



Models for zero-dimensional molecular magnets

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ABSTRACT

The beauty of molecular magnets lies on their simplicity in what concerns quantum description. Zero-dimensional clusters have, due to the well-known Hamiltonians (e.g., Heisenberg, asymmetric, anti-symmetric and others), analytical solution of the thermodynamic quantities (of course, for a reasonable size of the Hilbert space). The aim of this paper is to describe step-by-step of how to develop models to explain the magnetic behavior of these materials. In spite the possibility of hand calculation (that opens doors for mistakes), computational codes can help to optimize this process of modeling; and then we provide a fully automatize computational routine to do the whole process: the CARDAMOMO package. Nine different Hamiltonians are available, as well as three different methods to obtain the eigenvalues. Thermodynamic quantities are obtained automatically and then fitted to the experimental data. At the end of this paper, an appendix support the physical background behind the Hamiltonians.

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1. Introduction

Zero-dimensional molecular magnets attract attention due to their huge number of potential applications, namely: high density data storage [1], quantum information and computation [2–4], magnetic refrigeration [5,6] and spintronics [1], in addition to other interesting characteristics, such as photo-induced magnetism [7], that make these materials able to be used in devices.

However, a carefully understanding of the fundamental questions behind these materials still need attention, especially those related to some quantum behaviors (starting point for new technologies). In this sense, new magnetic phenomena challenges the well established concepts and then promises to arise revolutionary technologies. Thus, new materials still need to be synthesized and magnetically understood to then be used in those above mentioned applications (and other applications, of course). To this purpose, the research on this issue has a barrier to overcome, i.e., some difficulties to develop models on molecular magnetism to then understand the behavior of these amazing materials.

That is the aim of the present paper, to provide a survey and a solution to those who need to develop such models. Here we present the basis of how to model these material and, in addition, provide a stand-alone code, named CARDAMOMO package, to do this task automatically. It is important to cite other computational routines [8–11].

Section 2 describes the qualitative way to develop models to molecular magnets. The following section is a step-by-step description of the program developed to automatize this process: the CARDAMOMO package. Section 3.2 explains minor details of

the procedure and then, in Section 4, a practical example is presented, where the whole process is executed. At the end of the paper, Appendix A starts and then a detailed survey on the magnetic interactions is done, as well as its mathematical description (i.e., Hamiltonians – nine different contributions).

2. Qualitative description: general rules

This section presents a qualitative description of how to develop models for zero-dimensional molecular magnets, i.e., clusters.

1. *Geometric configuration*: The first step is to obtain the crystallographic structure of the molecular magnet under consideration, with special attention to the magnetic centers (both metallic and/or organic). Following, we must transfer the information of this structure (the whole crystal), to the geometrical configuration of spins. Based therefore on the angles and distances of the bonds between ions, we can associate one or more exchange interactions. Different angles/distances mean different exchange interactions (at least in first approximation).

2. *Hamiltonian*: From the geometric configuration of spins, it is possible then to write the Hamiltonian. A brief discussion on the physical meaning of some Hamiltonians is given in Appendix A. Those contributions are spin Hamiltonians, i.e., depend only on the spins of the system. The spin operators, expansion of the Hilbert space and all algebraic evaluation must be addressed.

3. *Eigenvalues*: There are several ways to do this task; and let us start from the more elegant and efficient manner (basis change). Following, we will discuss Perturbation Theory and then eig function, available on the MatLab platform.

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3.a. *Basis change*: Spin Hamiltonian containing S_x and S_y is not diagonal on the local basis $|s_1, s_2, \dots, s_i, m_{s_1}, m_{s_2}, \dots, m_{s_i}\rangle$ (only z component), and then basis change can be a useful and powerful way to obtain eigenvalues. For some cases, there is a coupled basis in which the Hamiltonian is diagonal and the Clebsch–Gordan coefficients for these two basis (local and coupled), can be used to change the basis of the Hamiltonian. There are two kinds of coupled basis: sequential and non-sequential. For the first case, the spins are summed up one-by-one sequentially. For instance, considering 4 spins (s_1, s_2, s_3 and s_4), it is possible to couple those as: $S_{12} = S_1 + S_2$, $S_{13} = S_{12} + S_3$ and $S_{14} = S = S_{13} + S_4$. Note that the spins are coupled sequentially. For the second case, the spins are coupled non-sequentially. Considering the spins above, it is possible to couple those as (other ways are possible): $S_{12} = S_1 + S_2$, $S_{34} = S_3 + S_4$ and $S = S_{12} + S_{34}$.

3.b. *Perturbation Theory*: This way to obtain the eigenvalues considers the zero-field Hamiltonian as the non-perturbed term and the Zeeman term as a perturbation.

In this case, we consider all terms, excluding the Zeeman contribution, as the main one. These contribution must be diagonal. The remaining term, i.e., Zeeman, is the perturbation and can be non-diagonal. From this approach, only the van Vleck susceptibility can be evaluated.

3.c. *eig function*: There is a third way to diagonalize the Hamiltonian: via the *eig* function of the MatLab platform. The technique used by this commercial software to obtain eigenvalues and eigenvectors is not detailed here and is available by the platform developer. In any case, it is important to emphasize that matrix with reasonable size (for instance, 32×32), and some symbolic variables (ca. 4–5), will take a long time to run and finish (several hours and even days).

4. *Thermodynamic quantities*: The previous step gave us the energy spectra and now we are able to obtain the thermodynamic quantities, namely magnetization, magnetic susceptibility, specific heat and entropy. Note an exception: cases in which perturbation theory is used, only the van Vleck susceptibility can be obtained. Analytical thermodynamic quantities were already found for interesting systems [12–14].

5. *Experimental data*: The analytical thermodynamic quantities obtained in the previous step can now be compared with experimental data. The free parameters to the fitting can be, for instance, the exchange integral J of the isotropic Heisenberg Hamiltonian, the Landé factor g and other quantities (see Appendix A for further details).

6. *Fitting to the experimental data*: At this level of the model, it is needed to use some least square procedure to get then the best fitting.

7. *Free parameters*: To conclude the model, the outputs are the optimized free parameters and a theoretical curve. With these values it is possible to understand the microscopic phenomena behind the magnetic behavior of a such molecular magnet.

Fig. 1 summarizes the seven steps described above.

3. Quantitative description: the CARDAMOMO package

A package with 20 (sub-)routines was developed to automatize the procedure of models development on molecular magnetism: the CARDAMOMO package, optimized to run on the MatLab platform [15,16].

3.1. Step-by-step

All of the routines provided by the package are stand-alone and are available for download [17]. The main program, in which you can execute your model, is named as *modelo*. Thus, type 'modelo' on the MatLab platform and follow the steps described below.

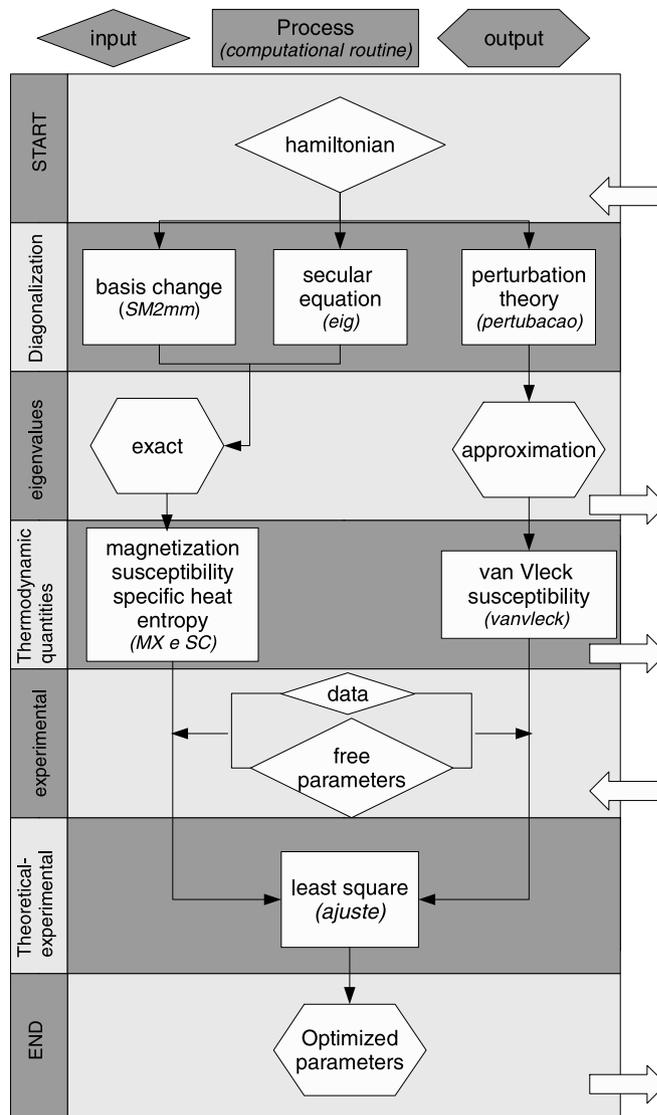


Fig. 1. Fluxogram to develop models. Lozenges mean information needed to run the model, i.e., inputs. Rectangles mean internal execution, i.e., neither input nor output. Heptagons mean outputs. Some of these seven levels have in and out arrows (right side of the diagram), and indicate that either input is required or output is available. Names between parenthesis are the computational routines that execute the corresponding task. See Section 3 for further details.

Step 1: The first input is to list the spins of the system. Considering five spins 1, for instance, labeled from s_1 up to s_5 , we must type '[1, 1, 1, 1, 1]', that means the spin value of $[s_1, s_2, s_3, s_4, s_5]$. Without " and with [].

Step 2: The package requires the user to enter the symbolic variables of the system. In general, these are the free parameters of the model; for instance, the exchange integrals, axial and rhombic components of the \mathcal{D} tensor and other quantities (see Appendix A for further details). Note, the magnetic field is not required to be declared (these are B_u , where $u = x, y, z$). The syntax is:

```
syms variables real
```

To resume the program, type 'return'.

Step 3: Enter the zero-field Hamiltonian of the system, except the Zeeman term.

There are several kinds of interactions managed by the CARDAMOMO package:

1. Name: Heisenberg, Ising and XY

Syntax: `hei(a, b, α , β , S)`

Corresponds to:

$$\vec{S}_a \cdot \vec{S}_b = \alpha(S_{ax}S_{bx} + S_{ay}S_{by}) + \beta(S_{az}S_{bz}) \quad (1)$$

Note 1: a and b must be integer numbers. α and β must be between 0 and 1. S is mandatory and is an internal variable.

Note 2: The exchange integral J is not included and must be multiplied by `hei`.

2. Name: bi-quadratic

Syntax: `biq(a, b, S)`

Corresponds to:

$$(\vec{S}_a \cdot \vec{S}_b)^2 \quad (2)$$

Note 1: a and b must be integer numbers. S is mandatory and is an internal variable. This contribution is isotropic, i.e., there is neither α nor β .

Note 2: The parameter j is not included and must be multiplied by `biq`.

3. Name: Anti-symmetric

Syntax: `anti(a, b, S, dx, dy, dz)`

Corresponds to:

$$\vec{d} \cdot (\vec{S}_a \times \vec{S}_b) \quad (3)$$

Note: a and b must be integer numbers. S is mandatory and is an internal variable. d_u ($u = x, y, z$) are components of the \vec{d} vector.

4. Name: Spin-orbit (local magneto-crystalline anisotropy)

Syntax: `assi(a, b, S, D, E)`

Corresponds to:

$$\vec{S}_a \cdot \vec{D} \cdot \vec{S}_b \quad (4)$$

Note: $a = b$ must be an integer number. S is mandatory and is an internal variable. D and E are the axial and rhombic parameters of the tensor \mathcal{D} .

5. Name: Dipolar

Syntax: `assi(a, b, S, D, E)`

Corresponds to:

$$\vec{S}_a \cdot \vec{D} \cdot \vec{S}_b \quad (5)$$

Note: $a \neq b$ must be integer numbers. S is mandatory and is an internal variable. D and E are the axial and rhombic parameters of the tensor \mathcal{D} .

Step 4: Enter the Zeeman Hamiltonian.

1. Name: Zeeman

Syntax: `zee(gx, gy, gz, S)`

Corresponds to:

$$\mu_B(g_x B_x S_x + g_y B_y S_y + g_z B_z S_z) \quad (6)$$

Note: $S_u = S_{1u} + S_{2u} + \dots + S_{iu}$, where $u = x, y, z$. S is mandatory and is an internal variable.

See [Appendix A](#) for further details on the physical meaning of each Hamiltonian.

Step 5: The program stops to the user verify how the Hamiltonians are. Type 'H{1}' to see the zero-field Hamiltonian and 'H{2}' to access the Zeeman term. To resume the program, type 'return'.

Step 6: The program asks if the user need to change the basis in which the Hamiltonian is written. If no, type '0' and then go to Step 7. Otherwise, if yes, type '1'.

The Hamiltonian is originally written on the local basis, i.e., the basis in which S_{iz} (where $i = 1, 2, \dots$ is the spin label), is diagonal:

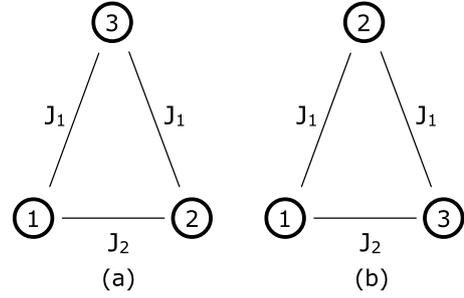


Fig. 2. Example of how the spin labels can change the way to diagonalize the Hamiltonian. See text for further details.

$$|s_1, s_2, \dots, s_n, m_{s_1}, m_{s_2}, \dots, m_{s_n}\rangle \quad (7)$$

In some cases, changing the basis of the system to a coupled basis (either sequential or non-sequential), can then diagonalize the operator. It is therefore an elegant way to diagonalize the Hamiltonian and then obtain the eigenvalues of the problem. Below, details on these coupled basis.

Step 6.1: At this stage, the program needs to know the kind of coupled basis you need to change the Hamiltonian to. There are two possibilities: sequential (type '1' and then go to Step 6.2), or non-sequential (type '2' and then go to Step 6.1.1), coupled basis. For the first case, the spins are coupled as follows:

$$S_{12} = S_1 + S_2$$

$$S_{13} = S_{12} + S_3$$

$$S_{14} = S_{13} + S_4$$

⋮

$$S = S_{1n} = S_{1,n-1} + S_n \quad (8)$$

and the basis is:

$$|s_1, s_2, \dots, s_n, s_{12}, s_{13}, \dots, s, m_s\rangle \quad (9)$$

where m_s is the projection of the S vector along the z -direction. Note that the number of quantum numbers remains the same, as expected.

For the second case, the spins are coupled non-sequentially, in order to satisfy some criteria (discussed below), to make the Hamiltonian diagonal under basis change. As an example, for four spins, the non-sequential basis can be:

$$S_{12} = S_1 + S_2$$

$$S_{34} = S_3 + S_4$$

$$S = S_{12} + S_{34} \quad (10)$$

This criteria mentioned above is, rudely speaking, when the Hamiltonian can be written in terms of the square of the spin operators, without bi-linear terms. The example below clarifies this idea.

Let us consider an isotropic trimer, as shown in Fig. 2(a). The Hamiltonian zero-field Hamiltonian is

$$\mathcal{H}_0 = -J_1(\vec{S}_1 \cdot \vec{S}_3 + \vec{S}_2 \cdot \vec{S}_3) - J_2 \vec{S}_1 \cdot \vec{S}_2 \quad (11)$$

and then it is not diagonal on the local basis $|s_1, s_2, s_3, m_{s_1}, m_{s_2}, m_{s_3}\rangle$, due to the x and y components of the spin operators. One way to diagonalize this Hamiltonian is changing the basis. Considering the sequential coupled basis $|s_1, s_2, s_3, s_{12}, s, m_s\rangle$, we must write:

$$\vec{S}_{12} = \vec{S}_1 + \vec{S}_2 \quad \text{and} \quad \vec{S} = \vec{S}_{12} + \vec{S}_3 \quad (12)$$

and therefore

$$\vec{S}_1 \cdot \vec{S}_2 = \frac{1}{2}(S_{12}^2 - S_1^2 - S_2^2) \quad (13)$$

and

$$\vec{S}_1 \cdot \vec{S}_3 + \vec{S}_2 \cdot \vec{S}_3 = \frac{1}{2}(S^2 - S_{12}^2 - S_3^2)$$

Thus, the Hamiltonian is:

$$\mathcal{H}_0 = -\frac{J_1}{2}(S^2 - S_{12}^2) - \frac{J_2}{2}S_{12}^2 \quad (14)$$

where the S_i^2 terms were omitted since those are energy constants. Since it can be written in terms of the square of the spin operator, it is diagonal at this basis.

However, the spins can be labeled in a different way, as shown in Fig. 2(b). Now, the zero-field Hamiltonian is:

$$\mathcal{H}_0 = -J_1(\vec{S}_1 \cdot \vec{S}_2 + \vec{S}_2 \cdot \vec{S}_3) - J_2\vec{S}_1 \cdot \vec{S}_3 \quad (15)$$

and it is easy to see that considering the sequential coupled basis as written above, it is not possible to write exclusively the Hamiltonian in terms of the square of the spin operator and then it is not diagonal. In this case, we must use the non-sequential basis $|s_1, s_2, s_3, s_{13}, s, m_s\rangle$, as follows:

$$\vec{S}_{13} = \vec{S}_1 + \vec{S}_3 \quad \text{and} \quad \vec{S} = \vec{S}_{13} + \vec{S}_2 \quad (16)$$

and then the Hamiltonian holds as:

$$\mathcal{H}_0 = -\frac{J_1}{2}(S^2 - S_{13}^2) - \frac{J_2}{2}S_{13}^2 \quad (17)$$

Now, it is diagonal.

Step 6.1.1: If the user chooses the non-sequential coupled basis, then the basis must be written at this stage. Following the previous example, the syntax is $\{\{s1, s3\}, \{vec1, s2\}, \{1, 3\}, \{0, 1, 2\}\}$, where 's' and 'vec' are mandatory, as well as the brackets {}.

Step 6.2: At this stage, the CARDAMOMO package allows the user to access several information: (1) dimension of the Hilbert space (type either 'a', if the user chooses sequential basis (scb), or 'aa', if the user chooses non-sequential basis (nscb)), local basis (type either 'b', for scb, or 'bb', for nscb), coupled basis (type either 'c', for scb, or 'cc', for nscb) and unitary matrix used to change the basis, i.e., that with the Clebsch–Gordan coefficients (type either 'd', for scb, or 'dd', for nscb). Verify that $d^\dagger d = I$, where I is an identity matrix with the dimension of the Hilbert space). The user now is also able to verify how the Hamiltonians are. Type `Hn{1}` to see the new zero-field Hamiltonian and `Hn{2}` to access the new Zeeman term, i.e., those at the coupled basis. To resume the program, type 'return'.

Step 7: At this stage, the CARDAMOMO package asks to choose the method to obtain the eigenvalues of energy. There are three options: `eig(H)` (type '0'), `diag(H)` (type '1') and Perturbation Theory (type '2'). The first option is a built in function of the MatLab and it returns the eigenvalues of a (non-)diagonal matrix (see Ref. [17] for further details). The second option just takes the diagonal elements of the Hamiltonian (zero-field plus Zeeman) and therefore it must be diagonal. Note that both cases return the exact eigenvalues, without approximations. Finally, the third option uses Perturbation Theory to obtain the energy levels. It returns the zero-field eigenvalues (this matrix must be diagonal), and the first and second-order corrections on energy, due to the Zeeman contribution. It is important to stress that the zero-field Hamiltonian must be diagonal, a mandatory requirement, while the Zeeman term can be (or not) diagonal.

If the zero-field term is not diagonal, the program does it via `eig` function. The program automatically changes the basis of the Zeeman contribution and then uses Perturbation Theory in accordance with the formalism of the theory.

Step 7.1: If the user changed the basis of the system to either sequential or non-sequential coupled basis, the program asks at this level to choose among the options of Step 7, on which basis it must work; either local (type '0'), or coupled (type '1').

Step 8: For any of the methods mentioned above, the energy eigenvalues are therefore evaluated and then allocated into the `ene` variable. To see these values, type 'ene'. The program automatically save the energy spectra at `c:\ene.mat`. Type 'return' to resume the program.

Step 9: Now the user has the eigenvalues of energy and can choose either evaluate the thermodynamic quantities (type '1'), or not (type '0'). If the user chooses to not evaluate the thermodynamic quantities, the program then is over.

Step 9.1: If the user obtained the eigenvalues of energy from Perturbation Theory, there is only one thermodynamic quantity available: the van Vleck susceptibility (saved at `c:\sus.mat`). On the other hand, if the user obtained the eigenvalues of energy from either basis change or `eig` function (i.e., an analytical result), there are three options: evaluate magnetization M and susceptibility χ (type '0' – result saved at `c:\magsus.mat`), specific heat C and entropy S (type '1' – result saved at `c:\entcal.mat`), and all of them (type '2' – result saved at `c:\entcalmagsus.mat`). Magnetization, susceptibility, specific heat and entropy are allocated, respectively, into the variables `mag`, `sus`, `cal` and `ent`, and saved at the paths mentioned above.

Step 10: Now the user has the thermodynamic functions. At this stage, the user can handle those quantities as desired. Type 'return' to resume the program.

Step 11: The program then asks if the user wishes to fit those thermodynamic quantities to the experimental data. Type '0' for no and then the program is over; or, for yes, type '1'.

Step 12: If the user chooses '1' at Step 11, then some instructions are displayed on the MatLab console. The experimental data must be in an ASCII file, at the same folder of the routines and must have the following format: temperature or magnetic field (first column) and the thermodynamic quantity (second column). Remarks concerning this file: do not use comma for decimal numbers; use dot instead. Be sure that the first and last lines contain numbers (and not text, symbols and even empty space). The program considers only the following units: $[M] = \mu_B/\text{FU}$, $[C] = k_B/\text{FU}$, $[\chi T] = \mu_B \text{K}/\text{FU-Oe}$, $[\chi] = \mu_B/\text{FU-Oe}$, $[B] = \text{Oe}$ and $[T] = \text{K}$, where FU means Formula Unity and must contain one magnetic cluster (i.e., a dimer, trimer or any other). Type 'return' to resume the program.

Step 13: The program at this level needs to know which thermodynamic quantity is the experimental data. The user can choose magnetization as a function of magnetic field (type '0'), specific heat as a function of temperature (type '1'), susceptibility times temperature as a function of temperature (type '2') and, finally, susceptibility as a function of temperature (type '3').

Step 13.1.a: If the user chooses $M(H)$, the program requests the temperature in which it was done.

Step 13.1.b: The program stops and the user has the possibility to handle the magnetization function and must create a new variable named `magr` and locate on it the magnetization function. The variable `magr` is mandatory. Type 'return' to resume the program.

Step 13.1.c: At this level, the program asks if the user desires to include a linear contribution (either positive or negative slope), to the magnetization. Type either '1', for yes, or '0', for no.

Step 13.2: If you choose C , the program considers $\Delta C = C(T, B) - C(T, 0)$, instead of only $C(T)$. It is easy to understand, because the specific heat contains a lot of contributions, like lattice, electrons and other; and this procedure eliminates this non-magnetic contributions. The value of the magnetic field is then requested.

Step 13.3.a: If you choose either χT or χ , the program pauses and the user can handle the thermodynamic quantities. For instance, the total susceptibility can be evaluated from an anisotropic case and therefore, the three components of the susceptibility χ_x , χ_y and χ_z are important; and the user must define at this stage $susr (= susx + susy + susz, \text{ for this example})$. The variable $susr$ is mandatory. Type 'return' to resume the program.

Step 13.3.b: The user has at this stage the opportunity to include a temperature independent contribution to the magnetic susceptibility, either positive (van Vleck paramagnetism), or negative (diamagnetic contribution).

Step 14: At this stage, the program requests to list the free parameters to the fitting, listed between square brackets [].

Step 15: Finally, the user is requested to introduce, also between square brackets, the initial values of the free parameters, listed following the order in which these parameters were listed in the previous step. Note that some parameters, like exchange interaction, must be multiplied by the Boltzmann constant k_B . Fig. 3 summarizes these steps.

3.2. Advanced configuration

The CARDAMOMO package has a configuration file. It contains some information on how some routines must run. Two control parameters are required to inform; one refers to how the spin matrix is built and the other is related to the degenerated eigenvalues used for Perturbation Theory. This information is written into the config.dat file as [a b], where both can assume either '0' or '1'. a is related to how the spin matrix is done and b is related to the degenerated eigenvalues used for Perturbation Theory.

Details concerning a control bit: It is related to how the spin operator (a matrix written on a basis $|s, m_s\rangle$), is built. For 'a = 1' the matrix is built decreasing m_s values:

- $\langle s, +s |$
- $\langle s, +s - 1 |$
- \vdots

- $\langle s, -s + 1 |$
- $\langle s, -s |$

and for 'a = 0', the matrix is built decreasing the absolute values of m_s . This last case can be either (for integer spins):

- $\langle s, +|s| |$
- $\langle s, -|s| |$
- $\langle s, +|s - 1| |$
- $\langle s, -|s - 1| |$
- \vdots

$\langle s, 0 |$

or (for half-integer spins):

- $\langle s, +|s| |$
- $\langle s, -|s| |$
- $\langle s, +|s - 1/2| |$
- $\langle s, -|s - 1/2| |$
- \vdots
- $\langle s, +1/2 |$
- $\langle s, -1/2 |$

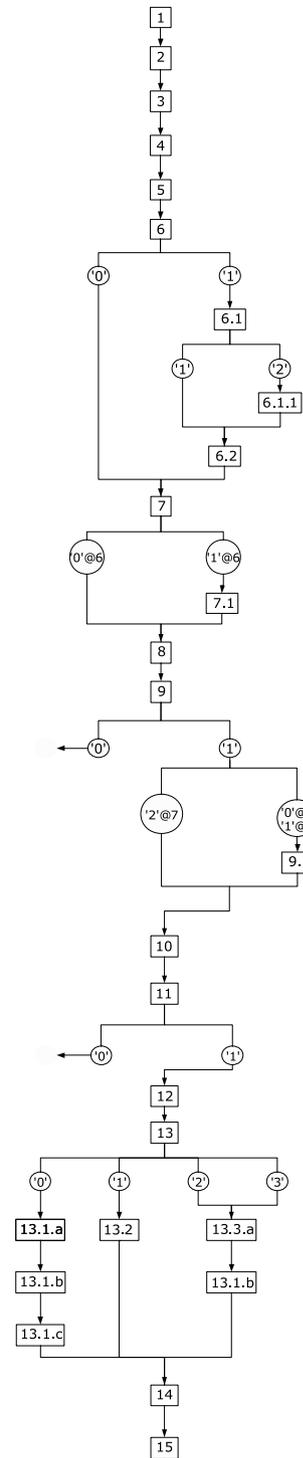


Fig. 3. Fluxogram of the step-by-step of the CARDAMOMO package. Numbers are inside squares and circles and represent, respectively, a step of the program and options of the previous question.

As an example, let us consider the S_x operator of $s = 3/2$ and the two possibilities to built it. For the 'a = 1' case it holds as:

$$\begin{pmatrix} 0 & \sqrt{3}/2 & 0 & 0 \\ \sqrt{3}/2 & 0 & 1 & 0 \\ 0 & 1 & 0 & \sqrt{3}/2 \\ 0 & 0 & \sqrt{3}/2 & 0 \end{pmatrix} \begin{matrix} \langle 3/2, +3/2 | \\ \langle 3/2, +1/2 | \\ \langle 3/2, -1/2 | \\ \langle 3/2, -3/2 | \end{matrix} \quad (18)$$

other important information, like the analytical thermodynamic functions and eigenvalues (see Section 3 for further details).

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Appendix A. Review on magnetic interactions

A.1. Heisenberg Hamiltonian

This interaction considers that the wave function of the ions in question is localized, i.e., the electron hopping is quite small. Metals, therefore, are not well described by this Hamiltonian; however, molecular magnets are in general isolators and Heisenberg interaction can be used.

Thus, let us consider the Heisenberg Hamiltonian between two spins \vec{S}_1 and \vec{S}_2 :

$$\begin{aligned}\mathcal{H}_{hei} &= -J\vec{S}_1 \cdot \vec{S}_2 \\ &= -J(S_{1x}S_{2x} + S_{1y}S_{2y} + S_{1z}S_{2z})\end{aligned}\quad (\text{A.1})$$

Note that this interaction is isotropic.

A.2. XY and Ising Hamiltonians

Heisenberg Hamiltonian can be generalized as:

$$\mathcal{H}_{hei} = -J[\alpha(S_{1x}S_{2x} + S_{1y}S_{2y}) + \beta S_{1z}S_{2z}] \quad (\text{A.2})$$

For the case in which $\alpha = 1$ and $\beta = 1$, we recover the isotropic Heisenberg case; $\alpha \neq \beta \neq 0$, anisotropic Heisenberg; $\alpha = 1$ and $\beta = 0$, XY Hamiltonian; and, finally, $\alpha = 0$ and $\beta = 1$, we find the famous Ising Hamiltonian.

A.3. Bi-quadratic Hamiltonian

The isotropic interaction between spins does not need to be restricted to the bi-linear term ($\vec{S}_1 \cdot \vec{S}_2$). Higher orders can also be considered and the bi-quadratic Hamiltonian is an example:

$$\mathcal{H}_{biq} = -j(\vec{S}_1 \cdot \vec{S}_2)^2 \quad (\text{A.3})$$

It is, in other words, a correction to the bi-linear Heisenberg term; also isotropic in character.

A.4. Anti-symmetric Hamiltonian

This interaction occurs in crystals of quite low symmetry. It is given by:

$$\mathcal{H}_{anti} = \vec{d} \cdot (\vec{S}_1 \times \vec{S}_2) \quad (\text{A.4})$$

$$\begin{aligned}&= d_x(S_{1y}S_{2z} - S_{1z}S_{2y}) \\ &\quad + d_y(S_{1z}S_{2x} - S_{1x}S_{2z})\end{aligned}\quad (\text{A.5})$$

$$+ d_z(S_{1x}S_{2y} - S_{1y}S_{2x}) \quad (\text{A.6})$$

and was proposed by Dzialoshinsky [22] and then further detailed by Moriya [23].

This interaction tends to align the neighbor spins perpendicular to each other, while the isotropic Heisenberg interaction aligns those in a parallel (or anti-parallel) fashion. Thus, Dzialoshinsky interaction is, in some cases, the origin of spin canting.

A.5. Spin-orbit Hamiltonian: local magneto-crystalline anisotropy

The spin-orbit coupling arises from the interaction of the spin of an electron and the magnetic field created by this electron due to its own orbit around the nucleus (obviously, it is a classical view of the problem). This interaction is given by:

$$E = -\left(2\frac{\mu_B}{\hbar}\right)\left(\frac{e}{4\pi mr^3}\right)\vec{L} \cdot \vec{S} \quad (\text{A.7})$$

Thus, this contribution represents the energy to change the spin to other direction than that along the angular moment. In other words, the energy is minimized when the spin is along the orbital moment, i.e., perpendicular to the orbit of the own electron. If this system is in a crystal lattice and there is a preferable plan to the orbit of the electron, the corresponding spin will be automatically fixed perpendicular to this plan and therefore an anisotropy arises. Remove the spin from this easy magnetization direction has energy consumption, given by the above equation. Due to the explained above, spin-orbit Hamiltonian is often called as local magneto-crystalline anisotropy.

The above words came from a classical view of the problem. However, the spin-orbit coupling arises naturally from the Dirac equation and has the form:

$$\mathcal{H}_{so} = \zeta\vec{L} \cdot \vec{S} \quad (\text{A.8})$$

where ζ is the spin-orbit coupling parameter. Let us now consider that this Hamiltonian is a perturbation. It is reasonable because in some cases the quench of the angular moment due to the crystal field is not perfect and therefore there is a small orbital contribution.

From the Perturbation Theory, second-order correction is:

$$-\zeta^2 \sum_{k \neq n} \frac{\langle k | \vec{L} \cdot \vec{S} | n \rangle \langle n | \vec{L} \cdot \vec{S} | k \rangle}{E_n - E_k} \quad (\text{A.9})$$

and can be re-written as:

$$\mathcal{H}_{la} = \vec{S} \cdot \vec{\mathcal{D}}_{la} \cdot \vec{S} \quad (\text{A.10})$$

where

$$\mathcal{D}_{la}^{(ab)} = -\zeta^2 \sum_{k \neq n} \frac{\langle k | L_a | n \rangle \langle n | L_b | k \rangle}{E_n - E_k} \quad (\text{A.11})$$

Due to the anisotropic character of this Hamiltonian, we renamed it as \mathcal{H}_{la} (local anisotropy). This kind of Hamiltonian is also often called as asymmetric, due to the tensor $\vec{\mathcal{D}}_{la}$ (further details on this tensor will be given in this appendix).

A.6. Zeeman Hamiltonian

Analogously to the spin-orbit coupling, the Zeeman Hamiltonian in its more complete form comes from the Dirac equation. Thus:

$$\mathcal{H}_z = \mu_B \vec{B} \cdot (\vec{L} + 2\vec{S}) \quad (\text{A.12})$$

It takes account on the interaction of the spin and angular moments with the external magnetic field \vec{B} .

The pure spin contribution is

$$\mathcal{H}_z^{(S)} = 2\mu_B \vec{B} \cdot \vec{S} = -\vec{\mu}_S \cdot \vec{B} \quad (\text{A.13})$$

where

$$\vec{\mu}_S = -g_s \mu_B \vec{S} \quad (g_s = 2) \quad (\text{A.14})$$

In a similar fashion, the pure orbital contribution is:

$$\mathcal{H}_z^{(L)} = \mu_B \vec{B} \cdot \vec{L} = -\vec{\mu}_L \cdot \vec{B} \quad (\text{A.15})$$

where

$$\vec{\mu}_L = -g_L \mu_B \vec{L} \quad (g_L = 1) \quad (\text{A.16})$$

Now, the total Zeeman Hamiltonian can be re-written as:

$$\mathcal{H}_z = \mathcal{H}_z^{(S)} + \mathcal{H}_z^{(L)} = -\vec{\mu}_J \cdot \vec{B} \quad (\text{A.17})$$

where

$$\vec{\mu}_J = -g_J \mu_B \vec{J} \quad (\text{A.18})$$

and

$$\vec{J} = \vec{L} + \vec{S} \quad (\text{A.19})$$

After some vectorial calculus, it is possible to determine the Landé factor:

$$g_J \equiv g = 1 + \frac{j(j+1) - l(l+1) + s(s+1)}{2j(j+1)} \quad (\text{A.20})$$

Finally, the Zeeman Hamiltonian holds:

$$\mathcal{H}_z = g \mu_B \vec{B} \cdot \vec{J} \quad (\text{A.21})$$

A.7. The g tensor

To discuss this issue, let us start considering the Zeeman and spin-orbit Hamiltonians:

$$\mathcal{H}_z = \mu_B \vec{B} \cdot (\vec{L} + 2\vec{S}) \quad (\text{A.22})$$

and

$$\mathcal{H}_{so} = \zeta \vec{L} \cdot \vec{S} \quad (\text{A.23})$$

Now, let us transform $\mathcal{H}_z + \mathcal{H}_{so}$ in a spin Hamiltonian, i.e., re-write it to collect into a single quantity all orbital dependence and leave only the spin operators. We must start from:

$$\mathcal{H} = \mathcal{H}_{so} + \mathcal{H}_z = 2\mu_B \vec{S} \cdot \vec{B} + \mu_B \vec{L} \cdot \vec{B} + \zeta \vec{L} \cdot \vec{S} \quad (\text{A.24})$$

The first term does not depend on the angular moment and therefore is already a spin Hamiltonian. The second and third terms must be re-written and, for this purpose, let us consider second-order correction from the Perturbation Theory. The reason is the same as before: the quench of the orbital moment cannot be perfect and therefore it is small, and can be considered as a perturbation. Thus:

$$\mathcal{H} = 2\mu_B \vec{S} \cdot \vec{B} - \sum_{k \neq n} \frac{\langle k | \mu_B \vec{L} \cdot \vec{B} + \zeta \vec{L} \cdot \vec{S} | n \rangle^2}{E_n - E_k} \quad (\text{A.25})$$

where the above written states $|n\rangle$ are those that diagonalize the first term of the Hamiltonian. Opening the second term of the above equation we find:

$$\mathcal{H} = -\mu_B^2 \vec{B} \cdot \overleftrightarrow{\mathcal{D}}_L \cdot \vec{B} - \zeta^2 \vec{S} \cdot \overleftrightarrow{\mathcal{D}}_L \cdot \vec{S} + \mu_B \vec{B} \cdot \overleftrightarrow{\mathcal{G}} \cdot \vec{S} \quad (\text{A.26})$$

where

$$\mathcal{D}_L^{(ab)} = \sum_{k \neq n} \frac{\langle k | L_a | n \rangle \langle n | L_b | k \rangle}{E_n - E_k} \quad (\text{A.27})$$

and

$$g^{(ab)} = 2(\mathbb{I} - \zeta \mathcal{D}_L^{(ab)}) \quad (\text{A.28})$$

Note that $\overleftrightarrow{\mathcal{A}}$ and $\mathcal{A}^{(ab)}$ are different ways to write a tensor (in this case, rank-2). As explained before, it is possible to note that

an orbital contribution promotes a deviation of the Lande factor from 2.

Considering the Hamiltonian written above (Eq. (A.26)), the second term is the spin-orbit coupling, representing the local magneto-crystalline anisotropy:

$$\mathcal{H}_{la} = -\zeta^2 \vec{S} \cdot \overleftrightarrow{\mathcal{D}}_L \cdot \vec{S} \quad (\text{A.29})$$

where

$$\overleftrightarrow{\mathcal{D}}_L = -\frac{1}{\zeta^2} \overleftrightarrow{\mathcal{D}}_{la} \quad (\text{A.30})$$

The third term represents the Zeeman interaction on its more complete form:

$$\mathcal{H}_z = \mu_B \vec{B} \cdot \overleftrightarrow{\mathcal{G}} \cdot \vec{S} \quad (\text{A.31})$$

Finally, the first term will be discussed below, when discuss the van Vleck paramagnetism.

A.8. Dipolar Hamiltonian

Dipolar Hamiltonian arises due to the interaction of a magnetic moment with the magnetic field created by other magnetic moment. Classically, this interaction is:

$$E = \frac{1}{r^3} \left[\vec{\mu}_1 \cdot \vec{\mu}_2 - 3 \frac{(\vec{\mu}_1 \cdot \vec{r})(\vec{\mu}_2 \cdot \vec{r})}{r^2} \right] \quad (\text{A.32})$$

where \vec{r} is a vector between these two spins.

From this energy, it is possible to write a spin Hamiltonian. Considering the isotropy of the tensor $\overleftrightarrow{\mathcal{G}}$ we have:

$$\vec{\mu}_i = -\mu_B g \vec{S}_i \quad (\text{A.33})$$

and then:

$$\mathcal{H}_d = \vec{S}_1 \cdot \overleftrightarrow{\mathcal{D}}_d \cdot \vec{S}_2 \quad (\text{A.34})$$

where $\overleftrightarrow{\mathcal{D}}$ is a tensor:

$$\mathcal{D}_d^{(ab)} = (g \mu_B)^2 \left\langle \frac{r^2 \delta_{ab} - 3ab}{r^5} \right\rangle \quad (\text{A.35})$$

and $\langle \dots \rangle$ represents an integration over the spatial wave functions.

It is important to emphasize that the parameters of the $\mathcal{D}_d^{(ab)}$ tensor are free to be determined when fitting the thermodynamic quantities to the experimental data.

Note the similarity between Hamiltonian of local magneto-crystalline anisotropy (Eq. (A.10)), and dipolar (Eq. (A.34)). Both are called as asymmetric.

A.9. The \mathcal{D} tensor

Now, further details on the \mathcal{D} tensor will be given. Let us considering the asymmetric Hamiltonian:

$$\mathcal{H} = \vec{S}_i \cdot \overleftrightarrow{\mathcal{D}} \cdot \vec{S}_j = \sum_u \sum_v \mathcal{D}_{uv} S_{iu} S_{jv} \quad (\text{A.36})$$

where $(u, v) = x, y, z$. Note that, if $i = j$, this asymmetric Hamiltonian is the local magneto-crystalline anisotropy; while, if $i \neq j$, we recover the dipolar Hamiltonian. Considering that crystal axis are the same of the $\overleftrightarrow{\mathcal{D}}$ tensor, this tensor is therefore diagonal (off-diagonal terms are zero). Thus:

$$\mathcal{H} = \mathcal{D}_{xx} S_{ix} S_{jx} + \mathcal{D}_{yy} S_{iy} S_{jy} + \mathcal{D}_{zz} S_{iz} S_{jz} \quad (\text{A.37})$$

We can define three parameters related to the diagonal of this tensor $\overleftrightarrow{\mathcal{D}}$:

$$D = \frac{1}{2}(-\mathcal{D}_{xx} - \mathcal{D}_{yy} + 2\mathcal{D}_{zz}) \quad (\text{A.38})$$

$$E = \frac{1}{2}(\mathcal{D}_{xx} - \mathcal{D}_{yy}) \quad (\text{A.39})$$

$$K = \frac{1}{3}(\mathcal{D}_{xx} + \mathcal{D}_{yy} + \mathcal{D}_{zz}) \quad (\text{A.40})$$

We can write this system as:

$$\begin{pmatrix} D \\ E \\ K \end{pmatrix} = \mathbb{T} \begin{pmatrix} \mathcal{D}_{xx} \\ \mathcal{D}_{yy} \\ \mathcal{D}_{zz} \end{pmatrix} \quad (\text{A.41})$$

where

$$\mathbb{T} = \begin{pmatrix} -1/2 & -1/2 & 1 \\ 1/2 & -1/2 & 0 \\ 1/3 & 1/3 & 1/3 \end{pmatrix} \quad (\text{A.42})$$

Consequently:

$$\begin{pmatrix} \mathcal{D}_{xx} \\ \mathcal{D}_{yy} \\ \mathcal{D}_{zz} \end{pmatrix} = \mathbb{T}^{-1} \begin{pmatrix} D \\ E \\ K \end{pmatrix} \quad (\text{A.43})$$

where

$$\mathbb{T}^{-1} = \begin{pmatrix} -1/3 & 1 & 1 \\ -1/3 & -1 & 1 \\ 2/3 & 0 & 1 \end{pmatrix} \quad (\text{A.44})$$

Thus, we find the elements of the diagonal of the tensor $\vec{\mathcal{D}}$ as a function of the parameters defined before:

$$\mathcal{D}_{xx} = -\frac{1}{3}D + E + K \quad (\text{A.45})$$

$$\mathcal{D}_{yy} = -\frac{1}{3}D - E + K \quad (\text{A.46})$$

$$\mathcal{D}_{zz} = \frac{2}{3}D + K \quad (\text{A.47})$$

We are now able to written the asymmetric Hamiltonian; however, in terms of these new parameters:

$$\mathcal{H} = D \left(S_{iz}S_{jz} - \frac{1}{3}\vec{S}_i \cdot \vec{S}_j \right) + E(S_{ix}S_{jx} - S_{iy}S_{jy}) + K(\vec{S}_i \cdot \vec{S}_j) \quad (\text{A.48})$$

To ensure the null trace of the tensor $\vec{\mathcal{D}}$, we can consider $K = 0$. Thus:

$$\mathcal{H} = D \left(S_{iz}S_{jz} - \frac{1}{3}\vec{S}_i \cdot \vec{S}_j \right) + E(S_{ix}S_{jx} - S_{iy}S_{jy}) \quad (\text{A.49})$$

It is easy to see that the parameter D will be on the diagonal, since $S_{iz}S_{jz}$ is diagonal on the basis $|s_i, s_j, s, m_s\rangle$; while the parameter E will be on the off-diagonal terms, since S_x and S_y are not diagonals. Due to this reason, D and E are called, respectively, as axial and rhombic parameters and assume:

$$D = \frac{3}{2}\mathcal{D}_{zz} = -\frac{3}{2}(\mathcal{D}_{xx} + \mathcal{D}_{yy}) \quad (\text{A.50})$$

$$E = \frac{1}{2}(\mathcal{D}_{xx} - \mathcal{D}_{yy}) \quad (\text{A.51})$$

The above results can be used directly to the dipolar Hamiltonian, when $i \neq j$. For the local magneto-crystalline anisotropy case, when $i = j$, it is:

$$\mathcal{H} = D \left(S_z^2 - \frac{1}{3}S^2 \right) + E(S_x^2 - S_y^2) \quad (\text{A.52})$$

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