following number-of-B-centers line(s) the isotropic g factors of the center(s) defined as B are read. The spin of the B center(s) is defined: $S = (N-1)/2$, where N is the corresponding number of states to be taken into the exchange coupling for this particular center. Some examples valid for mixed situations: the system consists of centers computed *ab initio* and isotropic centers (case F, False):

```
NNEQ
  2   F
  1   2
  2   2
  A   B
  2.3   2.3   2.3
```

There are two kinds of magnetic centers in the cluster; the center of the first type has been computed *ab initio*, while the centers of the second type are considered isotropic with $g_X = g_Y = g_Z$=2.3; the cluster consists of three magnetic centers: one center of the first kind and two centers of the second kind. Only the ground doublet state from each center is considered for the exchange coupling. As a result the $N_{exch} = 2^1 \times 2^2 = 8$. File `aniso_i.input` (for-type 1) must be present.

```
NNEQ
  3   F
  2   1   1
  4   2   3
  A   B   B
  2.3  2.3  2.0
  2.0  2.0  2.5
```

There are three kinds of magnetic centers in the cluster; the first center type has been computed *ab initio*, while the centers of the second and third types are considered empirically with $g_X = g_Y$ =2.3; g_Z=2.0 (second type) and $g_X = g_Y$ =2.0; g_Z=2.5 (third type); 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, four spin-orbit states are considered for the exchange coupling, two states from the second kind and three states from the center of the third kind. As a result the $N_{exch} = 4^2 \times 2^1 \times 3^1 = 96$. The file `aniso_i.input` must be present.

```
NNEQ
  6   T
  1   1   1   1   1   1
  2   4   3   5   2   2
  B   B   A   A   B   A
  2.12  2.12  2.12
  2.43  2.43  2.43
  2.00  2.00  2.00
```

There are six kinds of magnetic centers in the cluster; only three centers have been computed *ab initio*, while the other three centers are considered isotropic; the g factors of the first center is 2.12 (S=1/2); of the second center 2.43 (S=3/2); of the fifth center 2.00 (S=1/2); the entire cluster consists of six magnetic centers: one center of each kind. From the center of the first kind, two spin-orbit states are considered in the exchange coupling, 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 $N_{exch} = 2^1 \times 4^1 \times 3^1 \times 5^1 \times 2^1 \times 2^1 = 480$. Three files `aniso_3.input` and `aniso_4.input` and `aniso_6.input` must be present.

There is no maximal value for NNEQ, although the calculation becomes quite heavy in case the number of exchange functions is large.

SYMM Specifies rotation matrices to symmetry equivalent sites. This keyword is mandatory in the case more centers of a given type are present in the calculation. This keyword is mandatory when the calculated polynuclear compound has exact crystallographic point group symmetry. In other words, when the number of equivalent centers of any kind i is larger than 1, this keyword must be employed. Here the rotation matrices from the one center to all the other of the same type are declared. On the following line the program will read the number 1 followed on the next lines by as many 3×3 rotation matrices as the total number of equivalent centers of type 1. Then the rotation matrices of centers of type 2, 3 and so on, follow in the same format. When the rotation matrices contain irrational numbers (e.g. $\sin \frac{\pi}{6} = \frac{\sqrt{3}}{2}$), then more digits than presented in the examples below are advised to be given: $\frac{\sqrt{3}}{2} = 0.8660254$.

Examples:

```
NNEQ
  2   F
  1   2
  2   2
  A   B
  2.3   2.3   2.3
  SYMM
  1
  1.0 0.0 0.0
  0.0 1.0 0.0
  0.0 0.0 1.0
  2
  1.0 0.0 0.0
  0.0 1.0 0.0
  0.0 0.0 1.0
 -1.0 0.0 0.0
  0.0 -1.0 0.0
  0.0 0.0 -1.0
```

The cluster computed here is a tri-nuclear compound, with one center computed *ab initio*, while the other two centers, related to each other by inversion, are considered isotropic with $g_X = g_Y = g_Z = 2.3$. The rotation matrix for the first center is I (identity, unity) since the center is unique. For the centers of type 2, there are two matrices 3×3 since we have two centers in the cluster. The rotation matrix of the first center of type 2 is Identity while the rotation matrix for the equivalent center of type 2 is the inversion matrix.

```
NNEQ
  3   F
  2   1   1
  4   2   3
  A   B   B
  2.1 2.1 2.1
  2.0 2.0 2.0
  SYMM
  1
  1.0 0.0 0.0
  0.0 1.0 0.0
  0.0 0.0 1.0
  0.0 -1.0 0.0
 -1.0 0.0 0.0
  0.0 0.0 1.0
  2
  1.0 0.0 0.0
  0.0 1.0 0.0
  0.0 0.0 1.0
  3
  1.0 0.0 0.0
  0.0 1.0 0.0
  0.0 0.0 1.0
```

In this input a tetranuclear compound is defined, all centers are computed *ab initio*. There are two centers of type "1", related one to each other by C_2 symmetry around the Cartesian Z axis. Therefore the SYMM keyword is mandatory. There are two matrices for centers of type 1, and one matrix (identity) for the centers of type 2 and type 3.

```
NNEQ
  6   F
  1   1   1   1   1   1
  2   4   3   5   2   2
  B   B   A   A   B   A
  2.12 2.12 2.12
  2.43 2.43 2.43
```

```
2.00 2.00 2.00
```

In this case the computed system has no symmetry. Therefore, the SYMM keyword is not required. End of Input Specifies the end of the input file. No keywords after this one will be processed.

Keywords Defining the Magnetic Exchange Interactions

This section defines the keywords used to set up the interacting pairs of magnetic centers and the corresponding exchange interactions.

A few words about the numbering of the magnetic centers of the cluster in the POLY_ANISO. First all equivalent centers of the type 1 are numbered, then all equivalent centers of the type 2, etc. These labels of the magnetic centers are used further for the declaration of the magnetic coupling.

PAIR or LIN1

This keyword defines the interacting pairs of magnetic centers and the corresponding exchange interaction. A few words about the numbering of the magnetic centers of the cluster in the POLY_ANISO. First all equivalent centers of the type 1 are numbered, then all equivalent centers of the type 2, etc. These labels of the magnetic centers are used now for the declaration of the magnetic coupling. Interaction Hamiltonian is:

$$\hat{H}_{Lines} = - \sum_{p=1}^{N_{pairs}} J_p \hat{s}_i \hat{s}_j,$$

where i an j are the indices of the metal sites of the interacting pair p; J_p is the user-defined magnetic exchange interaction between the corresponding metal sites; $\hat{s}_i$ and $\hat{s}_j$ are the ab initio spin operators for the low-lying exchange eigenstates.

```
PAIR
3
1 2 -0.2
1 3 -0.2
2 3  0.4
```

The input above is applicable for a tri-nuclear molecule. Two interactions are antiferromagnetic while ferro-magnetic interaction is given for the last interacting pair.

LIN3

This keyword defines a more involved exchange interaction, where the user is allowed to define 3 parameters for each interacting pair. The interaction Hamiltonian is given by:

$$\hat{H}_{Lines} = - \sum_{p=1}^{N_{pairs}} \sum_{\alpha} J_{p,\alpha} \hat{s}_{i,\alpha} \hat{s}_{j,\alpha},$$

where the α defines the Cartesian axis x, y, z.

```
LIN3
1
1 2 -0.2 -0.4 -0.6 # i, j, Jx, Jy, Jz
```

The input above is applicable for a mononuclear molecule.

LIN9

This keyword defines a more involved exchange interaction, where the user is allowed to define 9 parameters for each interacting pair. The interaction Hamiltonian is given by:

$$\hat{H}_{Lines} = - \sum_{p=1}^{N_{pairs}} \sum_{\alpha,\beta} J_{p,\alpha,\beta} \hat{s}_{i,\alpha} \hat{s}_{j,\beta},$$

where the α and β defines the Cartesian axis x, y, z.

```
LIN9
1
1 2 -0.1 -0.2 -0.3 -0.4 -0.5 -0.6 -0.7 -0.8 -0.9
# i,j,Jxx,Jxy,Jxz,Jyx,Jyy,Jyz,Jzx,Jzy,Jzz
```

The input above is applicable for a mononuclear molecule.

COOR

The `COOR` keyword turns ON the computation of the dipolar coupling for those interacting pairs which were declared under `PAIR`, `LIN3` or `LIN9` keywords. On the NON-EQ lines following the keyword the program will read the symmetrised Cartesian coordinates of NON-EQ magnetic centers: one set of symmetrised Cartesian coordinates for each type of magnetic centers of the system. The *symmetrized Cartesian coordinates* are obtained by translating the original coordinates to the origin of Coordinate system, such that by applying the corresponding SYMM rotation matrix onto the input COOR data, the position of all other sites are generated.

```
COOR
6.489149     3.745763     1.669546
5.372478     5.225861     0.505625
```

The magnetic dipole-dipole Hamiltonian is computed as follows:

$$\hat{H}_{dip} = \mu_{Bohr}^2 \sum_{p=1}^{N_{pairs}} \frac{\hat{\mu}_i \hat{\mu}_j - 3(\hat{\mu}_i \vec{n}_{i,j})(\hat{\mu}_j \vec{n}_{i,j})}{r_{i,j}^3}$$

and is added to $\hat{H}_{exch}$ computed using other models. The $\hat{H}_{dip}$ is added for all magnetic pairs.

Optional General Keywords to Control the Input

Normally `POLY_ANISO` runs without specifying any of the following keywords. However, some properties are only computed if it is requested by the respective keyword. Argument(s) to the keyword are always supplied on the next line of the input file.

MLTP

The number of molecular multiplets (i.e. groups of spin-orbital eigenstates) for which g, D and higher magnetic tensors will be calculated (default `MLTP=1`). The program reads two lines: the first is the number of multiplets (N_{MULT}) and the second the array of N_{MULT} numbers specifying the dimension (multiplicity) of each multiplet. Example:

```
MLTP
10
2 4 4 2 2 2 2 2 2 2
```

`POLY_ANISO` will compute the EPR g and D- tensors for 10 groups of states. The groups 1 and 4-10 are doublets ($\tilde{S} = |1/2\rangle$), while the groups 2 and 3 are quadruplets, having the effective spin $\tilde{S} = |3/2\rangle$. For the latter cases, the ZFS (D-) tensors will be computed. We note here that large degeneracies are quite common for exchange coupled systems, and the data for this keyword can only be rendered after the inspection of the exchange spectra.

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 0.0 K)

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

- nT - number of temperature points (Default 301)

Example:

```
TINT
0.0 300.0 331
```

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

HINT

Specifies the field points for the evaluation of the molar magnetisation. The program will read three numbers: H_{min}, H_{max}, nH.

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

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

- nH - number of field points (Default 101)

Example:

```
HINT
0.0 20.0 201
```

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

TMAG

Specifies the temperature(s) at which the field-dependent magnetisation is calculated. Default is one temperature point, T = 2.0 K.

Example:

```
TMAG
6   1.8 2.0 2.4 2.8 3.2 4.5
```

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 exchange 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`.

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:
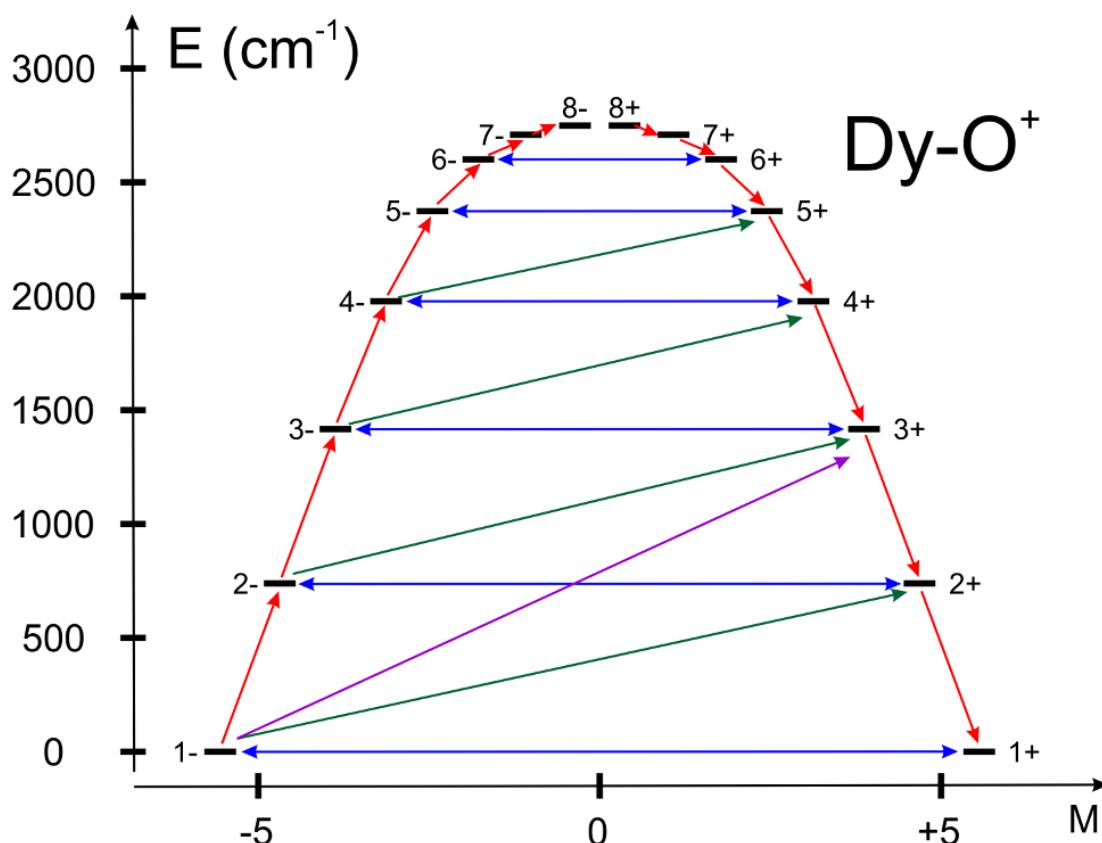
In this figure, a qualitative performance picture of the investigated single-molecular magnet is estimated by the strengths of the transition matrix elements of the magnetic moment connecting states with opposite magnetisations ($n+ \to n-$). The height of the barrier is qualitatively estimated by the energy at which the matrix element ($n+ \to n-$) 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 ($8+ \to 8-$). 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 (μ_{Bohr}). Example:

```
UBAR
```

ERAT

This flag is used to define the cut-off energy for the low-lying exchange-coupled 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`.

NCUT

This flag is used to define the cut-off energy for the low-lying exchange 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 exchange states(N_{exch}, 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.

MVEC

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

Example:

```
MVEC
4 # number of directions
1.0 0.0 0.0   # px, py, pz of each direction
0.0 1.0 0.0
0.0 0.0 1.0
1.0 1.0 1.0
```

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
6
1.0 0.0 0.0
0.0 1.0 0.0
0.0 0.0 1.0
0.0 1.0 1.0
1.0 0.0 1.0
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

This keyword allows computation of the magnetic susceptibility $\chi T(T)$ at experimental points. On the line below the keyword, the number of experimental points N_T is defined, and on the next N_T lines the program reads the experimental temperature (in K) and the experimental magnetic susceptibility (in $cm^3 K mol^{-1}$). The magnetic susceptibility routine will also print the standard deviation from the experiment.

```
TEXP
54
299.9901    55.27433
290.4001    55.45209
279.7746    55.43682
269.6922    55.41198
259.7195    55.39274
249.7031    55.34379
239.735     55.29292
229.7646    55.23266
219.7354    55.15352
209.7544    55.06556
...
```

HEXP

This keyword allows computation of the molar magnetisation $M_{mol}(H)$ at experimental points. On the line below the keyword, the number of experimental points N_H is defined, and on the next N_H lines the program reads the experimental field intensity (in Tesla) and the experimental magnetisation (in μ_{Bohr}). The magnetisation routine will print the standard deviation from the experiment.

```
HEXP
3  1.0  5.3  2.4  # temperature values
10 # numer of field points
0.30 4.17 1.26 2.51  # H(T) and M for each temperature
1.00 5.47 3.57 4.82
1.88 5.79 4.54 5.30
2.67 5.92 4.96 5.54
3.46 5.97 5.20 5.70
4.24 6.00 5.36 5.81
5.03 6.01 5.48 5.88
5.82 6.02 5.57 5.93
6.61 6.02 5.65 5.97
7.40 6.03 5.72 5.99
```

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
```

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.

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.

PRLV

This keyword controls the print level.

- 2 - normal. (Default)

- 3 or larger (debug)

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
```

5.36 DeltaSCF

`DeltaSCF` is a time-independent alternative to time-dependent DFT for the description of excited electronic states in a mean-field DFT framework and has been shown to yield better results than TDDFT in the common linear-response adiabatic approximation for the topology of an avoided crossing and a conical intersection in the ethylene molecule paradigmatic for photochemistry [758], as well as for charge transfer excited states, where the absolute error in TDDFT increases rapidly with the charge transfer distance, while a balanced description is obtained with `DeltaSCF` [759].

Typically, the SCF proceedure is used to obtain the ground electronic state represented by a minimum on the energy surface with respect to the electronic orbital rotation degrees of freedom. The idea behind ΔSCF is to converge to a higher-energy solution on the electronic energy surface, often a saddle point instead, in order to find mean-field representations of excited electronic states. As it is usually not sufficient to form an initial guess close to such an excited state solution and use conventional SCF approaches, several strategies have been developed and implemented in ORCA to make the SCF converge to the target saddle point and prevent so-called variational collapse, convergence to undesired lower-energy solutions.

One simple but often effective approach was introduced by the group of Peter Gill [760] as the Maximum Overlap Method (MOM). In ORCA, we also feature the more recent PMOM from the group of Hrant Hratchian [761]. Additionally, ORCA offers an SOSCF optimization technique that leverages the limited-memory symmetric rank-1 quasi-Newton method as well as the generalized mode following approach both capable of converging to saddle point solutions systematically. The excited state initial guess can be refined by constrained optimization within the freeze-and-release SOSCF strategy. ΔSCF has also been referred to as "orbital optimized DFT for electronic excited states" [762] and "excited state mean-field theory" [763].

Figure Fig. 5.67 shows the schematic representation of a generic HOMO-LUMO excitation in ΔSCF. First, the ground state is obtained in a regular SCF calculation. Then, the occupation numbers are changed to a non-aufbau occupation reflecting the desired excitation. For a HOMO-LUMO excitation, the HOMO in one of the two spin channels is chosen to be unoccupied, while the LUMO is occupied. This non-aufbau occupation together with the ground state orbitals is used as the initial guess for a variational saddle point search yielding a ΔSCF excited state solution.

Starting from some single reference wavefunction

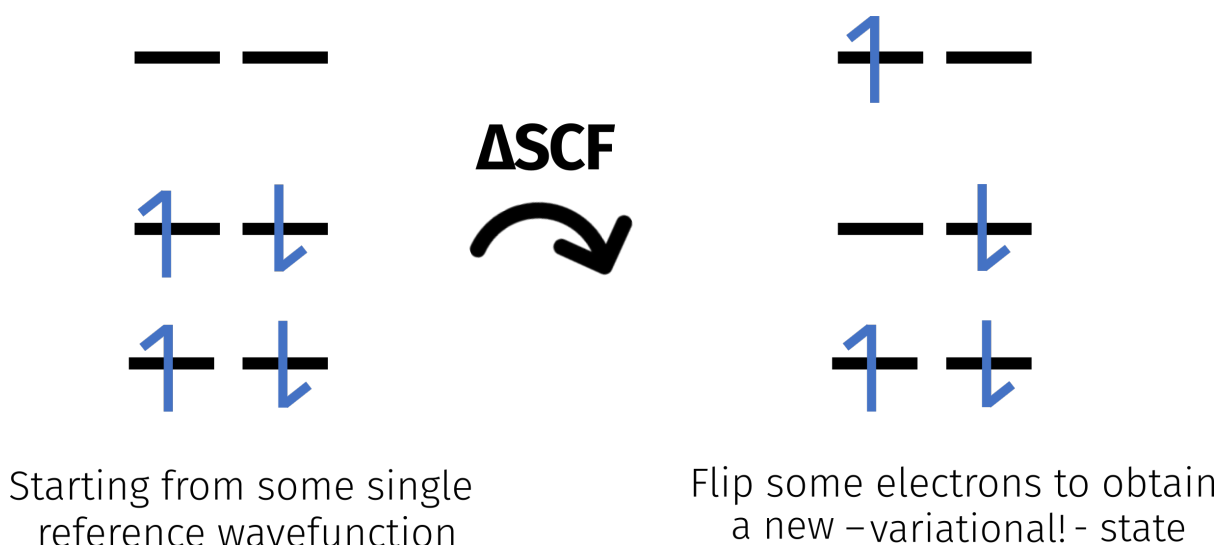Flip some electrons to obtain a new –variational! - state

Fig. 5.67: A simple scheme of a HOMO-LUMO excitation state using ΔSCF

Using ORCA's `DeltaSCF`, we can **choose** to converge the SCF to a HOMO/LUMO excited state. The excited state is obtained by fully relaxing the orbitals and can include any contributions such as the VV10 correlation or CPCM for solvation. Due to the variational optimization of the wave function, the Hellman-Feynman holds meaning that the gradient on the positions of the nuclei is available for geometry optimizations, molecular dynamics simulations, reaction path calculations, and all the other geometry search features ORCA has to offer. Additionally, all properties ORCA can calculate with a ground state SCF density can be computed with an excited state ΔSCF density as well.

> ⏸ **Important**
>
> ΔSCF states are represented by single-determinant wave functions within a DFT framework. As ground state DFT can struggle with multideterminantal cases, so can excited state DFT. Keep this in mind when tackling such cases!
>
> This description is, for instance, relatively reasonable when
>
> 1. the excited state can be described by a particle-hole interaction. That is for example **NOT** the case for the HOMO-LUMO excitation of a benzene molecule or most π-π^* excited states,
>
> 2. the occupied and virtual orbitals are separated in space such that the relevant exchange integral is zero. Examples include some n-π^* states, long-range charge transfer states etc.,
>
> 3. for closed-shell doubly excited states which can be represented by a single-determinant wavefunction.
>
> Furthermore, ΔSCF wave functions can break the symmetries of the Hamiltonian (this is true for ground and excited states). Open-shell singly excited states inherently break the spin symmetry and require spin purification [764].

5.36.1 Theory

In this section, the theory of behind the ΔSCF method is discussed.

SOSCF L-SR1 method

In ΔSCF, one searches a stationary point on the energy surface with respect to the electronic orbital rotation degrees of freedom collected in the orbital rotation matrix

$$\boldsymbol{\kappa} = \begin{pmatrix} \boldsymbol{\kappa}_{\mathrm{oo}} = 0 & \boldsymbol{\kappa}_{\mathrm{ov}} \\ -\boldsymbol{\kappa}_{\mathrm{ov}}^+ & \boldsymbol{\kappa}_{\mathrm{vv}} = 0 \end{pmatrix} \,,$$

where oo, ov, and vv represent the blocks of $\boldsymbol{\kappa}$ containing pairwise orbital rotations that mix two occupied, an occupied and a virtual, and two virtual orbitals, respectively. A stationary point is found as

$$\mathbf{C}_{\mathrm{stat}} = \mathbf{C}_0 e^{\boldsymbol{\kappa}} \,,$$

with the energy gradient being

$$\frac{\partial E}{\partial \kappa_{ij}} = \frac{2 - \delta_{ij}}{2} \left[\int_0^1 dt e^{t\boldsymbol{\kappa}} \mathbf{L} e^{-t\boldsymbol{\kappa}} \right]_{ji} = \frac{2 - \delta_{ij}}{2} \left[\mathbf{L} + \frac{1}{2!} \left[\boldsymbol{\kappa}, \mathbf{L} \right] + \frac{1}{3!} \left[\boldsymbol{\kappa}, \left[\boldsymbol{\kappa}, \mathbf{L} \right] \right] + ... \right]_{ji} \,,$$

where the right-hand side is a special case of the Baker-Campbell-Hausdorff formula and holds because the space of $\boldsymbol{\kappa}$ forms the Lie algebra corresponding to the Lie group of its exponential. Since the gradient is always zero for all elements of $\boldsymbol{\kappa}_{\mathrm{oo}}$ and $\boldsymbol{\kappa}_{\mathrm{vv}}$, those blocks of $\boldsymbol{\kappa}$ are dropped as degrees of freedoms in the optimization. As $e^{\boldsymbol{\kappa}}$ is required to be unitary, $\boldsymbol{\kappa}$ is required to be anti-Hermitian, dropping several orbital rotations as degrees of freedom in the optimization.

The saddle point search is performed using the L-SR1 quasi-Newton optimizer, which is capable of forming an indefinite model Hessian, starting from an excited state initial guess. To increase the performance of the method and make it more robust, the following standard SOSCF preconditioner is used and allowed to become indefinite as well:

$$\frac{\partial^2 E}{\partial \kappa_{ij}^2} \approx 2 \left(f_j - f_i \right) \left(\epsilon_i - \epsilon_j \right) \,,$$

where f_i is the occupation number of orbital i and ϵ_i its energy.

Generalized Mode Following

The generalized mode following (GMF) method [765, 766] is a more robust but also a bit more expensive saddle point search method that can be used to converge to ΔSCF excited state solutions. The method recasts the saddle point search as a minimization by modifying the gradient, such that it corresponds to a modified objective function that has a minimum where the energy function has the target saddle point. Now, a minimization can be performed to locate the target saddle point corresponding to the desired excited state, meaning the robust L-BFGS optimizer can be used instead of the L-SR1 optimizer, the preconditioner can be made positive-definite, and variational collapse to lower-energy solutions other than the targeted one becomes impossible by construction, making MOM unnecessary with GMF. For this to work, the saddle point order n of the target solution needs to be estimated at the start of the calculation, and the lowest n eigenpairs of the electronic Hessian need to be evaluated at every electronic optimization step with a finite difference Davidson method.

Once the lowest n eigenvectors v_i of electronic Hessian are evaluated at each optimization step, the modified gradient is calculated as

$$g^{\mathrm{mod}} = g - 2 \sum_{i=1}^{n} v_i v_i^{\mathrm{T}} g \,.$$

5.36.2 Freeze-and-release strategy

In tricky cases, particularly those where the excitation leads to a large amount of charge transfer, it can be advantageous to shift to a freeze-and-release SOSCF strategy [767], which converges the DeltaSCF in two steps:

```
1. A constrained optimization freezing all orbitals that are excited, i.e. those↵
 ↪orbitals
   for which the occupation numbers differ from the aufbau occupation. This step↵
 ↪reduces
   to a minimization for the unconstrained orbitals.

2. An unconstrained optimization as usual.
```

Step 1 accounts for the orbital relaxation effect due to the first-order change in the electron density after the excitation on the orbitals that are not involved in the excitation. It can be regarded as an elaborate way of generating a very good initial guess for the excited state saddle point search in step 2.

5.36.3 Input and examples

In this section, some example calculations are presented together with the input.

First Example: HOMO-LUMO Excited State of Formaldehyde

Let's begin by trying to converge to the first excited state of formaldehyde and optimize the geometry in that electronic state starting from the regular planar structure:

```
!PBE DEF2-TZVP OPT FREQ DELTASCF UHF
%SCF ALPHACONF 0,1 END
* XYZ 0 1
C      0.000000    0.000000   -0.602985
O      0.000000    0.000000    0.605394
H      0.000000    0.934673   -1.182175
H      0.000000   -0.934673   -1.182175
*
```

Besides the regular keywords such as method, basis set, `OPT` and `FREQ`, one needs to specify `DELTASCF` in the simple input and in this case `UHF` since the alpha and beta orbitals will be different due to the single excitation (for doubly-excited states `RHF` might be sufficient).

It is also necessary to add the `ALPHACONF` or `BETACONF` under the `%SCF` block. That is a minimal representation of the configuration you want to converge to. In this case, `0,1` means a HOMO/LUMO transition, where the HOMO has occupation zero and LUMO occupation one. For a HOMO-1/LUMO transition, it would be `ALPHACONF 0, 1,1`. For a HOMO/LUMO+1 it would be `ALPHACONF 0,0,1` and so on. Just picture what the frontier orbital occupation should look like. Any orbital below the first zero is assumed to be occupied and any orbital above the last occupied is assumed to be empty.

After the regular startup, the ΔSCF-specific print shows:

```
------------------------------
DELTA-SCF INITIAL CONFIGURATION
------------------------------

Alpha: 1.00 1.00 1.00 0.00 1.00 0.00 0.00 0.00
Beta : 1.00 1.00 1.00 1.00 0.00 0.00 0.00 0.00

Hessian update                            ... L-SR1
Aufbau metric                             ... MOM
Keep initial reference                    ... true
```

Here you can follow the initial configuration and some other important things:

1. `Hessian update` refers to which method will be used for the SOSCF Hessian update. ORCA's default is `L-BFGS`, which forces the electronic Hessian to be positive definite and will always push the system down to a minimum. As we want to go to a saddle point, the `L-SR1` is set by default for `DeltaSCF`. More details on Hessian updates and their consequences at this reference from the group of Hannes Jónsson [768].

2. `Aufbau metric` is the way one measures the "overlap" between the actual and reference wave functions (more details in [761]). It is `MOM` by default, but can be also set to `%SCF PMOM TRUE END` to use `PMOM`.

3. `Keep initial reference TRUE` means we will always try to keep the initial reference state defined after the guess phase. That is sometimes called `IMOM` in the literature [769]. If `%SCF KEEPINITIALREF FALSE END` is set, it is always the last SCF iteration that is taken as reference.

> ⏸ **Important**
>
> Here we are using the orbitals of the `PMODEL` guess because it is trivial. In general, we recommend always starting the SCF by reading the orbitals of a previously converged ground state SCF! Please check *Restarting SCF Calculations* for more info on that.

This calculation trivially converges in 12 steps:

```
-----------------------------------D-I-I-S-----------------------------------
↪--------
Iteration    Energy (Eh)           Delta-E    RMSDP    MaxDP    DIISErr   Damp ␣
↪Time(sec)
-----------------------------------------------------------------------------
↪--------
             ***  Starting incremental Fock matrix formation  ***
MOM changed the orbital occupation numbers
   1    -114.2533654537761123    0.00e+00  2.06e-03  6.64e-02  7.14e-02  0.700 ␣
↪0.1
MOM changed the orbital occupation numbers
   2    -114.2675698961360382   -1.42e-02  4.71e-04  1.46e-02  3.08e-02  0.700 ␣
↪0.1
                          ***Turning on AO-DIIS***
MOM changed the orbital occupation numbers
   3    -114.2754325617175226   -7.86e-03  1.98e-04  3.98e-03  2.21e-02  0.700 ␣
↪0.1
MOM changed the orbital occupation numbers
   4    -114.2806616906060100   -5.23e-03  4.98e-04  6.40e-03  1.60e-02  0.000 ␣
↪0.1
MOM changed the orbital occupation numbers
                        *** Initializing SOSCF ***
-----------------------------------S-O-S-C-F---------------------------------
↪---
Iteration    Energy (Eh)           Delta-E    RMSDP    MaxDP    MaxGrad   ␣
↪Time(sec)
-----------------------------------------------------------------------------
↪---
   5    -114.2932665018211225   -1.26e-02  7.19e-05  1.55e-03  2.33e-03    0.1
           *** Restarting incremental Fock matrix formation ***
                       *** Restarting Hessian update ***
   6    -114.2932913947584979   -2.49e-05  5.82e-05  1.33e-03  1.11e-03    0.1
   7    -114.2932671856877818    2.42e-05  2.54e-05  5.00e-04  2.58e-03    0.1
   8    -114.2932914986330530   -2.43e-05  1.76e-05  3.20e-04  1.02e-03    0.1
   9    -114.2932961472105404   -4.65e-06  2.13e-06  6.94e-05  6.42e-05    0.1
  10    -114.2932961779292640   -3.07e-08  2.99e-05  1.10e-03  8.27e-06    0.1
  11    -114.2932921911087050    3.99e-06  3.05e-05  1.12e-03  5.44e-04    0.1
  12    -114.2932961794015654   -3.99e-06  2.45e-08  5.31e-07  2.39e-07    0.1
              *** Gradient check signals convergence ***
```

> **ℹ Note**
>
> The statement `MOM changed the orbital occupation numbers` is normal, it is just printing what it is doing. Nothing to worry about.

and one can see from the spin contamination, that this is indeed an open-shell singlet:

```
----------------------
UHF SPIN CONTAMINATION
----------------------


Warning: in a DFT calculation there is little theoretical justification to
         calculate <S**2> as in Hartree-Fock theory. We will do it anyways
         but you should keep in mind that the values have only limited relevance

Expectation value of <S**2>     :     1.006910
Ideal value S*(S+1) for S=0.0   :     0.000000
Deviation                       :     1.006910
```

The gradient is then computed, and the geometry is optimized until convergence. Finally the frequencies show this is actually not a minimum, but a saddle point on the geometry space!

```
----------------------
VIBRATIONAL FREQUENCIES
----------------------


Scaling factor for frequencies =  1.000000000  (already applied!)

     0:        0.00 cm**-1
     1:        0.00 cm**-1
     2:        0.00 cm**-1
     3:        0.00 cm**-1
     4:        0.00 cm**-1
     5:        0.00 cm**-1
     6:     -591.31 cm**-1 ***imaginary mode***
     7:      799.56 cm**-1
     8:     1228.37 cm**-1
     9:     1271.29 cm**-1
    10:     2971.77 cm**-1
    11:     3067.96 cm**-1
```

The reason is: the HOMO/LUMO transition on formaldehyde populates the π^* LUMO, thus breaking the double bound and making the carbon atom pyramidal. If one starts from a slightly distorted structure, it then converges to the actual geometry minimum. Starting from a pyramidal structure:

```
!wB97M-D4 DEF2-TZVP DELTASCF UHF OPT FREQ
%SCF ALPHACONF 0,1 END
* XYZ 0 1
C         0.00000        0.00000       -0.60298
O        -0.74131       -0.10909        0.45746
H         0.00000        0.93467       -1.18217
H         0.00000       -0.93467       -1.18217
*
```

now converges to a minimum, as shown by the absence of negative frequencies:

```
----------------------
VIBRATIONAL FREQUENCIES
----------------------


Scaling factor for frequencies =  1.000000000  (already applied!)
```

```
 0:       0.00 cm**-1
 1:       0.00 cm**-1
 2:       0.00 cm**-1
 3:       0.00 cm**-1
 4:       0.00 cm**-1
 5:       0.00 cm**-1
 6:     713.25 cm**-1
 7:     826.75 cm**-1
 8:    1206.57 cm**-1
 9:    1292.70 cm**-1
10:    2826.06 cm**-1
11:    2893.16 cm**-1
```

The final geometry is surprisingly accurate for the gas phase formaldehyde, too! We will also show the results here using the range-corrected, meta-GGA hybrid `wB97M-D4` and the double-hybrid DFT `!B2PLYP DEF2-QZVPP AUTOAUX`, just to show that MP2 also works.

Table 5.23: Geometry of gas phase formaldehyde versus the DeltaSCF results, in Angstroem and degrees.

parameter	exp.	PBE	wB97M-D4	B2PLYP
r(C-O)	1.323	1.300	1.310	1.311
r(C-H)	1.098	1.113	1.093	1.090
∠HCH	118.8	115.0	117.0	116.8
∠OOP	34.0	41.1	36.5	37.0

- exp. taken from [760].

> **Important**
>
> We are using the default ground state SCF algorithm here, `AO-DIIS + SOSCF` because this is relatively simple. In general and for more complicated cases, we suggest using the approximate second-order method, to avoid escaping back to the ground state with `!NODIIS NOTRAH`, which is the default for ΔSCF.

> **Important**
>
> Do **NOT** combine ΔSCF wavefunctions with CCSD, or any such method with single excitations. It requires a speciallized version of CC which we don't have yet.

> **Important**
>
> When running the same calculation above with `wB97M-D4`, there will **not** be a virtual orbital between the alpha HOMO-1 and the HOMO (so no negative HOMO-LUMO gap). There is nothing wrong here, it just optimized the orbitals to the excited state such that the occupation numbers correspond to an aufbau occupation. Hybrid functionals tend to lower the energy of the occupied orbitals with respect to the virtual orbitals.
>
> The energy is still higher than the non-ΔSCF solution and if you plot the orbitals you will see that the alpha HOMO is now a π orbital instead of an n. The eigenvalues of the electronic Hessian indicate that this solution is a first-order saddle point.

Core-ionized States

Another big advantage of the ΔSCF is the possibility to converge to core-excited and/or core-ionized states. We have a simple keyword to remove electrons from any orbital, even the deep core ones:

```
%SCF IONIZEALPHA 2 END
```

and the electron from orbital number two will be removed. `IONIZEBETA` works for beta orbitals. One can start from an anion UHF electronic structure obtained by adding one extra electron and remove a core electron like this to obtain core-excited states too. Geometry optimization, EPR, and even TDDFT calculations are all valid for these states.

As an example, the input below will ionize the 1s electron from a water molecule, which corresponds to MO 0 here:

```
!PBE0 DEF2-TZVP DELTASCF NODIIS UHF
%SCF IONIZEALPHA 0 END
* xyz 0 1
  O     2.127880   -0.361920    0.104770
  H     3.117210   -0.387460    0.070360
  H     1.838520   -0.926280   -0.655730
*
```

> **ⓘ Note**
>
> If the orbital is not localized over a single atom, one might need to localized them first!

and one can see from the results that is exactly what it converges to.

```
----------------
ORBITAL ENERGIES
----------------
              SPIN UP ORBITALS
  NO   OCC        E(Eh)          E(eV)
   0  0.0000    -20.108086     -547.1688
   1  1.0000     -1.567415      -42.6515
   2  1.0000     -1.057257      -28.7694
   3  1.0000     -0.939315      -25.5601
   4  1.0000     -0.882871      -24.0241
   5  0.0000     -0.304254       -8.2792
   6  0.0000     -0.239285       -6.5113
   7  0.0000      0.044344        1.2066
       (...)
```

> **ⓘ Note**
>
> ORCA automatically adjusts charge and multiplicity here. **The input should contain those from the reference system!**

Here are some examples of binding energies for 1s electrons. The atom from where it was removed is highlighted in bold:

Table 5.24: Binding energies from 1s electrons found by DeltaSCF using wB97M-V/DEF2-TZVPP, in eV.

1s ionization	exp.	wB97M-V
H2**O**	539.82	541.17
CO2	297.69	299.10
NH3	405.56	406.82
CH3C**N**	405.64	406.92

- exp. taken from [770]

Diabatic Couplings

ΔSCF is also a quite accurate method to obtained diabatic couplings, which can later be used in Markus theory to compute electron transfer rates. These can be computed by calculating the energy difference between electron transfer states and using the Generalized Mulliken-Hush Approach (GMH). For more details please check for example this paper from the group of Blumberger [771].

There is not enough space to go through the details here, but one can get these diabatic coupling from essentially one regular SCF for the ground state + a ΔSCF for the excited state. For symmetric systems, this is trivial:

$$2|H_{ab}| = \Delta E_{12}$$

where states a and b are diabatic states, and ΔE_{12} is the energy difference between adiabatic states 1 and 2 (which are obtained via SCF solution). Here is an example of the diabatic couplings obtained for a benzene dimer, obtained by starting from the ground state cation and exciting the beta electron with:

```
%SCF BETACONF 0,1 END
```

Table 5.25: Diabatic couplings found by ΔSCF using wB97M-V/DEF2-TZVPP, in meV.

Distance in Ang	MRCI+Q	wB97M-V	TD-DFT
3.5	435.2	473.1	593
4.0	214.3	236.7	374
4.5	104.0	115.9	267.5
5.0	51.70	56.7	218.5

- MRCI+Q taken from [771]

Generalized Mode Following

For an example GMF calculation, we return to the formaldehyde molecule, this time targeting a HOMO-LUMO+1 excitation to keep it interesting and add the simple input keyword `GMF`:

```
!WB97X-D4 DEF2-SVP UKS DELTASCF GMF
%SCF ALPHACONF 0,0,1 END
* XYZ 0 1
O       -3.54418        1.61112         0.04891
C       -4.12047        0.61074        -0.35955
H       -3.36418       -0.41948        -0.79627
H       -4.84699        0.73407        -1.42962
*
```

If not provided in the input, the target saddle point order is estimated either by using the orbital energies or by evaluating the number of negative eigenvalues of the electronic Hessian. In the former case, the target saddle point order is approximated as the number of pairs of an occupied and a virtual orbital where the occupied orbital has a larger energy than the virtual orbital at the excited state initial guess after the excitation has been performed. In our example, this yields a saddle point order of 2, as is estimated by default and printed together with some other default input parameters in the `DeltaSCF` block:

```
------------------------------
DELTA-SCF INITIAL CONFIGURATION
------------------------------


Alpha: 1.00 1.00 1.00 0.00 0.00 1.00 0.00 0.00 0.00
Beta : 1.00 1.00 1.00 1.00 0.00 0.00 0.00 0.00 0.00
```

```
Hessian update                           ... L-BFGS/GMF
Generalized mode following:
 Target saddle point order               ... 2
 Finite difference generalized Davidson method:
  Finite difference mode                 ... Forward
  Finite difference step size            ... 1.000e-03
  Max. size of Krylov subspace           ... 20
  Convergence tolerance                  ... 1.000e-02
  Max. number of iterations              ... 100
Aufbau metric                            ... Fixed occupations
```

Before every optimization step, the lowest 2 (same as target saddle point order) eigenpairs of the electronic Hessian are evaluated, and once converged below the tolerance, the eigenvalues are printed, e.g. for the first optimization step:

```
Solving for 2 Hessian eigenvectors
    It.    Root MAX Err.:           1          2
    1                       6.520e-02  6.276e-02
    2                       3.193e-02  2.817e-02
    3                       1.511e-02  9.423e-03
    4                       3.889e-03  9.417e-03
    Eigenvalues:           -3.316e-01 -2.404e-01
```

After a few optimization steps, the evaluation of the Hessian eigenpairs requires no further adjustments, so that the Davidson runs converge immediately:

```
      Solving for 2 Hessian eigenvectors
          It.    Root MAX Err.:         1          2
          1                       5.165e-03  8.433e-03
          Eigenvalues:           -2.574e-01 -1.792e-01
   11    -114.1023998750192305   -1.06e-05  1.06e-03  1.96e-02  5.46e-04    1.3
      Solving for 2 Hessian eigenvectors
          It.    Root MAX Err.:         1          2
          1                       5.755e-03  8.231e-03
          Eigenvalues:           -2.575e-01 -1.791e-01
   12    -114.1024101850037624   -1.03e-05  6.43e-04  1.25e-02  3.11e-04    1.3
      Solving for 2 Hessian eigenvectors
          It.    Root MAX Err.:         1          2
          1                       6.190e-03  8.354e-03
          Eigenvalues:           -2.575e-01 -1.790e-01
   13    -114.1024129524389963   -2.77e-06  3.67e-04  7.30e-03  2.00e-04    1.3
      Solving for 2 Hessian eigenvectors
          It.    Root MAX Err.:         1          2
          1                       6.264e-03  8.286e-03
          Eigenvalues:           -2.574e-01 -1.790e-01
   14    -114.1024142211099530   -1.27e-06  8.68e-05  1.34e-03  1.46e-04    1.3
      Solving for 2 Hessian eigenvectors
          It.    Root MAX Err.:         1          2
          1                       6.396e-03  8.439e-03
          Eigenvalues:           -2.574e-01 -1.790e-01
   15    -114.1024145538739987   -3.33e-07  4.56e-05  7.31e-04  9.17e-05    1.3
          **** Energy Check signals convergence ****
```

In this simple example, one would expect the configuration to be conserved during the optimization. This is not the case here, again, because a hybrid functional is used. The occupied orbitals are stabilized with respect to the virtual ones leading to this configuration:

```
----------------
ORBITAL ENERGIES
----------------
            SPIN UP ORBITALS
  NO   OCC          E(Eh)            E(eV)
```

```
   0   1.0000     -19.374322     -527.2021
   1   1.0000     -10.431285     -283.8497
   2   1.0000      -1.258409      -34.2430
   3   1.0000      -0.755807      -20.5666
   4   1.0000      -0.635639      -17.2966
   5   1.0000      -0.591213      -16.0877
   6   1.0000      -0.584445      -15.9036
   7   0.0000      -0.143277       -3.8988
   8   1.0000      -0.113247       -3.0816
   9   0.0000      -0.061224       -1.6660
  10   0.0000       0.146574        3.9885
  11   0.0000       0.251438        6.8420
  12   0.0000       0.490702       13.3527
  13   0.0000       0.537161       14.6169
  14   0.0000       0.565655       15.3923
  15   0.0000       0.624632       16.9971
  16   0.0000       0.649717       17.6797
  17   0.0000       0.710983       19.3468
  18   0.0000       0.928559       25.2674
```

The two lowest eigenvalues of the Hessian at the last optimization step are clearly negative, so this solution is a second-order saddle point, as expected and targeted in the optimization. Do not rely on the configuration to determine the saddle point order if you use hybrid functionals!

Freeze-and-release strategy

Let's take a look at a tricky excited state of the 90-degrees-twisted N-phenylpyrrole molecule. We first perform a ground state SCF calculation without `DeltaSCF` using this input:

```
!UKS aug-cc-pVDZ PBE

*xyz 0 1
C      10.13954933     10.09711395     12.38421108
C      11.34646202     10.09711395     13.07460199
C       8.93263664     10.09711395     13.07460199
C      10.13954933     10.09711395     15.16101197
C      11.34465495     10.09711395     14.46510328
C       8.93444370     10.09711395     14.46510328
C      10.13954933     11.21630306     10.16939448
C      10.13954933      8.97792484     10.16939448
C      10.13954933     10.80761594      8.85675649
C      10.13954933      9.38661196      8.85675649
N      10.13954933     10.09711395     10.96513494
H      12.26979504     10.09711395     12.51888639
H       8.00930362     10.09711395     12.51888639
H      12.27909865     10.09711395     15.00190089
H       8.00000000     10.09711395     15.00190089
H      10.13954933     10.09711395     16.23847837
H      10.13954933     12.19422790     10.60962753
H      10.13954933      8.00000000     10.60962753
H      10.13954933     11.45309491      8.00000000
H      10.13954933      8.74113299      8.00000000
*
```

This calculation yields an energy of -440.702 E_h and a dipole moment of 2.181 D. Now we perform an excited state calculation with `DeltaSCF` starting from this converged ground state solution and exciting an electron from the HOMO to the LUMO in the alpha spin channel with this input:

```
!UKS aug-cc-pVDZ PBE DeltaSCF
!SOSCF NoDIIS NoTRAH
```

```
!MORead
!SCFCheckGrad

%moinp "gs.gbw"

%scf
AlphaConf 0,1
DoMOM false
SOSCFMaxStep 0.1
end

*xyz 0 1
C      10.13954933      10.09711395      12.38421108
C      11.34646202      10.09711395      13.07460199
C       8.93263664      10.09711395      13.07460199
C      10.13954933      10.09711395      15.16101197
C      11.34465495      10.09711395      14.46510328
C       8.93444370      10.09711395      14.46510328
C      10.13954933      11.21630306      10.16939448
C      10.13954933       8.97792484      10.16939448
C      10.13954933      10.80761594       8.85675649
C      10.13954933       9.38661196       8.85675649
N      10.13954933      10.09711395      10.96513494
H      12.26979504      10.09711395      12.51888639
H       8.00930362      10.09711395      12.51888639
H      12.27909865      10.09711395      15.00190089
H       8.00000000      10.09711395      15.00190089
H      10.13954933      10.09711395      16.23847837
H      10.13954933      12.19422790      10.60962753
H      10.13954933       8.00000000      10.60962753
H      10.13954933      11.45309491       8.00000000
H      10.13954933       8.74113299       8.00000000
*
```

This simple-seeming excitation leads to a large charge transfer from the phenyl group to the pyrrole group which makes this excited state tricky to converge. To this end, we reduce the maximum step size of the SOSCF optimization from 0.2 (default) to 0.1 with `SOSCFMaxStep 0.1` and deactivate MOM with `DoMOM false` since MOM tends to become counterproductive for cases with heavy charge transfer. We also use only SOSCF and deactivate DIIS and TRAH using the simple input `!SOSCF NoDIIS NoTRAH` and force a convergence check for the SOSCF gradient with `!SCFCheckGrad`. The latter amounts to personal preference.

This calculation converges to a solution with an excitation energy of 189 mE_h and a dipole moment difference to the ground state of 4.958 D, which are both smaller than expected for this heavy charge transfer state. This is known as a variational collapse, i.e. the calculation converged to a lower-energy solution than desired.

To counteract this variational collapse, we use the freeze-and-release SOSCF approach by adding `FreezeAndRelease` (or `FRSOSCF`) to the simple input line:

```
!UKS aug-cc-pVDZ PBE DeltaSCF FreezeAndRelease
!MORead
!SCFCheckGrad

%moinp "gs.gbw"

%scf
AlphaConf 0,1
DoMOM 0
SOSCFConvFactor 500
SOSCFMaxStep 0.1
end
```