)) (Gab(\chi(a), \chi(b))
\quad + h(x, z, dCab_0, dCab_1, dCab_2, dCab_3, dCab_4, dCab_5, aCab)) + h(x, z, ds_0, ds_1, ds_2, ds_3, ds_4, ds_5, aCss)),

g = \varepsilon(\rho(s), 0) (Gss(\chi(s)) \quad (386)
\quad + h(\chi(s), zs, dCss_0, dCss_1, dCss_2, dCss_3, dCss_4, dCss_5, aCss)) ds,

G = \varepsilon(\rho(s), 0) (Gss(\chi(s)) \quad (387)
\quad + h(\chi(s), zs, dCss_0, dCss_1, dCss_2, dCss_3, dCss_4, dCss_5, aCss)) ds.
C.32 M06-2X: M06-2X Meta-GGA Exchange Functional

\[ g = -\frac{3}{4} \frac{\sqrt{6} \sqrt{\pi^2} (\rho(s))^{4/3} F(S) F_S(ws)}{\pi}, \]  
(388)

\[ G = -\frac{3}{4} \frac{\sqrt{6} \sqrt{\pi^2} (\rho(s))^{4/3} F(S) F_S(ws)}{\pi}, \]  
(389)

\[ S = \frac{1}{12} \frac{X(s) 6^{2/3}}{\sqrt{\pi^2}}, \]  
(390)

\[ F(S) = 1 + R - R \left( 1 + \frac{\mu S^2}{R} \right)^{-1}, \]  
(391)

\[ R = 0.804, \]  
(392)

\[ \mu = \frac{1}{3} \delta \pi^2, \]  
(393)

\[ \delta = 0.066725, \]  
(394)

\[ n = 11, \]  
(395)

\[ A = [0.4600000, -0.2206052, -0.09431788, 2.164494, -2.556466, -14.22133, 15.55044, 35.98078, -27.22754, -39.24093, 15.22808, 15.22227], \]  
(396)

\[ F_S(ws) = \sum_{i=0}^{n} A_i w_{si}, \]  
(397)

\[ ws = \frac{ts - 1}{ts + 1}, \]  
(398)

\[ ts = \frac{ts{lsda}}{taus{MFM}}, \]  
(399)

\[ ts{lsda} = 3/106^{2/3} (\pi^{2/3} (\rho(s))^{5/3}, \]  
(400)

\[ taus{MFM} = 1/2 \tau(s). \]  
(401)
C.33 M06C: M06 Meta-GGA Correlation Functional

\[ T = [0.031091, 0.015545, 0.016887], \]  
\[ U = [0.21370, 0.20548, 0.11125], \]  
\[ V = [7.5957, 14.1189, 10.357], \]  
\[ W = [3.5876, 6.1977, 3.6231], \]  
\[ X = [1.6382, 3.3662, 0.88026], \]  
\[ Y = [0.49294, 0.62517, 0.49671], \]  
\[ P = [1, 1, 1], \]  
\[ \epsilon(\alpha, \beta) = (\alpha + \beta) \left( e(r(\alpha, \beta), T_1, U_1, V_1, W_1, X_1, Y_1, P_1) \right. \]
\[ - e(r(\alpha, \beta), T_3, U_3, V_3, W_3, X_3, Y_3, P_3) \omega(\zeta(\alpha, \beta)) (1 - (\zeta(\alpha, \beta))^4) \right. \]
\[ + \left. (e(r(\alpha, \beta), T_2, U_2, V_2, W_2, X_2, Y_2, P_2) \right. \]
\[ - e(r(\alpha, \beta), T_1, U_1, V_1, W_1, X_1, Y_1, P_1)) \omega(\zeta(\alpha, \beta)) (\zeta(\alpha, \beta))^4 \right), \]
\[ r(\alpha, \beta) = \frac{1}{4} \sqrt[3]{3} \sqrt[3]{\frac{1}{\pi (\alpha + \beta)}}, \]  
\[ \zeta(\alpha, \beta) = \frac{\alpha - \beta}{\alpha + \beta}, \]  
\[ \omega(z) = \frac{(1 + z)^{4/3} + (1 - z)^{4/3} - 2}{2 \sqrt[3]{2} - 2}, \]  
\[ e(r, t, u, v, w, x, y, p) = -2t (1 + 1/2 \frac{1}{t(v\sqrt{r + wr + xr^{3/2} + yr^{3/2})}}) \]  
\[ + ur) \ln \left( 1 + \frac{1}{t(v\sqrt{r + wr + xr^{3/2} + yr^{3/2})}} \right), \]  
\[ c = 1.709921, \]  
\[ G_{ab}(chia, chib) = \sum_{i=0}^{n} e^{Cab_i} \left( \frac{y^{Cab_i} (chia^2 + chib^2)}{1 + y^{Cab_i} (chia^2 + chib^2)} \right)^{1/c}, \]
\[ G_{ss} (\text{chis}) = \sum_{i=0}^{n} c_{Css, i} \left( \frac{y_{Css, i}^2}{1 + y_{Css, i}^2} \right), \]  

\( n = 4, \)  

\[ e_{Cab} = [3.741593, 218.7098, -453.1252, 293.6479, -62.87470], \]  

\[ e_{Css} = [0.5094055, -1.491085, 17.23922, -38.59018, 28.45044], \]  

\[ y_{Cab} = 0.0031, \]  

\[ y_{Css} = 0.06, \]  

\[ x = \sqrt{(\chi (a))^2 + (\chi (b))^2}, \]  

\[ \tau_{\text{ausMFM}} = 1/2 \tau (s), \]  

\[ \tau_{\text{auaMFM}} = 1/2 \tau (a), \]  

\[ \tau_{\text{aubMFM}} = 1/2 \tau (b), \]  

\[ z_s = 2 \frac{\tau_{\text{ausMFM}}}{(\rho (s))^{5/3}} - c_f, \]  

\[ z = 2 \frac{\tau_{\text{auaMFM}}}{(\rho (a))^{5/3}} + 2 \frac{\tau_{\text{aubMFM}}}{(\rho (b))^{5/3}} - 2 c_f, \]  

\[ c_f = \frac{3}{5} 6^{2/3} (\pi^2)^{2/3}, \]  

\[ d_s = 1 - \frac{(\chi (s))^2}{4 z_s + 4 c_f}, \]  

\[ h (x, z, d_0, d_1, d_2, d_3, d_4, d_5, \alpha) = \frac{d_0}{\lambda (x, z, \alpha)} + d_1 x^2 + d_2 z \left( \frac{\lambda (x, z, \alpha)}{\lambda (x, z, \alpha)^2} \right)^2 + d_3 x^4 + d_4 x^2 z + d_5 z^2 \left( \frac{\lambda (x, z, \alpha)}{\lambda (x, z, \alpha)^3} \right), \]  

\[ \lambda (x, z, \alpha) = 1 + \alpha (x^2 + z). \]
C  DENSITY FUNCTIONAL DESCRIPTIONS

\[ d_{\text{Cab}} = [\]
\[ \begin{array}{c}
-2.741539, \\
-0.6720113, \\
-0.07932688, 0.001918681, \\
-0.002032902, 0.001918681, \\
\end{array} ] \]

\[ d_{\text{Css}} = [0.4905945, \\
-0.1437348, 0.2357824, 0.001871015, \\
-0.003788963, 0.001918681], \]

\[ a_{\text{Cab}} = 0.003050, \]

\[ a_{\text{Css}} = 0.005151, \]

\[ f = (\varepsilon (\rho (a), \rho (b)) \\
- \varepsilon (\rho (a), 0) \\
- \varepsilon (\rho (b), 0)) (\varepsilon(a_{\text{Cab}})) \\
+ h(x, z, d_{\text{Cab}}0, d_{\text{Cab}}1, d_{\text{Cab}}2, d_{\text{Cab}}3, d_{\text{Cab}}4, d_{\text{Cab}}5, a_{\text{Cab}}), \]

\[ g = \varepsilon (\rho (s), 0) (G_{\text{ss}}(\chi (s)) \\
+ h(\chi (s), zs, d_{\text{Css}}0, d_{\text{CSS}}1, d_{\text{CSS}}2, d_{\text{CSS}}3, d_{\text{CSS}}4, d_{\text{CSS}}5, a_{\text{Css}})) ds, \]

\[ G = \varepsilon (\rho (s), 0) (G_{\text{ss}}(\chi (s)) \\
+ h(\chi (s), zs, d_{\text{Css}}0, d_{\text{CSS}}1, d_{\text{CSS}}2, d_{\text{CSS}}3, d_{\text{CSS}}4, d_{\text{CSS}}5, a_{\text{Css}})) ds. \]

C.34 M06-HF: M06-HF Meta-GGA Correlation Functional

\[ T = [0.031091, 0.015545, 0.016887], \]

\[ U = [0.21370, 0.20548, 0.11125], \]

\[ V = [7.5957, 14.1189, 10.357], \]

\[ W = [3.5876, 6.1977, 3.6231], \]

\[ X = [1.6382, 3.3662, 0.88026], \]

\[ Y = [0.49294, 0.62517, 0.49671], \]

\[ P = [1, 1, 1], \]

\[ \varepsilon (\alpha, \beta) = (\alpha \\
+ \beta) \left( e (r (\alpha, \beta), T1, U1, V1, W1, X1, Y1, P1) \\
- \varepsilon (r (\alpha, \beta), T3, U3, V3, W3, X3, Y3, P3) \omega (\zeta (\alpha, \beta)) (1 - (\zeta (\alpha, \beta))^4) \\
+ c (e (r (\alpha, \beta), T2, U2, V2, W2, X2, Y2, P2) \\
- \varepsilon (r (\alpha, \beta), T1, U1, V1, W1, X1, Y1, P1)) \omega (\zeta (\alpha, \beta)) (\zeta (\alpha, \beta))^4), \right) \]
C  DENSITY FUNCTIONAL DESCRIPTIONS

\[ r(\alpha, \beta) = \frac{1}{4\sqrt[3]{4^{2/3}}} \sqrt[3]{\frac{1}{\pi(\alpha + \beta)}} \quad \text{(447)} \]

\[ \zeta(\alpha, \beta) = \frac{\alpha - \beta}{\alpha + \beta} \quad \text{(448)} \]

\[ \omega(z) = \frac{(1 + z)^{4/3} + (1 - z)^{4/3} - 2}{2\sqrt{2} - 2} \quad \text{(449)} \]

\[ e(r, t, u, v, w, x, y, \rho) = -2t(1 + ur) \ln \left( \frac{1}{1 + \frac{1/2}{(v\sqrt{r + wr + x\rho^{3/2} + y\rho^{3/2})}} \right) \quad \text{(450)} \]

\[ c = 1.709921 \quad \text{(451)} \]

\[ Gab(chia, chib) = \sum_{i=0}^{n} c_{Cab_i} \left( \frac{y_{Cab_i}(chia^2 + chib^2)}{1 + y_{Cab_i}(chia^2 + chib^2)} \right)^i \quad \text{(452)} \]

\[ Gss(chis) = \sum_{i=0}^{n} c_{Css_i} \left( \frac{y_{Css_i}chis^2}{1 + y_{Css_i}chis^2} \right)^i \quad \text{(453)} \]

\[ n = 4 \quad \text{(454)} \]

\[ c_{Cab} = [1.674634, 57.32017, 59.55416, -231.1007, 125.5199] \quad \text{(455)} \]

\[ c_{Css} = [0.1023254, -2.453783, 29.13180, -34.94358, 23.15955] \quad \text{(456)} \]

\[ y_{Cab} = 0.0031 \quad \text{(457)} \]

\[ y_{Css} = 0.06 \quad \text{(458)} \]

\[ x = \sqrt{(\chi(a))^2 + (\chi(b))^2} \quad \text{(459)} \]

\[ tausMFM = 1/2 \tau(x) \quad \text{(460)} \]

\[ tauaMFM = 1/2 \tau(a) \quad \text{(461)} \]

\[ taubMFM = 1/2 \tau(b) \quad \text{(462)} \]
\[ zs = 2 \frac{tausMFm}{(\rho (s))^{5/3}} - cf, \]  
(463)

\[ z = 2 \frac{tauMFm}{(\rho (a))^{5/3}} + 2 \frac{taubMFm}{(\rho (b))^{5/3}} - 2 cf, \]  
(464)

\[ cf = 3/5 6^{2/3} (\pi^2)^{2/3}, \]  
(465)

\[ ds = 1 - \frac{\chi (s)^2}{4zs + 4cf}, \]  
(466)

\[ h(x, z, d0, d1, d2, d3, d4, d5, \alpha) = \]  
\[
\begin{align*}
    & d0 \\
    & \lambda (x, z, \alpha) \\
    & + d1 x^2 + d2 z \\
    & \left( \frac{\lambda (x, z, \alpha)}{f (x, \alpha)} \right)^2 \\
    & + d3 x^4 + d4 x^2 z + d5 z^2 \\
    & \left( \frac{\lambda (x, z, \alpha)}{f (x, \alpha)} \right)^3, \n\end{align*}
\]  
(467)

\[ \lambda (x, z, \alpha) = \]  
\[
\begin{align*}
    & 1 \\
    & + \alpha (x^2 \\
    & + z), \n\end{align*}
\]  
(468)

\[ dCab = [ \]  
\[
\begin{array}{c}
-0.6746338, \\
-0.1534002, \\
-0.09021521, \\
-0.001292037, \\
-0.0002352983, 0.0, \\
\end{array}
\]  
(469)

\[ dCss = [0.8976746, \]  
\[
\begin{array}{c}
-0.2345830, 0.2368173, \\
-0.0009913890, \\
-0.01146165, 0.0, \n\end{array}
\]  
(470)

\[ aCab = 0.003050, \]  
(471)

\[ aCss = 0.005151, \]  
(472)

\[ f = (\varepsilon (\rho (a), \rho (b)) \]  
\[
\begin{align*}
    & - \varepsilon (\rho (a), 0) \\
    & - \varepsilon (\rho (b), 0)) (Gab (\chi (a), \chi (b)) \\
    & + h(x, z, dCab0, dCab1, dCab2, dCab3, dCab4, dCab5, aCab)), \n\end{align*}
\]  
(473)

\[ g = \varepsilon (\rho (s), 0) (Gss (\chi (s)) \]  
\[
\begin{align*}
    & + h(\chi (s), zs, dCss0, dCss1, dCss2, dCss3, dCss4, dCss5, aCss)) ds, \n\end{align*}
\]  
(474)

\[ G = \varepsilon (\rho (s), 0) (Gss (\chi (s)) \]  
\[
\begin{align*}
    & + h(\chi (s), zs, dCss0, dCss1, dCss2, dCss3, dCss4, dCss5, aCss)) ds. \n\end{align*}
\]  
(475)
C.35 M06HFX: M06-HF Meta-GGA Exchange Functional

\[
g = -\frac{3}{4} \frac{\sqrt{6} \sqrt{\pi^2} \langle \rho(s) \rangle^{4/3} F(S) F_s(w_s)}{\pi} + eslsda(\chi(s), zs), \tag{476}
\]

\[
G = -\frac{3}{4} \frac{\sqrt{6} \sqrt{\pi^2} \langle \rho(s) \rangle^{4/3} F(S) F_s(w_s)}{\pi} + eslsda(\chi(s), zs), \tag{477}
\]

\[
S = 1/12 \frac{\chi(s) G^{2/3}}{\sqrt{\pi^2}}, \tag{478}
\]

\[
F(S) = 1 + R - R \left( 1 \right) + \left( \frac{\mu S^2}{R} \right)^{-1}, \tag{479}
\]

\[
R = 0.804, \tag{480}
\]

\[
\mu = 1/3 \delta \pi^2, \tag{481}
\]

\[
\delta = 0.066725, \tag{482}
\]

\[
n = 11, \tag{483}
\]

\[
A = [0.1179732, -1.066708, -0.1462405, 7.481848, 3.776679, -44.36118, -18.30962, 100.3903, 38.64360, -98.06018, -25.57716, 35.90404], \tag{484}
\]

\[
F_s(w_s) = \sum_{i=0}^{n} A_i w_s^i, \tag{485}
\]

\[
w_s = \frac{t_s - 1}{t_s + 1}, \tag{486}
\]

\[
t_s = \frac{tslsda}{tausMFM}, \tag{487}
\]

\[
slsda = 3/106 G^{2/3} \langle \pi^2 \rangle^{2/3} \langle \rho(s) \rangle^{5/3}, \tag{488}
\]

\[
eslsda = -3/8 \sqrt{3} G^{2/3} \sqrt{\pi^{-1}} \langle \rho(s) \rangle^{4/3}, \tag{489}
\]

\[
d = [\tag{490}
-0.1179732, -0.002500000, -0.01180065, 0.0, 0.0, 0.0, 0.0].
\]
\(\alpha = 0.001867,\)  
\(zs = 2 \frac{\text{tausMFM}}{(\rho (s))^3} - cf,\)

\(h(x, z)\)

\[
= \frac{d_0}{\lambda (x, z, \alpha)} + \frac{d_1 x^2 + d_2 z}{(\lambda (x, z, \alpha))^2} + \frac{d_3 x^4 + d_4 x^2 z + d_5 z^2}{(\lambda (x, z, \alpha))^3},
\]

\(\lambda (x, z, \alpha)\)

\[
= 1 + \alpha (x^2 + z),
\]

\(cf = \frac{3}{5} 6^{2/3} (\pi^2)^{2/3},\)

\(\text{tausMFM} = 1/2 \tau (s).\)

**C.36 M06LC: M06-L Meta-GGA Correlation Functional**

\[ T = [0.031091, 0.015545, 0.016887], \]

\[ U = [0.21370, 0.20548, 0.11125], \]

\[ V = [7.5957, 14.1189, 10.357], \]

\[ W = [3.5876, 6.1977, 3.6231], \]

\[ X = [1.6382, 3.3662, 0.88026], \]

\[ Y = [0.49294, 0.62517, 0.49671], \]

\[ P = [1, 1, 1], \]

\(\epsilon(\alpha, \beta)\)

\[
= (\alpha + \beta) \left( \epsilon(r(\alpha, \beta), T_1, U_1, V_1, W_1, X_1, Y_1, P_1) - \epsilon(r(\alpha, \beta), T_2, U_2, V_2, W_2, X_2, Y_2, P_2) \right) \omega(\zeta(\alpha, \beta)) (1 - (\zeta(\alpha, \beta))^4) \\
+ \epsilon(r(\alpha, \beta), T_1, U_1, V_1, W_1, X_1, Y_1, P_1) \omega(\zeta(\alpha, \beta)) (\zeta(\alpha, \beta))^4, \]

\(r(\alpha, \beta)\)

\[
= 1/4 \sqrt[3]{34^{2/3}} \frac{1}{\pi (\alpha + \beta)},
\]
\[ \zeta(\alpha, \beta) = \frac{\alpha - \beta}{\alpha + \beta}, \]  
\[ \omega(z) = \frac{(1 + z)^{4/3} + (1 - z)^{4/3} - 2}{2 \sqrt{2} - 2}, \]  
\[ e(r, t, u, v, x, y, p) = -2t(1 + ur) \ln \left(1 + \frac{1}{t (v \sqrt{r} + w + x r^{3/2} + y r p + 1)} \right), \]  
\[ c = 1.709921, \]  
\[ Gab(chia, chib) = \sum_{i=0}^{n} c_{Cab_i} \left( \frac{y_{Cab}(chia_2^2 + chib_2^2)}{1 + y_{Cab} (chia_2^2 + chib_2^2)} \right)^i, \]  
\[ Gss(chis) = \sum_{i=0}^{n} c_{Css_i} \left( \frac{y_{Css} chis_2^2}{1 + y_{Css} chis_2^2} \right)^i, \]  
\[ n = 4, \]  
\[ c_{Cab} = [0.6042374, 177.6783, -251.3252, 76.35173, -12.55699], \]  
\[ c_{Css} = [0.5349466, 0.5396620, -31.61217, 51.49592, -29.19613], \]  
\[ y_{Cab} = 0.0031, \]  
\[ y_{Css} = 0.06, \]  
\[ x = \sqrt{(\chi(a))^2 + (\chi(b))^2}, \]  
\[ \text{tausMFM} = 1/2 \tau(s), \]  
\[ \text{tauMFM} = 1/2 \tau(a), \]  
\[ \text{taubMFM} = 1/2 \tau(b), \]  
\[ zs = \frac{2 \cdot \text{tausMFM}}{(\rho(s))^{5/3}} - cf, \]
\[ z = 2 \frac{\tau_{aMFM}}{(\rho(a))^{5/3}} + 2 \frac{\tau_{bMFM}}{(\rho(b))^{5/3}} - 2 \epsilon_f, \] (522)

\[ \epsilon_f = 3/5 \cdot 6^{2/3} \cdot (\pi^2)^{2/3}, \] (523)

\[ ds = 1 - \frac{(\chi(s))^2}{4zs + 4 \epsilon_f}, \] (524)

\[ h(x, z, d0, d1, d2, d3, d4, d5, \alpha) = d0 \frac{\lambda(x, z, \alpha)}{\lambda(x, z, \alpha)^2} + d1 x^2 + d2 z + d3 x^4 + d4 x^2 z + d5 z^2 + \] (525)

\[ + \frac{d3 x^4 + d4 x^2 z + d5 z^2}{(\lambda(x, z, \alpha))^3}, \]

\[ \lambda(x, z, \alpha) = 1 + \alpha (x^2 + z), \] (526)

\[ d_{Cab} = [0.3957626, \] (527)

\[ -0.5614546, 0.0140396, 0.0009831, -0.0035771, 0.0], \]

\[ d_{Css} = [0.4650534, 0.1617589, 0.1833657, 0.0046921, 0.0, \] (528)

\[ -0.0049905, 0.0], \]

\[ a_{Cab} = 0.003050, \] (529)

\[ a_{Css} = 0.005151, \] (530)

\[ f = (\epsilon(\rho(a), \rho(b)), \] (531)

\[ - \epsilon(\rho(a), 0), - \epsilon(\rho(b), 0)) (G_{ab}(\chi(a), \chi(b)) + h(x, z, d_{Cab}, d_{Cab}, d_{Cab}, d_{Cab}, d_{Cab}, a_{Cab}, a_{Cab})), \]

\[ g = \epsilon(\rho(s), 0) (G_{ss}(\chi(s)), \] (532)

\[ + h(\chi(s), z, d_{Css}, d_{Css}, d_{Css}, d_{Css}, d_{Css}, a_{Css})) ds, \]

\[ G = \epsilon(\rho(s), 0) (G_{ss}(\chi(s)), \] (533)

\[ + h(\chi(s), z, d_{Css}, d_{Css}, d_{Css}, d_{Css}, d_{Css}, a_{Css})) ds. \]
C.37 M06-LX: M06-L Meta-GGA Exchange Functional

\[ g = -3/4 \pi \frac{\sqrt{6} \sqrt{\pi^2} (\rho(s))^{43/3} F(S) F_s(ws) + eslsda(\chi(s), zs)}{\rho(s) - \sqrt{\pi}^2}, \tag{534} \]

\[ G = -3/4 \pi \frac{\sqrt{6} \sqrt{\pi^2} (\rho(s))^{43/3} F(S) F_s(ws) + eslsda(\chi(s), zs)}{\rho(s) - \sqrt{\pi}^2}, \tag{535} \]

\[ S = \frac{1}{12} \frac{\chi(s) 6^{2/3}}{\sqrt{\pi^2}}, \tag{536} \]

\[ F(S) \]
\[ = 1 + R - R \left( 1 + \frac{\mu S^2}{R} \right)^{-1}, \tag{537} \]

\[ R = 0.804, \tag{538} \]

\[ \mu = 1/3 \delta \pi^2, \tag{539} \]

\[ \delta = 0.066725, \tag{540} \]

\[ n = 11, \tag{541} \]

\[ A = \begin{bmatrix} 0.3987756, 0.2548219, 0.3923994, \\
0.0013655, 0.97615, 0.97273, \\
-6.302147, 10.97615, 30.97273, \\
-3.18489, 21.60364, 34.21814, \\
-9.049762 \end{bmatrix}, \tag{542} \]

\[ F_s(ws) \]
\[ = \sum_{i=0}^{n} A_i ws^i, \tag{543} \]

\[ ws = \frac{ts - 1}{ts + 1}, \tag{544} \]

\[ ts = \frac{tlslsda}{tausMFM}, \tag{545} \]

\[ tlslsda = 3/106 2^{2/3} (\pi^2)^{2/3} (\rho(s))^{5/3}, \tag{546} \]

\[ eslsda = -3/8 \sqrt{3} 4^{2/3} \sqrt{\pi}^{-1} (\rho(s))^{4/3}, \tag{547} \]

\[ d = \begin{bmatrix} 0.6012244, 0.004748822, \\
-0.008635108, \\
0.00009308062, 0.0004482811, 0.0 \end{bmatrix}, \tag{548} \]
\( \alpha = 0.001867 \),

\( z_s = 2^{tausMFM} \frac{(\rho(s))^{5/3}}{\rho(s)} - cf \),

\[
\begin{align*}
    h(x, z) &= \frac{d_0}{\lambda(x, z, \alpha)} \\
    &= \frac{d_1 x^2 + d_2 z}{(\lambda(x, z, \alpha))^2} \\
    &= \frac{d_3 x^4 + d_4 x^2 z + d_5 z^2}{(\lambda(x, z, \alpha))^3},
\end{align*}
\]

\[
\begin{align*}
    \lambda(x, z, \alpha) &= 1 \\
    &= 1 + \alpha (x^2 + z),
\end{align*}
\]

\( cf = 3/5 \cdot 6^{2/3} \cdot (\frac{\pi}{3})^{2/3} \),

\( tausMFM = 1/2 \tau(s) \).

**C.38  M06X: M06 Meta-GGA Exchange Functional**

\[
\begin{align*}
    g &= -3/4 \sqrt[6]{\frac{\sqrt{\pi}}{\sqrt{\pi}^2}} (\rho(s))^{4/3} F(S) F_s(w_s) + eslsdah(\chi(s), z_s), \\
    G &= -3/4 \sqrt[6]{\frac{\sqrt{\pi}}{\sqrt{\pi}^2}} (\rho(s))^{4/3} F(S) F_s(w_s) + eslsdah(\chi(s), z_s), \\
    S &= 1/12 \frac{\chi(s) 6^{2/3}}{\sqrt{\pi}^2}, \\
    F(S) &= 1 \\
    &= 1 + R \\
    &= -R \left(1 + \frac{\mu S^3}{R}\right)^{-1},
\end{align*}
\]

\( R = 0.804 \),

\( \mu = 1/3 \delta \pi^2 \),

\( \delta = 0.066725 \),

\( n = 11 \).
\[ A = [0.5877943, -0.1371776, 0.2682367, -2.515898, -2.978892, 8.710679, 16.88195, -4.89724, -32.99983, -14.49050, 20.43747, 12.56504], \]

\[ Fs(ws) = \sum_{i=0}^{n} A_i ws^i, \] (564)

\[ ws = \frac{ts - 1}{ts + 1}, \] (565)

\[ ts = \frac{ts_{lsda}}{taus_{MFM}}, \] (566)

\[ ts_{lsda} = \frac{3}{106} \frac{2^{2/3}}{(\pi^2)^{2/3}} (\rho(s))^{5/3}, \] (567)

\[ es_{lsda} = -\frac{3}{8} \frac{\sqrt{3} 4^{2/3}}{\sqrt{\pi} \rho(s)}^{4/3}, \] (568)

\[ d = [0.1422057, 0.0007370319, -0.01601373, 0.0, 0.0, 0.0, 0.0], \] (569)

\[ \alpha = 0.001867, \] (570)

\[ zs = 2 \frac{taus_{MFM}}{(\rho(s))^{5/3}} - cf, \] (571)

\[ h(x,z) = \frac{d_0}{\lambda(x,z,\alpha)} + \frac{d_1 x^2 + d_2 z}{(\lambda(x,z,\alpha))^2} + \frac{d_3 x^4 + d_4 x^2 z + d_5 z^2}{(\lambda(x,z,\alpha))^3}, \] (572)

\[ \lambda(x,z,\alpha) = 1 + \alpha (x^2 + z), \] (573)

\[ cf = \frac{3}{5} 6^{2/3} (\pi^2)^{2/3}, \] (574)

\[ taus_{MFM} = \frac{1}{2} \tau(s). \] (575)

**C.39 Meta GGA Correlation Functional**

C.40 MK00: Exchange Functional for Accurate Virtual Orbital Energies

\[ g = -3 \frac{\pi (\rho(s))^3}{\tau(s) - 1/4 \upsilon(s)}. \] (576)

C.41 MK00B: Exchange Functional for Accurate Virtual Orbital Energies

MK00 with gradient correction of the form of B88X but with different empirical parameter.

\[ g = -3 \frac{\pi (\rho(s))^3}{\tau(s) - 1/4 \upsilon(s)} - \beta \frac{\rho(s)^{4/3} (\chi(s))^2}{1 + 6 \beta \chi(s) \text{arcsinh}(\chi(s))}. \] (577)

\[ \beta = 0.0016, \] (578)

\[ G = -3 \frac{\pi (\rho(s))^3}{\tau(s) - 1/4 \upsilon(s)} - \beta \frac{\rho(s)^{4/3} (\chi(s))^2}{1 + 6 \beta \chi(s) \text{arcsinh}(\chi(s))}. \] (579)

C.42 P86: Gradient correction to VWN.

\[ f = \rho e + e^{-\beta C(r)} \frac{\sigma}{d \rho^{4/3}}, \] (580)

\[ r = 1/4 \sqrt{3} \sqrt[3]{\frac{1}{\pi \rho}}, \] (581)

\[ x = \sqrt{r}, \] (582)

\[ \zeta = \frac{\rho(a) - \rho(b)}{\rho}, \] (583)

\[ k = [0.0310907, 0.01554535], \] (584)

\[ l = [ \frac{-1/6 \pi^{-2}}{1/6 \pi^{-2}} ], \] (585)

\[ m = [3.72744, 7.06042, 1.13107], \] (586)

\[ n = [12.9352, 18.0578, 13.0045], \] (587)

\[ e = \Lambda + \omega y (1 + h \zeta^{4/3}), \] (588)

\[ y = \frac{9}{8} (1 + \zeta^{4/3} + 9/4, \] (589)
\[ h = \frac{4/9}{\left(\sqrt{2} - 1\right)} \omega - 1, \]  
(590)

\[ \Lambda = q(k_1, l_1, m_1, n_1), \]  
(591)

\[ \lambda = q(k_2, l_2, m_2, n_2), \]  
(592)

\[ \omega = q(k_3, l_3, m_3, n_3), \]  
(593)

\[ q(A, p, c, d) = A \ln \left( \frac{x^2}{X(x, c, d)} \right) + 2c \arctan \left( \frac{Q(c, d)}{2x + c} \right) (Q(c, d))^{-1} \]  
\[ - cp \ln \left( \frac{(x - p)^2}{X(x, c, d)} \right) + 2(c + 2p) \arctan \left( \frac{Q(c, d)}{2x + c} \right) (Q(c, d))^{-1} \]  
\[ (X(p, c, d))^{-1} \right), \]  
(594)

\[ Q(c, d) = \sqrt{4d - c^2}, \]  
(595)

\[ X(i, c, d) = i^2 + ci + d, \]  
(596)

\[ \Phi = 0.007390075 \frac{z \sqrt{\sigma}}{C(r) \rho^{7/6}}, \]  
(597)

\[ d = \sqrt{2} \sqrt{(1/2 + 1/2 \xi)^{5/3} + (1/2 - 1/2 \xi)^{5/3}}, \]  
(598)

\[ C(r) = 0.001667 + 0.002568 + \frac{\alpha r + \beta r^2}{1 + \xi r + \delta r^2 + 10000 \beta r^3}, \]  
(599)

\[ z = 0.11, \]  
(600)

\[ \alpha = 0.023266, \]  
(601)

\[ \beta = 0.000007389, \]  
(602)

\[ \xi = 8.723, \]  
(603)

\[ \delta = 0.472. \]  
(604)
C.43 PBEC: PBE Correlation Functional

\[ f = \rho \left( \epsilon(\rho(a), \rho(b)) \right) + H(d, \rho(a), \rho(b)) \]  \hspace{1cm} (605)

\[ G = \rho \left( \epsilon(\rho(s), 0) \right) + C(Q, \rho(s), 0) \]  \hspace{1cm} (606)

\[ d = 1/12 \frac{\sqrt{\sigma^{3/6}}}{u(\rho(a), \rho(b)) \sqrt[3]{\pi^{1/6}}} \rho^{3/6} \]  \hspace{1cm} (607)

\[ u(\alpha, \beta) = 1/2 \left( \frac{1}{1 + \zeta(\alpha, \beta) 2/3} \right) \]  \hspace{1cm} (608)

\[ H(d, \alpha, \beta) = 1/2 \left( u(\rho(a), \rho(b)) \right)^3 \lambda^2 \ln \left( 1 + \frac{1}{\lambda} \frac{(d^2 + A(\alpha, \beta)d^4)}{(1 + A(\alpha, \beta)d^2 + (A(\alpha, \beta))^2d^4)} \right) \]  \hspace{1cm} (609)

\[ A(\alpha, \beta) = 2 \frac{\imath}{\lambda} \left( e^{-2 \frac{\imath \epsilon(\alpha, \beta)}{u(\rho(a), \rho(b))}} \right)^{1/2} \]  \hspace{1cm} (610)

\[ \imath = 0.0716, \]  \hspace{1cm} (611)

\[ \lambda = \nu \kappa, \]  \hspace{1cm} (612)

\[ \nu = 16 \frac{\sqrt{3} \sqrt{\pi^2}}{\pi}, \]  \hspace{1cm} (613)

\[ \kappa = 0.004235, \]  \hspace{1cm} (614)

\[ Z = -0.001667, \]  \hspace{1cm} (615)

\[ \phi(r) = \theta(r) - Z, \]  \hspace{1cm} (616)

\[ \theta(r) = \frac{1}{1000} \frac{2.568 + \Xi r + \Phi r^2}{1 + \Lambda r + \Upsilon r^2 + 10\Phi r^3}, \]  \hspace{1cm} (617)

\[ \Xi = 23.266, \]  \hspace{1cm} (618)

\[ \Phi = 0.007389, \]  \hspace{1cm} (619)
\[ \Lambda = 8.723, \]  
\[ Y = 0.472, \]  
\[ T = [0.031091, 0.015545, 0.016887], \]  
\[ U = [0.21370, 0.20548, 0.11125], \]  
\[ V = [7.5957, 14.1189, 10.357], \]  
\[ W = [3.5876, 6.1977, 3.6231], \]  
\[ X = [1.6382, 3.3662, 0.88026], \]  
\[ Y = [0.49294, 0.62517, 0.49671], \]  
\[ P = [1, 1, 1], \]  
\[ \varepsilon(\alpha, \beta) \]  
\[ = \varepsilon(r(\alpha, \beta), T_1, U_1, V_1, W_1, X_1, Y_1, P_1) \]  
\[ - \varepsilon(r(\alpha, \beta), T_3, U_3, V_3, W_3, X_3, Y_3, P_3) \omega(\zeta(\alpha, \beta))(1 - (\zeta(\alpha, \beta))^4) \]  
\[ + (\varepsilon(r(\alpha, \beta), T_2, U_2, V_2, W_2, X_2, Y_2, P_2) \]  
\[ - \varepsilon(r(\alpha, \beta), T_1, U_1, V_1, W_1, X_1, Y_1, P_1)) \omega(\zeta(\alpha, \beta))(\zeta(\alpha, \beta))^4, \]  
\[ r(\alpha, \beta) \]  
\[ = 1/4 \sqrt{3} \frac{4^{2/3}}{\sqrt{\pi (\alpha + \beta)}}, \]  
\[ \zeta(\alpha, \beta) \]  
\[ = \frac{\alpha - \beta}{\alpha + \beta}; \]  
\[ \omega(z) \]  
\[ = \frac{(1 + z)^{4/3} + (1 - z)^{4/3} - 2}{2 \sqrt{2} - 2}, \]  
\[ e(r, t, u, v, w, x, y, p) \]  
\[ = -2r(1 + ur) \ln \left(1 + \frac{1}{r \sqrt{T + wr + xr^{3/2} + yr^{3/2}}}, \right), \]  
\[ c = 1.709921, \]  
\[ C(d, \alpha, \beta) \]  
\[ = K(Q, \alpha, \beta) \]  
\[ + M(Q, \alpha, \beta), \]
\begin{align*}
M(d, \alpha, \beta) &= 0.5 \nu (\phi (r(\alpha, \beta))) \quad - \kappa \\
&
\quad - 3/7Z d^2 e^{-335.9789467 \frac{2r^3}{\pi^2 \rho}}, \\
K(d, \alpha, \beta) &= 0.2500000000 \lambda^2 \ln \left(1 + 2 \frac{1}{\lambda} \frac{d^2 + N(\alpha, \beta) d^4}{1 + N(\alpha, \beta) d^2 + (N(\alpha, \beta))^2 d^4} \right) r^{-1}, \\
N(\alpha, \beta) &= 2 \lambda^{-1} \left(e^{-4 \frac{r(\alpha, \beta)}{\lambda^2}} - 1\right)^{-1}, \\
Q &= 1/12 \frac{\sqrt{\sigma} \sqrt{23^{5/6}}}{\sqrt{\pi} \rho^{7/6}}.
\end{align*}

\textbf{C.44 PBESOLC: PBEsol Correlation Functional}

\textbf{C.45 PBESOLX: PBEsol Exchange Functional}

\textbf{C.46 PBEX: PBE Exchange Functional}

\begin{align*}
g &= 1/2 E(2 \rho (s)), \\
G &= 1/2 E(2 \rho (s)), \\
E(n) &= -3/4 \frac{\sqrt{3} \sqrt{\pi}^{-3/4} F(S)}{\pi}, \\
S &= 1/12 \frac{X(s) 6^{2/3}}{\sqrt{\pi}^2}, \\
F(S) &= 1 + R - R \left(1 + \frac{\mu S^2}{R}\right)^{-1}, \\
R &= 0.804, \\
\mu &= 1/3 \delta \pi^2, \\
\delta &= 0.066725.
\end{align*}
C.47 PBEXREV: Revised PBE Exchange Functional

Changes the value of the constant $R$ from the original PBEX functional

\[ g = \frac{1}{2} E (2 \rho (s)), \]  
(648)

\[ G = \frac{1}{2} E (2 \rho (s)), \]  
(649)

\[ E (n) = -\frac{3}{4} \sqrt[3]{\sqrt{\pi}^{4/3} n^{4/3} F (S)}, \]  
(650)

\[ S = \frac{1}{12} \frac{X (s) 6^{2/3}}{\sqrt{\pi^2}}, \]  
(651)

\[ F (S) = 1 + R - R \left( 1 + \frac{\mu S^2}{R} \right)^{-1}, \]  
(652)

\[ R = 1.245, \]  
(653)

\[ \mu = \frac{1}{3} \delta \pi^2, \]  
(654)

\[ \delta = 0.066725. \]  
(655)

C.48 PW86:

GGA Exchange Functional.

\[ g = \frac{1}{2} E (2 \rho (s)), \]  
(656)

\[ E (n) = -\frac{3}{4} \sqrt[3]{\sqrt{\pi}^{4/3} n^{4/3} F (S)}, \]  
(657)

\[ F (S) = 1 + 1.296 S^2 + 14 S^4 + 0.2 S^6 \left( \frac{1}{15} \right), \]  
(658)

\[ S = \frac{1}{12} \frac{X (s) 6^{2/3}}{\sqrt{\pi^2}}, \]  
(659)

\[ G = \frac{1}{2} E (2 \rho (s)). \]  
(660)
C.49  **PW91C**: Perdew-Wang 1991 GGA Correlation Functional

\[ f = \rho \left( \varepsilon(\rho(a), \rho(b)) + H(d, \rho(a), \rho(b)) \right), \]  
\[ G = \rho \left( \varepsilon(\rho(s), 0) + C(Q, \rho(s), 0) \right), \]  
\[ d = 1/12 \frac{\sqrt{\sigma^{3.56}}}{u(\rho(a), \rho(b))^{7/3}} \rho^{7/6}, \]  
\[ u(\alpha, \beta) = 1/2 \left(1 + \frac{1}{2} \left(1 + \frac{\zeta(\alpha, \beta)^{2/3}}{-\zeta(\alpha, \beta)^{2/3}}\right)\right) \]  
\[ H(d, \alpha, \beta) = L(d, \alpha, \beta) + J(d, \alpha, \beta), \]  
\[ L(d, \alpha, \beta) = \frac{1}{2} \left(1 + \frac{\zeta(\alpha, \beta)^{2/3}}{-\zeta(\alpha, \beta)^{2/3}}\right) \]  
\[ J(d, \alpha, \beta) = \frac{1}{2} \left(1 + \frac{\zeta(\alpha, \beta)^{2/3}}{-\zeta(\alpha, \beta)^{2/3}}\right) \]  
\[ A(\alpha, \beta) = 2 \lambda^{-1} \left(1 - \frac{1}{2} \left(1 - \frac{\zeta(\alpha, \beta)^{2/3}}{-\zeta(\alpha, \beta)^{2/3}}\right)\right)^{-1}, \]  
\[ \zeta = 0.09, \]  
\[ \lambda = \nu \kappa, \]  
\[ \nu = 16 \frac{\sqrt{3} \sqrt{\pi}}{\pi}, \]  
\[ \kappa = 0.004235, \]  
\[ Z = -0.001667, \]
\[ \phi (r) = \theta (r) - Z, \] (674)

\[ \theta (r) = \frac{1}{1000} \frac{2.568 + \Xi r + \Phi r^2}{1 + \Lambda r + \Upsilon r^2 + 10\Phi r^3}, \] (675)

\[ \Xi = 23.266, \] (676)

\[ \Phi = 0.007389, \] (677)

\[ \Lambda = 8.723, \] (678)

\[ \Upsilon = 0.472, \] (679)

\[ T = [0.031091, 0.015545, 0.016887], \] (680)

\[ U = [0.21370, 0.20548, 0.11125], \] (681)

\[ V = [7.5957, 14.1189, 10.357], \] (682)

\[ W = [3.5876, 6.1977, 3.6231], \] (683)

\[ X = [1.6382, 3.3662, 0.88026], \] (684)

\[ Y = [0.49294, 0.62517, 0.49671], \] (685)

\[ P = [1, 1, 1], \] (686)

\[ \epsilon (\alpha, \beta) = \epsilon (r(\alpha, \beta), T_1, U_1, V_1, W_1, X_1, Y_1, P_1) \] (687)

\[ - \epsilon (r(\alpha, \beta), T_3, U_3, V_3, W_3, X_3, Y_3, P_3) \omega (\zeta (\alpha, \beta)) (1 - (\zeta (\alpha, \beta))^4) \] (687)

\[ + (\epsilon (r(\alpha, \beta), T_2, U_2, V_2, W_2, X_2, Y_2, P_2) \] (687)

\[ - \epsilon (r(\alpha, \beta), T_1, U_1, V_1, W_1, X_1, Y_1, P_1) \omega (\zeta (\alpha, \beta)) (\zeta (\alpha, \beta))^4, \] (687)

\[ r(\alpha, \beta) = \frac{1}{4\sqrt{34}^{2/3}} \frac{1}{\sqrt{\pi (\alpha + \beta)}}, \] (688)

\[ \zeta (\alpha, \beta) = \frac{\alpha - \beta}{\alpha + \beta}, \] (689)

\[ \omega (z) = \frac{(1 + z)^{4/3} + (1 - z)^{4/3} - 2}{2\sqrt{2} - 2}, \] (690)
e(r,t,u,v,w,x,y,p) \\
= -2t(1 + \frac{1}{2}\ln \left(\frac{1}{(v\sqrt{r + wr + xr^{3/2} + yr^{1/2}})}\right),
\quad (691)
\]
\]
c = 1.709921,
\quad (692)
\]
\[
C(d,\alpha,\beta) = K(Q,\alpha,\beta) + M(Q,\alpha,\beta),
\quad (693)
\]
\[
M(d,\alpha,\beta) = 0.5 \nu(\phi(r(\alpha,\beta))) - \kappa - 3/7Zd^2e^{-335.9789467 \sqrt{\pi} \rho^{3/2}}
\quad (694)
\]
\[
K(d,\alpha,\beta) = 0.2500000000 \lambda^2 \ln \left(1 + 2 \frac{(d^2 + N(\alpha,\beta)d^4)}{\lambda (1 + N(\alpha,\beta)d^2 + (N(\alpha,\beta))^2d^4)}\right)^{-1},
\quad (695)
\]
\[
N(\alpha,\beta) = 24\lambda^{-1} \left( e^{-\frac{4\nu(\alpha,\beta)}{\lambda^2}} - 1 \right)^{-1},
\quad (696)
\]
\[
Q = 1/12 \sqrt[6]{\frac{\sigma(s)}{\pi}} \sqrt[4]{23\frac{5}{6}}
\quad (697)
\]
\]
\]
\[
C.50 \textbf{PW91X: Perdew-Wang 1991 GGA Exchange Functional}
\]
\[
g = 1/2 E(2\rho(s))\),
\quad (698)
\]
\[
G = 1/2 E(2\rho(s)),
\quad (699)
\]
\[
E(n) = -3/4 \sqrt{3} \sqrt{\pi} n^{4/3} F(S),
\quad (700)
\]
\[
S = 1/12 \sqrt{n(s) \sqrt{\pi}} \sqrt{23\frac{5}{6}}
\quad (701)
\]
\[
F(S) = \frac{1 + 0.19645 \text{Sarcsinh}(7.7956S) + \left(0.2743 - 0.1508 e^{-100S^2}\right)S^2}{1 + 0.19645 \text{Sarcsinh}(7.7956S) + 0.004 S^4}.
\quad (702)
\]
C.51 PW92C: Perdew-Wang 1992 GGA Correlation Functional

Electron-gas correlation energy.

\[ T = [0.031091, 0.015545, 0.016887], \]
\[ U = [0.21370, 0.20548, 0.11125], \]
\[ V = [7.5957, 14.1189, 10.357], \]
\[ W = [3.5876, 6.1977, 3.6231], \]
\[ X = [1.6382, 3.3662, 0.88026], \]
\[ Y = [0.49294, 0.62517, 0.49671], \]
\[ P = [1, 1, 1], \]
\[ f = \rho \varepsilon(\rho(a), \rho(b)), \]
\[ e(\alpha, \beta) = e(r(\alpha, \beta), T_1, U_1, V_1, W_1, X_1, Y_1, P_1) \]
\[ = e(r(\alpha, \beta), T_3, U_3, V_3, W_3, X_3, Y_3, P_3) \frac{c}{\omega(\zeta(\alpha, \beta)) (1 - (\zeta(\alpha, \beta))^4)} \]
\[ + (e(r(\alpha, \beta), T_2, U_2, V_2, W_2, X_2, Y_2, P_2) \]
\[ - e(r(\alpha, \beta), T_1, U_1, V_1, W_1, X_1, Y_1, P_1)) \omega(\zeta(\alpha, \beta)) (\zeta(\alpha, \beta))^4 , \]
\[ r(\alpha, \beta) = \frac{1}{4\sqrt{3}^3} \sqrt{\frac{1}{\pi (\alpha + \beta)}}, \]
\[ \zeta(\alpha, \beta) = \frac{\alpha - \beta}{\alpha + \beta}, \]
\[ \omega(z) = \frac{(1 + z)^{4/3} + (1 - z)^{4/3} - 2}{2\sqrt{2} - 2}, \]
\[ e(r, t, u, v, w, x, y, p) = -2t (1 + ur) \ln \left( \frac{1}{r \sqrt{r + wr + xr^{3/2} + yr^{3/2} + 1}} \right), \]
\[ c = 1.709921. \]

C.52 STEST: Test for number of electrons

\[ g = \rho(s). \]
C.53 TFKE: Thomas-Fermi Kinetic Energy

Automatically generated Thomas-Fermi Kinetic Energy.

\[ g = ctf(\rho(s))^{5/3}, \]

\[ ctf = 3/10^2 \pi^{2/3} (\pi^2)^{2/3}. \]

C.54 TH1: Tozer and Handy 1998

Density and gradient dependent first row exchange-correlation functional.

\[ t = [7/6, 4/3, 3/2, 5/3, 4/3, 3/2, 5/3, \frac{11}{6}, 3/2, 5/3, \frac{11}{6}, 2, 3/2, 5/3, \frac{11}{6}, 2, 7/6, 4/3, 3/2, 5/3, 1], \]

\[ u = [0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 1, 1, 1, 1, 0], \]

\[ v = [0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 1, 1, 1, 1, 0], \]

\[ w = [0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 1, 1, 1, 1, 0], \]

\[ \omega = [\]
\[ -0.728255, 0.331699, -0.0876221, 0.140854, -0.0353615, 0.0497930, -0.0645900, 0.219805, -3.72927, 1.94441, 0.128877], \]

\[ n = 21, \]

\[ R_i = (\rho(a))^6 + (\rho(b))^6, \]

\[ S_i = \left(\frac{\rho(a) - \rho(b)}{\rho}\right)^2 u, \]

\[ X_i = 1/2 \left(\frac{\sqrt{\sigma(aa)}}{\rho^{4/3} v_i} + \left(\frac{\sqrt{\sigma(bb)}}{\rho^{4/3} v_i}\right)^{v_i}\right)^{v_i}, \]

\[ Y_i = \left(\frac{\sigma(aa) + \sigma(bb) - 2\sqrt{\sigma(aa)}\sqrt{\sigma(bb)}}{\rho^{8/3}}\right)^{\frac{w_i}{v_i}}, \]

\[ f = \sum_{i=1}^{n} \omega_i R_i S_i X_i Y_i, \]

\[ G = \sum_{i=1}^{n} 1/2 \omega_i (\rho(s))^{1/3} \left(\frac{\sqrt{\sigma(ss)}}{(\rho(s))^{4/3}}\right)^{w_i} (\rho(s))^{(4/3)} v_i^{-1}. \]
C  DENSITY FUNCTIONAL DESCRIPTIONS

C.55  \textbf{TH2: .}

Density and gradient dependent first row exchange-correlation functional.

\[ t = \left[ \frac{13}{12}, \frac{7}{6}, 4/3, 3/2, 5/3, \frac{17}{12}, \frac{3}{2}, 5/3, \frac{11}{6}, \frac{5}{3}, \frac{11}{6}, 2, 5/3, \frac{11}{6}, 2, 7/6, 4/3, 3/2, 5/3 \right], \]  

\[ u = \left[ 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 1, 1, 1 \right], \]  

\[ v = \left[ 0, 0, 0, 0, 0, 1, 1, 1, 1, 2, 2, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0 \right], \]  

\[ w = \left[ 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 1, 1, 1, 0, 0, 0, 0, 0 \right]. \]  

\[ \omega = [0.678831, -1.75821, 1.27676, -1.60789, 0.365610, -0.181327, 0.146973, 0.147141, -0.0716917, -0.0407167, 0.0214625, -0.000768156, 0.0310377, -0.0720326, 0.0446562, -0.266802, 1.50822, -1.94515, 0.679078], \]  

\[ n = 19, \]  

\[ R_i = \left( \rho (a) \right)^{3i} + \left( \rho (b) \right)^{3i}, \]  

\[ S_i = \left( \frac{\rho (a) - \rho (b)}{\rho} \right)^{2v_i} \]  

\[ X_i = 1/2 \left( \sqrt{\sigma (aa)} \right)^{v_i} + \left( \sqrt{\sigma (bb)} \right)^{v_i}, \]  

\[ Y_i = \left( \sigma (aa) + \sigma (bb) - 2 \sqrt{\sigma (aa) \sigma (bb)} \right)^{w_i}, \]  

\[ f = \sum_{i=1}^{n} \omega_i R_i S_i X_i Y_i, \]  

\[ G = \sum_{i=1}^{n} 1/2 \omega_i \left( \rho (s) \right)^{3i} \left( \sqrt{\sigma (ss)} \right)^{v_i} \left( \frac{\sigma (ss)}{\rho (s)} \right)^{w_i} \left( \left( \rho (s) \right)^{4/3} v_i \right)^{-1} \]  

(732)  

(733)  

(734)  

(735)  

(736)  

(737)  

(738)  

(739)  

(740)  

(741)  

(742)  

(743)
Density and gradient dependent first and second row exchange-correlation functional.

\[ t = \left[ \frac{7}{6}, \frac{4}{3}, \frac{3}{2}, 5/3, \frac{17}{12}, \frac{3}{2}, 5/3, \frac{11}{6}, \frac{11}{6}, \frac{11}{6}, \frac{11}{6}, \frac{13}{12}, \frac{2}{7/6}, 4/3, \frac{3}{2}, 5/3, \frac{11}{6}, \frac{11}{6}, \frac{11}{6}, \frac{11}{6}, \frac{13}{12} \right] \]  
\hspace{1cm} (744)

\[ u = [0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 1, 1, 1, 1, 0], \]  
\hspace{1cm} (745)

\[ v = [0, 0, 0, 1, 1, 1, 1, 2, 2, 2, 0, 0, 0, 0, 0, 0, 0, 0], \]  
\hspace{1cm} (746)

\[ w = [0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 1, 1, 1, 0, 0, 0], \]  
\hspace{1cm} (747)

\[ \omega = [ \ldots ] \]  
\hspace{1cm} (748)

\[ n = 19, \]  
\hspace{1cm} (749)

\[ R_i = (\rho (a))^i \]  
\hspace{1cm} (750)

\[ + (\rho (b))^i, \]  
\hspace{1cm} (750)

\[ S_i = \left( \frac{\rho (a) - \rho (b)}{\rho} \right)^{2u_i}, \]  
\hspace{1cm} (751)

\[ X_i = 1/2 \left( \frac{\sqrt{\sigma (aa)}}{\rho^{3/3}} \right)^{v_i} + \left( \frac{\sqrt{\sigma (bb)}}{\rho^{3/3}} \right)^{v_i}, \]  
\hspace{1cm} (752)

\[ Y_i = \left( \frac{\sigma (aa) + \sigma (bb) - 2 \sqrt{\sigma (aa)} \sqrt{\sigma (bb)}}{\rho^{3/3}} \right)^{w_i}, \]  
\hspace{1cm} (753)

\[ f = \sum_{i=1}^{n} \omega_i R_i S_i X_i Y_i, \]  
\hspace{1cm} (754)

\[ G = \sum_{i=1}^{n} 1/2 \omega_i (\rho (s))^i \left( \frac{\sqrt{\sigma (ss)}}{\rho (s)^{3/3}} \right)^{v_i} \left( \frac{\sigma (ss)}{\rho (s)^{3/3}} \right)^{w_i} \left( (\rho (s))^{4/3} \right)^{-1}. \]  
\hspace{1cm} (755)
C.57 TH2:.

Density an gradient dependent first and second row exchange-correlation functional.

\[ t = \left[ \frac{7}{6}, \frac{3}{2}, \frac{25}{3}, \frac{17}{12}, \frac{3}{2}, \frac{5}{3}, \frac{11}{6}, \frac{11}{6}, \frac{2}{5}, \frac{8}{3}, \frac{2}{3}, \frac{13}{12} \right]. \]  

(756)

\[ u = [0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 1, 1, 1, 0], \]  

(757)

\[ v = [0, 0, 0, 0, 1, 1, 1, 2, 2, 2, 0, 0, 0, 0, 0, 0, 0], \]  

(758)

\[ w = [0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 1, 1, 0, 0, 0], \]  

(759)

\[ \omega = [0.0677353, \quad -1.06763, \quad -0.0419018, 0.0226313, \quad -0.222478, 0.283432, \quad -0.0165089, \quad -0.0167204, \quad -0.0332362, 0.0162254, \quad -0.0098419, 0.0376713, \quad -0.0653419, 0.0222835, 0.375782, \quad -1.90675, 3.22494, \quad -1.68698, \quad -0.0235810], \]  

(760)

\[ n = 19, \]  

(761)

\[ R_i = (\rho (a))^v_i + (\rho (b))^v_i, \]  

(762)

\[ S_i = \left( \frac{\rho (a) - \rho (b)}{\rho} \right) \rho^{2uv}, \]  

(763)

\[ X_i = 1/2 \left( \sqrt{\sigma (aa)} \right)^{v_i} + \left( \sqrt{\sigma (bb)} \right)^{v_i} \rho^{-3v}, \]  

(764)

\[ Y_i = \left( \sigma (aa) + \sigma (bb) - 2 \sqrt{\sigma (aa) \sigma (bb)} \right) \rho^{-3v}, \]  

(765)

\[ f = \sum_{i=1}^{n} \omega_i R_i S_i X_i Y_i, \]  

(766)

\[ G = \sum_{i=1}^{n} 1/2 \omega_i (\rho (s))^v_i \left( \sqrt{\sigma (ss)} \right)^{v_i} \left( \frac{\sigma (ss)}{(\rho (s))^{3v_i}} \right) \rho^{-3v_i} (\rho (s))^{4v_i} \]  

(767)
C.58 THGFC:

Density and gradient dependent first row exchange-correlation functional for closed shell systems. Total energies are improved by adding $DN$, where $N$ is the number of electrons and $D = 0.1863$.

$$t = [\frac{7}{6}, \frac{4}{3}, \frac{3}{2}, 5/3, 4/3, 3/2, 5/3, 11/6, 3/2, 5/3, 11/6, 2],$$  \hspace{1cm} (768)

$$v = [0, 0, 0, 0, 1, 1, 1, 2, 2, 2, 2],$$ \hspace{1cm} (769)

$$\omega = [$$
\begin{align*}
  &-0.864448, 0.565130, \\
  &-1.27306, 0.309681, \\
  &-0.287658, 0.588767, \\
  &-0.252700, 0.0223563, 0.0140131, \\
  &-0.0826608, 0.0556080, \\
  &-0.00936227; \\
\end{align*}

\hspace{1cm} (770)

$$n = 12,$$ \hspace{1cm} (771)

$$R_i = (\rho (a))^i + (\rho (b))^i,$$ \hspace{1cm} (772)

$$X_i = 1/2 \left( \sqrt{\sigma (aa)} \right)^{v_i} + \left( \sqrt{\sigma (bb)} \right)^{v_i} / \rho_{4/3v_i},$$ \hspace{1cm} (773)

$$f = \sum_{i=1}^{n} \omega_i R_i X_i,$$ \hspace{1cm} (774)

$$G = \sum_{i=1}^{n} 1/2 \omega_i (\rho (s))^i \left( \sqrt{\sigma (ss)} \right)^{v_i} / \rho_{4/3v_i}.$$ \hspace{1cm} (775)

C.59 THGFCFO:

Density and gradient dependent first row exchange-correlation functional. FCFO = FC + open shell fitting.

$$t = [\frac{7}{6}, \frac{4}{3}, \frac{3}{2}, 5/3, 4/3, 3/2, 5/3, 11/6, 3/2, 5/3, 11/6, 2, 7/6, 4/3, 3/2, 5/3],$$ \hspace{1cm} (776)

$$u = [0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 1, 1, 1, 1],$$ \hspace{1cm} (777)

$$v = [0, 0, 0, 0, 1, 1, 1, 1, 2, 2, 2, 0, 0, 0, 0, 0, 0],$$ \hspace{1cm} (778)

$$w = [0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 1, 1, 1, 0, 0, 0],$$ \hspace{1cm} (779)
\[ \omega = [ \\
-0.864448, 0.565130, \\
-1.27306, 0.309681, \\
-0.287658, 0.588767, \\
-0.252700, 0.0223563, 0.0140131, \\
-0.0826608, 0.0556080, \\
-0.0936227, \\
-0.00677146, 0.0515199, \\
-0.0874213, 0.431940, \\
-0.691153, \\
-0.637866, 1.07565 ], \] (780)

\[ n = 20, \quad (781) \]

\[ R_i = (\rho (a))^b_i + (\rho (b))^b_i, \quad (782) \]

\[ S_i = \left( \frac{\rho (a) - \rho (b)}{\rho} \right)^2 u_i, \quad (783) \]

\[ X_i = \frac{1/2 \left( \sqrt{\sigma (aa)} \right)^v_i + \left( \sqrt{\sigma (bb)} \right)^v_i}{\rho^{4/3} v_i}, \quad (784) \]

\[ Y_i = \left( \frac{\sigma (aa) + \sigma (bb) - 2 \sqrt{\sigma (aa)} \sqrt{\sigma (bb)}}{\rho^{8/3}} \right)^w_i, \quad (785) \]

\[ f = \sum_{i=1}^{n} \omega_i R_i S_i X_i Y_i, \quad (786) \]

\[ G = \sum_{i=1}^{n} 1/2 \omega_i (\rho (s))^4_i \left( \sqrt{\sigma (ss)} \right)^v_i \left( \frac{\sigma (ss)}{(\rho (s))^{8/3}} \right)^w_i \left( (\rho (s))^{4/3} \right)^{-1}. \quad (787) \]

**C.60 THGFco**: Density and gradient dependent first row exchange-correlation functional.

\[ t = [7/6, 4/3, 3/2, 5/3, 4/3, 3/2, 5/3, 11/6, 3/2, 5/3, 11/6, 2, 3/2, 5/3, 11/6, 2, 7/6, 4/3, 3/2, 5/3], \quad (788) \]

\[ u = [0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 1, 1, 1], \quad (789) \]

\[ v = [0, 0, 0, 0, 1, 1, 1, 2, 2, 2, 2, 0, 0, 0, 0, 0, 0, 0, 0, 0], \quad (790) \]

\[ w = [0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 1, 1, 1, 0, 0, 0, 0], \quad (791) \]
\[ \omega = [ \]
\[-0.962998, 0.860233, \]
\[-1.54092, 0.381602, \]
\[-0.210208, 0.391496, \]
\[-0.107660, \]
\[-0.0105324, 0.00837384, \]
\[-0.0617859, 0.0383072, \]
\[-0.00526905, \]
\[-0.00381514, 0.00837384, \]
\[-0.0617859, 0.0383072, \]
\[-0.328799, \]
\[-1.22595, 1.36412], \]
\[n = 20, \]
\[R_i = (\rho (a))^i + (\rho (b))^i, \]
\[S_i = \left( \frac{\rho (a) - \rho (b)}{\rho} \right)^2 u_i, \]
\[X_i = \frac{1}{2} \frac{\sqrt{\sigma (aa)}}{\rho^{4/3} v_i} + \left( \frac{\sqrt{\sigma (bb)}}{\rho^{4/3} v_i} \right) u_i, \]
\[Y_i = \left( \frac{\sigma (aa) + \sigma (bb) - 2 \sqrt{\sigma (aa) \sqrt{\sigma (bb)}}}{\rho^{8/3}} \right)^{w_i}, \]
\[f = \sum_{i=1}^{n} \omega_i R_i X_i Y_i, \]
\[G = \sum_{i=1}^{n} 1/2 \omega_i (\rho (s))^i \left( \frac{\sigma (ss)}{\rho^{8/3} (\rho (s))^{8/3}} \right)^{w_i} \left( (\rho (s))^{4/3} v_i \right)^{-1}. \]

C.61 THGFL: .

Density dependent first row exchange-correlation functional for closed shell systems.
\[ t = [7/6, 4/3, 3/2, 5/3], \]
\[\omega = [ \]
\[-1.06141, 0.898203, \]
\[-1.34439, 0.302369], \]
\[n = 4, \]
\[R_i = (\rho (a))^i + (\rho (b))^i, \]
\[f = \sum_{i=1}^{n} \omega_i R_i. \]
C.62 TPSSC: TPSS Correlation Functional


C.63 TPSSX: TPSS Exchange Functional


C.64 VSXC: .

\[ p = \begin{bmatrix} -0.98, 0.3271, 0.7035 \end{bmatrix}, \]  

\[ q = \begin{bmatrix} -0.003557, -0.03229, 0.007695 \end{bmatrix}, \]  

\[ r = [0.00625, -0.02942, 0.05153], \]  

\[ t = \begin{bmatrix} -0.00002354, 0.002134, 0.00003394 \end{bmatrix}, \]  

\[ u = \begin{bmatrix} -0.0001283, -0.005452, -0.001269 \end{bmatrix}, \]  

\[ v = [0.0003575, 0.01578, 0.001296], \]  

\[ \alpha = [0.001867, 0.005151, 0.00305], \]  

\[ g = (\rho(s))^{4/3} F(\chi(s), zs, p_1, q_1, r_1, t_1, u_1, v_1, \alpha_1) \]  

\[ + ds \varepsilon(\rho(s), 0) F(\chi(s), zs, p_2, q_2, r_2, t_2, u_2, v_2, \alpha_2), \]  

\[ G = (\rho(s))^{4/3} F(\chi(s), zs, p_1, q_1, r_1, t_1, u_1, v_1, \alpha_1) \]  

\[ + ds \varepsilon(\rho(s), 0) F(\chi(s), zs, p_2, q_2, r_2, t_2, u_2, v_2, \alpha_2), \]  

\[ f = F(x, z, p_3, q_3, r_3, t_3, u_3, v_3, \alpha_3) (\varepsilon(\rho(a), \rho(b)) \]  

\[ - \varepsilon(\rho(a), 0) \]  

\[ - \varepsilon(\rho(b), 0)), \]  

\[ x = (\chi(a))^2 \]  

\[ + (\chi(b))^2, \]  

\[ zs = \frac{\tau(s)}{(\rho(s))^{5/3}} - cf, \]  

\[ z = \frac{\tau(a)}{(\rho(a))^{5/3}} + \frac{\tau(b)}{(\rho(b))^{5/3}} - 2cf, \]
\[ ds = 1 - \frac{(\chi(s))^2}{4zs + 4cf}, \]  
\[ F(x, z, p, q, c, d, e, f, \alpha) = \frac{p}{\lambda(x, z, \alpha)} + \frac{q x^2 + cz}{(\lambda(x, z, \alpha))^2} + \frac{d x^4 + e x^2 z + f z^2}{(\lambda(x, z, \alpha))^3} \]  
\[ \lambda(x, z, \alpha) = 1 + \alpha (x^2 + z), \]  
\[ cf = 3/5 3^{2/3} (\pi^2)^{2/3}, \]  
\[ T = [0.031091, 0.015545, 0.016887], \]  
\[ U = [0.21370, 0.20548, 0.11125], \]  
\[ V = [7.5957, 14.1189, 10.357], \]  
\[ W = [3.5876, 6.1977, 3.6231], \]  
\[ X = [1.6382, 3.3662, 0.88026], \]  
\[ Y = [0.49294, 0.62517, 0.49671], \]  
\[ P = [1, 1, 1], \]  
\[ \varepsilon(\alpha, \beta) = (\alpha + \beta) \left(\varepsilon(I(\alpha, \beta), T_1, U_1, V_1, W_1, X_1, Y_1, P_1) \right) \]  
\[ = \varepsilon(I(\alpha, \beta), T_3, U_3, V_3, W_3, X_3, Y_3, P_3) \omega(\zeta(\alpha, \beta)) \left(1 - (\zeta(\alpha, \beta))^4\right) \]  
\[ + \varepsilon(I(\alpha, \beta), T_2, U_2, V_2, W_2, X_2, Y_2, P_2) \omega(\zeta(\alpha, \beta)) \left(1 - (\zeta(\alpha, \beta))^4\right), \]  
\[ I(\alpha, \beta) = 1/4 \sqrt{54} 3^{2/3} \sqrt{\frac{1}{\pi (\alpha + \beta)}}, \]  
\[ \zeta(\alpha, \beta) = \frac{\alpha - \beta}{\alpha + \beta}. \]
\[\omega(z) = \frac{(1 + z)^{4/3} + (1 - z)^{4/3} - 2}{2\sqrt{2} - 2}, \quad (832)\]

\[e(r,t,u,v,w,x,y,p) = -2t(1 + ur)\ln\left(1 + \frac{1}{t(v\sqrt{r} + wr + xr^{3/2} + yp^{1/2})}\right), \quad (833)\]

\[c = 1.709921. \quad (834)\]

C.65 \textbf{VW: von Weizsäcker kinetic energy}

Automatically generated von Weizsäcker kinetic energy.

\[g = \frac{c\sigma(ss)}{\rho(s)}, \quad (835)\]

\[G = \frac{c\sigma(ss)}{\rho(s)}, \quad (836)\]

\[c = 1/8. \quad (837)\]

C.66 \textbf{VWN3: Vosko-Wilk-Nusair (1980) III local correlation energy}

VWN 1980(III) functional

\[x = \frac{1}{4} \sqrt[6]{\frac{\rho}{34^{5/6}}} \sqrt{\frac{1}{\pi \rho}}, \quad (838)\]

\[\zeta = \frac{\rho(a) - \rho(b)}{\rho}, \quad (839)\]

\[f = \rho e, \quad (840)\]

\[k = [0.0310907, 0.0155453, \ldots, -1/6 \pi^{-2}], \quad (841)\]

\[l = [\ldots, -0.409286, -0.743294, -0.228344], \quad (842)\]

\[m = [13.0720, 20.1231, 1.06835], \quad (843)\]

\[n = [42.7198, 101.578, 11.4813], \quad (844)\]

\[e = \Lambda + z(\lambda), \quad (845)\]

\[- \Lambda), \quad (846)\]
\[ y = \frac{9}{8} \left( 1 + \zeta \right)^{4/3} + \frac{9}{8} \left( 1 - \zeta \right)^{4/3} - \frac{9}{4}, \]

\[ \Lambda = q(k_1, l_1, m_1, n_1), \]

\[ \lambda = q(k_2, l_2, m_2, n_2), \]

\[ q(A, p, c, d) = A \ln \left( \frac{x^2}{X(x, c, d)} \right) + 2c \arctan \left( \frac{Q(c, d)}{2x + c} \right) (Q(c, d))^{-1} - cp \ln \left( \frac{(x - p)^2}{X(x, c, d)} \right) + 2(c + 2p) \arctan \left( \frac{Q(c, d)}{2x + c} \right) (Q(c, d))^{-1} \left( X(p, c, d) \right)^{-1}, \]

\[ Q(c, d) = \sqrt{4d - c^2}, \]

\[ X(i, c, d) = i^2 + ci + d, \]

\[ z = 4 \frac{y}{9 \sqrt{2} - 9}. \]

**C.67 VWN5: Vosko-Wilk-Nusair (1980) V local correlation energy**

VWN 1980(V) functional. The fitting parameters for \( \Delta \varepsilon_c(r, \zeta)_V \) appear in the caption of table 7 in the reference.

\[ x = 1/4 \sqrt{34^{566} \frac{1}{\pi \rho}}, \]

\[ \zeta = \frac{\rho(a) - \rho(b)}{\rho}, \]

\[ f = \rho e, \]

\[ k = [0.0310907, 0.01554535, -1/6 \pi^{-2}], \]

\[ l = [-0.10498, -0.325, -0.0047584]. \]
\begin{align*}
m &= [3.72744, 7.06042, 1.13107], \quad (858) \\
n &= [12.9352, 18.0578, 13.0045], \quad (859) \\
e &= \Lambda + \alpha y (1 + h \zeta^4), \quad (860) \\
y &= \frac{9}{8} (1 + \frac{9}{8} (1 - \frac{9}{4})), \quad (861) \\
h &= 4/9 \frac{\lambda - \Lambda}{(\sqrt{\frac{\lambda}{2}} - 1)} \alpha - 1, \quad (862) \\
\Lambda &= q (k_1, l_1, m_1, n_1), \quad (863) \\
\lambda &= q (k_2, l_2, m_2, n_2), \quad (864) \\
\alpha &= q (k_3, l_3, m_3, n_3), \quad (865) \\
q(A, p, c, d) &= A \left( \ln \left( \frac{x^2}{X(x, c, d)} \right) \right. \\
&\quad + 2c \arctan \left( \frac{Q(c, d)}{2x + c} \right) (Q(c, d))^{-1} \\
&\quad - cp \left( \ln \left( \frac{(x - p)^2}{X(x, c, d)} \right) \right. \\
&\quad + 2 \left( \frac{c}{\sqrt{4d - c^2}} \right) + 2p \arctan \left( \frac{Q(c, d)}{2x + c} \right) (Q(c, d))^{-1} \left( X(p, c, d) \right)^{-1} \right), \quad (866) \\
Q(c, d) &= \sqrt{4d - c^2}, \quad (867) \\
X(i, c, d) &= i^2 + ci + d. \quad (868)
\end{align*}

C.68 \textbf{XC-M05: M05 Meta-GGA Exchange-Correlation Functional}


C.69 \textbf{XC-M05-2X: M05-2X Meta-GGA Exchange-Correlation Functional}

C.70  **XC-M06**: M06 Meta-GGA Exchange-Correlation Functional

Here it means M06 exchange-correlation part which excludes HF exact exchange term. Y. Zhao and D. G. Truhlar, Theor. Chem. Acc. 120, 215 (2008).

C.71  **XC-M06-2X**: M06-2X Meta-GGA Exchange-Correlation Functional

Here it means M06-2X exchange-correlation part which excludes HF exact exchange term. Y. Zhao and D. G. Truhlar, Theor. Chem. Acc. 120, 215 (2008).

C.72  **XC-M06-HF**: M06-HF Meta-GGA Exchange-Correlation Functional


C.73  **XC-M06-L**: M06-L Meta-GGA Exchange-Correlation Functional


C.74  **XC-M08-HX**: M08-HX Meta-GGA Exchange-Correlation Functional


C.75  **XC-M08-SO**: M08-SO Meta-GGA Exchange-Correlation Functional


C.76  **XC-M11-L**: M11-L Exchange-Correlation Functional


C.77  **XC-SOGGA**: SOGGA Exchange-Correlation Functional


C.78  **XC-SOGGA11**: SOGGA11 Exchange-Correlation Functional


C.79  **XC-SOGGA11-X**: SOGGA11-X Exchange-Correlation Functional

License information

The Molpro source code contains some external code which is listed in this section. Molpro binaries may, in some instances, contain compiled versions of this code also.

D.1 BLAS

Copies of some of the netlib BLAS routines are included in the Molpro source code. The source code is identical except for the addition of a revision control header, and renaming of the file suffix from .f to .fh. These routines are only used if the user does not provide an external BLAS library. In addition, as suggested in the comments, the STOP statement in subroutine XERBLA has been modified.
D.2 LAPACK

Copies of some of the netlib LAPACK routines are included in the Molpro source code. The source code is identical except for the addition of a revision control header, and renaming of the file suffix from .f to .fh. These routines are only used if the user does not provide an external LAPACK library. The license follows.

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