

(continued from previous page)

```

↪0.000 eV
AI-Root 14: E(AI)=      7.856 eV -> LF-Root 14:      7.856 eV   S= 1.000 Delta=  -
↪0.000 eV
RMS error for this block =      0.000 eV =      0.0 cm**-1

Total RMS error g=      0.000 eV =      0.0 cm**-1
Note: Dropped RMS error for the reference energy.

Confidence intervals (95) computed from the square root of the
diagonal elements of the covariance matrix:
H(dz2 ,dz2 )= 0.000000000 a.u. =      0.000 eV =      0.0 cm**-1
H(dxz ,dz2 )= 0.000000000 a.u. =      0.000 eV =      0.0 cm**-1
H(dxz ,dxz )= 0.000000000 a.u. =      0.000 eV =      0.0 cm**-1
H(dyz ,dz2 )= 0.000000000 a.u. =      0.000 eV =      0.0 cm**-1
H(dyz ,dxz )= 0.000000000 a.u. =      0.000 eV =      0.0 cm**-1
H(dyz ,dyz )= 0.000000000 a.u. =      0.000 eV =      0.0 cm**-1
H(dx2-y2,dz2 )= 0.000000000 a.u. =      0.000 eV =      0.0 cm**-1
H(dx2-y2,dxz )= 0.000000000 a.u. =      0.000 eV =      0.0 cm**-1
H(dx2-y2,dyz )= 0.000000000 a.u. =      0.000 eV =      0.0 cm**-1
H(dx2-y2,dx2-y2)= 0.000000000 a.u. =      0.000 eV =      0.0 cm**-1
H(dxy ,dz2 )= 0.000000000 a.u. =      0.000 eV =      0.0 cm**-1
H(dxy ,dxz )= 0.000000000 a.u. =      0.000 eV =      0.0 cm**-1
H(dxy ,dyz )= 0.000000000 a.u. =      0.000 eV =      0.0 cm**-1
H(dxy ,dx2-y2)= 0.000000000 a.u. =      0.000 eV =      0.0 cm**-1
H(dxy ,dxy )= 0.000000000 a.u. =      0.000 eV =      0.0 cm**-1
F2dd      = 0.000000000 a.u. =      0.000 eV =      0.0 cm**-1
F4dd      = 0.000000000 a.u. =      0.000 eV =      0.0 cm**-1
Pearson's correlation coefficient =      1.000 (should be close to 1)

```

```

Calculating statistical parameters          ... done

Reference energy AI-LFT =    -38.134345028 au
Reference energy AI      =    -38.134150221 au

-----
COMPARISON OF AB INITIO AND LIGAND FIELD RESULTS
-----

Block 1
-----
AI-Root 0: E(AI)=    -0.000 eV -> LF-Root 0:      0.000 eV   S= 0.933 Delta=  -
↪0.000 eV
AI-Root 1: E(AI)=      0.000 eV -> LF-Root 1:      0.000 eV   S= 0.769 Delta=  -
↪0.000 eV
AI-Root 2: E(AI)=      0.001 eV -> LF-Root 2:      0.000 eV   S= 0.773 Delta=  ↵
↪0.000 eV
AI-Root 3: E(AI)=      0.001 eV -> LF-Root 3:      0.000 eV   S= 0.742 Delta=  ↵
↪0.001 eV
AI-Root 4: E(AI)=      0.002 eV -> LF-Root 4:      0.000 eV   S= 0.750 Delta=  ↵
↪0.001 eV
AI-Root 5: E(AI)=      0.003 eV -> LF-Root 5:      0.001 eV   S= 0.931 Delta=  ↵
↪0.002 eV
AI-Root 6: E(AI)=      0.003 eV -> LF-Root 6:      0.001 eV   S= 0.998 Delta=  ↵
↪0.003 eV
AI-Root 7: E(AI)=      2.195 eV -> LF-Root 7:      2.266 eV   S= 1.000 Delta=  -
↪0.070 eV
AI-Root 8: E(AI)=      2.195 eV -> LF-Root 8:      2.266 eV   S= 0.998 Delta=  -
↪0.070 eV
AI-Root 9: E(AI)=      2.195 eV -> LF-Root 9:      2.266 eV   S= 0.998 Delta=  -
↪0.070 eV
RMS error for this block =      0.039 eV =     311.1 cm**-1

```

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```

Block      2
-----
AI-Root    0: E(AI)=      1.812 eV -> LF-Root    0:      1.875 eV      S= 0.825 Delta=  -
↳0.063 eV
AI-Root    1: E(AI)=      1.812 eV -> LF-Root    1:      1.875 eV      S= 0.938 Delta=  -
↳0.063 eV
AI-Root    2: E(AI)=      1.812 eV -> LF-Root    2:      1.875 eV      S= 1.000 Delta=  -
↳0.063 eV
AI-Root    3: E(AI)=      1.812 eV -> LF-Root    3:      1.875 eV      S= 1.000 Delta=  -
↳0.063 eV
AI-Root    4: E(AI)=      1.812 eV -> LF-Root    4:      1.875 eV      S= 0.773 Delta=  -
↳0.063 eV
AI-Root    5: E(AI)=      2.987 eV -> LF-Root    5:      2.932 eV      S= 0.955 Delta=  ⬇
↳0.056 eV
AI-Root    6: E(AI)=      2.987 eV -> LF-Root    6:      2.932 eV      S= 0.910 Delta=  ⬇
↳0.055 eV
AI-Root    7: E(AI)=      2.988 eV -> LF-Root    7:      2.932 eV      S= 0.874 Delta=  ⬇
↳0.056 eV
AI-Root    8: E(AI)=      2.988 eV -> LF-Root    8:      2.932 eV      S= 0.792 Delta=  ⬇
↳0.056 eV
AI-Root    9: E(AI)=      2.988 eV -> LF-Root    9:      2.932 eV      S= 0.796 Delta=  ⬇
↳0.056 eV
AI-Root   10: E(AI)=      2.988 eV -> LF-Root   10:      2.932 eV      S= 0.808 Delta=  ⬇
↳0.056 eV
AI-Root   11: E(AI)=      2.988 eV -> LF-Root   11:      2.932 eV      S= 0.971 Delta=  ⬇
↳0.056 eV
AI-Root   12: E(AI)=      2.988 eV -> LF-Root   12:      2.932 eV      S= 0.994 Delta=  ⬇
↳0.056 eV
AI-Root   13: E(AI)=      2.989 eV -> LF-Root   13:      2.932 eV      S= 0.994 Delta=  ⬇
↳0.057 eV
AI-Root   14: E(AI)=      7.122 eV -> LF-Root   14:      7.241 eV      S= 1.000 Delta=  -
↳0.119 eV
RMS error for this block =      0.064 eV =      519.6 cm**-1

Total RMS error g=      0.057 eV =      457.2 cm**-1
Note: Dropped RMS error for the reference energy.

Confidence intervals (95) computed from the square root of the
diagonal elements of the covariance matrix:
H(dz2      ,dz2      )= 0.000523387 a.u. =      0.014 eV =      114.9 cm**-1
H(dxz      ,dz2      )= 0.000393965 a.u. =      0.011 eV =      86.5 cm**-1
H(dxz      ,dxz      )= 0.000523387 a.u. =      0.014 eV =      114.9 cm**-1
H(dyz      ,dz2      )= 0.000393965 a.u. =      0.011 eV =      86.5 cm**-1
H(dyz      ,dxz      )= 0.000393965 a.u. =      0.011 eV =      86.5 cm**-1
H(dyz      ,dyz      )= 0.000523387 a.u. =      0.014 eV =      114.9 cm**-1
H(dx2-y2,dz2      )= 0.000393965 a.u. =      0.011 eV =      86.5 cm**-1
H(dx2-y2,dxz      )= 0.000393965 a.u. =      0.011 eV =      86.5 cm**-1
H(dx2-y2,dyz      )= 0.000393965 a.u. =      0.011 eV =      86.5 cm**-1
H(dx2-y2,dx2-y2)= 0.000523387 a.u. =      0.014 eV =      114.9 cm**-1
H(dxy      ,dz2      )= 0.000393965 a.u. =      0.011 eV =      86.5 cm**-1
H(dxy      ,dxz      )= 0.000393965 a.u. =      0.011 eV =      86.5 cm**-1
H(dxy      ,dyz      )= 0.000393965 a.u. =      0.011 eV =      86.5 cm**-1
H(dxy      ,dx2-y2)= 0.000393965 a.u. =      0.011 eV =      86.5 cm**-1
H(dxy      ,dxy      )= 0.000523387 a.u. =      0.014 eV =      114.9 cm**-1
F2dd      = 0.002351095 a.u. =      0.064 eV =      516.0 cm**-1
F4dd      = 0.003038264 a.u. =      0.083 eV =      666.8 cm**-1
Pearson's correlation coefficient =      1.000 (should be close to 1)

```

Several utilities are offered for more specialized tasks that provide better control of the AILFT inputs and outputs:

- Skipping orbital optimization or reading in previously computed orbitals can be requested in two ways:

1. By the !NoIter keyword in the command line
 2. By the AILFT_SkipOrbOpt in the ailft block (see example below)
- Estimating F0 SCPs or Racah A from single zeta Slater Exponents can be requested from the AILFT_EffectiveSlaterExponents true keyword in the ailft block
 - For the above task the knowledge of the principle quantum numbers is required. This can be specified in two ways:
 1. By the AILFT_PQN x keyword in the ailft block (x=3 for 3d)
 2. By the LFTCase x keyword (LFTCase 3d, omitting in this way the ActOrbs dOrbs keyword)

Let us see how all the above translates in the above example of the $\text{Ni}^{2+} d^8$ ion

```
!NoIter NEVPT2 def2-SVP def2-SVP/C

%casscf
  nel 8
  norb 5
  LFTCase 3d
  mult 3,1
  nroots 10,15
  ailft
    #AILFT_SkipOrbOpt true (An alternative to NoIter)
    #AILFT_PQNs 3 (Works together with ActOrbs dOrbs as an alternative to LFTCase 3d)
    AILFT_SlaterExponents true
  end
  rel
    dosoc true
  end
end

*xyz 2 3
Ni      0.0000000000      0.0000000000      0.0000000000
*
```

By running the above input the fitted 1-electron energies and SCP parameters also Racah parameters for 1-shells will be printed at the CASSCF and NEVPT2 levels of theory, including F0s and Racah A as estimated from single zeta effective Slater exponents from the fitted F2dd SCPs.

----- AILFT MATRIX ELEMENTS (CASSCF) -----

Ligand field one-electron matrix VLFT (a.u.) :

Orbital	dz2	dxz	dyz	dx2-y2	dxy
dz2	-7.974440	0.000000	-0.000000	0.000000	-0.000000
dxz	0.000000	-7.974440	-0.000000	-0.000000	0.000000
dyz	-0.000000	-0.000000	-7.974440	-0.000000	0.000000
dx2-y2	0.000000	-0.000000	-0.000000	-7.974440	0.000000
dxy	-0.000000	0.000000	0.000000	0.000000	-7.974440

Slater-Condon Parameters (electronic repulsion) :

Computed Single Zeta Slater Effective Exponents

...

kd(SZ) (from F2dd) = 3.134434893 a.u.

Computed F0s from Single Zeta Slater Effective Exponents

...

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```

F0dd(from F2dd kd(SZ)) = 0.809116820 a.u. = 22.017 eV = 177580.6 cm**--1
F2dd                    = 0.427107567 a.u. = 11.622 eV = 93739.3 cm**--1
F4dd                    = 0.264174069 a.u. = 7.189 eV = 57979.5 cm**--1

```

Racah Parameters :

```

A(from F2dd kd(SZ))    = 0.779764145 a.u. = 21.218 eV = 171138.4 cm**--1
B                      = 0.005721310 a.u. = 0.156 eV = 1255.7 cm**--1
C                      = 0.020966196 a.u. = 0.571 eV = 4601.5 cm**--1
C/B                    = 3.665

```

The ligand field one electron eigenfunctions:

Orbital	Energy (eV)	Energy (cm ⁻¹)	dz2	dxz	dyz	dx2-y2	dx2-y2
↪ dxy							
1	0.000	0.0	-0.999981	0.000787	-0.001735	0.004390	-0.
↪003810							
2	0.000	0.0	0.003811	0.000493	0.000955	0.000497	-0.
↪999992							
3	0.000	0.0	0.004388	0.000169	0.000080	0.999990	0.
↪000514							
4	0.000	0.0	-0.000750	-0.999810	-0.019460	0.000174	-0.
↪000514							
5	0.000	0.0	-0.001754	-0.019459	0.999809	-0.000069	0.
↪000939							

Ligand field orbitals were stored in ni.3d.casscf.lft.gbw

...

AILFT MATRIX ELEMENTS (NEVPT2)

Ligand field one-electron matrix VLFT (a.u.) :

Orbital	dz2	dxz	dyz	dx2-y2	dxy
dz2	-7.974812	-0.000000	-0.000000	0.000002	-0.000000
dxz	-0.000000	-7.974860	0.000000	0.000000	0.000000
dyz	-0.000000	0.000000	-7.974856	-0.000000	0.000000
dx2-y2	0.000002	0.000000	-0.000000	-7.974837	0.000000
dxy	-0.000000	0.000000	0.000000	0.000000	-7.974837

Slater-Condon Parameters (electronic repulsion) :

Computed Single Zeta Slater Effective Exponents

...

```

kd(SZ) (from F2dd)      = 3.126330433 a.u.

```

Computed F0s from Single Zeta Slater Effective Exponents

...

```

F0dd(from F2dd kd(SZ)) = 0.807024751 a.u. = 21.960 eV = 177121.5 cm**--1
F2dd                    = 0.426003229 a.u. = 11.592 eV = 93496.9 cm**--1
F4dd                    = 0.262001371 a.u. = 7.129 eV = 57502.7 cm**--1

```

Racah Parameters :

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```

A(from F2dd kd(SZ))    = 0.777913487 a.u. = 21.168 eV = 170732.3 cm**−1
B                      = 0.005723406 a.u. = 0.156 eV = 1256.1 cm**−1
C                      = 0.020793760 a.u. = 0.566 eV = 4563.7 cm**−1
C/B                    = 3.633

```

```

-----
The ligand field one electron eigenfunctions:
-----

```

Orbital	Energy (eV)	Energy (cm ^{−1})	dz2	dxz	dyz	dx2−y2
↪ dxy						
1	0.000	0.0	−0.000608	−0.999795	0.017518	0.010019
↪ 001244						
2	0.000	0.9	0.000003	−0.017532	−0.999696	−0.003661
↪ 016920						
3	0.001	4.9	0.065092	−0.009854	0.004898	−0.995782
↪ 063719						
4	0.001	5.0	−0.004126	0.002173	0.016617	0.063640
↪ 997824						
5	0.001	10.5	0.997871	0.000042	−0.000237	0.065225
↪ 000030						

```

Ligand field orbitals were stored in ni.3d.nevpt2.1ft.gbw

```

It is also possible to treat only the High Spin states in the d- and f- 1-shell AILFT. Note that not all the cases can be treated as this renders the different SCP parameters undefined. In the beginning, AILFT will check whether such case is detected and will drop a warning message

For example in the case of the Fe²⁺ d⁶ ion with an input like the following:

```

!NoIter def2-SVP def2-SVP/C

%casscf
  nel 6
  norb 5
  mult 5
  nroots 5
  LFTCase 3d
end

*xyz 2 3
Fe      0.0000000000      0.0000000000      0.0000000000
*

```

the following Warning will be printed in the beginning of the calculation

```

WARNING: In AILFT F2dd remains undefined when considering only the HS Multiplicity.
↪ block
Be Careful with the results!
TIP:      If possible use in addition a LS Multiplicity Block

```

Spin orbit coupling effects (SOC) can be introduced by parametrizing the effective SOC constant ζ . As long as SOC is requested in the rel CASSCF block the respective requested shell effective SOC constant ζ will be computed at the end of every AILFT calculation

Hence in the above examples one gets:

```

-----
SPIN ORBIT COUPLING (based on CASSCF orbitals)
-----

```

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```

AI-SOC-X integrals (cm-1)
0      1      2      3      4
0      0.000000  0.000000 1078.568273 -0.000000 -0.000000
1      -0.000000  0.000000 -0.000000 -0.000000 622.711683
2      -1078.568273  0.000000  0.000000 -622.711683  0.000000
3      0.000000  0.000000 622.711683  0.000000 -0.000000
4      0.000000 -622.711683 -0.000000  0.000000  0.000000
AI-SOC-Y integrals (cm-1)
0      1      2      3      4
0      -0.000000 -1078.568273 -0.000000  0.000000  0.000000
1      1078.568273  0.000000 -0.000000 -622.711683 -0.000000
2      0.000000  0.000000  0.000000 -0.000000 -622.711683
3      -0.000000 622.711683  0.000000  0.000000 -0.000000
4      -0.000000  0.000000 622.711683  0.000000  0.000000
AI-SOC-Z integrals (cm-1)
0      1      2      3      4
0      0.000000 -0.000000  0.000000 -0.000000  0.000000
1      0.000000 -0.000000 -622.711683 -0.000000  0.000000
2      -0.000000 622.711683  0.000000 -0.000000 -0.000000
3      0.000000  0.000000  0.000000 -0.000000 -1245.423365
4      -0.000000 -0.000000  0.000000 1245.423365  0.000000

Fit to the SOC matrix elements
a = 15.000000
b = 1.158 eV = 9340.7 cm**-1
SOC constant zeta = 0.077 eV = 622.7 cm**-1

LF-SOC-X integrals (cm-1)
0      1      2      3      4
0      0.000000 -0.000000 1078.568273 -0.000000 -0.000000
1      0.000000  0.000000 -0.000000 -0.000000 622.711683
2      -1078.568273  0.000000  0.000000 -622.711683 -0.000000
3      0.000000  0.000000 622.711683  0.000000 -0.000000
4      0.000000 -622.711683  0.000000  0.000000  0.000000
LF-SOC-Y integrals (cm-1)
0      1      2      3      4
0      0.000000 -1078.568273 -0.000000 -0.000000 -0.000000
1      1078.568273  0.000000 -0.000000 -622.711683 -0.000000
2      0.000000  0.000000  0.000000 -0.000000 -622.711683
3      0.000000 622.711683  0.000000  0.000000 -0.000000
4      0.000000  0.000000 622.711683  0.000000  0.000000
LF-SOC-Z integrals (cm-1)
0      1      2      3      4
0      0.000000 -0.000000 -0.000000 -0.000000 -0.000000
1      0.000000  0.000000 -622.711683 -0.000000 -0.000000
2      0.000000 622.711683  0.000000 -0.000000 -0.000000
3      0.000000  0.000000  0.000000  0.000000 -1245.423365
4      0.000000  0.000000  0.000000 1245.423365  0.000000

RMS error of nonzero matrix elements = 0.0 cm**-1

-----SOC-CONSTANTS-----
---All Values in cm-1---
ZETA_D = 622.71
-----

```

Starting from ORCA 5.0 it is also possible in addition to CASSCF and NEVPT2 to employ DCDCAS(2) and Hermitian QD-NEVPT2 Abinitio Hamiltonians in AILFT Example inputs are provided below for DCDCAS(2):

```

!def2-SVP def2-SVP/C

%casscf
  nel 8
  norb 5
  actorbs dorbs
  mult 3,1
  nroots 10,15
  dcdcas true
  corrorder 2
  rel
    dosoc true
  end
end

*xyz 2 3
Ni      0.0000000000      0.0000000000      0.0000000000
*

```

and Hermitian QD-NEVPT2:

```

!def2-SVP def2-SVP/C

%casscf
  nel 8
  norb 5
  actorbs dorbs
  mult 3,1
  nroots 10,15
  PTMethod  sc_nevpt2
  PTSettings
    QDType QD_VanVleck
  end
  rel
    dosoc true
  end
end

*xyz 2 3
Ni      0.0000000000      0.0000000000      0.0000000000
*

```

Running the above inputs the respective DCDCAS(2) and Hermitian QD-NEVPT2 Hamiltonians will be processed:

```

Calculating ab initio Hamiltonian matrices          ...
-----
DCDCAS correction for this block/order is calculated
DCDCAS Hamiltonian of block = 0 and order = 0 is passed
DCDCAS Hamiltonian diagonalized
-----
DCDCAS correction for this block/order is calculated
DCDCAS Hamiltonian of block = 0 and order = 1 is passed
DCDCAS Hamiltonian diagonalized
-----
DCDCAS correction for this block/order is calculated
DCDCAS Hamiltonian of block = 0 and order = 2 is passed
DCDCAS Hamiltonian diagonalized
-----
DCDCAS correction for this block/order is calculated

```

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```

DCDCAS Hamiltonian of block = 1 and order = 0 is passed
DCDCAS Hamiltonian diagonalized
-----
DCDCAS correction for this block/order is calculated
DCDCAS Hamiltonian of block = 1 and order = 1 is passed
DCDCAS Hamiltonian diagonalized
-----
DCDCAS correction for this block/order is calculated
DCDCAS Hamiltonian of block = 1 and order = 2 is passed
DCDCAS Hamiltonian diagonalized
-----
...
Calculating ab initio Hamiltonian matrices          ...
-----
Hermitian QD-NEVPT2 correction for this block is calculated
Hermitian QD-NEVPT2 Hamiltonian of block = 0 is passed
Hermitian QD-NEVPT2 Hamiltonian diagonalized
-----
Hermitian QD-NEVPT2 correction for this block is calculated
Hermitian QD-NEVPT2 Hamiltonian of block = 1 is passed
Hermitian QD-NEVPT2 Hamiltonian diagonalized
-----

```

It should be noted that NEVPT2 and Hermitian QD-NEVPT2 AILFT require a complete saturation of the excitation space. This implies that if less roots than the required are requested the AILFT analysis will be skipped in these cases. This is on the contrary not the case in CASSCF or DCDCAS(2) in which AILFT can operate under incomplete saturation of the excitation space.

```

Calculating ab initio Hamiltonian matrices          ...
WARNING: Number of NEVPT2 roots for block 0 (5) is not equal to the number of
↪CASSCF CSFs (10)!
Skipping AILFT analysis with NEVPT2 energies!

WARNING: Number of NEVPT2 roots for block 1 (2) is not equal to the number of
↪CASSCF CSFs (15)!
Skipping AILFT analysis with NEVPT2 energies!

```

In a similar fashion one can request a 2-shell AILFT calculation.

For this purpose the recommended steps are the following:

- In a first step the valence active space orbitals are optimized in the framework of SA-CASSCF calculation, e.g., the 3d MOs in a core 1s3d or 2p3d AILFT calculation, or the f MOs in an 4f5d AILFT calculation)
- In a second step the relevant core or virtual orbitals are rotated into the active space and the chosen CASSCF/AILFT problem is solved by saturating the excitation space with all the involved excitations/multiplicity.
- In the most of the cases the excitation space of two multiplicities the High-Spin one and the subsequent Low-Spin one are enough for a successful fitting of the parameters

It should be noted that 2-shell AILFT involves a 2-step fitting process following a bottom up shell angular momentum approach :

1. At first when possible an intra-shell fitting is performed
2. In following the respective effective Slater exponents are derived
3. In a last step an inter-shell fitting is performed and all the computed/fitted parameters are printed

This implies that:

- the flag of computing effective Slater exponents is always on by default in 2-shell AILFT
- the desired LFT problem is best requested by the LFTCase keywords (e.g. LFTCase 1s3d)

Let look at the case of 1s3d LFT problem of the $\text{Ni}^{2+} d^8$ ion. A relevant input is provided below:

```
!NoIter NEVPT2 def2-SVP def2-SVP/C

%method
  frozencore fc_none
end

%scf
  rotate
    {0,8,90}
  end
end

%casscf
  nel 10
  norb 6
  mult 3,1
  nroots 100,100
  LFTCase 1s3d
  rel
    dosoc true
  end
end

*xyz 2 3
Ni      0.0000000000      0.0000000000      0.0000000000
*
```

Like in 1-shell AILFT, 2-shells AILFT starts with a sanity check

```
---- THE CAS-SCF GRADIENT HAS CONVERGED ----
--- FINALIZING ORBITALS ---
---- DOING ONE FINAL ITERATION FOR PRINTING ----
--- sd-orbitals (depends on the molecular axis frame)
L-Center:  0 Ni [0.000, 0.000, 0.000]
L-Center:  0 Ni Active Orbital 0 is the s orbital ; l = 0 ; active shell = 0
L-Center:  0 Ni Active Orbital 1 is one d orbital ; l = 2 ; active shell = 7
L-Center:  0 Ni Active Orbital 2 is one d orbital ; l = 2 ; active shell = 7
L-Center:  0 Ni Active Orbital 3 is one d orbital ; l = 2 ; active shell = 7
L-Center:  0 Ni Active Orbital 4 is one d orbital ; l = 2 ; active shell = 7
L-Center:  0 Ni Active Orbital 5 is one d orbital ; l = 2 ; active shell = 7
--- The active space contains 1 s orbitals and 5 d orbitals : OK
Setting 8 active MO to AO s      (0)
Setting 9 active MO to AO dz2    (11)
Setting 10 active MO to AO dxz   (12)
Setting 11 active MO to AO dyz   (13)
Setting 12 active MO to AO dx2y2 (14)
Setting 13 active MO to AO dxy   (15)
--- Canonicalize Internal Space
--- Canonicalize External Space
```

In following the AI-LFT Hamiltonians are constructed and the LFT parameters are fitted at the CASSCF and at the NEVPT2 levels of theory

```
-----
AILFT MATRIX ELEMENTS (CASSCF)
```

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```

-----
Ligand field one-electron matrix VLFT (a.u.) with V(0,0) fixed :
0          1          2          3          4          5
0   -334.652557   -0.000000   0.000000   -0.000000   -0.000000   -0.000000
1    -0.000000  -10.085777   0.000000   0.000000   -0.000000   -0.000000
2     0.000000   0.000000  -10.085777  -0.000000   -0.000000   -0.000000
3    -0.000000   0.000000  -0.000000  -10.085777   0.000000   0.000000
4    -0.000000  -0.000000  -0.000000   0.000000  -10.085777  -0.000000
5    -0.000000  -0.000000  -0.000000   0.000000  -0.000000  -10.085777

```

```

-----
Slater-Condon Parameters (electronic repulsion) :
-----

```

```

F0ss          = 17.137989284 a.u. = 466.348 eV = 3761353.9 cm** -1
F0dd          = 0.809116820 a.u. = 22.017 eV = 177580.6 cm** -1
F2dd          = 0.427107567 a.u. = 11.622 eV = 93739.3 cm** -1
F4dd          = 0.278548413 a.u. = 7.580 eV = 61134.3 cm** -1
F0sd          = 1.285327742 a.u. = 34.976 eV = 282096.8 cm** -1
G2sd          = 0.001928559 a.u. = 0.052 eV = 423.3 cm** -1
R2sddd        = 0.003748289 a.u. = 0.102 eV = 822.7 cm** -1

```

```

-----
The ligand field one electron eigenfunctions:
-----

```

Orbital	Energy (eV)	Energy (cm ⁻¹)	s	dz ²	dxz	dyz	
↪ dx ² -y ²	0.000	0.0	-1.000000	-0.000000	0.000000	-0.000000	-
↪ 0.000000	0.000000						
2	8831.911	71234174.2	0.000000	-0.006282	0.006583	-0.271975	↪
↪ 0.962261	0.000000						
3	8831.911	71234174.2	0.000000	0.000000	0.000000	0.000000	↪
↪ 0.000000	1.000000						
4	8831.911	71234174.2	0.000000	-0.075508	-0.016185	-0.959327	-
↪ 0.271528	0.000000						
5	8831.911	71234174.2	-0.000000	0.071391	-0.997365	0.008467	↪
↪ 0.009682	0.000000						
6	8831.911	71234174.2	-0.000000	0.994566	0.070404	-0.075159	-
↪ 0.015232	-0.000000						

Ligand field orbitals were stored ni.1s3d.casscf.lft.gbw

...

```

-----
AILFT MATRIX ELEMENTS (NEVPT2)
-----

```

```

Ligand field one-electron matrix VLFT (a.u.) with V(0,0) fixed :
0          1          2          3          4          5
0   -334.652557   -0.000000   0.000000   0.000000   0.000000   0.000000
1    -0.000000  -10.298799   0.000008   0.000006  -0.000002  -0.000002
2     0.000000   0.000008  -10.293700  -0.000042  -0.000008  -0.000006
3     0.000000   0.000006  -0.000042  -10.293839  -0.000001   0.000008
4     0.000000  -0.000002  -0.000008  -0.000001  -10.293927  -0.000033
5     0.000000  -0.000002  -0.000006   0.000008  -0.000033  -10.293511

```

```

-----
Slater-Condon Parameters (electronic repulsion) :
-----

```

```

F0ss          = 16.677683435 a.u. = 453.823 eV = 3660328.4 cm** -1
F0dd          = 0.806859685 a.u. = 21.956 eV = 177085.2 cm** -1

```

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```

F2dd      = 0.425916096 a.u. = 11.590 eV = 93477.8 cm** -1
F4dd      = 0.277771367 a.u. = 7.559 eV = 60963.8 cm** -1
F0sd      = 1.424742585 a.u. = 38.769 eV = 312694.9 cm** -1
G2sd      = 0.025339297 a.u. = 0.690 eV = 5561.3 cm** -1
R2sddd    = 0.003739506 a.u. = 0.102 eV = 820.7 cm** -1

```

The ligand field one electron eigenfunctions:

Orbital	Energy (eV)	Energy (cm ⁻¹)	s	dz2	dxz	dyz	
↪ dx2-y2 dxz							
1	0.000	0.0	1.000000	0.000000	-0.000000	-0.000000	-
↪0.000000	-0.000000						
2	8826.114	71187421.2	-0.000000	0.999998	-0.001607	-0.001229	-
↪0.000405	0.000329						
3	8826.247	71188489.9	-0.000000	0.000330	-0.040203	-0.027545	-
↪0.995773	-0.077852						
4	8826.249	71188507.4	-0.000000	0.001631	0.264542	0.963492	-
↪0.035726	-0.020544						
5	8826.254	71188542.9	0.000000	-0.001223	-0.962932	0.264866	-
↪0.034492	-0.037635						
6	8826.258	71188582.5	0.000000	-0.000317	-0.034070	0.027728	-
↪0.077265	0.996042						

Ligand field orbitals were stored in ni.1s3d.nevpt2.1ft.gbw

As discussed above saturation of the excitation space is a requirement also in the case of 2-shell AILFT. It is usually enough to specify a large number of roots for two multiplicities (e.g. 100 singlets and triplets in the above example) The exact number of roots will be automatically detected.

```

Multiplicity          ...    3
#(Configurations)     ...   15
#(CSFs)               ...   15
#(Roots)              ...  100
WARNING (ORCA_CASSCF): NRoots > NCSFs. Adjusting to maximum number of roots.
↪Please check the output carefully!
#(Roots)              ...   15
ROOT=0 WEIGHT=        0.033333
ROOT=1 WEIGHT=        0.033333
ROOT=2 WEIGHT=        0.033333
ROOT=3 WEIGHT=        0.033333
ROOT=4 WEIGHT=        0.033333
ROOT=5 WEIGHT=        0.033333
ROOT=6 WEIGHT=        0.033333
ROOT=7 WEIGHT=        0.033333
ROOT=8 WEIGHT=        0.033333
ROOT=9 WEIGHT=        0.033333
ROOT=10 WEIGHT=       0.033333
ROOT=11 WEIGHT=       0.033333
ROOT=12 WEIGHT=       0.033333
ROOT=13 WEIGHT=       0.033333
ROOT=14 WEIGHT=       0.033333

BLOCK 2 WEIGHT=       0.5000
Multiplicity          ...    1
#(Configurations)     ...   21
#(CSFs)               ...   21
#(Roots)              ...  100
WARNING (ORCA_CASSCF): NRoots > NCSFs. Adjusting to maximum number of roots.
↪Please check the output carefully!
#(Roots)              ...   21
ROOT=0 WEIGHT=        0.023810

```

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```

ROOT=1 WEIGHT= 0.023810
ROOT=2 WEIGHT= 0.023810
ROOT=3 WEIGHT= 0.023810
ROOT=4 WEIGHT= 0.023810
ROOT=5 WEIGHT= 0.023810
ROOT=6 WEIGHT= 0.023810
ROOT=7 WEIGHT= 0.023810
ROOT=8 WEIGHT= 0.023810
ROOT=9 WEIGHT= 0.023810
ROOT=10 WEIGHT= 0.023810
ROOT=11 WEIGHT= 0.023810
ROOT=12 WEIGHT= 0.023810
ROOT=13 WEIGHT= 0.023810
ROOT=14 WEIGHT= 0.023810
ROOT=15 WEIGHT= 0.023810
ROOT=16 WEIGHT= 0.023810
ROOT=17 WEIGHT= 0.023810
ROOT=18 WEIGHT= 0.023810
ROOT=19 WEIGHT= 0.023810
ROOT=20 WEIGHT= 0.023810

```

However very often the required number of states to be computed in the framework of NEVPT2 type of calculations are quite large. In these cases a Hamiltonian reduction process on the basis of the Restrictive Active Space (RAS) is required. In fact all LFT parameters can be determined by considering up to double excitations from the donor-shell.

Let us consider the 2p3d case of the $\text{Fe}^{2+} d^6$ ion. Saturation of the active space requires to consider 70 triplet and 378 singlet states. Restriction of the active space to only up to double excitations from the 2p-shell results in 65 quintet and 330 triplet states. The Hamiltonian reduction can be requested in the ailft block:

```

ailft
  AILFT_Dimension 2 # Up to double excitations from the donor shell
                    Other options:
                    1   Up to single excitations from the donor shell
                    0   No excitations from the donor shell
end

```

Hence the relevant input can be now formulated as:

```

!NoIter MOREAD DKH2 DKH-def2-TZVP def2-TZVP/C NEVPT2

%moinp "fe.3d.gbw"

%pal
  nprocs 16
end

%method
  frozencore fc_none
end

%scf
  rotate
    {2,6,90}
    {3,7,90}
    {4,8,90}
  end
end

%casscf
  nel 12
  norb 8

```

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```

mult 5,3
nroots 65,330
LFTCase 2p3d
ailft
  AILFT_Dimension 2
end
rel
  dosoc true
  GTensor false
  DoDTensor false
end
end

*xyz 2 5
Fe      0.0000000000      0.0000000000      0.0000000000
*
```

Note that before running the above calculation:

- An initial SA-CASSCF calculation has been performed on the valence states of Fe in the 3d active space. These orbitals (fe.3d.gbw) are read in
- The computation of the g- and D- tensors is switched off. This is recommended if the magnetism analysis is not required
- As core spectroscopy is targeted the frozen core is switched off

At the NEVPT2 part the reduced AI and LFT Hamiltonians will be constructed

```

Calculating  ab initio Hamiltonian matrices      ...
-----
NRoots (NEVPT2) for this block = 65
NEVPT2 correction for this block is calculated
Full NEVPT2 Hamiltonian constructed
Full NEVPT2 Hamiltonian diagonalized
-----
NRoots (NEVPT2) for this block = 330
NEVPT2 correction for this block is calculated
Full NEVPT2 Hamiltonian constructed
Full NEVPT2 Hamiltonian diagonalized
-----
```

As a result the CASSCF and NEVPT2 LFT parameters will be determined in the requested reduced basis

```

-----
AILFT MATRIX ELEMENTS (CASSCF)
-----

-----
Slater-Condon Parameters (electronic repulsion) :
-----
F0pp      = 3.889665545 a.u. = 105.843 eV = 853682.9 cm**-1
F2pp      = 1.832901835 a.u. = 49.876 eV = 402275.5 cm**-1
F0dd      = 0.767706319 a.u. = 20.890 eV = 168492.1 cm**-1
F2dd      = 0.405248254 a.u. = 11.027 eV = 88941.7 cm**-1
F4dd      = 0.264292339 a.u. = 7.192 eV = 58005.5 cm**-1
F0pd      = 1.174187892 a.u. = 31.951 eV = 257704.5 cm**-1
F2pd      = 0.220959621 a.u. = 6.013 eV = 48495.0 cm**-1
G1pd      = 0.157243007 a.u. = 4.279 eV = 34510.9 cm**-1
G3pd      = 0.089473762 a.u. = 2.435 eV = 19637.2 cm**-1
```

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```

...

-----
AILFT MATRIX ELEMENTS (NEVPT2)
-----

-----
Slater-Condon Parameters (electronic repulsion) :
-----

F0pp      = 3.527444471 a.u. = 95.987 eV = 774184.6 cm**-1
F2pp      = 1.906123325 a.u. = 51.868 eV = 418345.7 cm**-1
F0dd      = 0.808248242 a.u. = 21.994 eV = 177390.0 cm**-1
F2dd      = 0.426649072 a.u. = 11.610 eV = 93638.6 cm**-1
F4dd      = 0.278249395 a.u. = 7.572 eV = 61068.7 cm**-1
F0pd      = 1.657417509 a.u. = 45.101 eV = 363761.1 cm**-1
F2pd      = 0.198646995 a.u. = 5.405 eV = 43598.0 cm**-1
G1pd      = 0.206111579 a.u. = 5.609 eV = 45236.3 cm**-1
G3pd      = 0.128174221 a.u. = 3.488 eV = 28131.0 cm**-1

...

```

In the above example inclusion of SOC will result in the computation of the effective SOC ζ constants of both p and d shells:

```

-----SOC-CONSTANTS-----
---All Values in cm-1---
ZETA_P = 65018.19
ZETA_D = 453.53
-----

```

One important feature of 1- and in particular of the 2-shell AILFT is that it is connected to the standalone orca_lft multiplet program. Hence every successful AILFT calculation will automatically construct relevant inputs for the orca_lft.

For example in the above 2p3d case of the $\text{Fe}^{2+} d^6$ ion the following inputs will be constructed

```

fe.2p3d.casscf.lft.inp
fe.2p3d.nevpt2.lft.inp

```

with the NEVPT2 one looking like this:

```

%lft

#-----Parameters-----
NEl= 12
Shell_PQN= 0, 2, 3, 0
Mult= 5, 3
NRoots= 65, 330
#-----

#---Slater-Condon Parameters---
#---All Values in eV---
PARAMETERS
F0pp = 95.9866
F2pp = 51.8683
F0dd = 21.9936
F2dd = 11.6097
F4dd = 7.5716
F0pd = 45.1006
F2pd = 5.4055

```

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```

G1pd = 5.6086
G3pd = 3.4878
end
#-----

#---LFT-Matrix Elelemnts---
#---All Values in eV---
FUNCTIONS
0 0 " 0.0000"
1 0 " -0.0146"
1 1 " 0.0947"
2 0 " 0.0210"
2 1 " 0.0061"
2 2 " 0.1155"
3 0 " 0.0000"
3 1 " -0.0000"
3 2 " -0.0000"
3 3 "1086.2398"
4 0 " 0.0000"
4 1 " -0.0000"
4 2 " -0.0000"
4 3 " 0.0323"
4 4 "1086.2181"
5 0 " -0.0000"
5 1 " 0.0000"
5 2 " 0.0000"
5 3 " -0.0356"
5 4 " -0.0154"
5 5 "1086.1183"
6 0 " 0.0000"
6 1 " -0.0000"
6 2 " -0.0000"
6 3 " -0.0767"
6 4 " -0.0080"
6 5 " 0.0341"
6 6 "1086.1219"
7 0 " -0.0000"
7 1 " 0.0000"
7 2 " 0.0000"
7 3 " 0.0050"
7 4 " -0.0023"
7 5 " 0.0026"
7 6 " -0.0038"
7 7 "1086.0688"
end
#-----

#---SOC-CONSTANTS---
#---All Values in eV---
PARAMETERS
ZETA_P = 8.06
ZETA_D = 0.06
end
#-----

#---SPECTRA/PROPERTIES---
DoABS true
#-----

```

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```

end

*xyz Charge Multiplicity
Atom 0.00 0.00 0.00
*
```

Further details regarding `orca_lft` can be found in the `orca_lft` section [Section 9.2.15](#) and the `orca_lft` tutorial. (*orca_lft*) and the `orca_lft` tutorial.

3.13.17 Extended Space Ab initio Ligand Field Theory (ESAILFT)

While the one- and two-shell AILFT approach has been remarkably effective in extracting interpretable parameters. There are still limitations to this approach. The nature of the AILFT extraction requires the CASCI or effective Hamiltonian matrix to be of the same dimension as the LFT Hamiltonian. This means that an extension of the CASSCF calculation, with the active space larger than the d-space to incorporate static correlations without increasing the number of AILFT parameters, is not possible with the original recipes.

We now provide a solution to this limitation by introducing another effective Hamiltonian that is based on partitioning the extended active spaces in CASSCF calculations. This method (esAILFT)[456] allows us to perform AILFT calculations on the basis of extended CASSCF active spaces to, in principle, any number of orbitals. The central idea is that esAILFT would allow for the inclusion of effects such as radial correlation of d-orbitals and reduce the overestimation of the ionic character in the CASSCF calculation.

The method of partitioning given by Löwdin presents one approach for building effective Hamiltonians. In this case, the Hilbert space is divided into a model (A) and an outer (B) space. The time-independent Schrödinger equation can be rewritten as:

$$\mathbf{H}^{AI} \begin{pmatrix} \mathbf{C}_A \\ \mathbf{C}_B \end{pmatrix} = \begin{pmatrix} \mathbf{H}_{AA} & \mathbf{H}_{AB} \\ \mathbf{H}_{BA} & \mathbf{H}_{BB} \end{pmatrix} \begin{pmatrix} \mathbf{C}_A \\ \mathbf{C}_B \end{pmatrix} = E^{(0)} \cdot \begin{pmatrix} \mathbf{C}_A \\ \mathbf{C}_B \end{pmatrix}$$

$$\mathbf{H}_{part}^{AI} = \mathbf{H}_{AA} - \mathbf{H}_{AB}(\mathbf{H}_{BB} - 1 \cdot E_0)^{-1} \mathbf{H}_{BA}$$

Here E_0 can be fixed to the lowest energy of the CASCI matrix but a bias-correction term becomes necessary to correct the energies of \mathbf{H}_{part}^{AI}

$$E_I^{BC} = [E_I - E_0] \times \sum_{k \in B} \frac{H_{IK}^{AI} H_{KI}^{AI}}{(E_K - E_0)^2}$$

The individual steps in the calculation are summarized as follows:

1. Orbital preparation Optimized CASSCF MOs are obtained by solving the CASSCF equations. We then exploit the unitary invariance of the active orbital space in order to make these orbitals suitable for the extended AILFT procedure by performing the following three steps
 1. The active orbitals are localized which will separate metal-based d- or from ligand-based orbitals
 2. The metal-d- orbitals are canonicalized by diagonalizing the matrix representation of the angular momentum operator L_z and then phase-adjusted to be consistent with the ligand field orbitals. Both steps 1.1. and 1.2. are already present in the original AILFT procedure.
 3. The remaining outer space orbitals are transformed to diagonalize the corresponding sub-block of the Fock operator. This step is optional but, in our experience, beneficial for the partitioning procedure and the interpretation of the results.
2. Generation of the effective Hamiltonian over the ligand field manifold space. The individual steps are as follows
 1. Calculations of the actual effective Hamiltonian
 2. Calculation of the bias correction
3. The original AILFT procedure is then used on the effective Hamiltonian.

We can illustrate this with an example for V^{2+} . The process begins with a converged minimal space CASSCF calculations.

```
!x2c x2c-TZVPall AUTOAUX
%maxcore 4000
%casscf
  # run the AILFT with the minimal active space
  actorbs dorbs
  # definition of the active space, multiplicity and number of roots
  nel 3
  norb 5
  mult 4,2
  nroots 10,40
  trafostep RI
  # optional properties such as SOC splitting and g-matrix
  rel
    dosoc false
    gtensor false
  end
end
# geometry block
*xyz 2 4
  V 0.0 0.0 0.0
*
# enable picture change
%rel
  picturechange true
end
```

We then run an extended space CASSCF:

```
!x2c x2c-TZVPall AUTOAUX moread
%moinp "V2p_min.gbwn" # contains the converged orbitals with the minimal active_
↪space
%maxcore 4000
%casscf
  # definition of the extended active space
  norb 9
  nel 11
  mult 4,2
  nroots 10,40
  trafostep RI
end
*xyz 2 4
  V 0.0 0.0 0.0
*
# enable picture change
%rel
  picturechange true
end
```

This can then be used for computing LFT parameters:

```
!x2c x2c-TZVPall AUTOAUX moread
%moinp "V2p_3s3p.gbwn" # converged casscf orbitals with the extended active space
%maxcore 4000
%casscf
  # run the esAILFT
  actorbs lmorbs
  ailft
  AILFT_SkipOrbOpt true
  NOrbInternal 4 # no of orbitals in the extended space to be labelled as internal
```

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```

NorbExternal 0 # no of orbitals in the extended space to be labelled as external
MinElectrons 3 # no of electrons in the active space after external + internal
are cut
end
# definition of the active space, multiplicity and number of roots
norb 9
nel 11
mult 4,2
nroots 10,40
trafostep RI
rel
  dosoc false
  gtensor false
end
end
*xyz 2 4
  V 0.0 0.0 0.0
*
%rel
  picturechange true
end

```

The output will include a block dedicated for ESAILFT. The information displayed is in an identical format to the one-shell case except it is extracted from the partitioned hamiltonian.

```

-----
AILFT MATRIX ELEMENTS (Hermitian HEffective)
-----

```

3.13.18 Core Excited Spectra: CAS-CI/RAS-CI XAS/RIXS

Starting from ORCA 4.1, a CASCI/NEVPT2 protocol can be used to compute core excited spectra, namely X-ray absorption (XAS) and resonant inelastic scattering (RIXS) spectra. RASCI calculations can also be easily specified.

The XAS/RIXS spectra calculations requires two steps:

- In a first step one needs to optimize the valence active space orbitals in the framework of SA-CASSCF calculations, e.g. including valence excited states in the range between 6 to 15 eV.
- In a second step the relevant core orbitals are rotated into the active space and the (C/R)ASCI/NEVPT2 problem is solved by saturating the excitation space with singly core-excited electronic configurations using the previously optimized sets of orbitals

Further information can be found in reference[457]

A relevant input for Fe L-edge XAS calculation of a Fe(III) complex like Fe(acac)₃ is given below for CASCI/NEVPT2:

```

%moinp "Fe_acac3_casscf.gbw"

%scf
rotate
{4,89,90,0,0}
{3,88,90,0,0}
{2,87,90,0,0}
end
end

%rel
picturechange true
FiniteNuc true

```

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```

end

%method FrozenCore FC_NONE
end

# CASSCF/NEVPT2 on the valence and L-edge excited states
%casscf
nel 11
norb 8
mult 6,4
nroots 16,173
maxiter 1
# account for spin-orbit coupling
rel
  DoSOC true
end
# adding the dynamical correlation with NEVPT2
PTMethod SC\_NEVPT2
end

* xyz 0 6
...
*
```

For RASCI/NEVPT2 calculations the valence d AS is set to RAS2. The RAS3 space is usually set empty. The RAS1 space contains the previously rotated core orbitals. To generate a single core hole, the number of maximum holes in the RAS1 space must be set to 1. Accordingly, the maximum number of particles in the RAS3 space must be 0. The RASCI input should thus look the following

```

%casscf
nel 11
norb 8
...
refs
  ras(11:3 1/5/0 0) # (Nel: NRAS1 MaxHoles / NRAS2 / NRAS3 MaxParticles)
end
...
end
```

As it is explicitly described in the respective ROCIS section RIXS spectra can be requested by the following keywords:

```

RIXS      true    # Request RIXS calculation (NoSOC)
RIXSSOC   true    # Request RIXS calculation (with SOC)
Elastic   true    # Request RIXS calculation (Elastic)
```

Please consult section [Section 5.7.4](#) for processing and analyzing the generated spectra.

3.13.19 Core Excited Spectra: CAS-CI/RAS-CI XES

Starting from ORCA 5.0 likewise to RASCI-XES (see section [Section 3.19.14](#)) orca features a CASCI-XES protocol.

Likewise to the RASCI-XES the CASCI-XES calculations requires two steps:

- In a first step one needs to optimize the valence active space orbitals in the framework of SA-CASSCF calculations, e.g. including valence excited states in the range between 6 to 15 eV.
- In a second step the relevant core orbitals e.g. metal 1s and 3p are rotated into the active space and the CASCI problem is solved for the ionized system by saturating the excitation space with singly core-excited electronic configurations using the previously optimized sets of orbitals. In CASCI-XES this can be achieved by defining reference configurations. or via the RAS functionality.

The XESSOC calculation is called by specifying the following keywords in the rel block:

```
rel
XESSOC true
XASMOs Number of the rotated 1s MO
end
```

Following a SA-CASSCF calculation:

```
! X2c x2c-TZVPall x2c/J def2-TZVP/C
! NormalPrint
! NoLoewdin NoMulliken

%casscf
nel 5
norb 5
nroots 1, 24
mult 6, 4
end

* xyz -3 6
Fe      0      0      0
Cl      2.40    0      0
Cl     -2.40    0      0
Cl      0      2.40    0
Cl      0     -2.40    0
Cl      0      0      2.40
Cl      0      0     -2.40
*
```

A relevant input for Fe XES calculation of a Fe(III) complex like FeCl_6 is given below:

```
! def2-SVP def2-SVP/C ZORA CPCM PAL8
! NormalPrint
! MOREAD
! NoLoewdin NoMulliken

%moinp "FeCl6_casscf.gbw"

%scf
#Rotate the 1s and 3p orbitals below the SOMOs by using the rotate option
rotate {0,59,90} {36,60,90} {37,61,90} {38,62,90} end
end

%casscf
nel 12
norb 9
nroots 1000, 1000
mult 7, 5
maxiter 1
refs
  1 2 2 2 0 0 1 2 2
  1 2 2 2 0 0 2 1 2
  1 2 2 2 0 0 2 2 1
  1 2 2 2 0 1 0 2 2
  1 2 2 2 0 1 1 1 2
  1 2 2 2 0 1 1 2 1
  1 2 2 2 0 1 2 0 2
  ...
  2 2 2 2 2 0 0 2 0
  2 2 2 2 2 0 1 0 1
```

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