MolForge 1.0.0-beta Manual

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CONTENTS

I. SPIRAL: SPIN-PHONON INTERACTION AND RELAXATION AT THE ATOMISTIC LEVEL

mpirun -n *ncores* **Spiral.x -spin_cpu** *ncpu* **-i** *input*

Options:

-i *input* ; file name of the input file

-spin_cpu *ncpu* ; Number of mpi processes dedicated to the distribution of spin matrices over cpu; -spin_cpu 1 would use all cores for phonon matrices

A.   Define a Spin Hamiltonian

&SPIN_H

&DEF_G *kind-i* .... Defines the g-tensor for S_i, optional, multiple blocks can be defined

g_{11} g_{12} g_{13}
g_{21} g_{22} g_{23}
g_{31} g_{32} g_{33}
&END

&DEF_DSI *kind-i* .... Defines the single-ion anisotropy tensor **D** for S_i, optional, multiple blocks can be defined

D_{11} D_{12} D_{13}
D_{21} D_{22} D_{23}
D_{31} D_{32} D_{33}
&END

&DEF_D2S *kind-i kind-j* .... Defines the anisotropic exchange tensor **D** for spins S_i S_j, optional, multiple blocks can be defined

D_{11} D_{12} D_{13}
D_{21} D_{22} D_{23}
D_{31} D_{32} D_{33}
&END

&DEF_O *kind-i l-order* .... Defines coefficients of the single ion crystal field tensor of order l, B_m^l, for spin S_i, optional, multiple blocks can be defined

$(-l)$ B_{-l}^l
$(-l+1)$ B_{-l+1}^l
...
(l) B_l^l
&END

SPINSPIN *cutoff* .... Turn on the calculation of dipolar spin-spin interactions for spins closer than *cutoff* expressed in Angstrom

EULER α β γ .... Euler's rotation angles, in radiants, for a rotation of the spin Hamiltonian. Convention ZYZ.

&END

Spiral allows to define a general spin Hamiltonian operator containing up to two-spin interaction terms:

$$\hat{H} = \sum_i \left[\vec{s}_i \cdot \mathbf{D_i} \cdot \vec{s}_i + \sum_{l=2}^{2|s_i|} \sum_{m=-l}^{m=l} B_m^l(i)\hat{O}_m^l(\vec{s}_i) + \vec{s}_i \cdot \mathbf{g_i} \cdot \vec{\mathbf{B}} \right] + \sum_{ij} \left[\vec{s}_i \cdot \mathbf{D_{ij}} \cdot \vec{s}_j + J_{ij}\vec{s}_i\vec{s}_j \right], \tag{1}$$

where $\mathbf{D_i}$ is a trace-less Cartesian tensor describing the single-ion anisotropy contribution to the Zero-Field splitting, $\mathbf{D_{ij}}$ is a trace-less Cartesian tensor describing the exchange anisotropy among spin i and spin j, $\mathbf{g_i}$ is the Landè tensor describing the Zeeman interaction with the external field $\vec{\mathbf{B}}$, and J_{ij} is the Heisenberg isotropic exchange coupling constant among two spins. Finally, $\hat{O}_m^l$ are generalized single-ion tesseral operators, which describes the zero field splitting at any order, and B_m^l are their coefficients, also know as crystal field parameters. It should be noted that $\mathbf{D_i}$ is equivalent to the set of coefficients $\{B_m^2\}$.

B. Define the Spin Systems

&SYSTEM

&DEF_SPINS

S *kind-id S-value* μ_B .... Define spin kinds: id, spin value and Bohr magneton.
Each line defines a new kind of spin

&END

&CELL .... Defines the unit-cell

A a_x a_y a_z
B b_x b_y b_z
C c_x c_y c_z

NREP N_A N_B N_C .... Multiply the cell N_AxN_BxN_C

&COORD .... Each line defines one spin kind and Cartesian coordinates.
S *kind-id* x_1 y_1 z_1
S *kind-id* x_2 y_2 z_2
...
S *kind-id* x_N y_N z_N
&END

&END

B B_x B_y B_z .... Defines the external static field in Tesla units

&END

C.   Define the Vibrational Hamiltonian

```
&SPH_H

  &PHONDY
    TEMP T  ...................  Phonons temperature in Kelvin
    K_MESH Nqx Nqy Nqz  .....  q-points mesh for Brillouin zone integration
    SMEAR smear  .............  Value of smear to apply to phonons' resonances (cm⁻¹)
    TYPE_SMEAR type  ........  type=1 for Gaussian smearing or type=0 for Lorentzian smearing
                               Filename of the file containing the harmonic force constants (see PHONDY
    FC2 FC2_FILE  .............  documentation for format)
    MAX_ENER max_ener  ......  Energy cutoff for phonons (cm⁻¹)
  &END

  &DSI_BATH kind-i  ...........  Modulation of a single-ion anisotropy tensor
    FILENAME SPH_FILE  .....  Filename of the file containing the Cartesian spin-phonon coupling coefficients
    NORDER order  ............  Order of spin-phonon coupling, 1 or 2 currently implemented
  &END

  &D2S_BATH kind-i kind-j ......  Modulation of Anisotropic Exchange Tensor
    FILENAME SPH_FILE  .....  Filename of the file containing the Cartesian spin-phonon coupling coefficients
    NORDER order  ............  Order of spin-phonon coupling, 1 or 2 currently implemented
  &END

  &G_BATH kind-i  .............  Modulation of Landè tensor
    FILENAME SPH_FILE  .....  Filename of the file containing the Cartesian spin-phonon coupling coefficients
    NORDER order  ............  Order of spin-phonon coupling, 1 or 2 currently implemented
  &END

  &O_BATH kind-i order-l  .......  Modulation of Crystal field operator of order l
    FILENAME SPH_FILE  .....  Filename of the file containing the Cartesian spin-phonon coupling coefficients
    ORDER order  ..............  Order of spin-phonon coupling, 1 or 2 currently implemented
  &END

  SECULAR  ....................  Turn on the diagonal approximation of the Redfield equations.
                               Mandatory for PT2 calculations

  PT2  .........................  Turn on the calculation of Raman rates due to second-order
                               time-dependent perturbation theory

&END
```

D. Build the Hilbert Space

&HILBERT_SPACE

FULLDIAG .... Diagonalize the spin Hamiltonian and express all quantities in its eigenbasis (required for spin-phonon relaxation)

NODIAG .... Do not diagonalize the Hamiltonian and work in the S_z eigenbasis

MAX_EX val .... val=-1,1,...,N Maximum number of spin excitations wrt to the fully polarized state, (val=-1 for the full Hilbert space)

DUMP_FREQ val .... Print out every val of steps

DUMP_S $FLAG$ .... FLAG=T or F. Print to disk the expectation values of the Spin operators

DUMP_MI M S_1 S_2 ... S_M .... Compute and print the spin operators of M selected spins

&END

E. Initialize and Propagate the Dynamics

&DENSITY_MATRIX
   TYPE *FLAG* .... *FLAG*=FULLY_POLARIZED all the spins are initialized along $-z$
                                           FLAG=THERMAL_POPULATION A Boltzman distribution of the
                                           diagonal levels of $\hat{\rho}$ is assumed
   TEMP *T* .... Initial spin temperature in Kelvin
&END

Build propagator with time step size *Step* in *ps*, and multiply it for itself *Nmult*
BUILD_PROPAGATOR *Step N* . times

PROPAGATE *N*   Propagate the spin dynamics for N number of steps

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II. PHONDY: PHONONS DYNAMICS AND LATTICE PROPERTIES FROM AB-INITIO SIMULATIONS

mpirun -n *ncores* **PhonDy.x -option** *option-arguments*

Options:

-restart *fc2-file-name* ; See below for the file format

-nk *nk1 nk2 nk3* ; Number of points for integrating the BZ along each direction

-smear *smear-val* ; σ value for Gaussian Smearing. Units in cm^{-1}

-dos1p *range-min range-max bin-size* ; units in cm^{-1}

-dos2p *range-min range-max bin-size* ; units in cm^{-1}

-path *BZ path file name* ; See below for the file format

-cart_disp *kp bn nsteps step-size* ; Print the atomic displacements for a mode

-dipole *Dipole-moment-Cartesian-derivatives-file*

III. TOOLS

A. get_FC: Calculation of lattice force constants

get_FC.x -option *option-arguments*

Options:

-xyz *filename; name of the file with unit-cell atoms positions*

-cell *filename; name of the file with the 3 by 3 matrix with unit-cell parameters*

-n *nx ny nz; three integer numbers representing the size of the supercell*

-step $step_size$; *onerealnumberrepresentingthesizeofthedisplacementforfinitedifferences*

-gen_disp *the lone keyword will activate the generation of all the distorted structures*

-read_forces *filename; name of the xyz file (excluded the column of lables) containing all the forces for the force constant calculation*

B. get_CF: Crystal Field and Spin Hamiltonian Parameters

The Tool CF.x is used to fit the parameters of a model Hamiltonian from the solutions of a CI ab-initio calculation.

The model Hamiltonian is defined as

$$\hat{H} = \sum_{lm} B_m^l \hat{O}_m^l(\vec{\mathbf{V}}) \,, \tag{2}$$

where $l \leq 2|V|$, $-l \leq m \leq l$ and $\vec{\mathbf{V}}$ can either be the total angular momentum $\vec{\mathbf{J}}$ or the spin operator $\vec{\mathbf{S}}$. In the former case $\hat{H}$ corresponds to the Crystal Field Hamiltonian $\hat{H}_{CF}(\vec{\mathbf{J}})$ and in the latter case it corresponds to the spin Hamiltonian $\hat{H}_{SH}(\vec{\mathbf{S}})$.

The generalized operators $\hat{O}_m^l(\vec{\mathbf{V}})$ are defined as Tesseral Tensor Operators (TTO) [App. Mag. Res. (2009), 35, 481-493]

$$\hat{O}_m^l = \hat{Y}_m^l \quad \text{if } l = 0 \tag{3}$$

$$\hat{O}_m^l = \frac{1}{\sqrt{2}}((-1)^m \hat{Y}_m^l + \hat{Y}_{-m}^l) \quad (m > 0) \tag{4}$$

$$\hat{O}_{-m}^l = \frac{i}{\sqrt{2}}((-1)^{m+1} \hat{Y}_m^l + \hat{Y}_{-m}^l) \quad (m > 0) \tag{5}$$

where $\hat{Y}_m^l(\vec{\mathbf{V}})$ are spherical tensor operators as defined in [J. Mag. Res. (1999) 140, 141-145]. The matrix elements of Y can conveniently be calculated exploiting the Wigner-Eckart theorem employing the definitions of Eqs. 17 and 20 of ref [J. Mag. Res. (1999) 140, 141-145].

The mapping between Eq. 2 and the CI results is performed by minimizing the deviation between the matrix elements of the model Hamiltonian and those of the CI solutions with respect to the basis set of the S (J) eigenfunctions $|S^2 M_S\rangle$ ($|J^2 M_J\rangle$) as discussed in ref [J. Chem. Theory Comput. (2009) 5, 11, 2977–2984].

The software CF.x reads 6 files: Lx.dat Lz.dat Lx.dat Lz.dat SOCI.dat SOCR.dat, containing the matrix elements of the spin and orbital angular momentum, and spin orbit coupling in the basis of the CI solutions. All these files can

automatically be extracted from output file of a CASSCF simulation carried out with the code ORCA by employing the scripts *get_SH_Orca.x* or *get_CF_Orca.x*. **NB:** The CASSCF calculation must be carried out with the *printlevel 3* keyword in the *rel* sub-block of the *casscf* block.

These scripts work as follows

> **get_CF_Orca.x** *2J+1 l_max* α β γ
>
>
> **Options:**
>
> 2J+1 = integer number, multiplicity of spin states of the model Hamiltonian
>
> l_max = max order or TTO used to defined the model Hamiltonian
>
> α β γ (optional) = Euler angles (radiants) for a ZYZ rotation of the TTO coefficients.

the script *get_SH_Orca.x* works analogously.

> **Example 1: Fitting of a second order SH for a high-spin (S=3/2) Co(II) single-ion compound**
>
> get_SH_Orca.x *orca.out* 4 2
>
> **Example 2: Fitting of a second order SH for a high-spin (S=3/2) Co(II) single-ion compound and rotating the SH by π along y**
>
> get_SH_Orca.x *orca.out* 4 2 0.00 3.14 0.00
>
> **Example 3: Fitting of a 14th order CF Hamiltonian for the $6H_{15/2}$ term of a Dy(III) single-ion compound**
>
> get_CF_Orca.x *orca.out* 16 14