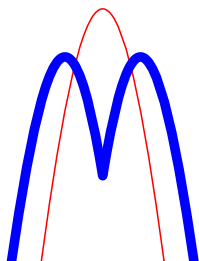


# MOLPRO



## *Recent Changes* *Version 2010.1*

H.-J. Werner

*Institut für Theoretische Chemie  
Universität Stuttgart  
Pfaffenwaldring 55  
D-70569 Stuttgart  
Federal Republic of Germany*

P. J. Knowles

*School of Chemistry  
Cardiff University  
Main Building, Park Place, Cardiff CF10 3AT  
United Kingdom*

*SHA1 833379180250ebe11052d872bd9ff53639690c67*

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## 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.

### 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.

### 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.

### 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`.

### 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:

cc-pVnZ-F12 (n=D-Q) cc-pCVnZ-F12 (n=D-Q)

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 Hättig 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 Hättig 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:

cc-pVTZ-DK cc-pwCVTZ-DK aug-cc-pVTZ-DK aug-cc-pwCVTZ-DK

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:

aug-cc-pVnZ-DK (n=D-5) cc-pCVnZ-DK (n=D-5) cc-pwCVnZ-DK (n=D-5) aug-cc-pCVnZ-DK (n=D-5) aug-cc-pwCVnZ-DK (n=D-5)

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:

cc-pCVnZ-F12 (n=D-Q) for B-Ne, Al-Ar cc-pCVnZ-F12/OptRI (n=D-Q) 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.).

### 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.

### 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.

### 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.

### 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.

## New features of MOLPRO2009.1

### 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.

## 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.

## 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.

## 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 as `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.

## 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.

## 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.
3. Correlation regions within a localized molecular orbital approach as described in *J. Chem. Phys.* 128, 144106 (2008).
4. Automated calculation of anharmonic vibrational frequencies and zero-point energies using VCI methods as described in *J. Chem. Phys.* 126, 134108 (2007) and references therein.
5. Coupling of DFT and coupled cluster methods as described in *Phys. Chem. Chem. Phys.* 10, 3353 (2008) 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.

## 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
8. Analytical DF-HF, DF-KS, DF-LMP2, and DF-SCS-LMP2 gradients
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 CASSCF and MRCI wavefunctions with different orbitals.
13. A new spin-orbit integral program for generally contracted basis sets.
14. Douglas-Kroll-Hess Hamiltonian up to arbitrary order.
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 ??).
17. An interface to the MRCC program of M. Kallay, allowing coupled-cluster calculations with arbitrary excitation level.
18. Automatic *embarrassingly parallel* computation of numerical gradients and Hessians (mppx Version).
19. Additional parallel codes, e.g. DF-HF, DF-KS, DF-LCCSD(T) (partly, including triples).
20. Additional output formats for tables (XHTML, L<sup>A</sup>T<sub>E</sub>X, 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.

### **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 SET command has changed (see sections ?? and ??).
5. The total charge of the molecule can be specified in a variable CHARGE or on the WF card, see section ??.
6. Improved numerical geometry optimization using symmetrical displacement coordinates (see sections ?? and ??).
7. Improved numerical frequency calculations using the symmetry (AUTO option, see section ??).

## 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  
G. Hetzer, P. Pulay, and H.-J. Werner, *Chem. Phys. Lett.* **290**, 143 (1998),  
M. Schütz, G. Hetzer, and H.-J. Werner, *J. Chem. Phys.* **111**, 5691 (1999),  
G. Hetzer, M. Schütz, H. Stoll, and H.-J. Werner, *J. Chem. Phys.* **113**, 9443 (2000),  
as well as LMP2 gradients as described in  
A. El Azhary, G. Rauhut, P. Pulay, and H.-J. Werner, *J. Chem. Phys.* **108**, 5185 (1998)  
are now available without special license. The linear scaling LCCSD(T) methods as described in  
M. Schütz and H.-J. Werner, *J. Chem. Phys.* **114**, 661 (2001),  
M. Schütz and H.-J. Werner, *Chem. Phys. Lett.* **318**, 370 (2000),  
M. Schütz, *J. Chem. Phys.* **113**, 9986 (2000)  
will be made available at a later stage.
2. QCISD gradients as described in *Phys. Chem. Chem. Phys.* **3**, 4853 (2001) are now available.
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.* **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* BASIS card, or a basis input block must be used. BASIS, NAME is now entirely equivalent to BASIS=NAME, i.e. a global default basis set is defined and the variable 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.

### 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.
5. New internally contracted multi-reference second-order perturbation theory code (author Paolo Celani) through command RS2C, as described in P. Celani and H.-J. Werner, J. Chem. Phys. 112, 5546 (2000).
6. EOM-CCSD for excited states (author Tatiana Korona).
7. QCISD dipole moments as true analytical energy derivatives (author Guntram Rauhut).
8. Linear scaling (CPU and memory) LMP2 as described by G. Hetzer, P. Pulay, and H.-J. Werner, Chem. Phys. Lett. 290, 143 (1998).  
M. Schütz, G. Hetzer, and H.-J. Werner, J. Chem. Phys. 111, 5691 (1999).
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 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 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.

## 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 diabaticization 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.