(continued from previous page)

```
↪-------------------------
TIP: Switch ON a Property calculation as DoProperty true:
------------------------------------------------------------------------------
↪-------------------------

------------------------------------------------------------------------------
↪-------------------------
General Input Parameters:
------------------------------------------------------------------------------
↪-------------------------
NEl                          Sets the number of electrons
Shell_PQN                    Sets the principle quantum number per type of shells␣
↪(s,p,d,f)
LFTCase                      !!!ALTERNATIVE TO Shell_PQN!!! Sets the given LFT␣
↪problem (2p3d, 1s3p3d, ...)
------------------------------------------------------------------------------
↪-------------------------
LFTCase WILL replace Shell_PQN
------------------------------------------------------------------------------
↪-------------------------
(e.g. Shell_PQN = 0,2,3,0 for a 2p3d calculation)
Mult                         Sets the Multiplicity/Multiplicities
NRoots                       Sets the number of Roots/Multiplicity
TMultiplets (0.01)           Threshold for the Multiplets grouping in eV
DoeV                         All values in eV. This is default. If set false the␣
↪cm-1 unit is used throughout
DoRAS                        Requests a RASCI calculation
RAS(nel: m1 h/ m2 / m3 p)    Computes the X-Ray Emission Spectra

RAS-reference with nel electrons
m1= number orbitals in RAS-1
h = max. number of holes in RAS-1
m2= number of orbitals in RAS-2 (any number of electrons or holes)
m3= number of orbitals in RAS-3
p = max. number of particles in RAS-3

DoElastic                    Computes in addition the Elastic Scattering terms in␣
↪RIXS/RIXSSOC calculations
------------------------------------------------------------------------------
↪-------------------------
Non Relativistic Spectroscopic Properties:
------------------------------------------------------------------------------
↪-------------------------
DoABS/DoXAS                  Computes the Absorption like Spectra
DoCD                         Computes the CD Spectra
DoXES                        Computes the X-Ray Emission Spectra
DoRIXS                       Computes the RIXS Spectra
DoQuadrupole                 Computes the ABS,XAS,RIXS Spectra beyond dipole␣
↪approximation
------------------------------------------------------------------------------
↪-------------------------
Relativistically Corrected Spectroscopic Properties:
------------------------------------------------------------------------------
↪-------------------------
DoSOC                        Requests the Spin Orbit Coupling Calculations
Note that this turned on automatically if zeta SOC
constant are provided
------------------------------------------------------------------------------
↪-------------------------
DoABS/DoXAS                  Computes the SOC Corrected Absorption like Spectra
DoCD                         Computes the SOC Corrected CD Spectra
```

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```
DoMCD/DoXMCD                    Computes the SOC Corrected MCD/XMCD Spectra
DoXESSOC:                       Computes the SOC Corrected XES Spectra
DoRIXSSOC:                      Computes the SOC Corrected RIXS Spectra
DoQuadrupole                    Computes the SOC Corrected ABS,XAS, XES RIXS Spectra␣
↪beyond dipole approximation
-------------------------------------------------------------------------------
↪-------------------------
Magnetic Properties:
-------------------------------------------------------------------------------
↪-------------------------
DoMagnetization                 Computes the Magnetization
DoSusceptibility                Computes the Susceptibilities
DoGTensor                       Computes the g-Tensors/Matrices
DoDTensor                       Computes the Zero-Field Splittings
DoATensor                       Computes the Hyperfine Tensors
DoEFGTensor                     Computes the Electric Field Gradient Tensors
(also Moesbauer Parameters in the presence of Fe centers)
-------------------------------------------------------------------------------
↪-------------------------
Variable Parameters (if they are not given, default values are used)
-------------------------------------------------------------------------------
↪-------------------------
Temperature(300)                Temperature to be used in the SOC calculations
MagneticField(0)                Magnetic Field (in Gauss)
NPointsPsi(10)                  Solid Angle Integration points Psi for MCD and XMCD
NPointsPhi(10)                  Solid Angle Integration points Phi for MCD and XMCD
NPointsTheta(10)                Solid Angle Integration points Theta for MCD and XMCD
-------------------------------------------------------------------------------
↪-------------------------
Variable Parameters needed for Magnetization and Susceptibility calculations
-------------------------------------------------------------------------------
↪-------------------------
LebedevIntegrationPoints(26)  Number for Integration points for Lebedev)
LebedevPrec(5)                  Precision of the grid for different field directions
(meaningful values range from 1 (smallest) to 10 (largest)
nPointsFStep (5)                Number of steps for numerical differentiation
(def: 5, meaningful values are 3, 5 7 and 9)
MAGTemperatureMIN(4.0)          Minimum Temperature (K) for Magnetization
MAGTemperatureMAX(4.0)          Maximum Temperature (K) for Magnetization
MAGTemperatureNPoints(1)        Number of Temperature points for Magnetization
MAGFieldStep(100.0)             Size of Field step for numerical differentiation␣
↪(def: 100 Gauss)
MAGFieldMin(0.0)                Minimum Field (Gauss) for Magnetization
MAGFieldMax(70000.0)            Minimum Field (Gauss) for Magnetization
MAGNPoints(15)                  Number of Field points for Magnetization
SUSTempMin(1)                   Minimum Temperature (K) for Susceptibility
SUSTempMxn(300.0)               Maximum Temperature (K) for Susceptibility
SUSNPoints(300)                 Number of Temperature points for Susceptibility
SUSStatFieldMIN(0.0)            Minimum Static Field (Gauss) for Susceptibility
SUSStatFieldMAX(1)              Maximum Static field (Gauss) for Susceptibility
SUSStatFieldNPoints(1)          Number of Static Fields for Susceptibility
-------------------------------------------------------------------------------
↪-------------------------
```

`orca_lft` can run standalone by processing an input file (`Basename.lft.inp`) with orca_lft

```
orca_lft BaseName.lft.inp -sim
```

Alternatively, one can call the main orca program like

```
orca BaseName.lft.inp
```

The different benefits of the two runs are provided in the `orca_lft` tutorial

`orca_lft` can also be used to automatically generate initial proper input files. For example, an initial bare input file `basename.lft_pd.inp` can be generated by running

```
orca_lft BaseName -pd_case
```

```
-------------------------------------------------------------
Initial Input: BaseName.lft_pd.inp for Orca_LFT has been generated:
-------------------------------------------------------------
```

The generated example input must be filled in with the required LFT parameters and the desired spectroscopic properties, after which the simulation can be started—just like in any standard multiplet program.

```
%lft


#-----Parameters------
NEl= 0
Shell_PQN= 0, 2, 3, 0
Mult= 0
NRoots= -1
#--------------------


#---Slater-Condon Parameters---
#---All Values in eV---
PARAMETERS
F0pp =  0.00
F2pp =  0.00
F0dd =  0.00
F2dd =  0.00
F4dd =  0.00
F0pd =  0.00
F2pd =  0.00
G1pd =  0.00
G3pd =  0.00
end
#--------------------


#---Diagonal LFT-Matrix Elelemnts---
#---All Values in eV---
FUNCTIONS
0   0 " 0.00"
1   1 " 0.00"
2   2 " 0.00"
3   3 " 0.00"
4   4 " 0.00"
5   5 " 0.00"
6   6 " 0.00"
7   7 " 0.00"
end
#--------------------


#---SPECTRA/PROPERTIES---
DoABS true
#---------
end
```

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```
*xyz 0 0
Atom 0.00 0.00 0.00
*
```

Special initial inputs based on an internal NEVPT2 database can also be generated. For the 2p3d LFT case of Ni(II), this can be done as follows:

```
orca_lft BaseName -atno28 -2p3d_case
```

```
-----------------------------------------------------------------------------
Creating input for Atom Ni(II) ...
-----------------------------------------------------------------------------


-------------------------------------------------------------
Initial Input: BaseName.lft_pd.inp for Orca_LFT has been generated:
-------------------------------------------------------------
```

The generated `BaseName.lft_pd.inp` file includes pre-filled LFT parameters from an internal NEVPT2 database, based on precomputed CASCI/NEVPT2 AILFT values. The resulting input-ready to runfor Ni^{II}-is as follows:

```
%lft


#-----Parameters------
NEl= 14
LFTCase 2p3d
Mult= 3, 1
NRoots= 25, 30
#--------------------


#---Slater-Condon Parameters---
#---All Values in eV---
PARAMETERS
F0pp =  85.88
F2pp =  54.77
F0dd =  23.31
F2dd =  13.89
F4dd =  9.14
F0pd =  33.03
F2pd =  7.76
G1pd =  6.42
G3pd =  2.11
end
#--------------------


#---Diagonal LFT-Matrix Elelemnts---
#---All Values in eV---
FUNCTIONS
0   0 " 0.00"
1   1 " 0.00"
2   2 " 0.00"
3   3 "1138.35"
4   4 "1138.35"
5   5 "1138.35"
6   6 "1138.35"
7   7 "1138.35"
end
#--------------------
```

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```
#---SPECTRA/PROPERTIES---
DoABS true
#---------
end


*xyz 2 3
Ni 0.00 0.00 0.00
*
```

Alternatively, as discussed in the Ab initio Ligand Field Theory section (*1- and 2-shell Abinitio Ligand Field Theory (AILFT)*), one may actually run a 2-shell AILFT calculation and produce the respective `.nevpt2.lft.inp` file

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


%method
frozencore fc_none
end

#--------------------
#Rotate Orbitals
#--------------------
%scf
rotate
{2,6,90}
{3,7,90}
{4,8,90}
end
end

#--------------------
#General Options
#--------------------
%casscf
nel 14
norb 8
mult 3,1
nroots 100,100

LFTCase 2p3d
rel
dosoc true
end
end


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

The structure of an `orca_lft` input is the following:

It contains:

- The General Parameters Block where the LFT problem is defined

```
-----Parameters------
NEl= 14
LFTCase 2p3d
```

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```
#Shells_PQN 0,2,3,0, Alternative definition using s,p,d,f main quantum numbers␣
↪Mult= 3, 1
NRoots= 25, 30
--------------------
```

- The PARAMETERS Block where the SCPs and SOC constant parameters are defined

```
---Slater-Condon Parameters---
---All Values in eV---
PARAMETERS
F0pp = 85.88
F2pp = 54.77
F0dd = 23.31
F2dd = 13.89
F4dd = 9.14
F0pd = 33.03
F2pd = 7.76
G1pd = 6.42
G3pd = 2.11
end
--------------------
```

```
---SOC-CONSTANTS---
---All Values in eV---
PARAMETERS
ZETA_P = 10.68
ZETA_D = 0.08
end
--------------------
```

- The FUNCTIONS Block where the LFT matrix is defined

```
---Diagonal LFT-Matrix Elelemnts---
---All Values in eV---
FUNCTIONS
0   0 " 0.00"
1   1 " 0.00"
2   2 " 0.00"
3   3 "1138.35"
4   4 "1138.35"
5   5 "1138.35"
6   6 "1138.35"
7   7 "1138.35"
end
--------------------
```

- The Properties Block where the desire simulation properties are specified

```
---SPECTRA/PROPERTIES---
DoABS true
--------------------
```

- The xyz Block where the ion, charge, multiplicity and coordinates (0. 0. 0.) are defined

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

Note

It should be emphasized the `orca_lft` through the FUNCTIONS and PARAMETERS subblocks provides

- Arbitrary parameterization of both the one-electron LFT matrix and the Slater–Condon parameters
- Powerful parameter scan capabilities

which helps to performs any kind of simulation without any symmetry restrictions. An example regarding the use of the FUNCTIONS and PARAMETERS subblocks is provided below, while a detailed `orca_lft` tutorial with worked out examples will be soon become available.

Let us perform the Ni^{2+} L-edge XAS spectrum simulation using the following input:

```
%lft


  #-----Parameters------
  NEl= 14
  LFTCase 2p3d
  Mult= 3, 1
  NRoots= 25, 30
  #--------------------


  #---Slater-Condon Parameters---
  #---All Values in eV---
  PARAMETERS
    F0pp =  85.88
    F2pp =  54.77
    F0dd =  23.31
    F2dd =  13.89
    F4dd =  9.14
    F0pd =  33.03
    F2pd =  7.76
    G1pd =  6.42
    G3pd =  2.11
  end
  #--------------------


  #---Diagonal LFT-Matrix Elelemnts---
  #---All Values in eV---
  FUNCTIONS
    0   0 " 0.00"
    1   1 " 0.00"
    2   2 " 0.00"
    3   3 "1138.35"
    4   4 "1138.35"
    5   5 "1138.35"
    6   6 "1138.35"
    7   7 "1138.35"
  end
  #--------------------

  #---SOC-CONSTANTS---
  #---All Values in eV---
  PARAMETERS
    ZETA_P = 11.341
    ZETA_D = 0.085
  end
  #--------------------

  #---SPECTRA/PROPERTIES---
  DoABS true
  Rel
```

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```
    DoSOC true
  End
  #---------
end


*xyz 2 3
Ni 0.00 0.00 0.00
*
```

Note

- From ORCA 6.1 orca_lft is properly connected with the QDPT driver
- This implies that all QDPT properties *Magnetic Properties Through Quasi Degenerate Perturbation Theory* can be requested within the Rel block

In the first step, the LFT problem at hand is defined:

```
------------------------------------------------------------------------------
                       L I G A N D    F I E L D    T H E O R Y
------------------------------------------------------------------------------


==============================================================================
                       LFT PARAMETERS DEFINITION BLOCK
==============================================================================


Number of electrons        = 14
Multiplicities             = 3 1
Roots                      = 25 30
Shells included            = 0 2 3 0


------------------------------------------------------------
Definition of the ligand field basis set:
------------------------------------------------------------
   0   = pz
   1   = px
   2   = py
   3   = dz2
   4   = dxz
   5   = dyz
   6   = dx2y2
   7   = dxy


------------------------------------------------------------
Definition of the static ligand field by the user:
There are 11 ligand field parameters

------------------------------------------------------------
  Nr.               Name       Initial Value
  ----------------------------------------
    1               F0PP          85.880000
    2               F2PP          54.770000
    3               F0DD          23.310000
    4               F2DD          13.890000
```

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```
    5               F4DD           9.140000
    6               F0PD          33.030000
    7               F2PD           7.760000
    8               G1PD           6.420000
    9               G3PD           2.110000
   10             ZETA_P          11.341000
   11             ZETA_D           0.085000


------------------------------------------------------------
Definition of the ligand field functions by the user:
There are 8 ligand field functions

------------------------------------------------------------
  Nr.      H-element         value   function
   ---------------------------------------------
 1   H(0,0)       0.000000000   0.00
 2   H(1,1)       0.000000000   0.00
 3   H(2,2)       0.000000000   0.00
 4   H(3,3)    1138.350000000  1138.35
 5   H(4,4)    1138.350000000  1138.35
 6   H(5,5)    1138.350000000  1138.35
 7   H(6,6)    1138.350000000  1138.35
 8   H(7,7)    1138.350000000  1138.35
```

After that, the CI problem is defined:

```
=> Defining the CI spaces and setting up the CI              ...
================================================================================
                            CI SETUP AND SOLUTION BLOCK
================================================================================


Making Checks...
   Multiplicty =   3, #(configurations) =     28 #(CSF's) =     28 #(Roots) =    ␣
↪25
   NRoots<NCSFs Adjussting  ==> (CSF's) =     25
Setting up CI...
   Multiplicty =   3, #(configurations) =     28 #(CSF's) =     25 #(Roots) =    ␣
↪25
================================================================================
                            CI SETUP AND SOLUTION BLOCK
================================================================================


Making Checks...
   Multiplicty =   1, #(configurations) =     36 #(CSF's) =     36 #(Roots) =    ␣
↪30
   NRoots<NCSFs Adjussting  ==> (CSF's) =     30
Setting up CI...
   Multiplicty =   1, #(configurations) =     36 #(CSF's) =     30 #(Roots) =    ␣
↪30
CI setup done
```

Then, the CI problem is solved:

```
-----------------------------
 LFT-CI TRANSITION ENERGIES
-----------------------------
```

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```
LOWEST ROOT (ROOT 0, MULT 3) =    460.113216547 Eh 12520.317 eV

STATE ROOT MULT  DE/a.u.     DE/eV    DE/cm**-1
   1:   1    3   0.000000     0.000       0.0
   2:   2    3   0.000000     0.000       0.0
   3:   3    3   0.000000     0.000       0.0
   4:   5    3   0.000000     0.000       0.0
   5:   4    3   0.000000     0.000       0.0
   6:   6    3   0.000000     0.000       0.0
   7:   0    1   0.086266     2.347   18933.2
   8:   1    1   0.086266     2.347   18933.2
   9:   2    1   0.086266     2.347   18933.2
  10:   3    1   0.086266     2.347   18933.2
  11:   4    1   0.086266     2.347   18933.2
  12:   7    3   0.099001     2.694   21728.2
  13:   8    3   0.099001     2.694   21728.2
  14:   9    3   0.099001     2.694   21728.2
  15:   5    1   0.132624     3.609   29107.7
  16:   6    1   0.132624     3.609   29107.7
  17:   7    1   0.132624     3.609   29107.7
  18:   8    1   0.132624     3.609   29107.7
  19:   9    1   0.132624     3.609   29107.7
  20:  10    1   0.132624     3.609   29107.7
  21:  12    1   0.132624     3.609   29107.7
  22:  11    1   0.132624     3.609   29107.7
  23:  13    1   0.132624     3.609   29107.7
  24:  14    1   0.331652     9.025   72789.3
  25:  15    1  29.897078   813.541 6561650.2
  26:  16    1  29.897078   813.541 6561650.2
  27:  17    1  29.897078   813.541 6561650.2
  28:  18    1  29.897078   813.541 6561650.2
  29:  19    1  29.897078   813.541 6561650.2
  30:  10    3  29.915627   814.046 6565721.2
  31:  11    3  29.915627   814.046 6565721.2
  32:  13    3  29.915627   814.046 6565721.2
  33:  12    3  29.915627   814.046 6565721.2
  34:  14    3  29.915627   814.046 6565721.2
  35:  15    3  29.915627   814.046 6565721.2
  36:  16    3  29.915627   814.046 6565721.2
  37:  17    3  29.978158   815.747 6579445.1
  38:  18    3  29.978158   815.747 6579445.1
  39:  19    3  29.978158   815.747 6579445.1
  40:  20    3  29.978158   815.747 6579445.1
  41:  21    3  29.978158   815.747 6579445.1
  42:  22    3  30.016020   816.777 6587754.9
  43:  23    3  30.016020   816.777 6587754.9
  44:  24    3  30.016020   816.777 6587754.9
  45:  20    1  30.087356   818.719 6603411.3
  46:  21    1  30.087356   818.719 6603411.3
  47:  22    1  30.087356   818.719 6603411.3
  48:  23    1  30.106270   819.233 6607562.6
  49:  24    1  30.106270   819.233 6607562.6
  50:  25    1  30.106270   819.233 6607562.6
  51:  26    1  30.106270   819.233 6607562.6
  52:  27    1  30.106270   819.233 6607562.6
  53:  29    1  30.106270   819.233 6607562.6
  54:  28    1  30.106270   819.233 6607562.6
```

accompanied by a multiplet analysis:

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

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```
Atomic calculation : Multiplet analysis (LFT)
-------------------------------------------------
11 multiplets found (Threshold = 0.01 eV)
  0 3F | E =     0.000 eV | 2p(6)3d(8)
  1 3P | E =     2.694 eV | 2p(6)3d(8)
  2 3F | E =   814.046 eV | 2p(5)3d(9)
  3 3D | E =   815.747 eV | 2p(5)3d(9)
  4 3P | E =   816.777 eV | 2p(5)3d(9)
  5 1D | E =     2.347 eV | 2p(6)3d(8)
  6 1G | E =     3.609 eV | 2p(6)3d(8)
  7 1S | E =     9.025 eV | 2p(6)3d(8)
  8 1D | E =   813.541 eV | 2p(5)3d(9)
  9 1P | E =   818.719 eV | 2p(5)3d(9)
 10 1F | E =   819.233 eV | 2p(5)3d(9)
-------------------------------------------------
```

This is followed by SOC computation in the QDPT framework:

```
************************************
Doing QDPT with ONLY SOC!
************************************

-----------------------------------
NONZERO SOC MATRIX ELEMENTS (cm**-1)
-----------------------------------

Bra                         Ket
<Block Root  S    Ms   | HSOC |  Block Root  S    Ms>    =  Real-part     Imaginary␣
↪part
-------------------------------------------------------------------------------------
↪---
0    1  1.0  1.0              0     0  1.0  1.0            0.000           -685.571
0    3  1.0  1.0              0     2  1.0  1.0            0.000            342.781
0    4  1.0  1.0              0     2  1.0  1.0            0.000              0.134
0    4  1.0  1.0              0     3  1.0  1.0            0.000             -2.946
0    5  1.0  1.0              0     2  1.0  1.0            0.000              0.987
0    5  1.0  1.0              0     3  1.0  1.0            0.000              7.920
0    5  1.0  1.0              0     4  1.0  1.0            0.000          -1022.995
0    6  1.0  1.0              0     2  1.0  1.0            0.000             -3.379

...

  1   29  0.0  0.0              0    17  1.0 -1.0        -2850.628           3039.
↪103
1   29  0.0  0.0              0    18  1.0 -1.0        -16745.172           2885.
↪219
1   29  0.0  0.0              0    19  1.0 -1.0        -1533.311           4672.283
1   29  0.0  0.0              0    20  1.0 -1.0          105.943            -43.140
1   29  0.0  0.0              0    21  1.0 -1.0           14.076             39.149

Note: In the following the full <I|HBO+SOC|J> are printed in the CI Basis.
I,J are compound indices for |Block/Mult, Ms, Root>, where the states
are ordered first by MultBlock, then Ms and finally Root.

...
```

The corrected SOC states are then printed out:

```
The threshold for printing is 0.0010
Eigenvectors:
                          Weight      Real          Image    : Block Root    Spin  ␣
```

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```
↪Ms
 STATE    0:       0.0000
                        0.014868    -0.121920     0.001813 :     0    0    1    1
                        0.158642     0.118778     0.380175 :     0    1    1    1
                        0.022316     0.003329     0.149347 :     0    2    1    1
                        0.073524    -0.037132     0.268598 :     0    3    1    1
                        0.071062    -0.251422     0.088592 :     0    4    1    1
                        0.068532    -0.250758     0.075180 :     0    5    1    1
                        0.010310     0.057750     0.083513 :     0    6    1    1
                        0.003333    -0.030103    -0.049264 :     0    0    1    0
                        0.007037     0.072029    -0.042999 :     0    1    1    0
                        0.245464     0.484256     0.104691 :     0    2    1    0
                        0.052920    -0.229815    -0.010229 :     0    3    1    0
                        0.017953     0.132002     0.022989 :     0    4    1    0
                        0.005423    -0.072174     0.014613 :     0    5    1    0
                        0.003723     0.024970     0.055669 :     0    6    1    0
                        0.018821     0.098122     0.095882 :     0    0    1   -1
                        0.081892    -0.206481     0.198135 :     0    1    1   -1
                        0.002458    -0.042784     0.025041 :     0    2    1   -1
                        0.057211    -0.099749     0.217397 :     0    3    1   -1
                        0.039565     0.098450     0.172838 :     0    4    1   -1
                        0.043388     0.182357     0.100666 :     0    5    1   -1
                        0.001044     0.019418     0.025827 :     0    6    1   -1
 STATE    1:       0.0000
                        0.042839    -0.206750    -0.009682 :     0    0    1    1
                        0.030129    -0.131357    -0.113467 :     0    1    1    1
                        0.004821    -0.067710    -0.015378 :     0    2    1    1
                        0.096567     0.259529     0.170915 :     0    3    1    1
                        0.019022    -0.134583    -0.030166 :     0    4    1    1
                        0.029125    -0.070877     0.155246 :     0    5    1    1
                        0.024443     0.150354     0.042856 :     0    6    1    1
                        0.126000    -0.140903    -0.325802 :     0    0    1    0
                        0.066620    -0.112104    -0.232493 :     0    1    1    0
                        0.034344    -0.075363    -0.169305 :     0    2    1    0
                        0.043496    -0.012839    -0.208161 :     0    3    1    0
                        0.035068    -0.017670     0.186428 :     0    4    1    0
                        0.088777    -0.019366    -0.297325 :     0    5    1    0
                        0.032394    -0.009435    -0.179735 :     0    6    1    0
                        0.033273    -0.179716    -0.031232 :     0    0    1   -1
                        0.038086    -0.175066     0.086245 :     0    1    1   -1
                        0.058972    -0.201976     0.134823 :     0    2    1   -1
                        0.091992     0.163866    -0.255226 :     0    3    1   -1
                        0.051908    -0.117870     0.194975 :     0    4    1   -1
                        0.015287    -0.106696    -0.062470 :     0    5    1   -1
                        0.036319     0.039383    -0.186462 :     0    6    1   -1
...
STATE 104: 6683223.2237
                        0.048335    -0.215907     0.041467 :     0   17    1    1
                        0.001350    -0.015566    -0.033287 :     0   18    1    1
                        0.058642    -0.018471    -0.241456 :     0   19    1    1
                        0.014743    -0.111453    -0.048181 :     0   20    1    1
                        0.019424    -0.128940     0.052904 :     0   21    1    1
                        0.013441    -0.042408    -0.107900 :     0   22    1    1
                        0.013136     0.106586    -0.042134 :     0   23    1    1
                        0.027360    -0.066625    -0.151399 :     0   24    1    1
                        0.030687     0.028711     0.172808 :     0   17    1    0
                        0.005134    -0.016659    -0.069691 :     0   18    1    0
                        0.006811    -0.016403    -0.080880 :     0   20    1    0
                        0.100510    -0.057415    -0.311791 :     0   21    1    0
                        0.054414    -0.044209    -0.229041 :     0   23    1    0
                        0.048345    -0.215766     0.042306 :     0   17    1   -1
```

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```
                        0.001057    -0.001549     0.032472 :     0   18    1   -1
                        0.060316     0.071066     0.235085 :     0   19    1   -1
                        0.015880    -0.093356     0.084643 :     0   20    1   -1
                        0.019274    -0.138702    -0.005996 :     0   21    1   -1
                        0.013436    -0.004756     0.115817 :     0   22    1   -1
                        0.013139     0.114517     0.004987 :     0   23    1   -1
                        0.026471    -0.005403     0.162611 :     0   24    1   -1
                        0.050526     0.219718    -0.047434 :     1   20    0    0
                        0.293497    -0.532819     0.097985 :     1   21    0    0
                        0.064015     0.249661    -0.041039 :     1   22    0    0
```

Then, the SOC-corrected absorption (here XAS) spectrum is provided:

```
-------------------------------------------------------------------------------
-----------------------
     SOC CORRECTED ABSORPTION SPECTRUM VIA TRANSITION ELECTRIC DIPOLE MOMENTS
-------------------------------------------------------------------------------
-----------------------
     Transition          Energy     Energy  Wavelength fosc(D2)      D2        |DX|␣
↪     |DY|       |DZ|
                          (eV)      (cm-1)    (nm)  (*population)  (au**2)     (au)␣
↪     (au)       (au)
-------------------------------------------------------------------------------
-----------------------
  1-3.0A  ->  2-3.0A    0.000000       0.0     0.0   0.000000000   0.00000   0.
↪00000   0.00000   0.00000
  0-3.0A  ->  1-3.0A    0.000000       0.0     0.0   0.000000000   0.00000   0.
↪00000   0.00000   0.00000
  0-3.0A  ->  2-3.0A    0.000000       0.0     0.0   0.000000000   0.00000   0.
↪00000   0.00000   0.00000
  1-3.0A  ->  3-3.0A    0.000000       0.0     0.0   0.000000000   0.00000   0.
↪00000   0.00000   0.00000
  2-3.0A  ->  3-3.0A    0.000000       0.0     0.0   0.000000000   0.00000   0.
↪00000   0.00000   0.00000
  0-3.0A  ->  3-3.0A    0.000000       0.0     0.0   0.000000000   0.00000   0.
↪00000   0.00000   0.00000
  1-3.0A  ->  4-3.0A    0.000000       0.0     0.0   0.000000000   0.00000   0.
↪00000   0.00000   0.00000
  2-3.0A  ->  4-3.0A    0.000000       0.0     0.0   0.000000000   0.00000   0.
↪00000   0.00000   0.00000
  2-3.0A  ->  5-3.0A    0.000000       0.0     0.0   0.000000000   0.00000   0.
↪00000   0.00000   0.00000
  2-3.0A  ->  6-3.0A    0.000000       0.0     0.0   0.000000000   0.00000   0.
↪00000   0.00000   0.00000
  0-3.0A  ->  4-3.0A    0.000000       0.0     0.0   0.000000000   0.00000   0.
↪00000   0.00000   0.00000
  1-3.0A  ->  7-3.0A    0.000000       0.0     0.0   0.000000000   0.00000   0.
↪00000   0.00000   0.00000
  1-3.0A  ->  6-3.0A    0.000000       0.0     0.0   0.000000000   0.00000   0.
↪00000   0.00000   0.00000
  2-3.0A  ->  7-3.0A    0.000000       0.0     0.0   0.000000000   0.00000   0.
↪00000   0.00000   0.00000
  1-3.0A  ->  5-3.0A    0.000000       0.0     0.0   0.000000000   0.00000   0.
↪00000   0.00000   0.00000
  0-3.0A  ->  6-3.0A    0.000000       0.0     0.0   0.000000000   0.00000   0.
↪00000   0.00000   0.00000
  0-3.0A  ->  7-3.0A    0.000000       0.0     0.0   0.000000000   0.00000   0.
↪00000   0.00000   0.00000
  0-3.0A  ->  5-3.0A    0.000000       0.0     0.0   0.000000000   0.00000   0.
↪00000   0.00000   0.00000
  1-3.0A  ->  8-3.0A    0.000000       0.0     0.0   0.000000000   0.00000   0.
```

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```
↪00000   0.00000   0.00000
  2-3.0A  ->  8-3.0A    0.000000       0.0     0.0   0.000000000   0.00000   0.
↪00000   0.00000   0.00000
  0-3.0A  ->  8-3.0A    0.000000       0.0     0.0   0.000000000   0.00000   0.
↪00000   0.00000   0.00000
  2-3.0A  ->  9-3.0A    0.171933    1386.7  7211.2   0.000000000   0.00000   0.
↪00000   0.00000   0.00000
  1-3.0A  ->  9-3.0A    0.171933    1386.7  7211.2   0.000000000   0.00000   0.
↪00000   0.00000   0.00000
  0-3.0A  ->  9-3.0A    0.171933    1386.7  7211.2   0.000000000   0.00000   0.
↪00000   0.00000   0.00000
  1-3.0A  -> 10-3.0A    0.171933    1386.7  7211.2   0.000000000   0.00000   0.
↪00000   0.00000   0.00000
  2-3.0A  -> 10-3.0A    0.171933    1386.7  7211.2   0.000000000   0.00000   0.
↪00000   0.00000   0.00000
  0-3.0A  -> 10-3.0A    0.171933    1386.7  7211.2   0.000000000   0.00000   0.
↪00000   0.00000   0.0

...

2-3.0A  -> 45-3.0A   808.419525 6520343.9     1.5   0.001132627   0.00052   0.
↪01199   0.00520   0.01856
1-3.0A  -> 45-3.0A   808.419525 6520343.9     1.5   0.000466250   0.00021   0.
↪00950   0.00818   0.00742
0-3.0A  -> 45-3.0A   808.419525 6520343.9     1.5   0.001659029   0.00075   0.
↪01729   0.00696   0.02018
2-3.0A  -> 46-3.0A   808.419525 6520343.9     1.5   0.001163057   0.00053   0.
↪01282   0.00222   0.01896
1-3.0A  -> 46-3.0A   808.419525 6520343.9     1.5   0.000718139   0.00033   0.
↪00902   0.01359   0.00780
0-3.0A  -> 46-3.0A   808.419525 6520343.9     1.5   0.000710800   0.00032   0.
↪01397   0.01112   0.00211
2-3.0A  -> 47-3.0A   808.419525 6520343.9     1.5   0.002893681   0.00132   0.
↪02588   0.01640   0.01943
1-3.0A  -> 47-3.0A   808.419525 6520343.9     1.5   0.001285542   0.00058   0.
↪02045   0.00869   0.00955
2-3.0A  -> 48-3.0A   808.419525 6520343.9     1.5   0.000921831   0.00042   0.
↪00885   0.01380   0.01228
```

By processing the `*.out` file as usual with orca_mapspc *orca_mapspc*, the *.dat and *.stk files are generated. The XAS spectrum plotted using these files is given in Fig. 9.10.

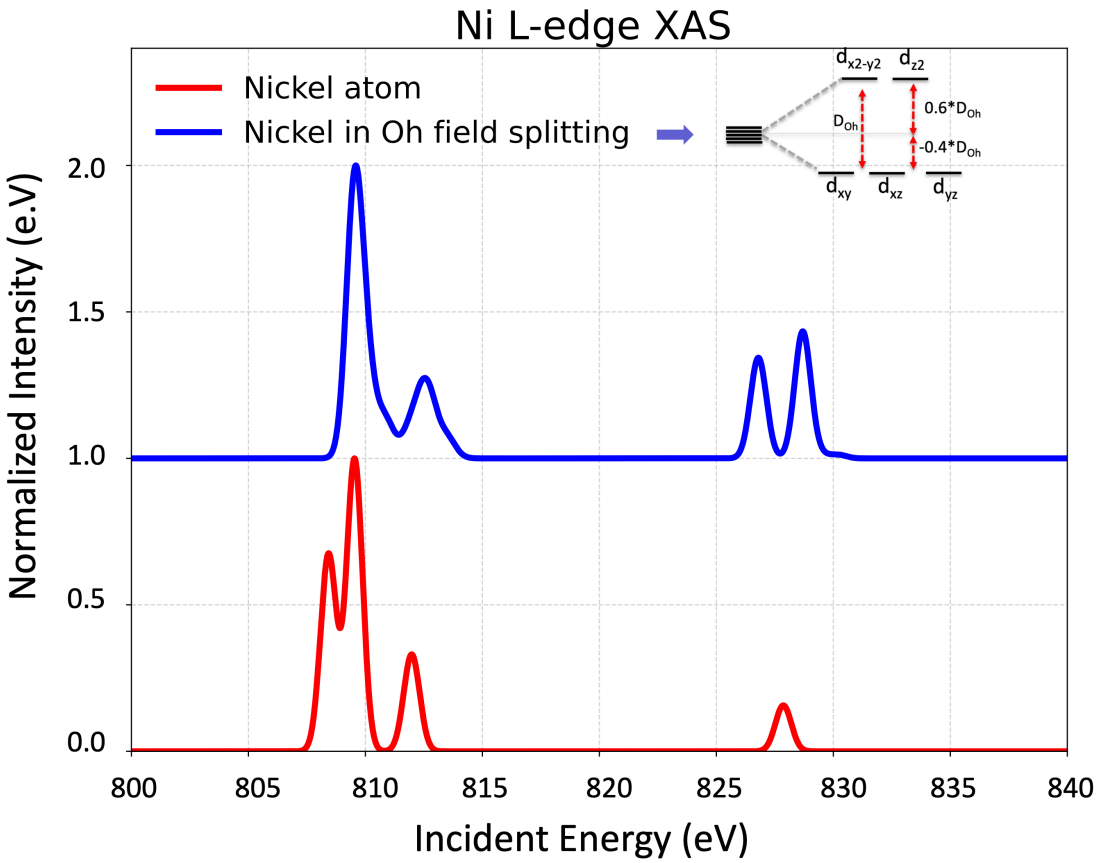

Fig. 9.10: orca_lft simulated Ni^{2+} L-edge XAS spectrum for the Nickel atom (red) and for the Nickel atom in the presence of an Oh field

The power of orca_lft stems from the fact that is entirely paramerizable. This flexibility is enabled through the intrinsic capabilities of the PARAMETERS and FUNCTIONS subblocks

- **Parameters Scanability** Any given parameter—for example, the `ZETA_D` spin-orbit coupling (SOC) constant in the D-shell can be:
- *Switched on/off*: `ZETA_D= 0.0`
- *Scanned over a range of parameters*: `ZETA_D= 0.0, 0.1, 11`, which spans the range 0.0-0.1 eV for 11 steps.
- **Definition of New Parameters**
- *Users may define any number or type of custom parameters within the PARAMETERS subblock*: e.g. `10Dq= 1.2`
- **Algebraic Relations in the PARAMETERS and FUNCTIONS Subblocks**
- *Algebraic relations in the PARAMETERS subblock*:

```
`DOh = 1.2`
`D1 = {-0.4*DOh}`
`D2 = {0.6*DOh}`
```

- *Algebraic relations in the FUNCTIONS subblock*:

```
`3   3 "1138.35 + D2" # => dz2`
`4   4 "1138.35 + D1" # => dxz`
```

This provides the necessary flexibility to set up arbitrarily parameterized ligand field theory (LFT) models tailored to specific experimental chemical problems.

As an example, let us revisit the nickel complex discussed above and introduce a barycentric octahedral ligand field splitting of the d-orbital shell with 10Dq=1.2 eV.

The input now reads:

```
%lft


  #-----Parameters------
  NEl= 14
  LFTCase 2p3d
  Mult= 3, 1
  NRoots= 25, 30
  #--------------------


  #---Slater-Condon Parameters---
  #---All Values in eV---
  PARAMETERS
    F0pp =  85.88
    F2pp =  54.77
    F0dd =  23.31
    F2dd =  13.89
    F4dd =  9.14
    F0pd =  33.03
    F2pd =  7.76
    G1pd =  6.42
    G3pd =  2.11
    DOh = 1.2
    D1 = {-0.4*DOh}
    D2 = {0.6*DOh}
  end
  #--------------------


  #---Diagonal LFT-Matrix Elelemnts---
  #---All Values in eV---
  FUNCTIONS
    0   0 " 0.00"
    1   1 " 0.00"
    2   2 " 0.00"
    3   3 "1138.35 + D2" # => dz2
    4   4 "1138.35 + D1" # => dxz
    5   5 "1138.35 + D1" # => dyz
    6   6 "1138.35 + D2" # => dx2-y2
    7   7 "1138.35 + D1" # => dxy
  end
  #--------------------

  #---SOC-CONSTANTS---
  #---All Values in eV---
  PARAMETERS
    ZETA_P = 11.341
    ZETA_D = 0.085
  end
  #--------------------

  #---SPECTRA/PROPERTIES---
  DoABS true
  Rel
    DoSOC true
  End
  #---------
```

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```
End

*xyz 2 3
Ni 0.00 0.00 0.00
*
```

By running the above inputone see that the new parameters `DOH`, `D1` and `D2` are succesfully defined:

```
------------------------------------------------------------
Definition of the ligand field basis set:
------------------------------------------------------------
   0  = pz
   1  = px
   2  = py
   3  = dz2
   4  = dxz
   5  = dyz
   6  = dx2y2
   7  = dxy


------------------------------------------------------------
Definition of the static ligand field by the user:
There are 14 ligand field parameters

------------------------------------------------------------
  Nr.               Name       Initial Value
  ----------------------------------------
    1               F0PP          85.880000
    2               F2PP          54.770000
    3               F0DD          23.310000
    4               F2DD          13.890000
    5               F4DD           9.140000
    6               F0PD          33.030000
    7               F2PD           7.760000
    8               G1PD           6.420000
    9               G3PD           2.110000
   10                DOH           1.200000
   11                 D1          -0.480000
   12                 D2           0.720000
   13             ZETA_P          11.341000
   14             ZETA_D           0.085000
```

And the Oh LFT splitting is take into account in the 1-electron LFT matrix as:

```
------------------------------------------------------------
Definition of the ligand field functions by the user:
There are 8 ligand field functions

------------------------------------------------------------
  Nr.      H-element         value   function
  ----------------------------------------------
 1   H(0,0)      0.000000000   0.00
 2   H(1,1)      0.000000000   0.00
 3   H(2,2)      0.000000000   0.00
 4   H(3,3)   1139.070000000  1138.35 + D2
 5   H(4,4)   1137.870000000  1138.35 + D1
 6   H(5,5)   1137.870000000  1138.35 + D1
 7   H(6,6)   1139.070000000  1138.35 + D2
 8   H(7,7)   1137.870000000  1138.35 + D1
```

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```
=> Defining the one-electron LFT matrix                    ... done
------------------------------------------------------------
The ligand field one electron eigenfunctions:
------------------------------------------------------------
Orbital    Energy (eV) Energy(cm-1)          pz         px         py         dz2 ␣
↪      dxz         dyz       dx2-y2       dxz
   1          0.000        0.0           1.000000   0.000000   0.000000   0.
↪000000   0.000000   0.000000   0.000000   0.000000
   2          0.000        0.0           0.000000   1.000000   0.000000   0.
↪000000   0.000000   0.000000   0.000000   0.000000
   3          0.000        0.0           0.000000   0.000000   1.000000   0.
↪000000   0.000000   0.000000   0.000000   0.000000
   4       1137.870  9177541.4           0.000000   0.000000   0.000000   0.
↪000000   1.000000   0.000000   0.000000   0.000000
   5       1137.870  9177541.4           0.000000   0.000000   0.000000   0.
↪000000   0.000000   1.000000   0.000000   0.000000
   6       1137.870  9177541.4           0.000000   0.000000   0.000000   0.
↪000000   0.000000   0.000000   0.000000   1.000000
   7       1139.070  9187220.1           0.000000   0.000000   0.000000   0.
↪000000   0.000000   0.000000   1.000000   0.000000
   8       1139.070  9187220.1           0.000000   0.000000   0.000000   1.
↪000000   0.000000   0.000000   0.000000   0.000000
```

Upon successful termination, one can process the Ni L-edge XAS spectrum and plot the resulting data, as shown in Fig. 9.10 (blue line), which indeed reproduces characteristic features of the Ni L-edge XAS spectrum of, for example, $Ni(H_2O)_6$.

Note

- A detailed tutorial will soon become available that further explores the capabilites of orca_lft

9.2.16 orca_crystalprep

ORCA features a utility program `orca_crystalprep` that can process crystallographic `.cif` files or `.xyz` supercell files and produce proper inputs for the embedded cluster calculations.

To perform an embedded cluster calculation conventionally or within the Ionic-Crystal-QMMM, one needs to define basically 3 regions:

1. The quantum cluster QC that will be treated quantum mechanically.
2. The point charge region PC that represents the solid's environment.
3. A boundary region BR or ECP that is located between the QC and PC with the main role to prevent charge communication between the QC and PC regions.

This implies that, in the first step, a SuperCell (.xyz) must be generated, with different regions separated according to the calculation design. In the second step, the charge of the system must be balanced. Finally, all these need to be combined into a proper calculation input.

This is clearly a multistep and many times multiplatform process that is

1. complicated,
2. time consuming,
3. not user friendly.

The `orca_crystalprep` utility is designed to automatically generate proper inputs for ORCA embedded cluster calculations with the aim to allow to a wide range of experienced and not experienced users the ability to setup an embedded cluster calculation with a minimal effort.

`orca_crystalprep` requires its own input. By simply executing it from the terminal:

```
orca_crystalprep
```

one gets printings for the usage

```
*****************************************************************************************
Generate initial ORCA CrystalPrep Input
*****************************************************************************************

=========================================================================================
Usage: orca_crystalprep [Basename Input] [options]
=========================================================================================

-----------------------------------------------------------------------------
↪--------------------------
[Options]:
-----------------------------------------------------------------------------
↪--------------------------
-geninput                     Generate Initial Input
-----------------------------------------------------------------------------
↪--------------------------

*****************************************************************************************
Generate ORCA Embedding Cluster Inputs using the CrystalPrep Utility
*****************************************************************************************

=========================================================================================
Usage: orca_crystalprep [CrystalPrep Input]
=========================================================================================
```

and the different options:

```
-----------------------------------------------------------------------------
↪--------------------------
[CrystalPrep Input Options]:
-----------------------------------------------------------------------------
↪--------------------------
General Definitions
-----------------------------------------------------------------------------
↪--------------------------
DoCIF                         true                    This will process a .cif file
DoXYZ                         true                    This will process a .xyz file
InputCIF                      "CIFFileName"           Set the name of the␣
↪CIFFileName
InputXYZ                      "XYZFileName"           Set the name of the␣
↪XYZFileName
-----------------------------------------------------------------------------
↪--------------------------
SuperCell Construction Definitions
-----------------------------------------------------------------------------
↪--------------------------
DoSuperCell                   true                    Flag to generate a SuperCell
SCDimension                   "axbxc"                 The Dimension of the␣
↪SuperCell (e.g. "1x1x1")
InputCIF                      "CIFFileName"           Set the name of the␣
↪CIFFileName
InputXYZ                      "XYZFileName"           Set the name of the␣
↪XYZFileName
-----------------------------------------------------------------------------
↪--------------------------
Special Tasks on SuperCells
-----------------------------------------------------------------------------
```

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```
↪--------------------------
DoFractional                 true                    Flag to Transform Cartesian␣
↪to Fractional coordinates
DoSymmetryOperations         true                    Flag to enforce using built␣
↪in Symmetry Operations
DoHemiSphereSC               true                    Flag to request a Hemisphere␣
↪Super Cell build
DoSymetricSC                 true/false              Flag to request a Symmetric␣
↪Super Cell build
                             false => Origin Build    :  0 - ra,   0 - rb,   0 -␣
↪rc  => Default for Now!
                             true  => Symmetric Build :  -ra - ra, -rb - rb, -rc -␣
↪rc
-------------------------------------------------------------------------------
↪--------------------------
Embedding Cluster Definitions
-------------------------------------------------------------------------------
↪--------------------------
DoEmbedding                  true                    Flag to generate the files␣
↪for the embedding approach
UseVolumeCriterion           true                    Volume Criterion to generate␣
↪layers
UseDistanceCriterion         true                    Distance Criterion to␣
↪generate layers
CellVolumeFraction           value                   Cell(UniCell/SuperCell)␣
↪fraction (default 1.0)
DoMolecularFragments         value                   Define Molecular Fragments␣
↪during the build
DoSimpleInput                true                    Flag to generate a␣
↪conventional Embedding Cluster input
DoICQMMMInput                true                    Flag to generate a Ionic-
↪Crystal-QMMM input
DoMCQMMMInput                true                    Flag to generate a Mol-
↪Crystal-QMMM input
WritePDB                     true                    Flag to run a Ionic-Crystal-
↪QMMM input from a PDF file
QCCharge                     Charge Number           Specify the total QC Charge
QCMult                       Multiplicity Number     Specify the total Multiplicity
-------------------------------------------------------------------------------
↪--------------------------
Special Tasks on Embedding Cluster Construction/Definition
-------------------------------------------------------------------------------
↪--------------------------
DoLayers                     true                    Request Layers Definition
1) Layers Definition. There are 2 Options:
             a) The Differnt regions are build in layers as multipoles of the␣
↪UnitCell
             b) The Differnt regions are build in layers around a predefined QC␣
↪cluster via a QCAtom List
QCLayers                     QC Layers Number        Specify the number of the QC␣
↪Layers
ECPLayers                    ECP Layers Number       Specify the number of the ECP␣
↪Layers
PCLayers                     PC Layers Number        Specify the number of the PC␣
↪Layers
HFLayers                     HF Layers Number        Specify the number of the HF␣
↪Layers
Example Input
QCLayers 1
2) Atoms Definition. This is alternative to Layers Definition (e.g. DoLayers false)
NQCAtoms                     QC Atoms  Number        Specify the number of the QC␣
```

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