Suscep

Introduction

Briefly, this code calculates the temperature dependence of magnetic susceptibility for a given system for which the exchange coupling constants have been determined. The following Hamiltonian is used to fulfil this purpose:

$$H_{E+Z} = -2\sum_{A=1,B=1}^{N,N} J_{AB}\langle I|\hat{S}_A.\hat{S}_B|J\rangle + \mu_B\vec{B}.\sum_{A=1}^{N} g_A\langle I|\hat{S}_A|J\rangle \quad (1)$$

where J_{AB} is the coupling constant between the magnetic centres A and B, I and J represent the particular M_s terms in the basis elements that the $\hat{S}_A.\hat{S}_B$ term operates on; $\vec{B}$ represents the applied magnetic field, g_A is the gyromagnetic tensor and μ_B is the unit Bohr Magneton. The first term accounts for the exchange coupling between Mn centres and the second term is the Zeeman term.

The basic working of this code involves setting up a matrix of all possible M_S (the magnetic spin quantum number) states for the given system. This is followed by operating each term of this matrix with eq. 1. Once this operation is complete, the matrix is diagonalised to obtain the eigenvalues which are then used to determine the magnetic susceptibility at different temperatures using the van Vleck equation. The details of the implementation of this procedure are given below.

Theory

Matrix Elements: The matrix elements are constructed using an uncoupled basis comprising of spin elements (the magnetic spin quantum number, M_s, value) for each magnetic centre. If a magnetic centre has N unpaired electron, then the magnetic spin quantum number values for that particular magnetic centre range from N/2 to –N/2; the consecutive values differing from each other by unity (total (N+1) values).

Hamiltonian: Only the two major contributors – the isotropic exchange term and the Zeeman term – to the Hamiltonian have been taken into consideration.

Isotropic Exchange term:

$$-2\sum_{A=1,B=1}^{N,N} J_{AB} < I|\hat{S}_A.\hat{S}_B|J > \quad (2)$$

where J_{AB} is the coupling constant between the magnetic centres A and B, I and J represent the particular M_s terms in the basis elements that $\hat{S}_A.\hat{S}_B$ operate on and

$$\hat{S}_A.\hat{S}_B = \frac{1}{2}\left(\hat{S}_{A,+}\hat{S}_{B,-} + \hat{S}_{A,-}\hat{S}_{B,+}\right) + \hat{S}_{A,z}.\hat{S}_{B,z} \quad (3)$$

where $\hat{S}_{A,+}$ and $\hat{S}_{B,-}$ are increment and decrement operators that are defined as follows:

$$\hat{S}_{A,+}|M_A\rangle = [(S_A(S_A+1) - M_A(M_A+1)]^{0.5}|S_A, M_A+1\rangle \quad (4)$$

$$\hat{S}_{A,-}|M_A\rangle = [(S_A(S_A+1) - M_A(M_A-1)]^{0.5}|S_A, M_A-1\rangle \quad (5)$$

$$\hat{S}_{A,z}|M_A\rangle = M_A|S_A, M_A\rangle \quad (6)$$

Zeeman term:

$$\mu_B \vec{B}. \sum_{A=1}^{N} g_A \langle I|\hat{S}_A|J\rangle \tag{7}$$

Here $\vec{B}$ represents the applied magnetic field, g_A is the gyromagnetic tensor and μ_B is the unit Bohr Magneton.

$$\begin{aligned}\langle S_A M_A|\vec{B}.g_A.\hat{S}_A|S_A M'_A\rangle = \\ +0.5\left[\left(B_x g_{Ax} + iB_y g_{Ay}\right)\{(S_A - M_A + 1)(S_A + M_A)\}^{0.5}\delta_{M'_A M_{A-1}}\right] \\ +0.5\left[\left(B_x g_{Ax} - iB_y g_{Ay}\right)\{(S_A + M_A + 1)(S_A - M_A)\}^{0.5}\delta_{M'_A M_{A+1}}\right] \\ +B_z g_{Az} M_A \delta_{M'_A M_A}\end{aligned} \tag{8}$$

where δ_{AB} is the kroenecker delta operator which is equal to 1 if A=B. Otherwise its value is 0. B_i and g_{Ai} represent the value of the magnetic field and the gyromagnetic tensor along a given direction.

The effective Hamiltonian is thus given as

$$H_{E+Z} = -2\sum_{A=1,B=1}^{N,N} J_{AB} < I|\hat{S}_A.\hat{S}_B|J > + \mu_B \vec{B}. \sum_{A=1}^{N} g_A \langle I|\hat{S}_A|J\rangle \tag{9}$$

The Hamiltonian matrix can thus be represented as

$$\sum_{I=1}^{N}\sum_{J=1}^{N}\langle A_I|H_{E+Z}|A_J\rangle \tag{10}$$

where A_I and A_J represent the elements of the basis and N is the total number of elements in the basis.

The eigenvalues ε_i and hence the energy levels of the various magnetic states are obtained by the diagonalisation of the Hamiltonian matrix. Once the eigenvalues are obtained, it can be used to plot the magnetic susceptibility with respect to temperature. To calculate the magnetic susceptibility, the Van Vleck equation is used which is:

$$\chi = \mu_0 N_A \frac{\sum_i [\frac{(-\epsilon_i^{(1)})^2}{kT} - 2\epsilon_i^{(2)}] exp(-\epsilon_i^{(0)}/kT)}{\sum_i exp(-\epsilon_i^{(0)}/kT)} \tag{11}$$

where $\epsilon_i^{(1)}$ and $\epsilon_i^{(2)}$ are the first and second derivative of energy with respect to the magnetic induction, μ_0 is the permeability of free space, N_A is the Avogadro's number, k is the Boltzmann constant and T is the temperature.

By Taylor expansion, the eigenvalues can be represented as:

$$\varepsilon_i = \epsilon_i^{(0)} + \epsilon_i^1 \Delta B + \epsilon_i^{(2)} \Delta B^2 + \epsilon_i^{(3)} \Delta B^3 + \cdots \tag{12}$$

with

$$\epsilon_i^{(n)} = \frac{1}{n!}\left(\frac{\partial^n \epsilon_i}{\partial B^n}\right) = C_i^{(n)} \tag{13}$$

being the coefficients to be determined. To obtain these coefficients, 5 sets of eigenvalues, $\varepsilon_{i,m}$ are generated using 5 different magnetic fields B_m, where

$$B_m = B_0 \pm N\delta \tag{14}$$

where N = 0, 1 and 2, and δ has been chosen to be equal $B_0/10$

Therefore,

$$\varepsilon_{i,m} = c_i^{(0)} + c_i^{(1)}\Delta B_m + \cdots + c_i^{(n)}(\Delta B_m)^n \tag{15}$$

for

$$\Delta B_m = B_m - B_0 \tag{16}$$

In matrix form,

$$\left(\varepsilon_{i,1}, \varepsilon_{i,2}, \ldots, \varepsilon_{i,m}\right) = \left(c_i^1, c_i^2, \ldots, c_i^n\right)\begin{pmatrix} 1 & 1 & \ldots & 1 \\ \Delta B_1 & \Delta B_2 & \ldots & \Delta B_m \\ \ldots & \ldots & \ldots & \ldots \\ \Delta B_1^n & \Delta B_2^n & \ldots & \Delta B_m^n \end{pmatrix} \tag{17}$$

or

$$e = cB \tag{18}$$

The matrix of coefficients can be calculated, provided the inverse of B exists, as follows:

$$c = eB^{-1} \tag{19}$$

By assembling the rows together, we obtain,

$$\begin{pmatrix} \varepsilon_{1,1} & \varepsilon_{1,2} & \ldots & \varepsilon_{1,m} \\ \varepsilon_{2,1} & \varepsilon_{2,2} & \ldots & \varepsilon_{2,m} \\ \ldots & \ldots & \ldots & \ldots \\ \varepsilon_{n,1} & \varepsilon_{n,2} & \ldots & \varepsilon_{n,m} \end{pmatrix} = \begin{pmatrix} c_1^0 & c_1^1 & \ldots & c_1^n \\ c_2^0 & c_2^1 & \ldots & c_2^n \\ \ldots & \ldots & \ldots & \ldots \\ c_m^0 & c_m^1 & \ldots & c_m^n \end{pmatrix}\begin{pmatrix} 1 & 1 & \ldots & 1 \\ \Delta B_1 & \Delta B_2 & \ldots & \Delta B_m \\ \ldots & \ldots & \ldots & \ldots \\ \Delta B_1^n & \Delta B_2^n & \ldots & \Delta B_m^n \end{pmatrix} \tag{20}$$

i.e.,

$$E = CB \tag{21}$$

Thus all the coefficients can be determined by the following equation:

$$C = EB^{-1} \tag{22}$$

These coefficients can then be used to calculate the magnetic susceptibility using the Van Vleck equation which can now be given as:

$$\chi = \mu_0 N_A \frac{\sum_i [\frac{(-c_i^{(1)})^2}{kT} - 2c_i^{(2)}] exp(-c_i^{(0)}/kT)}{\sum_i exp(-c_i^{(0)}/kT)} \tag{23}$$

Basic details

This code has been written in FORTRAN. It requires one input files that specifies the following:

1. Number of paramagnetic centres in the system.
2. The number of unpaired electrons on each centre.
3. The coupling behaviour between these centres and the coupling strength.
4. The g-value.
5. The strength of the applied magnetic field.

This code generates a .txt file that contains the value of χ and the χT product at different temperatures. The output also contains details about the size of Hamiltonian matrix and the M_s values associated with each paramagnetic centre.

For Users

The execution of the code is done as follows:

./suscep < input file >

The details of the format for the input file and an example input file are given below

<Input File>

magnetic centres
<number of paramagnetic centres>
spin
<spin on the first paramagnetic centre>
<spin on the second paramagnetic centre>
<spin on the third paramagnetic centre>
And so on
No. of J values
<number of J-values>
J-values
<1st J-value (in cm^{-1})>
<2nd J-value (in cm^{-1})>
<3rd J-value (in cm^{-1})>
And so on
g value
<g value>
Hamiltonian
<j1(paramagnetic centre A paramagnetic centre B + paramagnetic centre A paramagnetic centre C + ……) + j2(…….) + j3(……) + …….
Field Strength
< Field Strength (in Oersted)>

This is the format of the input file. The first line has to state 'magnetic centres' and the second line will specify how many magnetic centres are there. Then the spin (number of unpaired electrons/2) on each paramagnetic centre is specified. The line containing 'No. of J values' is followed by the strength of each J-value (in cm^{-1}) specified on separate lines. This is followed by the definition of the g value which is then followed by the definition of the Hamiltonian. The final term is the strength of the applied field (in Oersted).

Note: The terms 'magnetic centres', 'spin', 'No. of J values', 'J-values', 'g value', 'Hamiltonian' and 'Field Strength' are case-sensitive.

The following is an example input file for a Mn_6 system that requires 2 j-values and the Hamiltonian is written as follows:

$$H = -2J_1[\langle s_1.s_4\rangle + \langle s_2.s_5\rangle + \langle s_3.s_6\rangle] - 2J_2[\langle s_1.s_2\rangle + \langle s_1.s_3\rangle + \langle s_1.s_5\rangle + \langle s_1.s_6\rangle + \langle s_2.s_3\rangle + \langle s_2.s_4\rangle + \langle s_2.s_6\rangle + \langle s_3.s_4\rangle + \langle s_3.s_5\rangle + \langle s_4.s_5\rangle + \langle s_4.s_6\rangle + \langle s_5.s_6\rangle]$$

magnetic centres
6
spin
2.0
2.0
2.0
2.0
2.0
2.0
No. of J values
2
J values
-1.2772
-3.4727
g value
1.997
Hamiltonian
j1(12 + 13 + 15 + 16 + 23 + 24 + 26 + 34 + 35 + 45 + 46 + 56) + j2(14 + 25 + 36)
Field Strength
1000.0

For Developers

This code contains the following functions and subroutines:

1. **Init**: This subroutine reads in the input file and initialises the global variables.
2. **Printer**: This subroutine prints some basic details to the output file.
3. **SpinMatForm**: This subroutine determines the Ms values for each paramagnetic centre.
4. **FormBasis**: The subroutine calculates the basis that will be used to span the Hamiltonian matrix. Each basis element comprises of a Ms value for each paramagnetic centre.
5. **CheckPos and UpdatePos**: These subroutines are helper subroutines for the subroutine 'FormBasis' to cycle through all the possible combinations of Ms values for the paramagnetic centres.
6. **HamilForm**: This subroutine defines the Hamiltonian matrix using the various basis elements and operates each element with the exchange operator.
7. **Kron_del**: This function is used to determine the value of the kronecker delta function.
8. **Diag**: This helper subroutine is used for matrix diagonalisation using the LAPACK library.
9. **Zeeman**: This subroutine adds the Zeeman term to the elements of the Hamiltonian matrix.
10. **Suscep_calc**: This subroutine defines the B matrix (eq. 21), calculates the matrix of coefficients (C matrix, eq. 22) and then calculates the temperature dependence of susceptibility.