Suscep

A code for calculation of temperature dependence of magnetic susceptibility

Contents

1 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:[1]

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

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.

2 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]

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

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:[2]

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

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:[3]

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

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:[1]

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

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 and 1, 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:

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

3 Basic details

This code has been written in FORTRAN 2008. It requires one input file 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.

4 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.

4.1 Example Input file

To understand the construction of the input files, let us take the example of a {Mn_6} coordination complex[4] shown in **Figure 1**. The Mn centres in this complex interact with each other via the phosphonate ligands and the central Cl^- ion. Each of the six Mn centres in this complex has 1 trans- and 4 cis- neighbours and thus, one requires 2 J-values to account for these cis- and trans- interactions between Mn centres.[4]

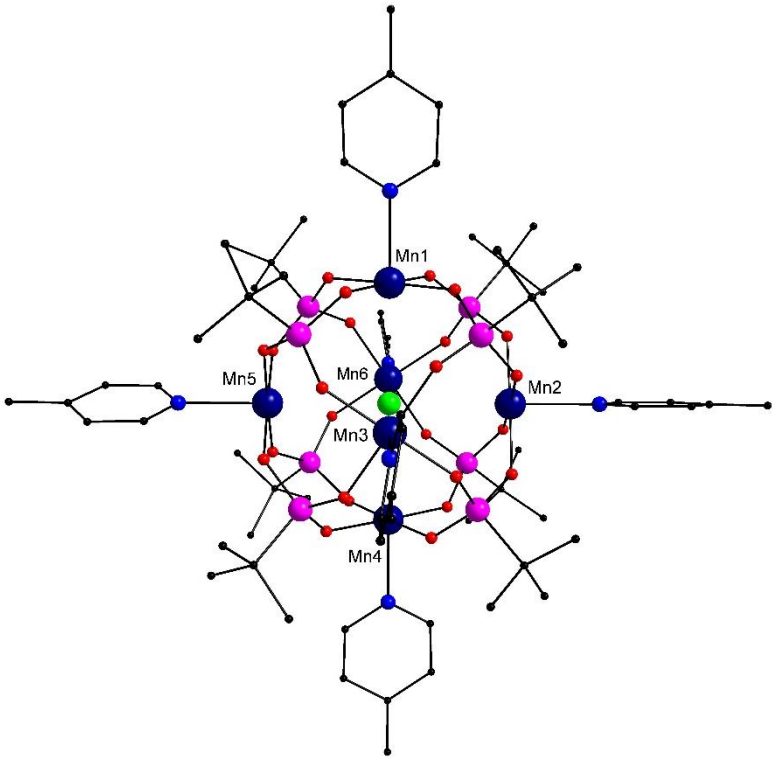

Figure 1: Structure of the {Mn_6} complex. Colour scheme: Mn (dark blue), P (pink), Cl (green), C (black), N (blue) and O (red). Hydrogen atoms have been removed for clarity.

This Hamiltonian for this complex can be written as follows:

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

The input file using the Hamiltonian mentioned above can be prepared as described below. The following additional parameters are used to complete the file – J_1: -3.48 cm^{-1}, J_2: -1.28 cm^{-1}, g-value: 1.997, field strength: 1000 oersted.

magnetic centres
6
spin
2.0
2.0
2.0
2.0
2.0
2.0
No. of J values
2
J values
-3.48
-1.28
g value
1.997
Hamiltonian
j1(14 + 25 + 36) + j2(12 + 13 + 15 + 16 + 23 + 24 + 26 + 34 + 35 + 45 + 46 + 56)
Field Strength
1000.0

Here the number 6 in the second line specifies that there are 6 magnetic centres. This is followed by the specification of the spin on each centre. In this example, each centre has 4 unpaired electrons and hence a spin value of 2. It is necessary to specify this value up to the first decimal place even if the spin value is a whole number. After specifying the spin on each centre, the details about the Hamiltonian are provided. In this example, 2 J-values are required and the magnitude of each J-value (-3.48 and -1.28 cm^{-1} respectively) is described following the number of J-values. This is followed by the specification of the g-value and the Hamiltonian which is then followed by the magnitude of the field strength in Oersted units (1000.0 in this case).
This example input file and the resultant output file have also been provided as separate files in the package.

5 Description of the output file

The format of the output file is as follows:

Output file sections	Description
Number of Magnetic centers: 6 The J values(cm-1) given are: - 3.47999999999999998 - 1.28000000000000003 g value: 1.99700000000000 …… ……	Details of the input parameters and the Hamiltonian that will be used.
J value (cm-1) with the pairs on which they act ……. …….. …….	This section specifies the interactions that are accounted for by a given J-value and should reflect the input Hamiltonian.
Temperature Chi Chi*Temp ……. …….. …….	This section gives the χ and χT values at different temperatures.

6 Limitations

The determination of the susceptibility for very large systems is limited by the available memory (RAM). This is because the size of the matrix containing Ms elements increases rapidly with the increase in the number of unpaired electrons and paramagnetic centres. The total number of elements in the matrix containing the Ms elements can be given as [(no. of unpaired electrons on centre 1) * (no. of unpaired electrons on centre 2) * (no. of unpaired electrons on centre 3) * ……..]^2. For example, for a {Mn^{III}_4} system, the matrix contains a total of (5*5*5*5)^2 =) 390,625 elements, for a {Mn^{III}_5} system, the matrix contains a total of (5^5*5^5 =) 9,765,625 elements while for a {Mn^{III}_6} system, the matrix contains (5^6*5^6 =) 244,140,625 elements. Since the calculation of susceptibility requires the exact diagonalisation of the whole matrix, the matrix needs to be stored in the memory and hence the limitation.

7 For Developers

The key global variables in this code are defined below:

Variable	Function
dimension	stores the number of magnetic centres.
no_of_j_val	stores the total number of unique J-values defined for the Hamiltonian.
totalspin	stores the row (or column) size of the spin hamiltonian matrix.
spin_mat_col	stores the column size of the spin matrix.
j_mat_col	stores the column size of the J value matrix.
spin	stores the S value (i.e. total number of unpaired e^-/2) for each metal centre.
jval	stores the different J-values in use.
jmat	stores information about which J-values are associated with different spin pairs.
hamil	stores the spin hamiltonian matrix.
g	stores the (isotropic) g-value
B	stores the magnetic induction in Wb m^{-2}.
vac_perm	stores the strength of the applied field.
field_str	permeability of free space in vacuum.
spinmat	stores all possible Ms values for each metal centre.
basis	stores all possible combinations of Ms values of all metal centres.

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.

8 References

1. R. Boca, in *Theoretical foundations of molecular magnetism*, Elsevier, Amsterdam; Oxford, 1999, ch. 6, pp. 315-344.
2. R. Boca, in *Theoretical foundations of molecular magnetism*, Elsevier, Amsterdam; Oxford, 1999, ch. 11, pp. 701-836.
3. O. Kahn, in *Molecular magnetism*, VCH Publishers, Inc., USA 1993, ch. 1, pp. 1-8.
4. S. Tandon, M. Venkatesan, W. Schmitt and G. W. Watson, *Dalton Trans.*, 2020, **49**, 8086-8095.