2. Powder magnetic susceptibility function $\chi(T)$.

3. Magnetisation vector $\vec{M}(\vec{H})$ for specified directions of the applied magnetic field $\vec{H}$.

4. Powder magnetisation $\overline{M_{mol}}(H, T)$.

5. Magnetisation torque function $\vec{\tau}_{mol}(H, T)$.

The magnetic Hamiltonians are defined for a desired group of $N$ low-lying electronic states obtained in `CASSCF/ SOC` calculation to which a *pseudospin* $\tilde{S}$ is subscribed according to the relation $N = 2\tilde{S} + 1$. The *pseudospin* $\tilde{S}$ reduces to a true spin $S$ in the absence of spin-orbit coupling. For instance, the two wave functions of a Kramers doublet correspond to the pseudospin $\tilde{S} = 1/2$. The implementation is done for *any* dimension of the pseudospin $\tilde{S}$, and controlled by the keyword `MLTP`.

The calculation of magnetic properties takes into account the contribution of excited states (the ligand-field and charge transfer states of the complex or mononuclear fragment which were included in the `CASSCF/CASPT2` calculation) via their thermal population and Zeeman admixture. The effect of intermolecular exchange interaction between magnetic molecules on the resulting magnetic properties in a crystal is described by a phenomenological parameter $zJ$ specified by the user.

### 5.34.2 Running `SINGLE_ANISO` Calculations

The `SINGLE_ANISO` is, in principle, a stand-alone utility (`otool_single_aniso`) that can be called directly from the shell with its own input file, provided that the *ab initio* datafile is available:

```
bash:$
bash:$  $ORCA/x86_64/otool_single_aniso < single_aniso.input > single_aniso.output
bash:$
```

However, this usage may not be so convenient, as the file `single_aniso.input` must include the true name of the datafile. For the user's convenience, a deeper integration between `SINGLE_ANISO` and `CASSCF` program in ORCA was implemented, as described below.

As a prerequisite for using the `SINGLE_ANISO` module to calculate the magnetic properties of the investigated compound, **spin-orbit coupling and other relativistic effects are already taken fully into account at the stage of quantum chemistry calculation of the investigated compound**. The necessary information of the *ab initio* calculation is provided in a form of a "datafile": energy spectra, angular momentum integrals, etc. The interface with ORCA generates the required `datafile` automatically. The following naming conventions were adopted for the `datafile` in function of the employed computational method:

- `CASSCF+SOC+SINGLE_ANISO` => `"$orca_input_name.CASSCF.anisofile"`

- `CASSCF+QD-NEVPT2+SOC+SINGLE_ANISO` => `"$orca_input_name.NEVPT2.anisofile"`

Note that if the `CASSCF+QD-NEVPT2+SOC+SINGLE_ANISO` calculation is requested, then the `SINGLE_ANISO` will be executed twice, and the above two datafiles will be generated. The interface will generate the `SINGLE_ANISO` input file with the keywords information provided in the `CASSCF/aniso` subblock. These filename of the `datafile` is included automatically in the input file for the `SINGLE_ANISO` utility (keyword `DATA`), also generated automatically by the interface. The naming convention for the generated input files for the `SINGLE_ANISO` utility is "$orca_input_name.anisofile".

All keywords of the `SINGLE_ANISO` program are possible to be specified within the `CASSCF/ANISO` subblock. They are referenced in Section *Reference List of CASSCF/ANISO Keywords*. Optionally, a working `SINGLE_ANISO` input file can be passed directly to the `CASSCF` module setting the filename with keyword `InputNameOnDisk` in the `ANISO` subblock.

An example of the full ORCA input for performing magnetic properties calculations within the `CASSCF/SOC/ SINGLE_ANISO` methodology for a hypothetical Co(II) compound is provided below:

```
! 6-31G TightSCF   # basis set and other global ORCA settings

%maxcore 2000
```

```
%casscf nel 7
  norb 5            # 7 electrons in 5 orbitals (3d shell)
  mult 4, 2
  nroots 10, 40     # 10 quartet and 40 doublet states

  rel
  dosoc true        # include spin-orbit coupling
  end

  ANISO
    doaniso true      # generate datafile/input and call
                      # the SINGLE_ANISO module
    MLTP 2,2,2,2      # group of spin-orbit states for which the pseudospin
                      # Hamiltonian is computed: 4 low-lying spin-orbit doublet␣
→states.

    TINT 0, 300, 301 # 301 steps in the temperature interval [0-300]
                     # for magnetic susceptibility (in Kelvin)
    HINT 0, 7.0, 71  # 71 steps in the field interval [0-7]
                     # for molar magnetisation (in Tesla)
    TMAG 1.0,1.2,1.8,2.5,3.6  # temperature points for which molar magnetisation
                                          # is computed
     CRYS_element "Co"
     CRYS_charge 2
     PLOT true         # requires the ANISO to produce gnuplot scripts,
                              # datafiles and plots of various quantities

    # Alternative to the snippet above. Provide separate input file:
    # InputFile "$orca_input_name.anisoinput"
  end
end

*xyz 0 4   # charge is 0 for this neutral compound
Co   -2.80118000    9.91634000   19.40386000
O    -3.59660000   12.00284000   20.51731000
O    -5.12835000   10.85934000   19.53431000
O    -5.70975000   12.39302000   20.99406000
O    -1.30202341   11.67611386   19.17300658
O    -3.84191000    9.45315000   21.48634000
O    -1.27500262    8.12582233   19.18634310
O    -3.94611990    9.65426823   17.48476360
N    -4.85020000   11.78071000   20.36823000
H    -1.23636310   12.09677337   18.41017549
H    -1.07910455    7.59540828   19.85227241
H    -3.30514987    9.28034259   22.26327382
H    -4.79957696    9.43862752   21.55163236
H    -4.64801074    9.00163025   17.42987361
H    -3.73273676   10.19508893   16.72083912
H    -0.75470916   11.94100908   19.91589125
*
```

The input above utilises the following keywords: `MLTP` keyword requires the computation of the $g$ tensor for 4 groups of spin-orbit states, the dimensionality of each group being 2 (Kramers or Ising doublets). `TINT` requires computation of the magnetic susceptibility in the temperature interval 0 K - 300 K distributed equally in 300 temperature intervals. `TMAG` requires computation of powder molar magnetisation at 6 temperature points, in Kelvin (K): 1.0 K, 1.2 K, 1.8 K, 2.5 K, 2.9 K and 3.6 K. `HINT` defines the range for the magnetic field strength, in Tesla. `PLOT` keyword invokes the plotting function of the module. `CRYS_element + CRYS_charge` request for the computation of the crystal field parameters for the ground term of the $Co^{2+}$ ion. For more information about the keywords in `SINGLE_ANISO` module, you can refer to section *Reference List of CASSCF/ANISO Keywords*.

**Please always check the obtained orbitals after `CASSCF` calculation**. In this particular case, the active orbitals

(45-49) are localised on the Co site and display dominant $3d$ character.

```
               45        46        47        48        49
            -0.37264  -0.36672  -0.36520  -0.36153  -0.35018
             1.40513   1.40270   1.39998   1.39823   1.39395

            --------  --------  --------  --------  --------
0 Co s          0.0       0.0       0.0       0.0       0.2
0 Co pz         0.1       0.1       0.1       0.0       0.0
0 Co px         0.0       0.2       0.0       0.0       0.1
0 Co py         0.1       0.1       0.0       0.0       0.1
0 Co dz2       23.6      39.5      10.0       2.0      23.5
0 Co dxz       12.8      30.8      48.6       4.4       2.2
0 Co dyz       46.5      10.4      19.3      20.8       2.4
0 Co dx2y2      6.9       0.3      21.2      69.2       1.6
0 Co dxy        9.5      17.6       0.2       2.8      68.0
```

We see that in the above output section, the five active orbitals have dominant contribution from the Co-$3d$ basis functions. This is OK and is expected for common transition metal compounds. For lanthanide compounds, the seven active orbitals should have dominant contribution from the $4f$ shell. Larger active spaces must be carefully inspected and analysed. We refer here to the respective section of this manual describing the CASSCF method and how to achieve convergence *Complete and Incomplete Active Space Self-Consistent Field (CASSCF and RAS/ORMAS)*.

The results calculated by using `SINGLE_ANISO` module are placed after the `SOC` section in ORCA output. Here is the explanation for these results.

```
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
CALCULATION OF PSEUDOSPIN HAMILTONIAN TENSORS FOR THE MULTIPLET 1 ( effective S = ␣
↪1/2)
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
The pseudospin is defined in the basis of the following spin-orbit states:
spin-orbit state 1. energy(1) =       0.000 cm-1.
spin-orbit state 2. energy(2) =       0.000 cm-1.

g TENSOR:
|------------------------------------------------------|
|    MAIN VALUES    |           MAIN MAGNETIC AXES     |  x , y , z  -- initial␣
↪Cartesian axes
|-------------------|----|----- x ------- y ------- z ---|  Xm, Ym, Zm -- main␣
↪magnetic axes
| gX =   0.09871069 | Xm | -0.456536 -0.363638  0.811998 |
| gY =   0.11729280 | Ym |  0.643532  0.495246  0.583605 |
| gZ =  11.21949040 | Zm | -0.614361  0.788985  0.007914 |
|------------------------------------------------------|
The sign of the product gX * gY * gZ for multiplet 1: < 0.
```

The section above shows the $g$ tensor for the ground Kramers doublet. Since the $g_X$ and $g_Y$ are much smaller than the $g_Z$ component, the $Zm$ axis is denoted as the $main\,magnetic\,axis$ of the computed molecule. The "Zm | -0.614361 0.788985 0.007914 |" denotes the Cartesian components of the $Zm$ vector.

In the case the computation of the parameters of the crystal field is requested by `CRYS_element` and `CRYS_charge`, the following section will be found in the output:

```
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
    CALCULATION OF CRYSTAL-FIELD PARAMETERS OF THE GROUND ATOMIC TERM, L =  3.
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%


The parameters of the Crystal Field matrix are written in the coordinate system:
(Xm, Ym, Zm) --  the main magnetic axes of the ground pseudo-L = | 3> orbital␣
↪multiplet.
Rotation matrix from the initial coordinate system to the employed coordinate␣
↪system is:
-----------------------------------------------------------------|
x , y , z  -- initial Cartesian axes                             |
```

(continues on next page)

```
Xm, Ym, Zm -- main magnetic axes                                          |
                    x                y                z          |
    | Xm | -0.61155332461133 -0.79120321735748  0.00000000001900 |
 R = | Ym |  0.79120321735748 -0.61155332461133 -0.00000000000264 |
    | Zm |  0.00000000001371  0.00000000001342  1.00000000000000 |
--------------------------------------------------------------------|
Quantization axis is Zm.



---------------------------------------------------------------------------------
↪----------|
  Ab Initio Crystal-Field Splitting Matrix written in the basis of Pseudo-L⌋
↪Eigenfunctions   |
---------------------------------------------------------------------------------
↪----------|
        |                   | -3 >             |                   | -2 >  ⌋
↪              |
----------|---------- REAL ----------- IMAGINARY ---|---------- REAL -----------⌋
↪IMAGINARY ---|
  < -3 | | -777.2218617165776    0.0000000000000 |   -0.0000000454613    0.⌋
↪0000000351393 |
  < -2 | |     -0.0000000454613  -0.0000000351393 |  285.4563720817839    0.⌋
↪0000000000000 |
  < -1 | |      0.0285952366255  -0.0055088548681 |    0.0000000002580   -0.⌋
↪0000000024089 |
  <  0 | |     -0.0000000160911   0.0000000604843 |    0.0001933353720   -0.⌋
↪0013498718536 |
  <  1 | |      0.0116130821579  -0.0096419531309 |   -0.0000000005651   -0.⌋
↪0000000026613 |
  <  2 | |      0.0000000070279  -0.0000000332291 |    0.0141002831881   -0.⌋
↪0117070160056 |
  <  3 | |     -0.0000002782243   0.0000001745761 |   -0.0000000070278    0.⌋
↪0000000332291 |
---------------------------------------------------------------------------------
↪----------|
---------------------------------------------------------------------------------
↪----------|
        |                   | -1 >             |                   | 0 >  ⌋
↪         |
----------|---------- REAL ----------- IMAGINARY ---|---------- REAL -----------⌋
↪IMAGINARY ---|
  < -3 | |      0.0285952366255   0.0055088548681 |   -0.0000000160911   -0.⌋
↪0000000604843 |
  < -2 | |      0.0000000002580   0.0000000024089 |    0.0001933353720    0.⌋
↪0013498718536 |
  < -1 | |    347.8121781289439  -0.0000000000000 |    0.0000000069613   -0.⌋
↪0000000861891 |
  <  0 | |      0.0000000069613   0.0000000861891 |  287.9066230116981    0.⌋
↪0000000000000 |
  <  1 | |     -0.0106576508828   0.0003303251251 |   -0.0000000069613   -0.⌋
↪0000000861891 |
  <  2 | |      0.0000000005651   0.0000000026613 |    0.0001933353720   -0.⌋
↪0013498718536 |
  <  3 | |      0.0116130821579  -0.0096419531309 |    0.0000000160911   -0.⌋
↪0000000604843 |
---------------------------------------------------------------------------------
↪----------|
---------------------------------------------------------------------------------
↪----------|
        |                   | 1 >              |                   | 2 >  ⌋
↪           |
```

**Chapter 5. Spectroscopy and Properties**

```
---------|---------- REAL ----------- IMAGINARY ---|---------- REAL -----------␣
↪IMAGINARY ---|
  < -3 | |     0.0116130821579    0.0096419531309 |    0.0000000070279     0.
↪0000000332291 |
  < -2 | |    -0.0000000005651    0.0000000026613 |    0.0141002831881     0.
↪0117070160056 |
  < -1 | |    -0.0106576508828   -0.0003303251251 |    0.0000000005651    -0.
↪0000000026613 |
  <  0 | |    -0.0000000069613    0.0000000861891 |    0.0001933353720     0.
↪0013498718536 |
  <  1 | |   347.8121781289439   -0.0000000000000 |   -0.0000000002580    -0.
↪0000000024089 |
  <  2 | |    -0.0000000002580    0.0000000024089 |  285.4563720817837     0.
↪0000000000000 |
  <  3 | |     0.0285952366255   -0.0055088548681 |    0.0000000454613     0.
↪0000000351392 |
-----------------------------------------------------------------------------
↪-----------|
----------------------------------------------------|
         |                       |  3 >             |
---------|---------- REAL ----------- IMAGINARY ---|
  < -3 | |    -0.0000002782241   -0.0000001745761 |
  < -2 | |    -0.0000000070278   -0.0000000332291 |
  < -1 | |     0.0116130821579    0.0096419531309 |
  <  0 | |     0.0000000160911    0.0000000604843 |
  <  1 | |     0.0285952366255    0.0055088548681 |
  <  2 | |     0.0000000454613   -0.0000000351392 |
  <  3 | |  -777.2218617165773    0.0000000000000 |
----------------------------------------------------|
```

In the above section, the low-lying CASSCF states of the $Co^{2+}$ site originating from the free ion $^4F$ term are transformed towards the eigenstates of the ($\tilde{L} = 3$), and the low-lying CASSCF *diagonal* $7 \times 7$ energy matrix is re-written in this basis. The *non-diagonal* "Ab Initio Crystal-Field Splitting Matrix" is printed in the above section. In the subsequent output sections, the obtained crystal field matrix is decomposed in a linear combination of Irreducible Tensorial Operators (ITOs) and the obtained expansion coefficients are listed in the output.

$$\hat{H}_{CF} = \sum_{k}^{2L} \sum_{q}^{-k,+k} B_k^q \hat{O}_k^q(\tilde{L})$$

The parameters are given for several sets of ITOs.

```
*****************************************************************************
The Crystal-Field Hamiltonian:
   Hcf = SUM_{k,q} * [ B(k,q) * O(k,q) ];
where:
   O(k,q) =  Extended Stevens Operators (ESO)as defined in:
         1. Rudowicz, C.; J.Phys.C: Solid State Phys.,18(1985) 1415-1430.
         2. Implemented in the "EasySpin" function in MATLAB, www.easyspin.org.
   k - the rank of the ITO, = 2, 4, 6, 8, 10, 12.
   q - the component of the ITO, = -k, -k+1, ... 0, 1, ... k;
Knm are proportionality coefficients between the ESO and operators defined in
J. Chem. Phys., 137, 064112 (2012).
----------------------------------------------|
 k |  q  |    (K)^2    |        B(k,q)        |
----|-----|------------|----------------------|
 2 | -2  |      1.50   |  0.44029016547734E-03 |
 2 | -1  |      6.00   |  0.24547763681975E-08 |
 2 |  0  |      1.00   | -0.43693326103120E+02 |
 2 |  1  |      6.00   | -0.84162317914775E-08 |
 2 |  2  |      1.50   |  0.12672200639220E-02 |
----|-----|------------|----------------------|
```

```
  4 |  -4 |      17.50 |   0.20185049671189E-03 |
  4 |  -3 |     140.00 |  -0.24080325997038E-08 |
  4 |  -2 |      10.00 |   0.53646717565242E-04 |
  4 |  -1 |      20.00 |   0.99248109880376E-09 |
  4 |   0 |       1.00 |  -0.67496280141952E+00 |
  4 |   1 |      20.00 |  -0.53708624488205E-09 |
  4 |   2 |      10.00 |   0.33333801678482E-03 |
  4 |   3 |     140.00 |  -0.66502585057483E-09 |
  4 |   4 |      17.50 |   0.24311509626065E-03 |
----|-----|------------|------------------------|
  6 |  -6 |      57.75 |  -0.48493356946616E-09 |
  6 |  -5 |     693.00 |   0.45219078679397E-09 |
  6 |  -4 |      31.50 |   0.11222605476277E-05 |
  6 |  -3 |     105.00 |  -0.14936428088413E-09 |
  6 |  -2 |      26.25 |   0.68538037767693E-06 |
  6 |  -1 |      42.00 |  -0.24067665895440E-09 |
  6 |   0 |       1.00 |  -0.18259217459128E-02 |
  6 |   1 |      42.00 |   0.11394843516111E-11 |
  6 |   2 |      26.25 |   0.48314159464149E-05 |
  6 |   3 |     105.00 |  -0.33636623245296E-10 |
  6 |   4 |      31.50 |   0.13517294099051E-05 |
  6 |   5 |     693.00 |   0.95637007025194E-10 |
  6 |   6 |      57.75 |  -0.77284500243776E-09 |
-------------------------------------------------|
```

In the sections below, the weight of various expansion terms on the total energy splitting of the corresponding term or multiplet is analysed.

```
CUMULATIVE WEIGHT OF INDIVIDUAL-RANK OPERATORS ON THE CRYSTAL FIELD SPLITTING:
  O2 :----------------------------------------:  70.094642 %.
  O2 + O4 :-----------------------------------:  99.417093 %.
  O2 + O4 + O6 :------------------------------: 100.000000 %.
```

```
ENERGY SPLITTING INDUCED BY CUMULATIVE INDIVIDUAL-RANK OPERATORS (in cm-1).
```

| L = 3 | RASSCF INITIAL | ONLY O2 | ONLY O2+O4 | ONLY O2+O4+O6 |
|-------|----------------|---------|------------|---------------|
| w.f.  1 |    0.00000000 |    0.00000000 |    0.00000000 |    0.00000000 |
| w.f.  2 |    0.00000220 |    0.00000000 |    0.00000149 |    0.00000220 |
| w.f.  3 | 1062.65990786 |  655.39989137 | 1058.22649805 | 1062.65990786 |
| w.f.  4 | 1062.69656233 |  655.39989157 | 1060.35861560 | 1062.69656233 |
| w.f.  5 | 1065.12848829 | 1048.63177735 | 1060.39653667 | 1065.12848829 |
| w.f.  6 | 1125.02338078 | 1048.64787570 | 1129.62295551 | 1125.02338078 |
| w.f.  7 | 1125.04470493 | 1179.71980502 | 1129.64777494 | 1125.04470493 |

```
WEIGHT OF INDIVIDUAL-RANK OPERATORS ON THE CRYSTAL FIELD SPLITTING:
  O2  :----------------------------------------:  70.094642 %.
  O4  :----------------------------------------:  29.322451 %.
  O6  :----------------------------------------:   0.582907 %.
```

```
ENERGY SPLITTING INDUCED BY INDIVIDUAL-RANK OPERATORS (in cm-1).
```

| L = 3 | RASSCF INITIAL | ONLY O2 | ONLY O4 | ONLY O6 |
|-------|----------------|---------|---------|---------|
| w.f.  1 |    0.00000000 |    0.00000000 |    0.00000000 |    0.00000000 |
| w.f.  2 |    0.00000220 |    0.00000000 |  121.49328633 |    0.00351330 |

```
w.f.   3  | 1062.65990786 |  655.39989137 |  121.49330341 |    4.60307936 |
w.f.   4  | 1062.69656233 |  655.39989157 |  202.46860036 |    4.60307986 |
w.f.   5  | 1065.12848829 | 1048.63177735 |  202.50909974 |    6.90310777 |
w.f.   6  | 1125.02338078 | 1048.64787570 |  526.45202593 |    6.90437338 |
w.f.   7  | 1125.04470493 | 1179.71980502 |  526.48994463 |   11.50506445 |
----------|---------------|---------------|---------------|---------------|


WEIGHT OF INDIVIDUAL CRYSTAL FIELD PARAMETERS ON THE CRYSTAL FIELD SPLITTING: (in␣
→descending order):
CFP are given in ITO used in J. Chem. Phys. 137, 064112 (2012).
-----------------------------------------------------|
  k |  q  |         B(k,q)         |    Weight (in %)  |
----|-----|-----------------------|-------------------|
2 |    0 | -0.43693326103120E+02 |  70.08577012260780 |
4 |    0 | -0.67496280141952E+00 |  29.31873954450217 |
6 |    0 | -0.18259217459128E-02 |   0.58283348856981 |
4 |    2 |  0.10541073637635E-03 |   0.00457878555457 |
4 |    4 |  0.58115623682363E-04 |   0.00252440109385 |
4 |   -4 |  0.48251497695683E-04 |   0.00209592749496 |
2 |    2 |  0.10346808494753E-02 |   0.00165966774870 |
4 |   -2 |  0.16964581649793E-04 |   0.00073690009261 |
2 |   -2 |  0.35949541472835E-03 |   0.00057664442705 |
6 |    2 |  0.94299583491020E-06 |   0.00030100389209 |
6 |    4 |  0.24084325388052E-06 |   0.00007687706999 |
6 |   -4 |  0.19995783180553E-06 |   0.00006382645967 |
6 |   -2 |  0.13377255211448E-06 |   0.00004270014495 |
6 |    6 | -0.10169893585902E-09 |   0.00000003246226 |
6 |   -6 | -0.63812572794630E-10 |   0.00000002036895 |
6 |   -1 | -0.37137214734348E-10 |   0.00000001185418 |
4 |   -1 |  0.22192552033089E-09 |   0.00000000963990 |
4 |   -3 | -0.20351589971646E-09 |   0.00000000884023 |
2 |    1 | -0.34359122410183E-08 |   0.00000000551133 |
6 |   -5 |  0.17177307577593E-10 |   0.00000000548299 |
4 |    1 | -0.12009613533364E-09 |   0.00000000521668 |
6 |   -3 | -0.14576461261073E-10 |   0.00000000465280 |
4 |    3 | -0.56204942711777E-10 |   0.00000000244141 |
2 |   -1 |  0.10021582557877E-08 |   0.00000000160750 |
6 |    5 |  0.36329494838219E-11 |   0.00000000115964 |
6 |    3 | -0.32825983078827E-11 |   0.00000000104780 |
6 |    1 |  0.17582625268298E-12 |   0.00000000005612 |
----|-----|-----------------------|-------------------|
```

In the case of lanthanide compounds, the same keywords (CRYS_element and CRYS_charge) trigger the energy decomposition of the lowest energy matrix corresponding to the ground $J-$ multiplet of the respective lanthanide ion.

```
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
→%%%%%%%%%%%%%
CALCULATION OF THE MAGNETIC SUSCEPTIBILITY
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
→%%%%%%%%%%%%%

  Temperature dependence of the magnetic susceptibility will be calculated in 301␣
→points,
  equally distributed in temperature range  0.0 --- 300.0 K.


|-------------------------------------------------------------------------------
→------|
|     |      T     | STATISTICAL |     X*T     |     X*T     |      X      |    1/
→X      |
```

```
|     |               | SUM (Z)    |   (zJ=0)    |              |              |     ↵
↪     |
|-----|------------------------------------------------------------------------
↪------|
|Units|   Kelvin    |    ---      | cm3*K/mol  | cm3*K/mol  |   cm3/mol   |   mol/
↪cm3   |
|-----|------------------------------------------------------------------------
↪------|
|     |    0.000100 | 0.20000E+01 |  3.93592010 |  3.93592010 | 0.39359E+05 | 0.
↪25407E-04 |
|     |    1.000000 | 0.20000E+01 |  3.94046247 |  3.94046247 | 0.39405E+01 | 0.
↪25378E+00 |
|     |    2.000000 | 0.20000E+01 |  3.94500530 |  3.94500530 | 0.19725E+01 | 0.
↪50697E+00 |
|     |    3.000000 | 0.20000E+01 |  3.94954814 |  3.94954814 | 0.13165E+01 | 0.
↪75958E+00 |
|     |    4.000000 | 0.20000E+01 |  3.95409097 |  3.95409097 | 0.98852E+00 | 0.
↪10116E+01 |
|     |    5.000000 | 0.20000E+01 |  3.95863380 |  3.95863380 | 0.79173E+00 | 0.
↪12631E+01 |
|     |    6.000000 | 0.20000E+01 |  3.96317663 |  3.96317663 | 0.66053E+00 | 0.
↪15139E+01 |
|     |    7.000000 | 0.20000E+01 |  3.96771946 |  3.96771946 | 0.56682E+00 | 0.
↪17642E+01 |
|     |    8.000000 | 0.20000E+01 |  3.97226229 |  3.97226229 | 0.49653E+00 | 0.
↪20140E+01 |
|     |    9.000000 | 0.20000E+01 |  3.97680512 |  3.97680512 | 0.44187E+00 | 0.
↪22631E+01 |
|     |   10.000000 | 0.20000E+01 |  3.98134795 |  3.98134795 | 0.39813E+00 | 0.
↪25117E+01 |
...
```

This section shows the computed magnetic susceptibility. The formula used for this calculation assumes the zero-field limit, $i.e. H = 0.0$ Tesla. A picture called "XT_no_field.png" using the above data will be created in the working directory whenever the PLOT keyword is included in the SINGLE_ANISO input. The picture shows the temperature dependence of the magnetic susceptibility.

```
|-------------------------------------------------------------------------------
↪-------------------|
|                      VAN VLECK SUSCEPTIBILITY TENSOR FOR zJ = 0,  in cm3*K/mol  ↵
↪                   |
|-------------------------------------------------------------------------------
↪-------------------|
|  T(K)    | |        SUSCEPTIBILITY TENSOR     |  MAIN VALUES  |             ↵
↪MAIN AXES         |
|----------|-|----- x --------- y --------- z ---|---------------|------ x --------
↪- y --------- z ----|
|          |x|  4.456611   -5.721848   -0.057261 | X:   0.000914 |  0.45654560  0.
↪36364537 -0.81199025 |
| 0.000100 |y| -5.721848    7.349367    0.073827 | Y:   0.001291 |  0.64352653  0.
↪49524178  0.58361733 |
|          |z| -0.057261    0.073827    0.001782 | Z:  11.805555 | -0.61436123  0.
↪78898519  0.00791499 |
|----------|-|----- x --------- y --------- z ---|---------------|------ x --------
↪- y --------- z ----|
|          |x|  4.461142   -5.718873   -0.057275 | X:   0.007129 |  0.48578721  0.
↪38619740 -0.78413160 |
| 1.000000 |y| -5.718873    7.351927    0.074460 | Y:   0.008275 |  0.62173382  0.
↪47788368  0.62054351 |
|          |z| -0.057275    0.074460    0.008319 | Z:  11.805983 | -0.61437598  0.
↪78897323  0.00796220 |
```

```
|----------|-|----- x --------- y --------- z ---|--------------|------ x --------
→- y --------- z ----|
|        |x|  4.465674   -5.715898   -0.057290 | X:   0.013344 | -0.49137357 -0.
→39055217  0.77847352 |
| 2.000000 |y| -5.715898    7.354486    0.075093 | Y:   0.015261 |  0.61731357  0.
→47435127  0.62762635 |
|        |z| -0.057290    0.075093    0.014856 | Z:  11.806411 | -0.61439073  0.
→78896126  0.00800947 |
...
```

The section above shows how the main axes of the susceptibility tensor evolves with temperature.

```
          HIGH-FIELD POWDER MAGNETIZATION
              (Units: Bohr magneton)


|----------|--------------|--------------|--------------|--------------|------
→---------|
|   H(T)   |STATISTICAL SUM|   1.000 K.  |    1.200 K.  |    1.800 K.  |    ␣
→2.500 K.  |
|----------|--------------|--------------|--------------|--------------|------
→---------|
| 0.000100 |    1.9995371 | 0.0007055560 | 0.0005880989 | 0.0003923371 | 0.
→0002827105 |
| 0.100000 |    1.6293687 | 0.6863212310 | 0.5768343572 | 0.3889480349 | 0.
→2814379254 |
| 0.200000 |    1.3961049 | 1.2730827904 | 1.0928431358 | 0.7585259147 | 0.
→5554332924 |
| 0.300000 |    1.2492960 | 1.7176941099 | 1.5137449727 | 1.0936561795 | 0.
→8154486026 |
| 0.400000 |    1.1568991 | 2.0312460704 | 1.8358752195 | 1.3858429640 | 1.
→0565149122 |
| 0.500000 |    1.0987474 | 2.2456644189 | 2.0736324473 | 1.6329635867 | 1.
→2755212118 |
| 0.600000 |    1.0621485 | 2.3917509695 | 2.2464760254 | 1.8374994655 | 1.
→4711430994 |
| 0.700000 |    1.0391143 | 2.4924803644 | 2.3720174309 | 2.0044495622 | 1.
→6435265950 |
| 0.800000 |    1.0246173 | 2.5633469179 | 2.4639356325 | 2.1396808073 | 1.
→7938697856 |
| 0.900000 |    1.0154934 | 2.6144012337 | 2.5321303741 | 2.2489088878 | 1.
→9240150206 |
| 1.000000 |    1.0097510 | 2.6521008670 | 2.5835380488 | 2.3371993536 | 2.
→0361143785 |
| 1.100000 |    1.0061370 | 2.6806180412 | 2.6229602467 | 2.4088035375 | 2.
→1323879997 |
| 1.200000 |    1.0038624 | 2.7026854246 | 2.6537186141 | 2.4671744880 | 2.
→2149684436 |
| 1.300000 |    1.0024309 | 2.7201250266 | 2.6781249799 | 2.5150622492 | 2.
→2858129074 |
| 1.400000 |    1.0015299 | 2.7341759016 | 2.6978046065 | 2.5546323752 | 2.
→3466634357 |
...
```

This section shows the field dependence of the powder molar magnetisation. A picture named "MH.png" can be created by using the PLOT keyword in the SINGLE_ANISO input file.

Running CASSCF calculations on lanthanides compounds in ORCA might be a bit more cumbersome compared to transition metal compounds, due to the convergence of this method. However, following the instructions in the *Complete and Incomplete Active Space Self-Consistent Field (CASSCF and RAS/ORMAS)* section and the related tips in this manual and on the Forum, the calculations could be performed. From our experience, the main reason for the poor convergence of CASSCF calculation originates from the wrong orbitals occupying the active space. This issue can be overcame by performing a proper rotation of the molecular orbitals such that the seven orbitals with dominant

$4f$ contribution are placed in the active space. As soon as the active orbitals acquire the dominant $4f$ weight, the convergence is quite straightforward.

Below we describe the calculation on a lanthanide fragment $[\text{Ce(COT)}_2]^-$ $(\text{COT}=(\text{C}_8\text{H}_8)^{2-})$ as an example:

```
!DKH DKH-DEF2-SVP slowconv KDIIS BP

%basis
newgto Ce "SARC2-DKH-QZVP" end
end

%scf
MaxIter 500
end

*xyz -1 2
Ce   5.97600100    5.09133100    13.17268800
C    5.47882500    2.98632700    11.42941100
C    4.38424700    3.88677900    11.27367600
H    4.21867900    4.06431900    10.35453600
C    3.47138800    4.59373300    12.09958800
H    2.87027600    5.12178400    11.58692300
C    3.21937800    4.72005000    13.49499100
C    3.84198900    4.08874200    14.61728000
H    3.46926600    4.38472800    15.43857500
C    4.86395700    3.14327700    14.81900800
H    4.97094200    2.92197400    15.73690500
C    5.77247800    2.44085400    13.98883400
H    6.34594800    1.86846400    14.48498500
C    6.03182900    2.38537000    12.60408600
H    6.75450600    1.80396200    12.40022700
C    6.40698800    7.65195200    12.14877700
C    6.11546300    7.83965300    13.53689900
H    5.47247100    8.52635500    13.66635300
C    6.52698400    7.27593700    14.77461400
H    6.07344100    7.67704500    15.50605500
C    7.44425200    6.26569500    15.21837900
C    8.37896000    5.47470700    14.49350900
H    8.88315100    4.90771300    15.06566300
C    8.74883600    5.31701900    13.13468700
H    9.45277500    4.68873000    13.02529900
C    8.32602800    5.86701900    11.90372100
H    8.81295200    5.51473700    11.16784000
C    7.36115600    6.80638600    11.50204100
H    7.33662500    6.90506000    10.55697400
H    5.93270067    2.68976505    10.50694264
H    5.83417492    8.22959522    11.45371334
H    2.43475960    5.39234559    13.77300645
H    7.40021961    6.07954201    16.27114118
*
```

This is the first step of the calculation. For heavier elements like lanthanides, we must consider relativistic effect by using `DKH` keyword. We explicitly use `KDIIS` in the calculation to smoothen out convergence. The orbital file called "CeCOT2_1.gbw" will be generated after this step. We further use this gbw file to do the `CASSCF` calculation.

```
!DKH DKH-DEF2-SVP TightSCF conv Moread

%moinp "CeCOT2_1.gbw"

%basis
newgto Ce "SARC2-DKH-QZVP" end
end
```

(continues on next page)

```
%casscf nel 1
   norb 7  # 1 electrons in 7 f orbitals
   mult 2
   nroots 7  # 7 doublet states

   rel
     dosoc true  # include spin-orbit coupling
   end
end

*xyz -1 2
......
*
```

We need to check the orbitals after the `CASSCF` step with the orbital file named "CeCOT2_2.gbw" obtained.

|         | 85      | 86      | 87      | 88      | 89      | 90      | 91      |
|---------|---------|---------|---------|---------|---------|---------|---------|
|         | 0.45543 | 0.45310 | 0.27655 | 0.45085 | 0.45251 | 0.45760 | 0.45713 |
|         | 0.14286 | 0.14286 | 0.14286 | 0.14286 | 0.14286 | 0.14286 | 0.14286 |
|         | -------- | -------- | -------- | -------- | -------- | -------- | -------- |
| 0 Ce f0 | 26.2    | 0.9     | 0.0     | 1.3     | 3.3     | 0.5     | 6.6     |
| 0 Ce f+1 | 5.4    | 20.2    | 0.0     | 24.0    | 3.4     | 5.6     | 39.1    |
| 0 Ce f-1 | 0.4    | 30.4    | 0.0     | 52.8    | 10.7    | 0.6     | 3.9     |
| 0 Ce f+2 | 3.8    | 0.2     | 0.7     | 1.4     | 4.7     | 76.7    | 10.7    |
| 0 Ce f-2 | 50.7   | 0.7     | 0.0     | 2.1     | 4.2     | 4.0     | 1.3     |
| 0 Ce f+3 | 8.2    | 22.0    | 0.0     | 1.2     | 55.8    | 0.0     | 11.6    |
| 0 Ce f-3 | 4.7    | 25.3    | 0.0     | 16.5    | 17.1    | 10.1    | 25.2    |

Orbitals 85, 86, 88-91 and 130 are occupied and strongly metal based $4f$-orbitals. For comparison, the converged `CASSCF` orbitals are pure $4f$-orbitals (99% metal-based). The orbitals need to be rotated in order to fit the active space (85-91). Then we can use the results of `CASSCF/SOC` calculation to call for the `SINGLE_ANISO` program.

```
!DKH DKH-DEF2-SVP TightSCF conv Moread
%moinp "CeCOT2_2.gbw"

%basis
newgto Ce "SARC2-DKH-QZVP" end
end

%scf rotate {87,130,90} end
end

%casscf nel 1
   norb 7
   mult 2
   nroots 7

   rel
   dosoc true
   end

   ANISO
     doaniso true
     MLTP 2,2,2    # 3 Kramers doublets, J=5/2
     MAVE 1, 12   # nsym=1, Lebedev grid number 12
     XFIE 0.1       # the applied magnetic field is 0.1 T
     CRYS_element "Ce"
     CRYS_charge 3
     NCUT 14
     ABCC_abc     11.0735, 12.6738, 22.4854, 84.436, 86.690, 83.969
     ABCC_center  0.82682, 0.31234, 0.78619
```

```
    ZJPR  -0.120
    HEXP_temp  2.0, 3.0
    HEXP_H  0.0, 1.0, 2.0, 3.0, 4.0
    HEXP_M[0]= 0.0, 2.46, 2.86, 2.95, 2.98
    HEXP_M[1]= 0.0, 2.04, 2.68, 2.87, 2.94
    TEXP_temp  0.0, 10.0, 20.0, 30.0, 40.0, 50.0
    TEXP_chiT  4.5, 4.5, 4.58, 4.62, 4.66, 4.70
    UBAR true
    PLOT true
    ZEEM[0]=1.0, 0.0, 0.0
    ZEEM[1]=0.0, 0.0, 1.0
    ZEEM[2]=0.0, 1.0, 0.0
    ZEEM[3]=0.75, 0.0, 0.25
  end
end

*xyz -1 2
......
*
```

The order of the keywords listed in the `CASSCF/ANISO` subblock does not matter.

### 5.34.3 Reference List of CASSCF/ANISO Keywords

The only required keyword for `SINGLE_ANISO` is the `DATA`, specifying the name of the datafile containing the *ab initio* information. The ORCA interface includes this keyword automatically and therefore it is not referenced here. All other keywords are extra and allow various customisation of the execution. For the computation of the EPR $g$-tensor, the only unknown variable for `SINGLE_ANISO` is the dimension (multiplicity) of the pseudospin(s). This information can be provided by the `MLTP` keyword. For example, in cases where spin-orbit coupling is weak, the multiplicity of the effective spin Hamiltonian is usually the same as the multiplicity of the lowest term (e.g. high spin $Fe^{3+}$: $S = \tilde{S} = 5/2$), while in the cases with strong anisotropy (lanthanide, actinide complexes, $Co^{2+}$ complexes, cases with near-orbital degeneracy, etc.) the lowest energy levels form a group of states which may differ drastically from the spins of the lowest term. In these cases the user should specify the multiplicity corresponding to a chosen value of pseudospin ($2\tilde{S}+1$). For instance, in $Dy^{3+}$ the spin of the ground state term is $S = 5/2$, but in most of real compounds only the ground Kramers doublet is considered. In such case, the multiplicity of the pseudospin equals to 2 (see `MLTP` keyword). For the calculation of the parameters of the crystal field corresponding to the ground atomic multiplet $J$ for lanthanides should be requested with the keywords `CRYS_element` and `CRYS_charge`. Similarly, the parameters of the crystal field corresponding to the ground atomic term $L$ for lanthanides and transition metals compounds can be requested with same keywords: `CRYS_element` and `CRYS_charge`.

Note that the keywords/syntax in the ORCA CASSCF/ANISO block are slightly different from the genuine `SINGLE_ANISO` input, where some of the keywords are grouped together. We aimed at keeping the control keywords as close as possible.

Optional general keywords to control the input within the ORCA interface (CASSCF/ANISO subblock):

**InputNameOnDisk**

> This keyword reads the name of the input file for `SINGLE_ANISO`, a string given between quotations. Example:

```
InputNameOnDisk "my_input_for_aniso.inp"
```

> The interface with ORCA will add the `DATA` keyword with specific name of the datafile for the performed calculation. All the other keywords provided inside this file must follow their original names, as in `MOLCAS`.

**MLTP**

> The number of molecular multiplets (*i.e.* groups of spin-orbit eigenstates) for which $g$, $D$ and higher magnetic tensors will be calculated (default `MLTP=1`). With `MLTP` an comma separated list of numbers specifying the dimension of each multiplet is passed. The default is to select one multiplet which has the dimension equal

to the multiplicity of the ground term. In cases of strong spin-orbit coupling the usage of this keyword is mandatory. Example:

```
MLTP 4, 4, 2, 2
```

SINGLE_ANISO will compute the $g$ tensor for 4 groups of states: 2 groups having the effective spin $S = |3/2>$, and other 2 groups of states being Kramers doublets.

**TINT**

Specifies the temperature points for the evaluation of the magnetic susceptibility. The program will read three numbers: $T_{min}$, $T_{max}$, and $nT$.

- $T_{min}$ - the minimal temperature (Default 0.0K)

- $T_{max}$ - the maximal temperature (Default 300.0K)

- $nT$ - number of temperature points (Default 101)

Example:

```
TINT 0.0, 330.0, 331
```

SINGLE_ANISO will compute temperature dependence of the magnetic susceptibility in 331 points evenly distributed in temperature interval: 0.0K - 330.0K.

**HINT**

Specifies the field points for the evaluation of the magnetisation in a certain direction. The program will read three numbers: $H_{min}$, $H_{max}$ and $nH$.

- $H_{min}$ - the minimal field (Default 0.0T)

- $H_{max}$ - the maximal filed (Default 10.0T)

- $nH$ - number of field points (Default 101)

Example:

```
HINT 0.0, 20.0, 201
```

SINGLE_ANISO will compute the molar magnetisation in 201 points evenly distributed in field interval: 0.0T - 20.0T.

**TMAG**

Specifies the temperature(s) at which the field-dependent magnetisation is calculated. The program will read the temperatures (in Kelvin) at which magnetisation is to be computed. Default is to compute magnetisation at one temperature point (2.0 K). Example:

```
TMAG 1.8, 2.0, 3.0, 4.0, 5.0
```

SINGLE_ANISO will compute the molar magnetisation at 5 temperature points (1.8 K, 2.0 K, 3.4 K, 4.0 K, and 5.0 K).

**ENCU**

The keyword expects to read two integer numbers. The two parameters (NK and MG) are used to define the cut-off energy for the lowest states for which Zeeman interaction is taken into account exactly. The contribution to the magnetisation coming from states that are higher in energy than $E$ (see below) is done by second order perturbation theory. The program will read two integer numbers: $NK$ and $MG$. Default values are: $NK = 100, MG = 100$.

$$E = NK \cdot k_{Boltz} \cdot \text{TMAG}_{max} + MG \cdot \mu_{Bohr} \cdot H_{max}$$

The field-dependent magnetisation is calculated at the maximal temperature value given by TMAG keyword. Example:

```
ENCU 250, 150
```

If $H_{max}$ = 10 T and `TMAG` = 1.8 K, then the cut-off energy is: $E = 250 \cdot k_{Boltz} \cdot 1.8 + 150 \cdot \mu_{Bohr} \cdot 10 = 1013.06258(cm^{-1})$

This means that the magnetisation arising from all spin-orbit states with energy lower than $E = 1013.06258(cm^{-1})$ will be computed exactly (i.e. are included in the exact Zeeman diagonalisation) The keywords `NCUT`, `ERAT` and `ENCU` have similar purpose. If two of them are used at the same time, the following priority is defined: `NCUT > ENCU > ERAT`.

**NCUT**

This flag is used to define the cut-off energy for the low-lying spin-orbit states for which Zeeman interaction is taken into account exactly. The contribution to the magnetisation arising from states that are higher in energy than lowest $N_{CUT}$ states, is done by second-order perturbation theory. The program will read one integer number. In case the number is larger than the total number of spin-orbit states($N_{SS}$, then the $N_{CUT}$ is set to $N_{SS}$ (which means that the molar magnetisation will be computed exactly, using full Zeeman diagonalisation for all field points). The field-dependent magnetisation is calculated at the temperature value(s) defined by `TMAG`. Example:

```
NCUT 32
```

The keywords `NCUT`, `ERAT` and `ENCU` have similar purpose. If two of them are used at the same time, the following priority is defined: `NCUT > ENCU > ERAT`.

**ERAT**

This flag is used to define the cut-off energy for the low-lying spin-orbit states for which Zeeman interaction is taken into account exactly. The program will read one single real number specifying the ratio of the energy states which are included in the exact Zeeman Hamiltonian. As example, a value of 0.5 means that the lowest half of the energy states included in the spin-orbit calculation are used for exact Zeeman diagonalisation.

Example:

```
ERAT 0.333
```

The keywords `NCUT`, `ERAT` and `ENCU` have similar purpose. If two of them are used at the same time, the following priority is defined: `NCUT > ENCU > ERAT`.

**MVEC_x MVEC_y MVEC_z**

`MVEC_x`, `MVEC_y` and `MVEC_z` define a number of directions for which the magnetisation vector will be computed. The directions are given as unitary vectors specifying the direction *i* of the applied magnetic field).

Example:

```
MVEC_x 0.00, 1.57, 1.57, 0.425
MVEC_y 0.00, 0.00, 1.57, 0.418
MVEC_z 0.00, 0.00, 1.57, 0.418
```

**ZEEM**

This keyword allows to compute Zeeman splitting spectra along certain directions of applied field. Directions of applied field are given as three real number for each direction, specifying the projections along each direction: Example:

```
ZEEM[0] 1.0, 0.0, 0.0
ZEEM[1] 0.0, 1.0, 0.0
ZEEM[2] 0.0, 0.0, 1.0
ZEEM[3] 0.0, 1.0, 1.0
ZEEM[4] 1.0, 0.0, 1.0
ZEEM[5] 1.0, 1.0, 0.0
```

The above input will request computation of the Zeeman spectra along six directions: Cartesian axes X, Y, Z (directions 1,2 and 3), and between any two Cartesian axes: YZ, XZ and XY, respectively. The program will re-normalise the input vectors according to unity length. In combination with `PLOT` keyword, the corresponding `zeeman_energy_xxx.png` images will be produced.

**MAVE**

The keyword requires two integer numbers, denoted `MAVE_nsym` and `MAVE_ngrid`. The parameters `MAVE_nsym` and `MAVE_ngrid` specify the grid density in the computation of powder molar magnetisation. The program uses Lebedev-Laikov distribution of points on the unit sphere. The parameters are integer numbers: $n_{sym}$ and $n_{grid}$. The $n_{sym}$ defines which part of the sphere is used for averaging. It takes one of the three values: 1 (half-sphere), 2 (a quarter of a sphere) or 3 (an octant of the sphere). $n_{grid}$ takes values from 1 (the smallest grid) till 32 (the largest grid, i.e. the densest). The default is to consider integration over a half-sphere (since $M(H) = -M(-H)$): $n_{sym} = 1$ and $n_{sym} = 15$ (i.e 185 points distributed over half-sphere). In case of symmetric compounds, powder magnetisation may be averaged over a smaller part of the sphere, reducing thus the number of points for the integration. The user is responsible to choose the appropriate integration scheme. Note that the program's default is rather conservative.

Example:

```
MAVE 1, 8
```

**TEXP_temp TEXP_chiT**

The parameters `TEXP_temp` and `TEXP_chiT` allow the computation of the magnetic susceptibility $\chi T(T)$ at experimental points. The experimental temperature (in $K$) and the experimental magnetic susceptibility (in $cm^3 K mol^{-1}$ ) are read as comma separated list. In the case both `TEXP` and `TINT` keywords are given, the `TEXP` will be used while the `TINT` input will be ignored.

Example:

```
TEXP_temp 0.0, 10.0, 20.0, 30.0, 40.0, 50.0
TEXP_chiT 4.5, 4.5, 4.58, 4.62, 4.66, 4.70
```

**HEXP_temp HEXP_H HEXP_M**

The three keywords `HEXP_temp`, `HEXP_H` and `HEXP_M` enable the computation of the molar magnetisation $M_{mol}(H)$ at experimental points. The experimental field strength (in Tesla) and the experimental magnetisation (in $\mu_{Bohr}$) are read as a comma separated list. In the case both `HEXP` and `HINT` keywords are given, the `HEXP` will be used while the `HINT` input will be ignored. The magnetisation routine will print the standard deviation from the experiment. Example:

```
HEXP_temp 2.0, 3.0
HEXP_H 0.0, 1.0, 2.0, 3.0, 4.0
HEXP_M[0]= 0.0, 2.46, 2.86, 2.95, 2.98  # exp. M at T=2.0 K
HEXP_M[1]= 0.0, 2.04, 2.68, 2.87, 2.94  # exp. M at T=3.0 K
```

**ZJPR**

This keyword specifies the value (in $cm^{-1}$) of a phenomenological parameter of a mean molecular field acting on the spin of the complex (the average intermolecular exchange constant). It is used in the calculation of all magnetic properties (not for spin Hamiltonians) (Default is 0.0).

```
ZJPR -0.02
```

**TORQ**

This keyword specifies the number of angular points for the computation of the magnetisation torque function, $\vec{\tau}_\alpha$ as function of the temperature, field strength and field orientation.

```
TORQ 55
```

The torque is computed at all temperature given by `TMAG` or `HEXP_temp` inputs. Three rotations around Cartesian axes X, Y and Z are performed.

**PrintLevel**

This keyword controls the print level.

- 2 - normal. (Default)
- 3 or larger (debug)

**CRYS_element CRYS_charge**

> The keywords `CRYS_element` and `CRYS_charge` request the computation of all 27 Crystal-Field parameters acting on the ground atomic multiplet of a lanthanide. With `CRYS_element` the chemical symbol of the lanthanide is set. **Note that the element symbol must be enclosed in quotation marks**. The charge is defined with `CRYS_charge`. By default the program will not compute the parameters of the Crystal-Field.

> Example:

```
CRYS_element "Dy" CRYS_charge 3
```

**QUAX**

> This keyword controls the quantisation axis for the computation of the Crystal-Field parameters acting on the ground atomic multiplet of a lanthanide. On the next line, the program will read one of the three values: 1, 2 or 3.

> - 1 - quantisation axis is the main magnetic axis $Zm$ of the ground pseudospin multiplet, whose size is specified within the `MLTP` keyword. (Default)

> - 2 - quantisation axis is the main magnetic axis $Zm$ of the entire atomic multiplet $|J, M_J >$.

> - 3 - quantisation axis is the original Cartesian Z axis. Rotation matrix is unity.

> Example:

```
QUAX 3
```

**UBAR**

> With `UBAR` set to "true", the blocking barrier of a single-molecule magnet is estimated. The default is not to compute it. The method prints transition matrix elements of the magnetic moment according to the Figure below:
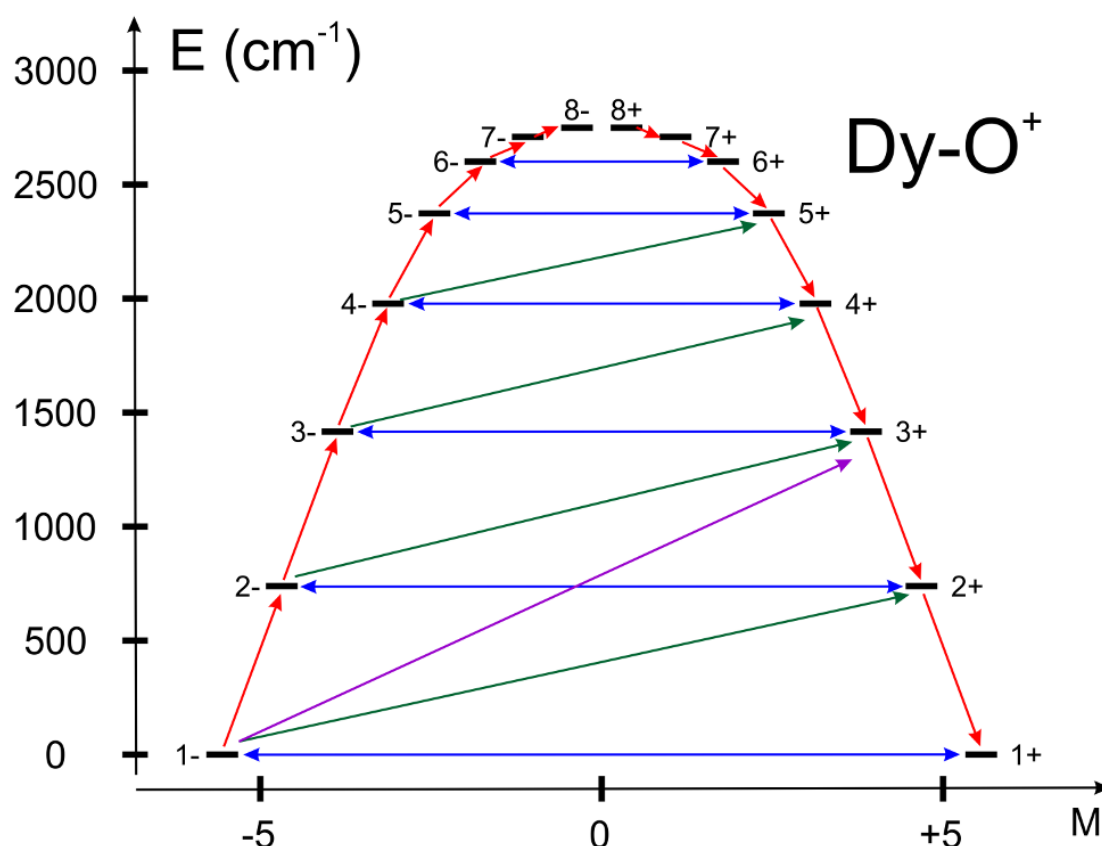


In this figure, a qualitative performance picture of the investigated single-molecular magnet is estimated by the strengths of the transition matrix elements of the magnetic moment connecting states with opposite magnetisaskytions ($n+ \rightarrow n-$). The height of the barrier is qualitatively estimated by the energy at which the

matrix element ($n+ \rightarrow n-$) is large enough to induce significant tunnelling splitting at usual magnetic fields (internal) present in the magnetic crystals (0.01-0.1 Tesla). For the above example, the blocking barrier closes at the state ($8+ \rightarrow 8-$).

All transition matrix elements of the magnetic moment are given as $((|\mu_X| + |\mu_Y| + |\mu_Z|)/3)$. The data is given in Bohr magnetons ($\mu_{Bohr}$).

Example:

```
UBAR true
```

**ABCC_abc ABCC_center**

    The keywords `ABCC_abc` and `ABCC_center` set the computation of magnetic and anisotropy axes in the crystallographic $abc$ system. With `ABCC_abc`, the program reads six real values, namely $a, b, c, \alpha, \beta$, and $\gamma$, defining the crystal lattice. The values must be separated by a comma. With `ABCC_center`, the program reads the fractional coordinates of the magnetic center (from the CIF file) - again separated by comma. It is assumed that the XYZ coordinates used for the *ab initio* calculations did not rotate or translate the molecule from its crystallographic position. This input will ensure that all tensors computed by `SINGLE_ANISO` are given also in the $abc$ system. The computed values in the output correspond to the crystallographic position of three "dummy atoms" located on the corresponding anisotropy axes, at the distance of 1.0 $\mathring{A}$ from the metal site. Example:

```
ABCC_abc 12.977, 12.977, 16.573, 90, 90, 120
ABCC_center 0.666667, 0.333333, 0.20413
```

**XFIE**

    This keyword specifies the value (in T) of applied magnetic field for the computation of magnetic susceptibility by $dM/dH$ and $M/H$ formulas. A comparison with the usual formula (in the limit of zero applied field) is provided. (Default is 0.0). Example:

```
XFIE 0.35
```

    This keyword together with the keyword `PLOT` will enable the generation of two additional plots: `XT_with_field_dM_over_dH.png` and `XT_with_field_M_over_H.png`, one for each of the two above formula used, alongside with respective `gnuplot` scripts and gnuplot datafiles.

**PLOT**

    Set to "true", the program generates a few plots (png or eps format) via an interface to the linux program *gnuplot*. The interface generates a datafile, a *gnuplot* script and attempts execution of the script for generation of the image. The plots are generated only if the respective function is invoked. The magnetic susceptibility, molar magnetisation and blocking barrier (`UBAR`) plots are generated. The files are named: `XT_no_field.dat`, `XT_no_field.plt`, `XT_no_field.png`, `MH.dat`, `MH.plt`, `MH.png`, `BARRIER_TME.dat`, `BARRIER_ENE.dat`, `BARRIER.plt` and `BARRIER.png`, `zeeman_energy_xxx.png` etc. All files produced by `SINGLE_ANISO` are referenced in the corresponding output section. Example:

```
PLOT true
```

## 5.34.4 How to cite

We would appreciate if you cite the following papers in publications resulting from the use of `SINGLE_ANISO`:

- Chibotaru, L. F.; Ungur, L. *J. Chem. Phys.*, **2012**, *137*, 064112.

- Ungur, L. Chibotaru, L. F. *Chem. Eur. J.*, **2017**, *23*, 3708-3718.

In addition, useful information like the definition of pseudospin Hamiltonians and their derivation can be found in this paper.

# 5.35 Interface to POLY_ANISO Module

## 5.35.1 General Description

The `POLY_ANISO` is a stand-alone utility allowing for a semi-*ab initio* description of the (low-lying) electronic structure and magnetic properties of polynuclear compounds. The model behind it is based on the *localised* nature of the magnetic orbitals (i.e. the $d$ and $f$ orbitals containing unpaired electrons). For many compounds of interest, the localised character of the magnetic orbitals leads to very weak character of the exchange interaction between magnetic centers. Due to this weakness of the inter-site interaction, the molecular orbitals and corresponding localised ground and excited states may be optimized in the absence of the magnetic interaction at all. For this purpose, various fragmentation models may be applied. The most commonly used fragmentation model is exemplified in Fig. 5.66:
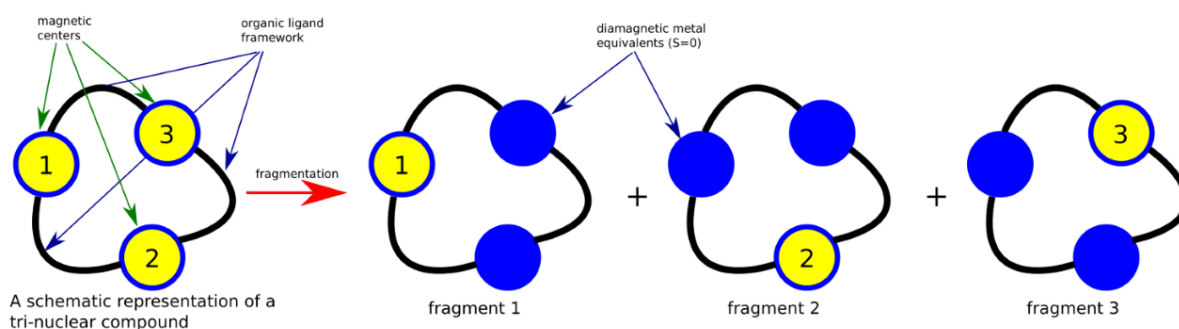


Fig. 5.66: Fragmentation model of a polynuclear compound.

The upper scheme shows a schematic overview of a tri-nuclear compound and the resulting three mononuclear fragments obtained by *diamagnetic atom substitution method*. By this scheme, the neighbouring magnetic centers, containing unpaired electrons are computationally replaced by their diamagnetic equivalents. As example, transition metal (TM) sites are best described by either a diamagnetic Zn(II) or Sc(III), in function of which one is the closest (in terms of charge and atomic radius). For lanthanides (LN), the same principle is applicable, La(III), Lu(III) or Y(III) are best suited to replace a given magnetic lanthanide. Individual mononuclear metal fragments are then investigated by the common CASSCF+SOC/NEVPT2+ SOC/SINGLE_ANISO computational method. A single `datafile` for each magnetic site, produced by the SINGLE_ANISO run, is needed by the POLY_ANISO code as input.

Magnetic interaction between metal sites is very important for accurate description of low-lying states and their properties. While the full exchange interaction is quite complex (e.g. requiring a multipolar description employing a large set of parameters [755, 756]), in a simplified model it can be viewed as a sum of various interaction mechanisms: magnetic exchange, dipole-dipole interaction, antisymmetric exchange, etc. In the POLY_ANISO code we have implemented several mechanisms, which can be invoked simultaneously for each interacting pair.

The description of the magnetic exchange interaction is done within the Lines model[757]. This model is exact in three cases:

1. interaction between two isotropic spins (Heisenberg),
2. interaction between one Ising spin (only $S_Z$ component) and one isotropic (i.e. usual) spin, and
3. interaction between two Ising spins.

In all other cases when magnetic sites have intermediate anisotropy (i.e. when the spin-orbit coupling and crystal field effects are of comparable strengths), the Lines model represents an approximation. However, it was successfully applied for a wide variety of polynuclear compounds so far.

In addition to the magnetic exchange, magnetic dipole-dipole interaction can be accounted exactly, by using the *ab initio* computed magnetic moment for each metal site (as available inside the `datafile`). In the case of strongly anisotropic lanthanide compounds (like $Ho^{3+}$ or $Dy^{3+}$), the magnetic dipole-dipole interaction is usually the dominant one. For example, a system containing two magnetic dipoles $\vec{\mu}_1$ and $\vec{\mu}_2$, separated by distance $\vec{r}$ have a total

energy:

$$E_{dip} = \frac{\mu_{Bohr}^2}{r^3}[\vec{\mu}_1 \cdot \vec{\mu}_2 - 3(\vec{\mu}_1 \vec{n}_{1,2}) \cdot (\vec{\mu}_2 \vec{n}_{1,2})],$$

where $\vec{\mu}_{1,2}$ are the magnetic moments of sites 1 and 2, respectively; $r$ is the distance between the two magnetic dipoles, $\vec{n}_{1,2}$ is the directional vector connecting the two magnetic dipoles (of unit length). $\mu_{Bohr}^2$ is the square of the Bohr magneton; with an approximate value of 0.43297 in $cm^{-1}$/T. As inferred from the above Equation, the dipolar magnetic interaction depends on the distance and on the angle between the magnetic moments on magnetic centers. Therefore, the Cartesian coordinates of all non-equivalent magnetic centers must be provided in the input.

In brief, the POLY_ANISO is performing the following operations:

1. read the input and information from the datafiles

2. build the exchange coupled basis

3. compute the magnetic exchange, magnetic dipole-dipole, and other magnetic Hamiltonians using the *ab initio*-computed spin and orbital momenta of individual magnetic sites and the input parameters

4. sum up all the magnetic interaction Hamiltonians and diagonalise the total interaction Hamiltonian

5. rewrite the spin and magnetic moment in the exchange-coupled eigenstates basis

6. use the obtained spin and magnetic momenta for the computation of the magnetic properties of entire poly-nuclear compound

The actual values of the inter-site magnetic exchange could be derived from e.g. broken-symmetry DFT calculations. Alternatively, they could be regarded as fitting parameters, while their approximate values could be extracted by minimising the standard deviation between measured and calculated magnetic data.

## 5.35.2 Files

POLY_ANISO is called independently of ORCA for now. In the future versions of ORCA we will aim for a deeper integration, for a better experience.

```
bash:$
bash:$  $ORCA/x86_64/otool_poly_aniso  <  poly_aniso.input  >  poly_aniso.output
bash:$
```

The actual names of the poly_aniso.input and poly_aniso.output are not hard coded, and can take any names. A bash script for a more convenient usage of POLY_ANISO can be provided upon request or made available on the Forum.

### Input Files

The program POLY_ANISO needs the following files:

**aniso_i.input**
> This is an ASCII text file generated by the CASSCF/SOC/ SINGLE_ANISO run. It should be provided for POLY_ANISO as aniso_i.input (i=1,2,3, etc.): one file for each magnetic center. In cases when the entire polynuclear cluster or molecule has exact point group symmetry, only aniso_i.input files for crystallographically non-equivalent centers should be given. This saves computational time since equivalent metal sites do not need to be computed *ab initio*.

**poly_aniso.input**
> The standard input file defining the computed system and various input parameters. This file can take any name.

**Output Files**

## 5.35.3 List of Keywords

This section describes the keywords used to control the `POLY_ANISO` input file. Only two keywords `NNEQ`, `PAIR` (and `SYMM` if the polynuclear cluster has symmetry) are mandatory for a minimal execution of the program, while the other keywords allow customisation of the execution of the `POLY_ANISO`.

The format of the "poly_aniso.input" file resembles to a certain extent the input file for `SINGLE_ANISO` program. The input file must start with "`&POLY_ANISO`" text.

### Mandatory Keywords Defining the Calculation

*Keywords defining the polynuclear cluster:*

`NNEQ` This keyword defines several important parameters of the calculation. On the first line after the keyword the program reads 2 values: 1) the number of types of different magnetic centers (NON-EQ) of the cluster and 2) a letter `T` or `F` in the second position of the same line. The number of NON-EQ is the total number of magnetic centers of the cluster which cannot be related by point group symmetry. In the second position the answer to the question: "Have all NON-EQ centers been computed *ab initio*?" is given: T for True and F for False. On the following line the program will read NON-EQ values specifying the number of equivalent centers of each type. On the following line the program will read NON-EQ integer numbers specifying the number of low-lying spin-orbit functions from each center forming the local exchange basis.

Some examples valid for situations where all sites have been computed *ab initio* (case T, True):

```
NNEQ
  2  T
  1  2
  2  2
```

There are two kinds of magnetic centers in the cluster; both have been computed *ab initio*; the cluster consists of 3 magnetic centers: one center of the first kind and two centers of the second kind. From each center we take into the exchange coupling only the ground doublet. As a result, the $N_{exch} = 2^1 \times 2^2 = 8$, and the two datafiles `aniso_1.input` (for-type 1) and `aniso_2.input` (for-type 2) files must be present.

```
NNEQ
  3  T
  2  1  1
  4  2  3
```

There are three kinds of magnetic centers in the cluster; all three have been computed *ab initio*; the cluster consists of four magnetic centers: two centers of the first kind, one center of the second kind and one center of the third kind. From each of the centers of the first kind we take into exchange coupling four spin-orbit states, two states from the second kind and three states from the third center. As a result the $N_{exch} = 4^2 \times 2^1 \times 3^1 = 96$. Three files `aniso_i.input` for each center ($i = 1, 2, 3$) must be present.

```
NNEQ
  6  T
  1  1  1  1  1  1
  2  4  3  5  2  2
```

There are six kinds of magnetic centers in the cluster; all six have been computed *ab initio*; the cluster consists of 6 magnetic centers: one center of each kind. From the center of the first kind we take into exchange coupling two spin-orbit states, four states from the second center, three states from the third center, five states from the fourth center and two states from the fifth and sixth centers. As a result the $N_{exch} = 2^1 \times 4^1 \times 3^1 \times 5^1 \times 2^1 \times 2^1 = 480$. Six files `aniso_i.input` for each center ($i = 1, 2, ..., 6$) must be present.

Only in cases when some centers have NOT been computed *ab initio* (i.e. for which no `aniso_i.input` file exists), the program will read an additional line consisting of NON-EQ letters ($A$ or $B$) specifying the type of each of the NON-EQ centers: $A$ - the center is computed *ab initio* and $B$ - the center is considered isotropic. On the