Readme

The following program aims at simulating magnetic susceptibility and magnetic Mössbauer data for powder samples of mononuclear transition metal systems with several low-lying electronic configurations. It provides a more robust and physically meaningful description of the magnetism for cases where the usual spin Hamiltonian fails.

The user defines a set of parameters in an input file which models are provided (see input-mos-model for a typical Mossbauer spectrum simulation and input-mag-model for a typical magnetic susceptibility simulation input). The user then executes the program :

./call.exe < input-file > outputfile

The calculated Mossbauer spectra or magnetic susceptibility data points are returned in a list. No graphic interface is available yet, but any software like excel should allow the user to visualize the spectra/data points.

IMPORTANT: The software uses the LAPACK subroutine zheev for matrix diagonalization.

In details, the user defines a set of electronic configurations with their relative energies. The software will then set up an effective Hamiltonian in the space spanned by the $|S, M_S\rangle$ eigenstates of each electronic configuration (S is always taken as the maximum for a given electronic configuration). The electronic Hamiltonian operator is defined as:

$$H_{\text{EH}} = H_\Delta + H_{\text{soc}} + H_{\text{Zee}} \tag{1}$$

$$H_{\text{soc}} = \zeta \sum_i \sum_{l=x,y,z} \hat{l}_l(i) \cdot \hat{s}_l(i) \tag{1a}$$

$$H_{\text{Zee}} = \sum_i \mu_B \left(g_e \vec{s}(i) + \vec{l}(i) \right) \cdot \overrightarrow{B_{\text{ext}}} \tag{1b}$$

Here, H_Δ corresponds to the vertical excitation energies. H_{soc} and H_{Zee} correspond to the spin-orbit coupling and Zeeman Hamiltonians, respectively.

ζ is the spin-orbit coupling constant of the metal, $\hat{l}_l$ the lth component of the orbital angular momentum operator of the electron, $\hat{s}_l$ the spin angular momentum operator of the electron, μ_B the Bohr magneton, g_e the gyromagnetic factor of the electron (~2.0) and $\overrightarrow{B_{\text{ext}}}$ is the applied field.

To calculate the magnetization/magnetic susceptibility, the Hamiltonian is then diagonalized and the partition function is calculated. The molar magnetization is then calculated from the derivative of the partition function,[i] and averaged over all possible applied field directions to yield the final powder-averaged macroscopic magnetization.

To calculate the Mössbauer spectrum under an applied field, the internal field expectation values are calculated from the electronic Hamiltonian eigenvectors:[ii]

$$\overrightarrow{B_{\text{int}}} = -2\mu_B \langle r_{\text{d}}^{-3}\rangle \langle \vec{L}\rangle - 2\mu_B \langle r_{\text{d}}^{-3}\rangle \langle \left[\sum_i \frac{3(\vec{r_i}\cdot\vec{s_i})\vec{r_i}}{r_i^2} - \vec{s_i}\right]\rangle - A_{\text{FC}}\langle \vec{S}\rangle \tag{2}$$

Where $\langle r_{\text{d}}^{-3}\rangle$ is the averaged radius^{-3} of the d-electron, $\langle \vec{L}\rangle$ the orbital angular momentum expectation value, $\langle \left[\sum_i \frac{3(\vec{r_i}\cdot\vec{s_i})\vec{r_i}}{r_i^2} - \vec{s_i}\right]\rangle$ the spin-dipole operator expectation value, A_{FC} the proportionality constant between the spin angular momentum and the fermi-contact component of the internal field.

Of note, for high temperature measurements, we have only implemented the fast electron relaxation limit, where the total hyperfine field is the Boltzmann average of the expectation values of $\overrightarrow{B_{\text{int}}}$ for all populated states, or:

$$\langle \overrightarrow{B_{\text{int}}}\rangle = \frac{\sum \overrightarrow{B_{\text{int}\,i}}\, e^{-\frac{E_i}{k_B T}}}{\sum e^{-\frac{E_i}{k_B T}}} \tag{3}$$

The nuclear Hamiltonian is then calculated

$$H_{\text{nuc}} = H_\delta + H_Q - \beta_N g_N \vec{I} \cdot \overrightarrow{B_{\text{eff}}} = H_\delta + H_Q - \beta_N g_N \vec{I} \cdot \left(\overrightarrow{B_{\text{int}}} + \overrightarrow{B_{\text{ext}}}\right) \tag{4}$$

$$H_Q = \frac{eQ}{2I(2I-1)}\left(V_{zz}\hat{I_z}^2 + V_{xx}\hat{I_x}^2 + V_{yy}\hat{I_y}^2\right) \tag{4a}$$

Where H_δ is the isomer shift and corresponds to a vertical shift of the energies of the $|I = \frac{3}{2}, M_I\rangle$ magnetic states, H_Q is the usual quadrupolar interactions Hamiltonian, β_N is the nuclear magneton, g_N the gyromagnetic factor of the iron nucleus, $\vec{I}$ the nuclear spin vector operator, e the elementary charge Q the quadrupolar moment of the iron nucleus, I the nuclear spin quantum number, $V_{\alpha\alpha}$ the principal components of electric field gradient tensor, and $\hat{I}_\alpha$ the α-components of the nuclear spin operator.

The nuclear Hamiltonian is then diagonalized, and the absorption function is calculated as a function of (1) the nuclear Hamiltonian eigenstates and energies, and (2) the direction of the incident gamma-wave propagation vector.[iii] Finally, the absorption function is averaged over (1) all possible directions of the gamma-wave propagation vector (in perpendicular mode) and (2) all possible directions of the applied field to yield the final powder-averaged spectrum.

For the magnetic susceptibility module, the user must define:
1) All electronic configurations to be included in the effective Hamiltonian

2) All energies relative to the lowest electronic configuration (the first configuration defined by the user)

3) The value of ζ

4) The field intensity

5) The temperatures at which the function must be calculated

More details in the file input-mag-model and blahblah.txt

For the Mossbauer module, the user must define:

1) All of the above

2) ΔE_Q (quadrupole splitting)

3) η (asymmetry parameter

4) δ (isomer shift)

5) $\langle r_d^{-3} \rangle$

6) A_{FC} (although a typical value is +21.5 T)

More details in the file input-mos-model.

The effective Hamiltonian also relies on the following approximations:

1) The d-orbitals are treated as pure d-orbitals and covalency is neglected (implementation of the treatment of covalency is on the way)

2) The $|S, M_S\rangle$ eigenstates of each electronic configuration are treated as pure restricted-open-shell determinants where the core subshells are closed shell

3) The individual radius^{-3} of the d-orbitals are replaced with a unique $\langle r_d^{-3} \rangle$ expectation values

4) The nuclear and electronic spin are completely decoupled.

Any question further question or comment are welcomed by the author of the program at the following email address:

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[i] Kahn, O., *Molecular Magnetism*, VCH publishers, 1993.

[ii] Neese, F. in Magnetism: Molecules to Material IV, J. S. Miller and M. Drillon, 2002

[iii] Gütlich, P.; Bill, E.; Trautwein, A. X. Mössbauer spectroscopy and transition metal chemistry, Springer-Verlag Berlin Heidelberg, 2011.