which gives the reference value 108 cm^{-1}. We now compare that to several other methods which only have the two "magnetic" orbitals (the 1s's on the hydrogens) in the active space:

```
... same as above
%mrci  EWin       -10,1000
       CIType     MRDDCI3
       ... same as previously
       NewBlock 1 *
          NRoots 1
          refs CAS(2,2) end
          end
       NewBlock 3 *
          NRoots 1
          refs CAS(2,2) end
          end
       end
```

This gives the result:

```
Method      S-T gap
MR-CI+Q  :  98 cm-1
MR-CI    :  93 cm-1
MR-ACPF  :  98 cm-1
MR-ACPF2 :  98 cm-1
MR-ACPF2a:  97 cm-1
MR-AQCC  :  95 cm-1
SORCI    : 131 cm-1
MR-DDCI2 :  85 cm-1
MR-DDCI3 : 130 cm-1
```

All these methods give good results with SORCI leading to a somewhat larger error than the others. The (difference dedicated CI) DDCI2 method slightly underestimates the coupling which is characteristic of this method. It is nice in a way that DDCI3 gives the same result as SORCI since SORCI is supposed to approximate the DDCI3 (or better the IDDCI3) result which it obviously does.

This splitting can also be studied using broken symmetry HF and DFT methods as explained elsewhere in this manual:

```
Method    S-T gap
 UHF     :  70 cm-1
 B3LYP/G : 240 cm-1
 BP86    : 354 cm-1
 PW91    : 234 cm-1
 PBE     : 234 cm-1
 PBE0    : 162 cm-1
 RPBE    : 242 cm-1
```

This confirms the usual notions; UHF underestimates the coupling and DFT overestimates it, less so for hybrid functionals than for GGAs. The BP86 is worse than PW91 or PBE. The PBE0 hybrid may be the best of the DFT methods. For some reason most of the DFT methods give the best results if the BS state is simply taken as an approximation for the true open-shell singlet. This is, in our opinion, not backed up by theory but has been observed by other authors too.

Now let us study the dependence on T_{sel} as this is supposed to be critical (we use the DDCI3 method):

```
Tsel      S-T gap
   1e-04     121
   1e-05     128
   1e-06     132
   1e-07     131
   1e-08     131
   1e-10     131
   1e-12     131
   0         131
```

The convergence is excellent once `AllSingles` are included.

3.19.10 Potential Energy Surfaces

Another situation where multireference approaches are necessary is when bond breaking is studied and one wants to calculate a full potential energy surface. Say we want to compute the potential energy surface of the CH molecule. First we have to figure out which states to include. Hence, let us first determine a significant number of roots for the full valence CASSCF reference state (we use a small basis set in order to make the job fast).

```
! ANO-pVDZ VeryTightSCF NoPop Conv

%casscf nel      5
        norb     5
        nroots   2
        mult     2
        end

%mrci  CIType      MRCI
       NewBlock 2 *
         excitations none
         NRoots 15
         refs CAS(5,5) end
         end
       NewBlock 4 *
         excitations none
         NRoots 15
         refs CAS(5,5) end
         end
       end

* xyz 0 2
C  0 0 0
H  0 0 1.15
*
```

This yields:

```
------------------
TRANSITION ENERGIES
------------------

The lowest energy is   -38.308119994 Eh

State Mult Irrep Root Block    mEh          eV       1/cm
  0    2    -1    0    0      0.000       0.000       0.0
  1    2    -1    1    0      0.000       0.000       0.0
  2    4    -1    0    1     14.679       0.399     3221.6
  3    2    -1    2    0    126.464       3.441    27755.7
  4    2    -1    3    0    126.464       3.441    27755.7
  5    2    -1    4    0    132.689       3.611    29121.8
  6    2    -1    5    0    164.261       4.470    36051.2
  7    2    -1    6    0    305.087       8.302    66958.9
  8    2    -1    7    0    305.087       8.302    66958.9
  9    4    -1    1    1    328.911       8.950    72187.7
 10    4    -1    2    1    452.676      12.318    99350.8
 11    4    -1    3    1    452.676      12.318    99350.8
 12    2    -1    8    0    460.116      12.520   100983.9
 13    2    -1    9    0    463.438      12.611   101712.9
 14    2    -1   10    0    463.438      12.611   101712.9
 ...
```

Thus, if we want to focus on the low-lying states we should include five doublet and one quartet root. Now we run a second job with these roots and scan the internuclear distance.

```
! ano-pVDZ VeryTightSCF NoPop Conv MRCI+Q

%casscf nel     5
        norb    5
        nroots  5,1
        mult    2,4
        shiftup 2
        end

%paras R = 0.8,2.5,25
        end

* xyz 0 2
C   0 0 0
H   0 0 {R}
*
```

The surfaces obtained in this run are shown in Fig. 3.43. You can nicely see the crossing of the $^2\Sigma$ and $^2\Delta$ states fairly close to the equilibrium distance and also the merging of the $^4\Sigma$ state with $^2\Pi$ and $^2\Sigma$ towards the asymptote that where C-H dissociates in a neutral C-atom in its ^3P ground state and a neutral hydrogen atom in its ^2S ground state. You can observe that once `AllSingles` is set to true (the default), the default settings of the MRCI module yield fairly smooth potential energy surfaces.
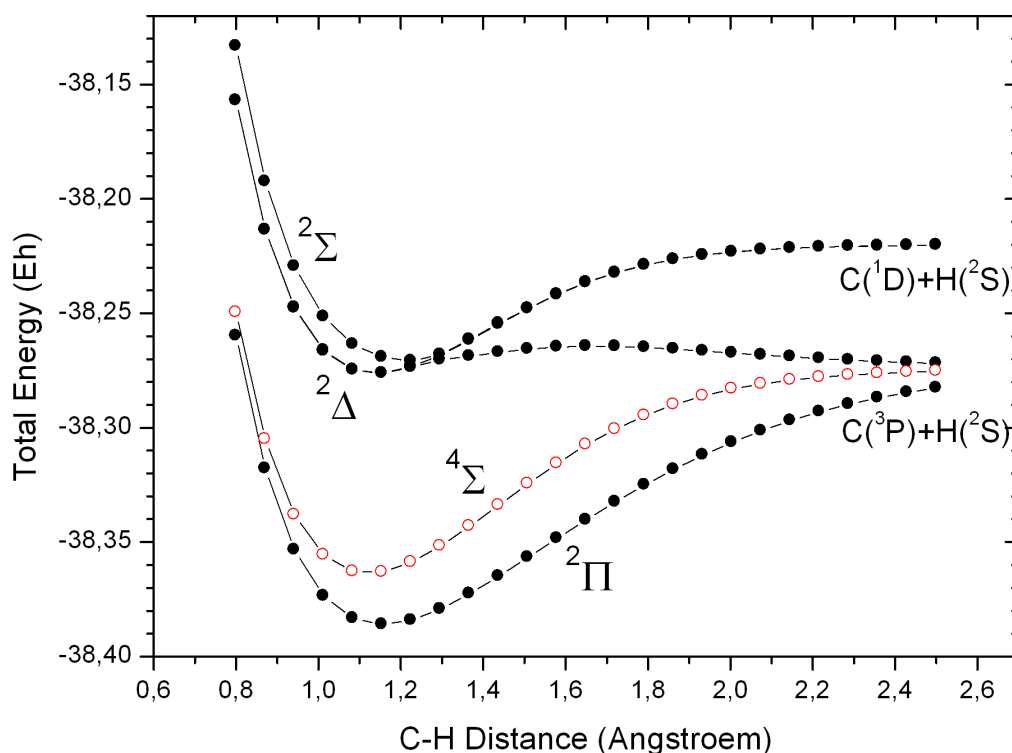

Fig. 3.43: Potential energy surfaces for some low-lying states of CH using the MRCI+Q method

In many cases one will focus on the region around the minimum where the surface is nearly quadratic. In this case one

can still perform a few (2, 3, 5,) point polynomial fitting from which the important parameters can be determined. The numerical accuracy and the behavior with respect to T_{sel} has to be studied in these cases since the selection produces some noise in the procedure. We illustrate this with a calculation on the HF molecule:

```
! ano-pVDZ VeryTightSCF NoPop Conv MRCI+Q

%paras  R = 0.85,1.1,7
        end

%casscf nel     8
        norb    5
        nroots  1  mult    1
        shiftup 2.5 shiftdn 2.5 switchstep nr gtol    1e-5
        end

%mrci   tsel 1e-8
        tpre 1e-5
        end

* xyz 0 1
F  0 0 0
H  0 0 {R}
*
```

The output contains the result of a Morse fit:

```
Morse-Fit Results:
 Re             =   0.93014 Angstroem
 we             =   4111.2 cm**-1
 wexe           =     79.5 cm**-1
```

Which may be compared with the CCSD(T) values calculated with the same basis set:

```
Morse-Fit Results:
 Re             =   0.92246 Angstroem
 we             =   4209.8 cm**-1
 wexe           =     97.6 cm**-1
```

The agreement between MRCI+Q and CCSD(T) results is fairly good.

3.19.11 Multireference Systems - Ozone

The ozone molecule is a rather classical multireference system due to its diradical character. Let us look at the three highest occupied and lowest unoccupied MO (the next occupied MO is some 6 eV lower in energy and the next virtual MO some 10 eV higher in energy):
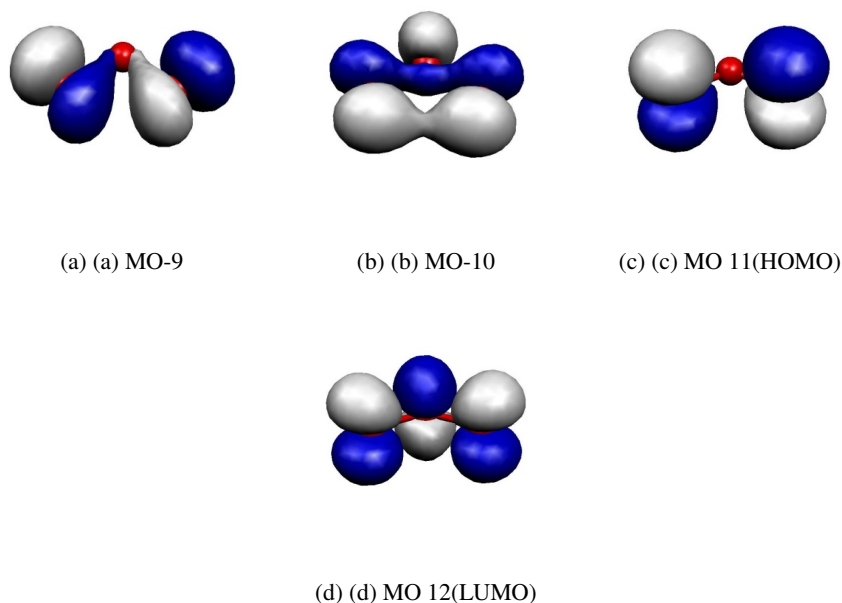
(a) (a) MO-9   (b) (b) MO-10   (c) (c) MO 11(HOMO)

(d) (d) MO 12(LUMO)

Fig. 3.44: Frontier MOs of the Ozone Molecule.

These MOs are two σ lone pairs which are high in energy and then the symmetric and antisymmetric combinations of the oxygen π lone pairs. In particular, the LUMO is low lying and will lead to strong correlation effects since the $(HOMO)^2 \rightarrow (LUMO)^2$ excitation will show up with a large coefficient. Physically speaking this is testimony of the large diradical character of this molecule which is roughly represented by the structure ↑O-O-O↓. Thus, the minimal active space to treat this molecule correctly is a CAS(2,2) space which includes the HOMO and the LUMO. We illustrate the calculation by looking at the RHF, MP2 MRACPF calculations of the two-dimensional potential energy surface along the O–O bond distance and the O-O-O angle (experimental values are 1.2717 Å and 116.78°).

```
! ano-pVDZ VeryTightSCF NoPop MRCI+Q Conv

%paras R     = 1.20,1.40,21
        Theta = 100,150,21
        end

%casscf nel    2
        norb   2
        mult   1
        nroots 1
        end

%mrci   tsel   1e-8
        tpre   1e-5
        end

* int 0 1
O  0 0 0  0    0         0
O  1 0 0 {R}   0         0
O  1 2 0 {R}  {Theta}    0
*
```

This is a slightly lengthy calculation due to the 441 energy evaluations required. RHF does not find any meaningful minimum within the range of examined geometries. MP2 is much better and comes close to the desired minimum but underestimates the O–O distance by some 0.03 Å. CCSD(T) gives a very good angle but a O–O distance that is too long. In fact, the largest doubles amplitude is ≈ 0.2 in these calculations (the HOMO–LUMO double excitation) which indicates a near degeneracy calculation that even CCSD(T) has problems to deal with. Already the

CAS(2,2) calculation is in qualitative agreement with experiment and the MRCI+Q calculation then gives almost perfect agreement.

The difference between the CCSD(T) and MRCI+Q surfaces shows that the CCSD(T) is a bit lower than the MRCI+Q one suggesting that it treats more correlation. However, CCSD(T) does it in an unbalanced way. The MRCI calculation employs single and double excitations on top of the HOMO-LUMO double excitation, which results in triples and quadruples that apparently play an important role in balancing the MR calculation. These excitations are treated to all orders explicitly in the MRCI calculation but only approximately (quadruples as simultaneous pair excitations and triples perturbatively) in the coupled-cluster approach. Thus, despite the considerable robustness of CC theory in electronically difficult situations it is not applicable to genuine multireference problems.

This is a nice result despite the too small basis set used and shows how important it can be to go to a multireference treatment with a physically reasonable active space (even if is only 2×2) in order to get qualitatively and quantitatively correct results.

(a) (a) RHF   (b) (b) CASSCF(2,2)   (c) (c) MP2   (d) (d) CCSD(T)   (e) (e) MRCI+Q
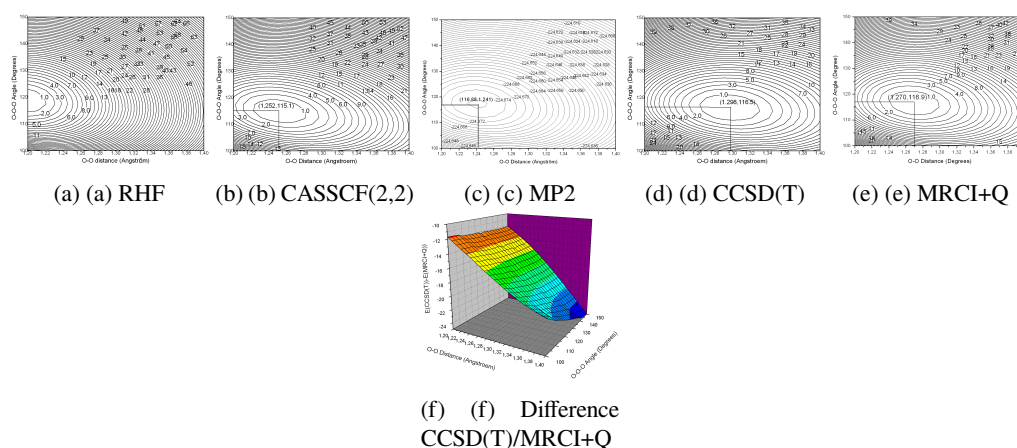

(f) (f) Difference CCSD(T)/MRCI+Q

Fig. 3.45: 2D potential energy surface for the O_3 molecule calculated with different methods

3.19.12 Size Consistency

Finally, we want to study the size consistency errors of the methods. For this we study two non-interacting HF molecules at the single reference level and compare to the energy of a single HF molecule. This should give a reasonably fair idea of the typical performance of each method (energies in Eh)[5]:

```
E(HF)          E(HF+HF)   |Difference|
  CISD+Q   -100.138 475  -200.273 599    0.00335
  ACPF     -100.137 050  -200.274 010    0.00000
  ACPF2    -100.136 913  -200.273 823    0.00000
  AQCC     -100.135 059  -200.269 792    0.00032
```

The results are roughly as expected – CISD+Q has a relatively large error, ACPF and ACPF/2 are perfect for this type of example; AQCC is not expected to be size consistent and is (only) about a factor of 10 better than CISD+Q in this respect. CEPA-0 is also size consistent.

―――――――――

[5] Most of these numbers were obtained with a slightly older version but will not change too much in the present version.

3.19.13 Efficient MR-MP2 Calculations for Larger Molecules

Uncontracted MR-MP2 approaches are nowadays outdated. They are much more expensive than internally contracted e.g. the NEVPT2 method described in section *N-Electron Valence State Perturbation Theory (NEVPT2)*. Moreover, MR-MP2 is prone to intruder states, which is a major obstacle for practical applications. For historical reasons, this section is dedicated to the traditional MR-MP2 approach that is available since version 2.7.0 ORCA. The implementation avoids the full integral transformation for MR-MP2 which leads to significant savings in terms of time and memory. Thus, relatively large RI-MR-MP2 calculations can be done with fairly high efficiency. However, the program still uses an uncontracted first order wavefunction which means that for very large reference space, the calculations still become untractable.

Consider for example the rotation of the stilbene molecule around the central double bond

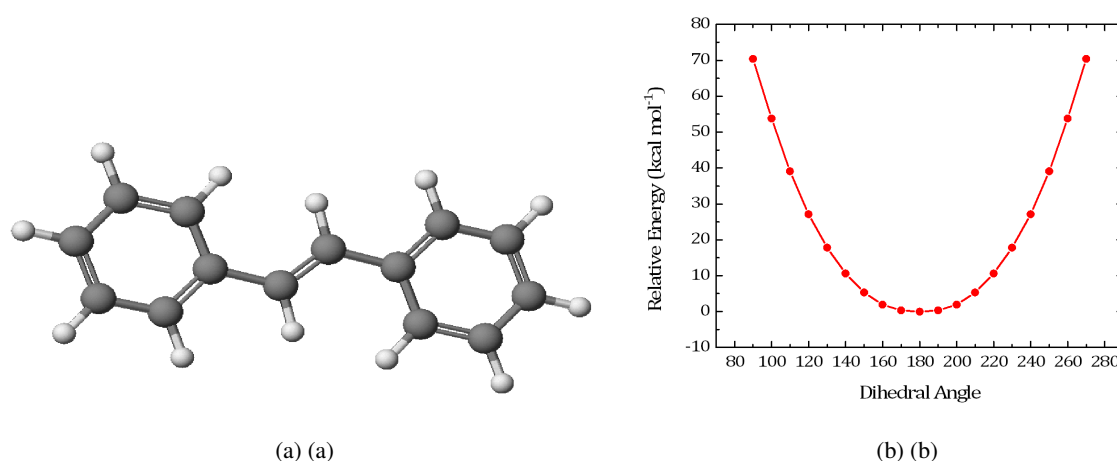(a) (a)   (b) (b)

Fig. 3.46: Rotation of stilbene around the central double bond using a CASSCF(2,2) reference and correlating the reference with MR-MP2.

The input for this calculation is shown below. The calculation has more than 500 basis functions and still runs through in less than one hour per step (CASSCF-MR-MP2). The program takes care of the reduced number of two-electron integrals relative to the parent MRCI method and hence can be applied to larger molecules as well. Note that we have taken a "JK" fitting basis in order to fit the Coulomb and the dynamic correlation contributions both with sufficient accuracy. Thus, this example demonstrates that MR-MP2 calculations for not too large reference spaces can be done efficiently with ORCA (as a minor detail note that the calculations were started at a dihedral angle of 90 degrees in order to make sure that the correct two orbitals are in the active space, namely the central carbon p-orbitals that would make up the pi-bond in the coplanar structure).

```
#
# Stilbene rotation using MRMP2
#
! def2-TZVP def2/JK RIJCOSX RI-MRMP2

%casscf nel          2
        norb         2
        end

%mrci   maxmemint 2000
        tsel 1e-8
        end


%paras  DIHED = 90,270, 19
        end

* int 0 1
```

(continues on next page)

```
C     0    0    0    0.000000     0.000      0.000
C     1    0    0    1.343827     0.000      0.000
C     2    1    0    1.490606   125.126      0.000
C     1    2    3    1.489535   125.829    \{DIHED\}
C     4    1    2    1.400473   118.696    180.000
C     4    1    2    1.400488   122.999      0.000
C     6    4    1    1.395945   120.752    180.000
C     5    4    1    1.394580   121.061    180.000
C     8    5    4    1.392286   120.004      0.000
C     3    2    1    1.400587   118.959    180.000
C     3    2    1    1.401106   122.779      0.000
C    11    3    2    1.395422   120.840    180.001
C    12   11    3    1.392546   120.181      0.000
C    13   12   11    1.392464   119.663      0.000
H     1    2    3    1.099419   118.266      0.000
H     2    1    3    1.100264   118.477    179.999
H     5    4    1    1.102119   119.965      0.000
H     6    4    1    1.100393   121.065      0.000
H     7    6    4    1.102835   119.956    180.000
H     8    5    4    1.102774   119.989    180.000
H     9    8    5    1.102847   120.145    180.000
H    10    3    2    1.102271   120.003      0.000
H    11    3    2    1.100185   121.130      0.000
H    12   11    3    1.103001   119.889    180.000
H    13   12   11    1.102704   120.113    180.000
H    14   13   12    1.102746   119.941    180.000
*
```

3.19.14 Properties Calculation Using the SOC Submodule

Zero-Field Splitting

The spin-orbit coupling (SOC) and spin-spin coupling (SSC) contributions to the zero-field splitting (ZFS) can be calculated very accurately using a wavefunction obtained from a multiconfigurational calculation of a multi-reference type such as CASSCF, MRCI, or MRPT as is described in QDPT Magnetic Properties Section *Magnetic Properties Through Quasi Degenerate Perturbation Theory*.

```
# In case that you want to run QDPT-SOC calculation with manually adjusted␣
↪diagonal
# energies you can copy the following part into the %mrci soc block and modify it␣
↪as needed
# (energies are given in wavenumbers relative to the lowest state).           ␣
↪
#                                                                             ␣
↪
# NOTE: It is YOUR responsibility to make sure that the CAS-CI state that you may␣
↪want to dress
#       with these energies correlates properly with the energies printed here.␣
↪The order of states
#       or even the identity of states may change with and without inclusion of␣
↪dynamic correlation.
#       In the case that dynamic correlation strongly mixes, different CAS-CI␣
↪states there may not
#        even be a proper correlation!                                         ␣
↪
#                                                                             ␣
↪
    EDiag[  0]    -149.526236244  # root    0 of block 0
    EDiag[  1]    -149.359818263  # root    1 of block 0
```

```
    EDiag[  2]    -149.359818263  # root   2 of block 0
    EDiag[  3]    -149.496737695  # root   0 of block 1
    EDiag[  4]    -149.496737695  # root   1 of block 1
    EDiag[  5]    -149.474844108  # root   2 of block 1
```

Those transition energies can be substituted by a more accurate energies provided in the input file as follows:

```
%soc
dosoc true
dossc true
    EDiag[  0]    -149.526236244  # root   0 of block 0
    EDiag[  1]    -149.359818263  # root   1 of block 0
    EDiag[  2]    -149.359818263  # root   2 of block 0
    EDiag[  3]    -149.496737695  # root   0 of block 1
    EDiag[  4]    -149.496737695  # root   1 of block 1
    EDiag[  5]    -149.474844108  # root   2 of block 1
end
```

Accurate diagonal energies generally improve the accuracy of the SOC and SSC splittings.

Local Zero-Field Splitting

The submodule can also be used to calculate the local ZFS splitting parameters of atomic centers. The method, referred to as local complete active space configuration interaction (L-CASCI), can be used to separate into atomic contributions the SOC part of the total ZFS tensor. The rational behind it and additional details are described in the original publication [509]; below are listed only the steps required to reproduce the calculation for the dimer complex presented there.

1. The first step consists in obtaining the molecular orbitals that are going to be used in the configuration interaction (CI) procedure. A good set of orbitals can be obtained from a restricted open-shell spin-averaged Hartree-Fock (SAHF) calculation. The relevant part of the input is listed below:

```
! def2-TZVP

% scf
   hftyp rohf
   rohf_case sahf
   rohf_numop 2
   rohf_nel[1] 9
   rohf_norb[1] 10
   end
```

For the present Mn(II)Mn(III) dimer there are a total of 9 electrons distributed into 10 d-orbitals.

2. Next, the molecular orbitals are localized using one of the implemented localization schemes. Below is the `orca_loc` input used in this case:

```
sahf.gbw
sahf.loc
0
200 # first of the 10 d-orbitals
209 # last of the 10 d-orbitals
128
0.000001
0.75
0.65
2
```

3. Following this, the localized orbitals are made locally canonical by block diagonalizing the Fock matrix using the `orca_blockf` utility.

```
orca_blockf sahf.gbw sahf.loc 200 204 205 209
```

The first two numbers define the range of molecular orbitals localized on one center; the last two are for the second center.

4. The recanonicalized orbitals stored in the `sahf.loc` file can be then used to calculate the SOC contribution to the local ZFS of the Mn(III) center using the following MRCI input:

```
! ZORA-def2-TZVP def2-TZVP/C ZORA
! nomulliken noloewdin
! moread noiter allowrhf
! moread

% mrci
    citype mrci
    tsel 0
    tpre 0
    intmode ritrafo
    solver diis
    soc
        intmode ritrafo
        dosoc true
        end
    newblock 10 *
        nroots 5
        excitations none
        refs
            #  Mn(II)    Mn(III)
            {1 1 1 1 1  1 1 1 1 0}
            {1 1 1 1 1  1 1 1 0 1}
            {1 1 1 1 1  1 1 0 1 1}
            {1 1 1 1 1  1 0 1 1 1}
            {1 1 1 1 1  0 1 1 1 1}
            end
        end
    newblock 8 *
        nroots 45
        excitations none
        refs
            #  Mn(II)    Mn(III)
            {1 1 1 1 1  2 1 1 0 0}
            {1 1 1 1 1  2 1 0 1 0}
            {1 1 1 1 1  2 1 0 0 1}
            {1 1 1 1 1  2 0 1 1 0}
            {1 1 1 1 1  2 0 1 0 1}
            {1 1 1 1 1  2 0 0 1 1}
            {1 1 1 1 1  1 2 1 0 0}
            {1 1 1 1 1  1 2 0 1 0}
            {1 1 1 1 1  1 2 0 0 1}
            {1 1 1 1 1  1 1 2 0 0}
            {1 1 1 1 1  1 1 1 1 0}
            {1 1 1 1 1  1 1 1 0 1}
            {1 1 1 1 1  1 1 0 2 0}
            {1 1 1 1 1  1 1 0 1 1}
            {1 1 1 1 1  1 1 0 0 2}
            {1 1 1 1 1  1 0 2 1 0}
            {1 1 1 1 1  1 0 2 0 1}
            {1 1 1 1 1  1 0 1 2 0}
            {1 1 1 1 1  1 0 1 1 1}
            {1 1 1 1 1  1 0 1 0 2}
            {1 1 1 1 1  1 0 0 2 1}
            {1 1 1 1 1  1 0 0 1 2}
```

(continues on next page)

```
          {1 1 1 1 1  0 2 1 1 0}
          {1 1 1 1 1  0 2 1 0 1}
          {1 1 1 1 1  0 2 0 1 1}
          {1 1 1 1 1  0 1 2 1 0}
          {1 1 1 1 1  0 1 2 0 1}
          {1 1 1 1 1  0 1 1 2 0}
          {1 1 1 1 1  0 1 1 1 1}
          {1 1 1 1 1  0 1 1 0 2}
          {1 1 1 1 1  0 1 0 2 1}
          {1 1 1 1 1  0 1 0 1 2}
          {1 1 1 1 1  0 0 2 1 1}
          {1 1 1 1 1  0 0 1 2 1}
          {1 1 1 1 1  0 0 1 1 2}
          end
       end
    end
```

5. The three second order ZFS components printed at the end of the calculation (`Second order D-tensor: component 0`, etc.) are scaled using the S value for the complex, which in this case is 4.5 (9 electrons $\times$ 0.5). In order to obtain the correct local value of the ZFS, the three matrices have to be rescaled using the S value for Mn(III), which is to 2. Note that the three matrices have different scaling prefactors, and the dependence on S is not the same:

$\mathbf{D}^{SOC-(0)} \propto \frac{1}{S^2}$

$\mathbf{D}^{SOC-(-1)} \propto \frac{1}{S(2S-1)}$

$\mathbf{D}^{SOC-(+1)} \propto \frac{1}{(S+1)(2S+1)}$

These equations can be used to calculate the required prefactors. For example in the case of the *SOC*-(0) the prefactor is equal to:

$\mathbf{D}^{SOC-(0)}_{\text{Mn(III)}} = \frac{4.5^2}{2^2} \cdot \mathbf{D}^{SOC-(0)}_{\text{dimer}} = 5.0625 \cdot \mathbf{D}^{SOC-(0)}_{\text{dimer}}$

The final step is to scale the two remaining matrices using the appropriate prefactors, sum all three of them up, diagonalize the resulting the matrix, and use its eigenvalues to calculate the D and E parameters. These represent the local ZFS parameters of the Mn(III) center.

Zero-Field Splitting from an excited Multiplet

For an excited state Multiplet the Calculationof ZFS can be requested by

```
Lowest eigenvalue of the SOC matrix:    -149.86223277 Eh
Energy stabilization:    -2.54512 cm-1
Eigenvalues:      cm-1         eV       Boltzmann populations at T =  300.000 K
   0:            0.00       0.0000        3.36e-01
   1:            2.37       0.0003        3.32e-01
   2:            2.37       0.0003        3.32e-01
   3:         7757.65       0.9618        2.33e-17
   4:         7757.66       0.9618        2.33e-17
   5:        11913.81       1.4771        5.15e-26
```

```
soc
 DTensor true
 IStates 3,4,5
end
```

```
*****************************************
 EXCITED STATE ZERO-FIELD SPLITTING:
*****************************************
```

```
--------------------------------------------
Computing Excited State D Tensors of
Excited State Multiplet Consisting of States :  3  4  5
--------------------------------------------
          0          4
          1          5
          2          0
          3          1
          4          0
          5          2



--------------------------------------------
         ZERO-FIELD SPLITTING
(2ND ORDER SPIN-ORBIT COUPLING CONTRIBUTION)
--------------------------------------------


D   =   -2.668445   cm-1
E/D =    0.000103



...


---------------------------------------------------------
               ZERO-FIELD SPLITTING
EFFECTIVE HAMILTONIAN SOC CONTRIBUTION
---------------------------------------------------------


D   =   -2.674495   cm-1
E/D =    0.009610


...
```

g-Tensor

The `orca_mrci` program contains an option to calculate g-tensors using MRCI wavefunctions. For a system with an odd number of electrons, the doubly degenerate eigenvalues obtained from the QDPT procedure represent Kramers pairs, which are used to build the matrix elements of the total spin operator and the total angular momentum operator from the Zeeman Hamiltonian. Denoting Ψ as a solution and $\bar{\Psi}$ as its Kramers partner and using matrix element notations

$$\Phi_{11}^k = \langle \Psi | \, \hat{L}_k + g_e \hat{S}_k \, | \Psi \rangle , \; \Phi_{12}^k = \langle \Psi | \, \hat{L}_k + g_e \hat{S}_k \, | \bar{\Psi} \rangle , \; k = x, y, z \tag{3.133}$$

The elements of g-matrix are obtained as:

$$g_{kz} = 2\Phi_{11}^k, \; g_{ky} = -2\Im\left(\Phi_{12}^k\right), \; g_{kx} = 2\Re\left(\Phi_{12}^k\right) \tag{3.134}$$

Then, the true tensor G is built from g-matrices:

$$G = gg^T \tag{3.135}$$

G is subjected further to diagonalization yielding positive eigenvalues, the square roots of which give the principal values of g-matrix.

$$g_{xx} = \sqrt{G_{xx}}, \; g_{yy} = \sqrt{G_{yy}}, \; g_{zz} = \sqrt{G_{zz}} \tag{3.136}$$

A typical mrci block of the input file for a g-tensor calculation should (e.g. for a S=3/2 problem) look as the following:

```
%mrci   ewin -4,1000
        citype mrci
        cimode direct2
        intmode fulltrafo
        solver diis
        etol 1e-8
        rtol 1e-8
        tsel 1e-6
        tpre 1e-5
        soc
          PrintLevel 2
          GTensor true      # make g-tensor calculations
          NDoubGTensor 2    # number of Kramers doublets to account
                            # for every pair a separate
                            # calculation is performed
        end
        newblock 4 *
          excitations cisd
          nroots 10
          refs  cas(7,5) end
        end
end
```

The result for the first Kramers pair is printed as follows:

```
--------------
KRAMERS PAIR 1
--------------


Matrix elements Re<1|S|1>   -0.072128    0.024511   -2.998843
Matrix elements Re<1|S|2>   -0.001088    0.000366   -0.002010
Matrix elements Im<1|S|2>   -0.000354   -0.001037   -0.000173
Matrix elements Re<1|L|1>   -0.027067    0.009209   -1.123531
Matrix elements Re<1|L|2>   -0.000031    0.000010   -0.000763
Matrix elements Im<1|L|2>   -0.000006   -0.000011   -0.000065


-------------------
ELECTRONIC G-MATRIX
-------------------


g-matrix:
-0.002240     0.000754   -0.005551
0.000720     0.002100    0.000477
-0.198556     0.067498   -8.251703

g-factors:
0.002220     0.002222    8.254370 iso =     2.752937

g-shifts:
-2.000100    -2.000098    6.252051 iso =     0.750618

Eigenvectors:
0.057426     0.998060    0.024055
0.998327    -0.057244   -0.008177
0.006784    -0.024484    0.999677
```

Here for the L and S matrix elements indices 1 and 2 are assumed to denote Kramers partners, and three numbers in the first row stand for x, y, z contributions.

In addition the g-tensor is calculated within the Effective Hamiltonian formalism.

```
----------------------------------------------
```

```
ELECTRONIC G-MATRIX FROM EFFECTIVE HAMILTONIAN
----------------------------------------------

g-matrix:
1.978874    -0.000345     0.018908
-0.000345     1.977899    -0.006433
0.018879    -0.006418     2.763402

g-factors:
1.977789     1.978477     2.763909 iso =     2.240058

g-shifts:
-0.024530    -0.023843     0.761590 iso =     0.237739

Eigenvectors:
0.288884     0.957062     0.024060
0.957364    -0.288770    -0.008181
0.000882    -0.025397     0.999677

# The g-factors are square roots of the eigenvalues of gT*g
# Orientations are the eigenvectors of gT*g
```

Finally and only within the MRCI module the g-tensor is evaluated by using the Sum Over States formalism[510]:

```
--------------------------------------------------------------------------------
SUM OVER STATES CALCULATION OF THE SPIN HAMILTONIAN (for g and HFC tensors)
--------------------------------------------------------------------------------


Ground state index       =    0
Ground state multiplicity =    4
Ground state spin density = P[  1]
State =   1  <0|P|I>=   2  <0|Q|I>=  19
State =   2  <0|P|I>=   3  <0|Q|I>=  27
State =   3  <0|P|I>=   4  <0|Q|I>=  34
State =   4  <0|P|I>=   5  <0|Q|I>=  40
State =   5  <0|P|I>=   6  <0|Q|I>=  45
State =   6  <0|P|I>=   7  <0|Q|I>=  49
State =   7  <0|P|I>=   8  <0|Q|I>=  52
State =   8  <0|P|I>=   9  <0|Q|I>=  54
State =   9  <0|P|I>=  10  <0|Q|I>=  55


Origin for angular momentum        ... ( -0.0006, -0.0010,  0.0021)
Kinetic Energy                     ... done
Relativistic mass correction       ... done
Gauge correction                   ... done
Angular momentum integrals         ... done
Reading Spin-Orbit Integrals       ... done
----------------------
MATRIX ELEMENT PRINTING
----------------------

Energy differences (DE=EI-E0) and spin-orbit matrix elements (SO=<I|HSO|0>) are
printed in cm**-1. Orbital Zeeman matrix elements (L=<I|L|0>) are printed in au.

State     DE          LX        LY        LZ          SOX        SOY        SOZ

1    1349.3     0.0464   -0.0158    1.9264     -23.432      7.965   -974.312
2   13026.2    -0.6596    0.6888    0.0214     337.028   -351.116    -10.966
3   13615.1    -0.6961   -0.6514    0.0113     354.225    332.219     -5.736
4   56686.3    -0.0053    0.0077    0.0971       1.794     -1.696    -36.786
```

```
  5    56954.2    -0.0516   -0.0048   -0.0042     28.211      5.821      1.459
  6    56994.0    -0.0418    0.0233   -0.0025     15.185     -2.144      1.145
  7    63371.5    -0.0211    0.0226    0.0078      3.833     -2.948     -2.724
  8    64176.0    -0.0652    0.0032   -0.0002     32.779      6.146      0.063
  9    74309.9    -0.0007    0.0032    0.0380      0.183     -1.058    -13.517


-------------------
ELECTRONIC G-MATRIX
-------------------


raw-matrix :
 2.025533   -0.000738    0.021755
-0.000738    2.024537   -0.007389
 0.021755   -0.007389    2.928943

g-factors:
 2.024122     2.025363    2.929527 iso =     2.326338

g-shifts:
 0.021803     0.023044    0.927208 iso =     0.324018

Eigenvectors:
 0.533896    -0.845208    0.024064
 0.845530     0.533866   -0.008182
-0.005932     0.024715    0.999677


Euler angles w.r.t. molecular frame (degrees):
-76.5038       1.4564     -161.2223


---------------------------
CONTRIBUTIONS TO THE G-MATRIX
---------------------------


Term                                g1          g2          g3
--------------------------------------------------------------------
Relativistic mass correction:   -0.0008220  -0.0008220  -0.0008220
Gauge correction          :      0.0000000   0.0000000   0.0000000
g(OZ/SOC)                 :      0.0226250   0.0238662   0.9280297

State   1                     :     0.0000000  -0.0000000   0.9279829
State   2                     :     0.0013767   0.0223913   0.0000000
State   3                     :     0.0212332   0.0014408   0.0000000
State   4                     :     0.0000000   0.0000004   0.0000418
State   5                     :     0.0000074   0.0000099   0.0000001
State   6                     :     0.0000002   0.0000078   0.0000001
State   7                     :     0.0000000   0.0000015   0.0000002
State   8                     :     0.0000076   0.0000144   0.0000000
State   9                     :     0.0000000   0.0000000   0.0000046
--------------------------------------------
Total g-shifts            :      0.0218030   0.0230442   0.9272077


# The g-factors are square roots of the eigenvalues of gT*g
# Orientations are the eigenvectors of gT*g
```

Note that within the SOS formalism in addition to the second order (SOC) contributions the bilinear to the field terms: Relativistic mass correction and diamagnetic spin-orbit term (Gauge) are evaluated. As can be seen these corrections are rather negligible in comparison to the second order SOC contributions and most of the time can be safely omitted. Moreover further insight is obtained by printing the individual contribution of each excited state to the g-tensor. In the example above the first excited state contributes to the g_z component while the next two to both the g_x and g_y

components, respectively.

So to summarize the g-tensor calculations in the framework of wavefunction based methods like MRCI and/or CASSCF can be evaluated:

- via the QDPT approach within an individual Kramers doublet. This is valid analysis only for non-integer spin cases. In particular for systems with well isolated Kramers doublets where the EPR spectrum originates only from one Kramers doublet defined within the pseudo spin 1/2 formalism. This analysis has been proven useful in determining the sign of the ZFS and the electronic structure of the system under investigation.[511]

- within the effective Hamiltonian approach. This is a valid analysis for all spin cases as it provides the principal g-values of the system under investigation evaluated in the molecular axis frame. These g-values can be directly compared with the experimentally determined ones.[512]

- within the sum over states formalism (SOS). As above this analysis is valid for all spin cases and is only available via the MRCI module.

Magnetization and Magnetic Susceptibility

The MRCI and CASSCF modules of ORCA allow for the calculation of magnetization and magnetic susceptibility curves at different fields and temperatures by differentiation of the QDPT Hamiltonian with respect to the magnetic field. For magnetic susceptibility, calculations are performed in two ways when a static field different from zero is defined: (i) as the second derivative of energy with respect to the magnetic field and (ii) as the magnetization divided by the magnetic field. Although the first method corresponds to the definition of magnetic susceptibility, the second approach is widely used in the experimental determination of $\chi * T$ curves. If the static field is low, both formulas tend to provide similar values.

The full list of keywords is presented below.

```
%mrci
     citype mrci
     newblock 3 *
     excitations none
     refs cas(2,7) end
     end
     soc
       dosoc true
       domagnetization true      # Calculate magnetization (def: false)
       dosusceptibility true      # Calculate susceptiblity (def: false)
       LebedevPrec            5   # Precision of the grid for different field
                                  # directions (meaningful values range from 1
                                  # (smallest) to 10 (largest))
       nPointsFStep           5   # number of steps for numerical differentiation
                                  # (def: 5, meaningful values are 3, 5 7 and 9)
       MAGFieldStep       100.0   # Size of field step for numerical⌟
→differentiation
                                  # (def: 100 Gauss)
       MAGTemperatureMIN    4.0   # minimum temperature (K) for magnetization
       MAGTemperatureMAX    4.0   # maximum temperature (K) for magnetization
       MAGTemperatureNPoints  1   # number of temperature points for magnetization
       MAGFieldMIN          0.0   # minimum field (Gauss) for magnetization
       MAGFieldMAX      70000.0   # maximum field (Gauss) for magnetization
       MAGNpoints            15   # number of field points for magnetization
       SUSTempMIN           1.0   # minimum temperature (K) for susceptibility
       SUSTempMAX         300.0   # maximum temperature (K) for susceptibility
       SUSNPoints           300   # number of temperature points for⌟
→susceptibility
       SUSStatFieldMIN      0.0   # minimum static field (Gauss) for⌟
→susceptibility
       SUSStatFieldMAX      0.0   # maximum static field (Gauss) for⌟
→susceptibility
       SUSStatFieldNPoints    1   # number of static fields for susceptibility
```

(continues on next page)

```
      end
end
```

The same keywords apply for CASSCF calculations in rel block (instead of soc in MRCI). Although different aspects of integration and grid precision can be modified through keywords, default values should provide an accurate description of both properties. Calculated magnetization and susceptibility are printed in .sus and .mag files, respectively and also in the output file.

```
------------------------------------------------------------------------------
FIELD DEPENDENT MAGNETIZATION AND MEAN SUSCEPTIBILITY (chi=M/B)
------------------------------------------------------------------------------
TEMPERATURE (K)   M. FIELD (Gauss)   MAGNETIZATION (B.M.)   chi*T (cm3*K/mol)
------------------------------------------------------------------------------

4.00                 0.00               0.000000                  inf
4.00              5000.00               0.350759             1.567189
4.00             10000.00               0.688804             1.538788
4.00             15000.00               1.003466             1.494496
4.00             20000.00               1.287480             1.438115
4.00             25000.00               1.537346             1.373773
4.00             30000.00               1.752841             1.305282
4.00             35000.00               1.936067             1.235764
4.00             40000.00               2.090450             1.167516
4.00             45000.00               2.219920             1.102067
4.00             50000.00               2.328368             1.040315
4.00             55000.00               2.419335             0.982690
4.00             60000.00               2.495883             0.929301
4.00             65000.00               2.560582             0.880052
4.00             70000.00               2.615538             0.834730
-------------------------------------------------------------
```

```
-------------------------------------------------------------
  TEMPERATURE DEPENDENT MAGNETIC SUSCEPTIBILITY
  ---------------------------------------------------------
  STATIC  FIELD    TEMPERATURE        chi*T (cm3*K/mol)
  (Gauss)           (K)        M/B         d2E/dB2
  ---------------------------------------------------------

  0.00      1.00            ----        1.576836
  0.00      2.00            ----        1.576910
  0.00      3.00            ----        1.576951
  0.00      4.00            ----        1.576988
  0.00      5.00            ----        1.577023
  0.00      6.00            ----        1.577057
  0.00      7.00            ----        1.577091
  0.00      8.00            ----        1.577125
  0.00      9.00            ----        1.577159
  0.00     10.00            ----        1.577193
  0.00     11.00            ----        1.577227
  .....
  0.00    300.00            ----        1.586942
  1000.00      1.00      1.570517       1.558042
  1000.00      2.00      1.575324       1.572178
  1000.00      3.00      1.576246       1.574845
  1000.00      4.00      1.576590       1.575802
  1000.00      5.00      1.576768       1.576264
  1000.00      6.00      1.576880       1.576530
  1000.00      7.00      1.576961       1.576704
  1000.00      8.00      1.577026       1.576829
  .....
```

Note that the CASSCF module also supports the calculation of susceptibility tensors at non-zero user-defined magnetic fields. This is not yet possible with the MRCI module.

MCD and Absorption Spectra

The MRCI module of the ORCA program allows calculating MCD spectra and the SOC effects on absorption spectra. The formalism is described in detail by Ganyushin and Neese[513]. The approach is based on the direct calculation of the transition energies and transition probabilities between the magnetic levels. Namely, the differential absorption of LCP- and RCP photons for transitions from a manifold of initial states A to a manifold of final states J. Using Fermi's golden rule, the Franck-Condon approximation, assuming a pure electronic dipole mechanism and accounting for the Boltzmann populations of the energy levels, the basic equation of MCD spectroscopy may be written as (atomic units are used throughout):

$$\frac{\Delta\varepsilon}{E} = \gamma \sum_{a,j} (N_a - N_j) \left(|\langle \Psi_a | m_{\mathrm{LCP}} | \Psi_j \rangle|^2 - |\langle \Psi_a | m_{\mathrm{RCP}} | \Psi_j \rangle|^2 \right) f(E) \tag{3.137}$$

Here a and j label members of the initial and state manifold probed in the experiments.

$$N_a(B,T) = \frac{\exp(-E_a/kT)}{\sum_i \exp(-E_i/kT)} \tag{3.138}$$

denotes the Boltzmann population and if the a-th ground state sublevel at energy E_a, $f(E)$ stands for a line shape function, and γ denotes a collection of constants. The electric dipole operators are given by:

$$m_{\mathrm{LCP}} \equiv m_x - im_y \tag{3.139}$$

$$m_{\mathrm{RCP}} \equiv m_x + im_y \tag{3.140}$$

They represent linear combinations of the dipole moment operator:

$$\vec{m} = \sum_N Z_N \vec{R}_N - \sum_i \vec{r}_i \tag{3.141}$$

where N and i denotes summations of nuclei (at positions $\vec{R}_N$ with charges Z_N) and electrons (at positions $\vec{r}_i$) respectively. The calculated transition dipole moment are subjected to the space averaging over the Euler angles which is performed by a simple summation over three angular grids.

$$\left(\frac{\Delta\varepsilon}{E}\right)_{ev} = \frac{1}{8\pi^2} \int_{\psi=0}^{2\pi} \int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} \left(\frac{\Delta\varepsilon}{E}\right) \sin\theta \, d\theta \, d\phi \, d\psi \approx \sum_{\mu\eta\tau} \left(\frac{\Delta\varepsilon}{E}\right)_{\mu\eta\tau} \sin\theta_\tau \tag{3.142}$$

Finally, every transition is approximated by a Gaussian curve with a definite Gaussian shape width parameter. Hence, the final calculated MCD spectrum arises from the superposition of these curves.

As an illustration, consider calculation of a classical example of MCD spectrum of $[\mathrm{Fe(CN)}_6]^{3-}$. The mrci block of the input file is presented below.

```
%mrci   ewin -4,10000
        citype mrddci2
        intmode ritrafo
        Tsel  1e-6
        Tpre  1e-5
        etol 1e-8
        rtol 1e-8
        cimode direct2
        maxmemint 300
        solver diis
        davidsonopt 0
        nguessmat 150
        MaxIter 50
```

(continues on next page)

```
        LevelShift 0.5
        PrintLevel 3
        soc
        printlevel 3
        Domcd true        # perform the MCD calculation
        NInitStates 24    # number of SOC and SSC state to account
                          # Starts from the lowest state
        NPointsTheta 10   # number of integration point for
        NPointsPhi 10     # Euler angles
        NPointsPsi 10     #
        B 43500           # experimental magnetic field strength
                          # in Gauss
        Temperature 299.0 # experimental temperature (in K)
        end
        newblock 2 *
         nroots 12
         excitations cisd
         refs cas(23,12) end
         end
        end
```

The parameters B and Temperature can be assigned in pairs, i.e. B = 1000, 2000, 3000…, Temperature = 4, 10, 300…. The program calculates the MCD and absorption spectra for every pair. Now for every point of the integration grid the program prints out the Euler angles, the orientation of the magnetic field in the coordinate system of a molecule, and the energy levels.

```
Psi = 36.000 Phi = 72.000 Theta = 20.000

Bx = 8745.0 By = 12036.5 Bz = 40876.6

Energy levels (cm-1,eV):Boltzmann populations for T = 299.000   K
  0 :        0.000    0.0000         4.53e-01
  1 :        3.943    0.0005         4.45e-01
  2 :      454.228    0.0563         5.09e-02
  3 :      454.745    0.0564         5.08e-02
  4 :     1592.142    0.1974         2.13e-04
  5 :     1595.272    0.1978         2.10e-04
  6 :    25956.363    3.2182         2.59e-55
  7 :    25958.427    3.2184         2.56e-55
  8 :    25985.656    3.2218         2.25e-55
  9 :    25987.277    3.2220         2.23e-55
 10 :    26070.268    3.2323         1.49e-55
 11 :    26071.484    3.2325         1.49e-55
 12 :    31976.645    3.9646         6.78e-68
 13 :    31979.948    3.9650         6.67e-68
 14 :    32018.008    3.9697         5.56e-68
 15 :    32021.074    3.9701         5.48e-68
 16 :    32153.427    3.9865         2.90e-68
 17 :    32157.233    3.9870         2.84e-68
 18 :    42299.325    5.2444         1.81e-89
 19 :    42303.461    5.2450         1.78e-89
 20 :    42346.521    5.2503         1.45e-89
 21 :    42348.023    5.2505         1.44e-89
 22 :    42456.119    5.2639         8.53e-90
 23 :    42456.642    5.2640         8.51e-90
```

In the next lines, ORCA calculates the strength of LCP and RCP transitions and prints the transition energies, the difference between LCP and RCP transitions (denoted as C), and sum of LCP and RCP transitions (denoted as D), and C by D ratio.

```
dE     Na          C          D       C/D

  0 -> 1         3.943 4.53e-01  1.14e-13  8.13e-13   0.00e+00
  0 -> 2       454.228 4.53e-01  5.01e-09  9.90e-09   5.06e-01
  0 -> 3       454.745 4.53e-01 -4.65e-09  7.00e-09  -6.65e-01
  0 -> 4      1592.142 4.53e-01 -8.80e-08  1.02e-07  -8.67e-01
  0 -> 5      1595.272 4.53e-01 -2.29e-08  2.97e-08  -7.71e-01
  0 -> 6     25956.363 4.53e-01  1.22e+01  9.60e+01   1.27e-01
  0 -> 7     25958.427 4.53e-01  3.44e+01  3.52e+01   9.77e-01
  0 -> 8     25985.656 4.53e-01  3.83e+01  1.70e+02   2.25e-01
  0 -> 9     25987.277 4.53e-01 -7.73e+00  6.03e+01  -1.28e-01
  0 ->10     26070.268 4.53e-01 -6.11e+00  2.85e+01  -2.14e-01
  0 ->11     26071.484 4.53e-01  6.17e+00  9.21e+00   6.70e-01
  0 ->12     31976.645 4.53e-01  2.45e+01  6.21e+01   3.95e-01
  0 ->13     31979.948 4.53e-01 -6.58e+01  6.93e+01  -9.50e-01
  0 ->14     32018.008 4.53e-01  3.42e-01  1.07e+02   3.21e-03
  0 ->15     32021.074 4.53e-01 -6.16e+00  3.24e+01  -1.90e-01
  0 ->16     32153.427 4.53e-01 -4.73e+01  1.37e+02  -3.46e-01
  0 ->17     32157.233 4.53e-01 -1.02e+00  5.97e+01  -1.71e-02
  0 ->18     42299.325 4.53e-01  6.47e+00  2.11e+01   3.07e-01
  0 ->19     42303.461 4.53e-01 -2.59e+00  7.61e+00  -3.40e-01
  0 ->20     42346.521 4.53e-01  1.90e+01  8.99e+01   2.11e-01
  0 ->21     42348.023 4.53e-01  3.36e+00  3.55e+00   9.48e-01
  0 ->22     42456.119 4.53e-01  2.52e-01  4.86e-01   5.20e-01
  0 ->23     42456.642 4.53e-01 -2.01e+00  2.91e+00  -6.91e-01
  1 -> 2       450.285 4.45e-01  4.59e-09  6.87e-09   6.69e-01
  1 -> 3       450.802 4.45e-01 -4.96e-09  9.73e-09  -5.09e-01
```

All C and D values are copied additionally into the text files input.1.mcd, input.2.mcd…, for every pair of Temperature and B parameters. These files contain the energies and C and D values for every calculated transition. These files are used by the program `orca_mapspc` to calculate the spectra lines. The `orca_mapspc` program generates from the raw transitions data into spectra lines. The main parameters of the `orca_mapspc` program are described in section 7.18.1. A typical usage of the `orca_mapspc` program for MCD spectra calculation for the current example may look as the following:

```
orca_mapspc input.1.mcd MCD -x020000 -x150000 -w2000
```

Here the interval for the spectra generation is set from 20000 cm^{-1} to 50000 cm^{-1}, and the line shape parameter is set to 2000 cm^{-1}.

Very often, it is desirable to assign different line width parameters to different peaks of the spectra to obtain a better fitting to experiment. `orca_mapspc` can read the line shape parameters from a simple text file named as input.1.mcd.inp. This file should contain the energy intervals (in cm^{-1}) and the line shape parameters for this energy interval in the form of:

```
20000 35000 1000
35000 40000 2000
40000 50000 1000
```

This file should not be specified in the executing command; `orca_mapspc` checks for its presence automatically:

```
orca_mapspc input.1.mcd MCD -x020000 -x150000
Mode is MCD
Number of peaks            ... 276001
Start wavenumber [cm-1]    ...  20000.0
Stop wavenumber [cm-1]     ...  50000.0
Line width parameters are taken from the file:input.1.mcd.inp
Number of points           ... 1024
```

Finally, the `orca_mapspc` program generates the output text file input.1.mcd.dat which contains seven columns of numbers: transition energies, intensities of MCD transitions (the MCD spectrum), intensities of absorption transitions