Problems with MOLPRO

May 21, 2009

Abstract

I am trying to compute the spin-orbit matrix for the states dissociating to the ground state and spin-orbit excited state of Br along the IBr potential curve. I am using one of the pseudopotentials of the Stuttgarg-Cologne group. I have found that the diagonal terms ("diabatic") of the spin-orbit coupling matrix are not affected by any change in the input file but the eigenstates of the spin-orbit matrix are very different for some of the geometries.

I present the results obtained for the same IBr distance but using different geometry in the input file. One of the calculations uses XYZ geometry and the other one uses Z-matrix. I would like to point out that I don't think the problem is only related with the use of XYZ geommetry or Z-matrix, since I have found the same problem when using the geommetry which here presents good results. I have chosen just this example because it is the one which should present the same (or very similar) results since nothing is different in the input but the geometry card.

Another point is that a proper CI, without the NOEXC option, presents the same problems.

1 Problems with MOLPRO

I have done the calculation of the energies and spin-orbit couplings using either cartesian coordinates or Z-matrix specifying the geometry. The inputs look like:

Cartesian coordinates

```
gprint,orbitals,civector
basis
include,/home/csanz/IBr/pot/Br10MDF-I28MDF/BasisVTZ/ecp10mdf.pl,1
include,/home/csanz/IBr/pot/Br10MDF-I28MDF/BasisVTZ/basis-ecp10mdf_vtz.pl,1
include,/home/csanz/IBr/pot/Br10MDF-I28MDF/BasisVTZ/ecp28mdf.pl,1
include,/home/csanz/IBr/pot/Br10MDF-I28MDF/BasisVTZ/basis-ecp28mdf_vtz.pl,1
end

text, IBr

!---------------------------------------
! Files where to store and read the orbitals and weights
!---------------------------------------
orbit=2100.2-1.0
wei=7100.2-0.0

!---------------------------------------
! Description of the electrid field
```

```
!---------------------------------------
! fs=field strenght
! I include the field in the plane YZ, the calculation chooses the IBr lying on the Y-axis

angs=0.5291772108
fs=0.0
the=0.0
ex=fs*sin(the)
ey=fs*cos(the)
ez=0.0

!---------------------------------------
! Description of coordinates
!---------------------------------------
r=[12.0,11.0,10.0,8.0,7.5,7.0,6.8,6.6,6.4,6.2,6.0,5.8,5.6,5.4,5.2,5.0,4.8,4.6,4.4,4.2,4.0,3.8] bohr

do j=1,#r
geomtyp=xyz
geometry={noorient;
2           ! number of atoms
Geometry input for IBr in cartesian coordinates
I,0.0001*angs,0.0,0.0
Br,0.0001*angs,r(j)*angs,0.0
}
!text, adding the dipole electric field
dip,ex,ey,ez

!!
! HF calculation
!!

if(j.eq.0)then
   {hf;wf,50,2,0;}
endif
!!
! MCSCF calculations
!!
orbit=orbit+1
wei=wei+1

!!
! A''
!!

{multi;occ,19,9;closed,13,6;save,ref=wei;wf,50,2,0;state,5;orbital,orbit;}
if(status.lt.0)then
   {multi;maxiter,50;occ,19,9;closed,13,6;save,ref=wei;wf,50,2,0;state,4;orbital,orbit;}
endif
table, 'SCF1App', r(j),energy(1),energy(2),energy(3),energy(4)

{multi;occ,19,9;closed,13,6;save,ref=wei;wf,50,2,2;state,5;orbital,orbit+100}
if(status.lt.0)then
   {multi;maxiter,50;occ,19,9;closed,13,6;save,ref=wei;wf,50,2,2;state,4;orbital,orbit+100}
endif
table, 'SCF3App', r(j),energy(1),energy(2),energy(3),energy(4)
```

```
!!
! A'
!!
{multi;occ,19,9;closed,13,6;save,ref=wei;wf,50,1,0;state,5;orbital,orbit;}
if(status.lt.0)then
   {multi;maxiter,50;occ,19,9;closed,13,6;save,ref=wei;wf,50,1,0;state,5;orbital,orbit;}
endif
table, 'SCF1Ap', r(j),energy(1),energy(2),energy(3),energy(4),energy(5)

{multi;occ,19,9;closed,13,6;save,ref=wei;wf,50,1,2;state,5;orbital,orbit+100}
if(status.lt.0)then
   {multi;maxiter,50;occ,19,9;closed,13,6;save,ref=wei;wf,50,1,2;state,5;orbital,orbit+100}
endif
table, 'SCF3Ap', r(j),energy(1),energy(2),energy(3),energy(4),energy(5)


{ci,nocheck;noexc;maxiter,32,600;o11.0,10.0,8.0,7.5,7.0,6.8,6.6,6.4,6.2,6.0,5.8,5.6,5.4,5.2,5.0,4.8,4.6,4.4,4.2,4.0
en(1)=energd(1)
{ci,nocheck;noexc;maxiter,32,600;occ,19,9;closed,13,6;wf,50,1,0;state,1,2;orbit,,ignore_error;save,3001.2;}
en(2)=energd(1)
{ci,nocheck;noexc;maxiter,32,600;occ,19,9;closed,13,6;wf,50,1,0;state,1,3;orbit,,ignore_error;save,3002.2;}
en(3)=energd(1)
{ci,nocheck;noexc;maxiter,32,600;occ,19,9;closed,13,6;wf,50,1,0;state,1,4;orbit,,ignore_error;save,3003.2;}
en(4)=energd(1)
{ci,nocheck;noexc;maxiter,32,600;occ,19,9;closed,13,6;wf,50,1,0;state,1,5;orbit,,ignore_error;save,3004.2;}
en(5)=energd(1)
table,'CI1Ap',r(j),en(1),en(2),en(3),en(4),en(5)

{ci,nocheck;noexc;maxiter,32,600;occ,19,9;closed,13,6;wf,50,1,2;state,1,1;orbit,,ignore_error;save,3100.2;}
en(1)=energd(1)
{ci,nocheck;noexc;maxiter,32,600;occ,19,9;closed,13,6;wf,50,1,2;state,1,2;orbit,,ignore_error;save,3101.2;}
en(2)=energd(1)
{ci,nocheck;noexc;maxiter,32,600;occ,19,9;closed,13,6;wf,50,1,2;state,1,3;orbit,,ignore_error;save,3102.2;}
en(3)=energd(1)
{ci,nocheck;noexc;maxiter,32,600;occ,19,9;closed,13,6;wf,50,1,2;state,1,4;orbit,,ignore_error;save,3103.2;}
en(4)=energd(1)
{ci,nocheck;noexc;maxiter,32,600;occ,19,9;closed,13,6;wf,50,1,2;state,1,5;orbit,,ignore_error;save,3104.2;}
en(5)=energd(1)
table,'CI3Ap',r(j),en(1),en(2),en(3),en(4),en(5)

{ci,nocheck;noexc;maxiter,32,600;occ,19,9;closed,13,6;wf,50,2,0;state,1,1;orbit,,ignore_error;save,3200.2;}
en(1)=energd(1)
{ci,nocheck;noexc;maxiter,32,600;occ,19,9;closed,13,6;wf,50,2,0;state,1,2;orbit,,ignore_error;save,3201.2;}
en(2)=energd(1)
{ci,nocheck;noexc;maxiter,32,600;occ,19,9;closed,13,6;wf,50,2,0;state,1,3;orbit,,ignore_error;save,3202.2;}
en(3)=energd(1)
{ci,nocheck;noexc;maxiter,32,600;occ,19,9;closed,13,6;wf,50,2,0;state,1,4;orbit,,ignore_error;save,3203.2;}
en(4)=energd(1)
table,'CI1App',r(j),en(1),en(2),en(3),en(4)
{ci,nocheck;noexc;maxiter,32,600;occ,19,9;closed,13,6;wf,50,2,2;state,1,1;orbit,,ignore_error;save,3300.2;}
en(1)=energd(1)
{ci,nocheck;noexc;maxiter,32,600;occ,19,9;closed,13,6;wf,50,2,2;state,1,2;orbit,,ignore_error;save,3301.2;}
en(2)=energd(1)
{ci,nocheck;noexc;maxiter,32,600;occ,19,9;closed,13,6;wf,50,2,2;state,1,3;orbit,,ignore_error;save,3302.2;}
```

```
en(3)=energd(1)
{ci,nocheck;noexc;maxiter,32,600;occ,19,9;closed,13,6;wf,50,2,2;state,1,4;orbit,,ignore_error;save,3303.2;}
en(4)=energd(1)
table,'CI3App',r(j),en(1),en(2),en(3),en(4)

{ci;print,hls=2,vls=0;options,hlstrans=0,matel=1;
hlsmat,ecpls,3000.2,3001.2,3002.2,3003.2,3004.2,3100.2,3101.2,3102.2,3103.2,3104.2,3200.2,3201.2,3202.2,3203.2,3300.2,

enddo

---
```

Z-matrix

```
gprint,orbitals,civector
basis
include,/home/csanz/IBr/pot/Br10MDF-I28MDF/BasisVTZ/ecp10mdf.pl,1
include,/home/csanz/IBr/pot/Br10MDF-I28MDF/BasisVTZ/basis-ecp10mdf_vtz.pl,1
include,/home/csanz/IBr/pot/Br10MDF-I28MDF/BasisVTZ/ecp28mdf.pl,1
include,/home/csanz/IBr/pot/Br10MDF-I28MDF/BasisVTZ/basis-ecp28mdf_vtz.pl,1
end

text, IBr

!---------------------------------------
! Files where to store and read the orbitals and weights
!---------------------------------------
orbit=2100.2-1.0
wei=7100.2-0.0

!---------------------------------------
! Description of the electrid field
!---------------------------------------
! fs=field strenght
! I include the field in the plane YZ, the calculation chooses the IBr lying on the Y-axis

angs=0.5291772108
fs=0.0
the=0.0
ex=0.0
ey=fs*sin(the)
ez=fs*cos(the)

!---------------------------------------
! Description of coordinates
!---------------------------------------
r=[12.0,11.0,10.0,8.0,7.5,7.0,6.8,6.6,6.4,6.2,6.0,5.8,5.6,5.4,5.2,5.0,4.8,4.6,4.4,4.2,4.0,3.8] bohr

do j=1,#r

geometry={X;
I;
Br,I,r(j);
}
```

```
!text, adding the dipole electric field
dip,ex,ey,ez

!!
! HF calculation
!!

if(j.eq.0)then
   {hf;wf,50,2,0;}
endif
!!
! MCSCF calculations
!!
orbit=orbit+1
wei=wei+1

!!
! A''
!!

{multi;occ,19,9;closed,13,6;save,ref=wei;wf,50,2,0;state,5;orbital,orbit;}
if(status.lt.0)then
   {multi;maxiter,50;occ,19,9;closed,13,6;save,ref=wei;wf,50,2,0;state,4;orbital,orbit;}
endif
table, 'SCF1App', r(j),energy(1),energy(2),energy(3),energy(4)

{multi;occ,19,9;closed,13,6;save,ref=wei;wf,50,2,2;state,5;orbital,orbit+100}
if(status.lt.0)then
   {multi;maxiter,50;occ,19,9;closed,13,6;save,ref=wei;wf,50,2,2;state,4;orbital,orbit+100}
endif
table, 'SCF3App', r(j),energy(1),energy(2),energy(3),energy(4)

!!
! A'
!!
{multi;occ,19,9;closed,13,6;save,ref=wei;wf,50,1,0;state,5;orbital,orbit;}
if(status.lt.0)then
   {multi;maxiter,50;occ,19,9;closed,13,6;save,ref=wei;wf,50,1,0;state,5;orbital,orbit;}
endif
table, 'SCF1Ap', r(j),energy(1),energy(2),energy(3),energy(4),energy(5)

{multi;occ,19,9;closed,13,6;save,ref=wei;wf,50,1,2;state,5;orbital,orbit+100}
if(status.lt.0)then
   {multi;maxiter,50;occ,19,9;closed,13,6;save,ref=wei;wf,50,1,2;state,5;orbital,orbit+100}
endif
table, 'SCF3Ap', r(j),energy(1),energy(2),energy(3),energy(4),energy(5)


{ci,nocheck;noexc;maxiter,32,600;occ,19,9;closed,13,6;wf,50,1,0;state,1,1;orbit,,ignore_error;save,3000.2;}
en(1)=energd(1)
{ci,nocheck;noexc;maxiter,32,600;occ,19,9;closed,13,6;wf,50,1,0;state,1,2;orbit,,ignore_error;save,3001.2;}
en(2)=energd(1)
{ci,nocheck;noexc;maxiter,32,600;occ,19,9;closed,13,6;wf,50,1,0;state,1,3;orbit,,ignore_error;save,3002.2;}
en(3)=energd(1)
{ci,nocheck;noexc;maxiter,32,600;occ,19,9;closed,13,6;wf,50,1,0;state,1,4;orbit,,ignore_error;save,3003.2;}
```

```
en(4)=energd(1)
{ci,nocheck;noexc;maxiter,32,600;occ,19,9;closed,13,6;wf,50,1,0;state,1,5;orbit,,ignore_error;save,3004.2;}
en(5)=energd(1)
table,'CI1Ap',r(j),en(1),en(2),en(3),en(4),en(5)

{ci,nocheck;noexc;maxiter,32,600;occ,19,9;closed,13,6;wf,50,1,2;state,1,1;orbit,,ignore_error;save,3100.2;}
en(1)=energd(1)
{ci,nocheck;noexc;maxiter,32,600;occ,19,9;closed,13,6;wf,50,1,2;state,1,2;orbit,,ignore_error;save,3101.2;}
en(2)=energd(1)
{ci,nocheck;noexc;maxiter,32,600;occ,19,9;closed,13,6;wf,50,1,2;state,1,3;orbit,,ignore_error;save,3102.2;}
en(3)=energd(1)
{ci,nocheck;noexc;maxiter,32,600;occ,19,9;closed,13,6;wf,50,1,2;state,1,4;orbit,,ignore_error;save,3103.2;}
en(4)=energd(1)
{ci,nocheck;noexc;maxiter,32,600;occ,19,9;closed,13,6;wf,50,1,2;state,1,5;orbit,,ignore_error;save,3104.2;}
en(5)=energd(1)
table,'CI3Ap',r(j),en(1),en(2),en(3),en(4),en(5)

{ci,nocheck;noexc;maxiter,32,600;occ,19,9;closed,13,6;wf,50,2,0;state,1,1;orbit,,ignore_error;save,3200.2;}
en(1)=energd(1)
{ci,nocheck;noexc;maxiter,32,600;occ,19,9;closed,13,6;wf,50,2,0;state,1,2;orbit,,ignore_error;save,3201.2;}
en(2)=energd(1)
{ci,nocheck;noexc;maxiter,32,600;occ,19,9;closed,13,6;wf,50,2,0;state,1,3;orbit,,ignore_error;save,3202.2;}
en(3)=energd(1)
{ci,nocheck;noexc;maxiter,32,600;occ,19,9;closed,13,6;wf,50,2,0;state,1,4;orbit,,ignore_error;save,3203.2;}
en(4)=energd(1)
table,'CI1App',r(j),en(1),en(2),en(3),en(4)

{ci,nocheck;noexc;maxiter,32,600;occ,19,9;closed,13,6;wf,50,2,2;state,1,1;orbit,,ignore_error;save,3300.2;}
en(1)=energd(1)
{ci,nocheck;noexc;maxiter,32,600;occ,19,9;closed,13,6;wf,50,2,2;state,1,2;orbit,,ignore_error;save,3301.2;}
en(2)=energd(1)
{ci,nocheck;noexc;maxiter,32,600;occ,19,9;closed,13,6;wf,50,2,2;state,1,3;orbit,,ignore_error;save,3302.2;}
en(3)=energd(1)
{ci,nocheck;noexc;maxiter,32,600;occ,19,9;closed,13,6;wf,50,2,2;state,1,4;orbit,,ignore_error;save,3303.2;}
en(4)=energd(1)
table,'CI3App',r(j),en(1),en(2),en(3),en(4)

{ci;print,hls=2,vls=0;options,hlstrans=0,matel=1;
hlsmat,ecpls,3000.2,3001.2,3002.2,3003.2,3004.2,3100.2,3101.2,3102.2,3103.2,3104.2,3200.2,3201.2,3202.2,3203.2,3300.2,

enddo

---
```

The energies obtained without any spin-orbit coupling consideration, after well converged calculations are:

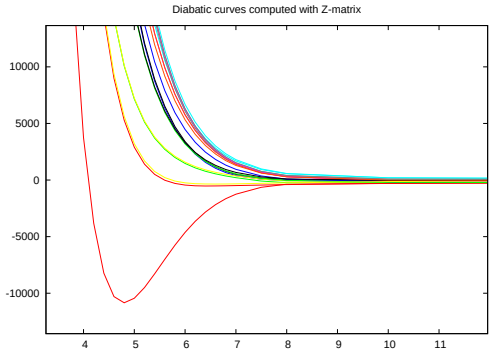
Cartesians coordinates

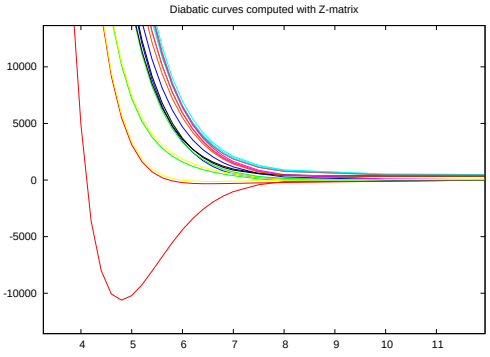
Symmetry	R_{IBr}	State 1	State 2	State 3	State 4	State 5
$^1A'$	12.0	-710.1680370	-710.1678354	-710.1673972	-710.1672712	-710.1660709
$^1A''$	12.0	-710.1672540	-710.1669714	-710.1669029	-710.1665208	
$^3A'$	12.0	-710.1680378	-710.1678330	-710.1673979	-710.1672712	-710.1660709
$^3A''$	12.0	-710.1672550	-710.1669718	-710.1669030	-710.1665208	

Z-matrix

Symmetry	R_{IBr}	State 1	State 2	State 3	State 4	State 5
$^1A'$	12.0	-710.1668328	-710.1668328	-710.1666614	-710.1666614	-710.1645973
$^1A''$	12.0	-710.1665194	-710.1651953	-710.1651953	-710.1647895	
$^3A'$	12.0	-710.1673303	-710.1667489	-710.1667072	-710.1664155	-710.1644560
$^3A''$	12.0	-710.1665202	-710.1651960	-710.1651960	-710.1647896	

The energies differ a little bit already, what I don't understand, but in relative energies along the curves, differences are not very large as can be seen in the curves plot below:





Something very different is obtained for the energies of the eigenstates of the spin-orbit matrix. The tables below show the eigenstates obtained for both calculations:

Cartesian coordinates

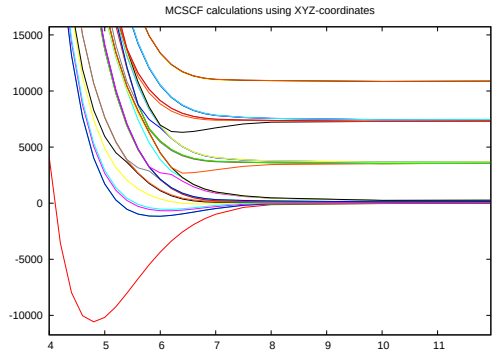
Nr	E (au)	E-E0 (au)	E-E0 (cm-1)	E-E(1) (au)	E-E(1) (cm-1)	E-E(1) (eV)
1	-710.18406124	-0.01602343	-3516.74	0.00000000	0.00	0.0000
2	-710.18405914	-0.01602133	-3516.28	0.00000210	0.46	0.0001
3	-710.18404750	-0.01600969	-3513.72	0.00001374	3.01	0.0004
4	-710.18404376	-0.01600595	-3512.90	0.00001748	3.84	0.0005
5	-710.18355997	-0.01552216	-3406.72	0.00050127	110.02	0.0136
6	-710.18354638	-0.01550856	-3403.74	0.00051486	113.00	0.0140
7	-710.18352789	-0.01549007	-3399.68	0.00053335	117.06	0.0145
8	-710.18352756	-0.01548974	-3399.61	0.00053368	117.13	0.0145
9	-710.18346160	-0.01542379	-3385.13	0.00059964	131.61	0.0163
10	-710.18345354	-0.01541573	-3383.36	0.00060769	133.37	0.0165
11	-710.18344547	-0.01540766	-3381.59	0.00061577	135.15	0.0168
12	-710.18342252	-0.01538470	-3376.55	0.00063872	140.18	0.0174
13	-710.18286387	-0.01482606	-3253.94	0.00119736	262.79	0.0326
14	-710.18286091	-0.01482310	-3253.29	0.00120033	263.44	0.0327
15	-710.18285989	-0.01482208	-3253.07	0.00120134	263.66	0.0327
16	-710.18285725	-0.01481944	-3252.49	0.00120399	264.24	0.0328
17	-710.16785796	0.00017985	39.47	0.01620328	3556.21	0.4409
18	-710.16785703	0.00018078	39.68	0.01620421	3556.41	0.4409
19	-710.16785692	0.00018089	39.70	0.01620431	3556.44	0.4409
20	-710.16785634	0.00018147	39.83	0.01620489	3556.56	0.4410
21	-710.16728937	0.00074844	164.26	0.01677187	3681.00	0.4564
22	-710.16728889	0.00074893	164.37	0.01677235	3681.11	0.4564
23	-710.16728884	0.00074897	164.38	0.01677240	3681.12	0.4564
24	-710.16728865	0.00074916	164.42	0.01677259	3681.16	0.4564
25	-710.15069338	0.01734443	3806.66	0.03336786	7323.40	0.9080
26	-710.15068962	0.01734819	3807.49	0.03337162	7324.22	0.9081
27	-710.15068162	0.01735619	3809.24	0.03337961	7325.98	0.9083
28	-710.15067939	0.01735842	3809.73	0.03338185	7326.47	0.9084
29	-710.15006021	0.01797761	3945.63	0.03400103	7462.36	0.9252
30	-710.15005946	0.01797836	3945.79	0.03400178	7462.53	0.9252
31	-710.15005734	0.01798047	3946.26	0.03400390	7462.99	0.9253
32	-710.15005536	0.01798246	3946.69	0.03400588	7463.43	0.9253
33	-710.13448128	0.03355654	7364.81	0.04957996	10881.54	1.3491
34	-710.13447715	0.03356066	7365.71	0.04958408	10882.45	1.3493
35	-710.13447008	0.03356774	7367.27	0.04959116	10884.00	1.3494
36	-710.13445779	0.03358002	7369.96	0.04960344	10886.70	1.3498

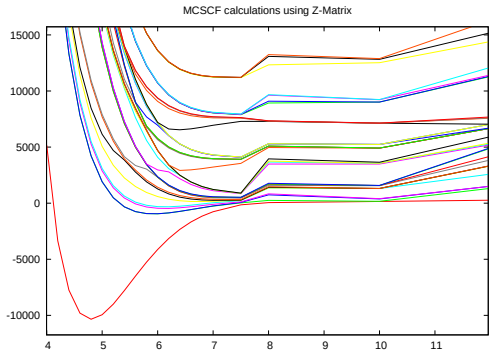
Z-matrix

Nr	E (au)	E-E0 (au)	E-E0 (cm-1)	E-E(1) (au)	E-E(1) (cm-1)	E-E(1) (eV)
1	-710.19606209	-0.02922925	-6415.08	0.00000000	0.00	0.0000
2	-710.19123628	-0.02440345	-5355.94	0.00482581	1059.14	0.1313
3	-710.19037636	-0.02354353	-5167.21	0.00568573	1247.87	0.1547
4	-710.19037358	-0.02354075	-5166.60	0.00568850	1248.48	0.1548
5	-710.18545437	-0.01862153	-4086.95	0.01060772	2328.13	0.2887
6	-710.18215221	-0.01531938	-3362.21	0.01390988	3052.87	0.3785
7	-710.18201448	-0.01518164	-3331.99	0.01404761	3083.09	0.3823
8	-710.18198581	-0.01515298	-3325.69	0.01407628	3089.39	0.3830
9	-710.17968654	-0.01285371	-2821.06	0.01637555	3594.02	0.4456
10	-710.17819221	-0.01135938	-2493.10	0.01786987	3921.98	0.4863
11	-710.17494779	-0.00811496	-1781.03	0.02111429	4634.05	0.5745
12	-710.17473413	-0.00790129	-1734.13	0.02132796	4680.95	0.5804
13	-710.17349865	-0.00666582	-1462.98	0.02256344	4952.10	0.6140
14	-710.17313185	-0.00629901	-1382.47	0.02293024	5032.61	0.6240
15	-710.17278694	-0.00595411	-1306.78	0.02327514	5108.30	0.6333
16	-710.17024231	-0.00340948	-748.29	0.02581978	5666.79	0.7026
17	-710.16683282	0.00000002	0.00	0.02922927	6415.08	0.7954
18	-710.16683100	0.00000183	0.40	0.02923109	6415.48	0.7954
19	-710.16683100	0.00000183	0.40	0.02923109	6415.48	0.7954
20	-710.16683100	0.00000183	0.40	0.02923109	6415.48	0.7954
21	-710.16666140	0.00017144	37.63	0.02940069	6452.71	0.8000
22	-710.16519600	0.00163683	359.24	0.03086609	6774.32	0.8399
23	-710.16519600	0.00163683	359.24	0.03086609	6774.32	0.8399
24	-710.16519600	0.00163683	359.24	0.03086609	6774.32	0.8399
25	-710.16519532	0.00163751	359.39	0.03086677	6774.47	0.8399
26	-710.16274100	0.00409183	898.05	0.03332109	7313.13	0.9067
27	-710.16258868	0.00424415	931.48	0.03347341	7346.56	0.9109
28	-710.16222222	0.00461061	1011.91	0.03383987	7426.99	0.9208
29	-710.14578282	0.02105002	4619.94	0.05027927	11035.02	1.3682
30	-710.14559887	0.02123396	4660.32	0.05046322	11075.40	1.3732
31	-710.14517186	0.02166098	4754.03	0.05089023	11169.11	1.3848
32	-710.14211253	0.02472030	5425.48	0.05394955	11840.56	1.4680
33	-710.13274256	0.03409027	7481.95	0.06331952	13897.03	1.7230
34	-710.13160156	0.03523128	7732.37	0.06446053	14147.45	1.7541
35	-710.12803593	0.03879690	8514.94	0.06802615	14930.01	1.8511
36	-710.12295096	0.04388188	9630.96	0.07311113	16046.04	1.9895

Both tables are very different, I would like to emphasise the fact that no degeneracy is found in the second set of results, look column number 6 on the tables above.

Because the problems with the spin-orbit couplings is not happening for all configurations or all calculations, I include below the plot of the 36 eigenstates for both calculations along the potential curve:





Must be noticed that the values for distances shorter that 7.5 a.u. present not many differences.

Is there anything I could do to avoid this problem? Is it due to the fact ot using Pseudopotentials?

Please let me know if you would require the output files, I have not included them because they are very long with all the spin-orbit couplings.