IOP Conf. Series: Journal of Physics: Conf. Series **869** (2017) 012037 doi:10.1088/1742-6596/869/1/012037

Magnetic phenomena in exchange coupled spin systems

S Sakhi and A Patel

Department of Physics, American University of Sharjah, United Arab Emirates, POBOX 26666
Email: ssakhi@aus.edu

Abstract. We study theoretically a cluster of several interacting spins modelling a hypothetical single-molecule magnet. Starting from a spin Hamiltonian, we obtain the individual energy levels and their evolution in an applied magnetic field. By substituting the energy levels into the partition function, we compute macroscopic observables like the magnetisation and the susceptibility of the system.

1. Introduction

Low-dimensional magnetic materials [1] attract interest because their fascinating physical properties show potential applications in areas such as high-density information storage, quantum computing, and biomedical applications such as magnetic resonance imaging [2]. Of particular interest are single-molecule magnets [3] which can be synthesized in a bottom-up approach using an increasing number of magnetic centres [4] such as transition metals or rare earth ions with spins equalling 5/2 or 7/2. These nano-magnets reveal a slow relaxation of the magnetization at low temperature and offer a controllable approach to nanoscale magnetism, where the energy barrier to magnetization reorientation is derived from the anisotropy of the molecular spin rather than the movement of domain walls, as in bulk magnets.

Theoretically these nano-magnets are remarkable because they offer enough complexity to yield new types of properties while simple enough to study in detail. They proved to be testing grounds for theories of the coexistence of quantum and classical phenomena [5]. The magnetic interactions in molecular systems are in principle the same as those in continuous lattices. However, the pair interactions are strongly localized in molecular systems with a predominantly electrostatic origin.

In this paper, we theoretically investigate a cluster of several interacting spins modelling a hypothetical single-molecule magnet. Starting from an effective spin Hamiltonian, we obtain the individual energy levels and their evolution in an applied magnetic field. In the effective spin Hamiltonian, all orbital coordinates are eliminated and replaced by spin coordinates while taking advantage of the symmetry properties of the system. We use a basis consisting of eigenfunctions of the total spin operator to ensure that the Hamiltonian is block-diagonal. This is straightforward in principle, but the problem rapidly grows in complexity as in general there are $(2S_i + 1)^N$ states for N spins. We also utilize an irreducible tensor method which exploits the symmetry of the full rotation group to derive the energy levels of the system.

2. The spin model

The interaction between localized spin magnetic moments in the strong exchange limit is described by the Heisenberg model.

$$H = -2\sum_{ij} J_{ij}\vec{S}_i \cdot \vec{S}_j + g\mu_B \vec{B}\cdot\sum_i \vec{S}_i \tag{1}$$

J_{ij} is a symmetric matrix containing the exchange parameters between spins at sites i and j. $J_{ij} < 0$ corresponds to antiferromagnetic and $J_{ij} > 0$ to ferromagnetic coupling. The first sum in (1) runs over all possible terms (i, j). The vector operators $\vec{S}_i$ are the single-particle spin operators. The last term (Zeeman) describes the interaction with an external magnetic field which is assumed to be along the z-axis. The dimensionless spin operators in (1) obey the commutation relations

$$\left[S_i^{\alpha}, S_j^{\beta}\right] = i\delta_{ij}\varepsilon^{\alpha\beta\gamma}S_i^{\gamma} \tag{2}$$

where α, β, γ refer to the Cartesian coordinates and $\varepsilon^{\alpha\beta\gamma}$ is the totally anti-symmetric Levi-Civita symbol. For a large cluster, the general problem of finding the eigenvalues of Hamiltonian (1) is challenging because of the lack of translation symmetry which prevents the reduction of the size of the matrix. Here we consider clusters comprising a reduced number of exchange-coupled spins and special topologies which allow exact solution of equation (1).

2.1. Two spin Cluster

The Hamiltonian for a pair of spins in the strong exchange limit *is*

$$H = -2J\vec{S}_i \cdot \vec{S}_j + g\mu_B B_z(S_i^z + S_j^z) \tag{3}$$

It can be exactly solved by using the total spin $\vec{S} = \vec{S}_i + \vec{S}_j$ whose square has eigenvalues $\vec{S}^2 = S(S+1)$ in the basis $|S_i, S_j; SM>$ with $0 \le S \le 2s$ and $S_i = S_j = s$. S_z has eigenvalues M with $-2s \le M \le 2s$. The eigenvalues of the pair Hamiltonian (3) are

$$E = -J\left[S(S+1) - 2s(s+1)\right] + g\mu_B B_z M \tag{4}$$

The magnetisation and the susceptibility are found from the partition function which is given by

$$Z = \mathrm{Tr}e^{-\beta\hat{H}} = \sum_{S=0}^{S=2s}\sum_{M=-S}^{M=+S} e^{\beta JS(S+1)-\beta g\mu_B B_z M} = \sum_{S=0}^{S=2s}\frac{\sinh(xS + x/2)}{\sinh(x/2)}e^{\beta JS(S+1)} \tag{5}$$

where the summation over M is performed and $x = \beta g\mu_B B_z$, $\beta = 1/(k_B T)$. The free energy is

$$F = -k_B T \ln Z \tag{6}$$

To find the magnetic susceptibility defined below in (8) as the second derivative with B_z as $B_z \to 0$, it is sufficient to expand the partition function in B_z and keep terms up to B_z^2. This gives

$$Z = \sum_{S=0}^{S=2s}\left[2S+1 + S(S+1)(2S+1)B_z^2/6\right]e^{\beta JS(S+1)} \tag{7}$$

The magnetic susceptibility is

$$\chi = -\frac{\partial^2 F}{\partial B_z^2} = \frac{k_B T}{3}\frac{\sum_{S=0}^{S=2s}\left[S(S+1)(2S+1)\right]e^{\beta JS(S+1)}}{\sum_{S=0}^{S=2s}\left[2S+1\right]e^{\beta JS(S+1)}} \tag{8}$$

For a cluster of two spins s=1/2, the partition function reduces to

$$Z = 1 + e^{\beta J}(1 + 2\cosh x) \tag{9}$$

The average pair magnetization is

$$< \mathcal{M} >= \frac{4\sinh(x)}{e^{-\beta J} + 1 + 2\cosh(x)} \tag{10}$$

2.2. Three spin cluster

The Hamiltonian for a three spin cluster in the strong exchange limit is

$$H = -2J_1\vec{S}_1 \cdot \vec{S}_2 - 2J_2\vec{S}_1 \cdot \vec{S}_3 - 2J_3\vec{S}_2 \cdot \vec{S}_3 + g\mu_B B_z(S_1^z + S_2^z + S_3^z) \tag{11}$$

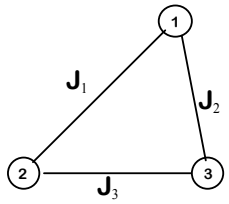

Figure1. Three spin cluster.

The eigenstates of (11) are found in the basis that diagonalizes $\vec{S}^2$ and S_z where $\vec{S}$ is the total spin operator. These states though are not uniquely determined by S and M_z, but require an additional quantum number which depends on the coupling scheme of the spins. Here, we first couple $\vec{S}_1$ with $\vec{S}_2$ to give $\vec{S}_{12} = \vec{S}_1 + \vec{S}_2$ and then $\vec{S}_{12}$ with $\vec{S}_3$ to give $\vec{S} = \vec{S}_{12} + \vec{S}_3$. The resulting states are labeled by the eigenvalues of the commuting set $\left\{\vec{S}_1^{\,2}, \vec{S}_2^{\,2}, \vec{S}_{12}^{\,2}, \vec{S}_3^{\,2}, \vec{S}^2, S_z\right\}$ as |$S_1S_2S_{12}S_3$SM>, and (11) reduces to

$$H = -J_1\left(\vec{S}_{12}^2 - \vec{S}_1^2 - \vec{S}_2^2\right) - J_2\left(\vec{S}^2 - \vec{S}_{12}^2 - \vec{S}_3^2\right) + g\mu_B B_z S^z + 2(J_2 - J_3)\vec{S}_2 \cdot \vec{S}_3 \tag{12}$$

For a symmetric spin arrangement for which $J_2 = J_3$, (12) is completely diagonal with eigenvalues

$$E = J_1\left(\tilde{S}_1 + \tilde{S}_2 - \tilde{S}_{12}\right) + J_2(\tilde{S}_3 + \tilde{S}_{12} - \tilde{S}) + g\mu_B B_z M_z \tag{13}$$

Here $\tilde{S}_\alpha = S_\alpha(S_\alpha + 1)$, $|S_1 - S_2| \le S_{12} \le S_1 + S_2$ and $|S_{12} - S_3| \le S \le S_{12} + S_3$. When $J_2 \neq J_3$, the last term in (12) is not diagonal. Its matrix elements can be obtained by Wigner-Eckart [6] theorem

$$\begin{aligned} &< S_{12}'S'M' | \vec{S}_2 \cdot \vec{S}_3 | S_{12}SM >= \delta_{S'S}\delta_{M'M}(-1)^{2S-2M+1}\left[(2S+1)(2S'+1)(2S_{12}+1)(2S_{12}'+1)(2S_1+1)\right]^{1/2} \\ &\times\left[(2S_2+1)S_2(S_2+1)(2S_3+1)S_3(S_3+1)\right]^{1/2} \begin{Bmatrix} S_1 & S_1 & 0 \\ S_2 & S_2 & 1 \\ S_{12} & S_{12}' & 1 \end{Bmatrix} \begin{Bmatrix} S_{12} & S_{12}' & 1 \\ S_3 & S_3 & 1 \\ S & S' & 0 \end{Bmatrix} \end{aligned} \tag{14}$$

The curly brackets are 9-j symbols whose numerical values are given in tables such as in Ref. [7], and some packages such as in Mathematica. For a cluster of three S =1/2 spins, $S_{12} = 0$, 1 and S = 3/2, 1/2. In this case we obtain compact expressions for the eigenvalues of (12) as follows

$$E(S=3/2,M)=-(J_1+J_2+J_3)/2+g\mu_B B_z M;\quad M=\pm 3/2,\pm 1/2 \tag{15}$$

$$E(S=1/2,M)=(J_1+J_2+J_3)/2\pm g\mu_B B_z M\pm\Delta;\quad M=\pm 1/2 \tag{16}$$

and $\Delta=[(J_1-J_2)^2+(J_2-J_3)^2+(J_1-J_2)(J_2-J_3)]^{1/2}$. The magnetic susceptibility for $B_z\to 0$ is

$$\chi=\frac{(g\mu_B)^2}{4k_BT}\frac{5+e^{-(J_1+J_2+J_3)/k_BT}\cosh(\Delta/k_BT)}{1+e^{-(J_1+J_2+J_3)/k_BT}\cosh(\Delta/k_BT)} \tag{17}$$

For a linear cluster, we put J_2=0, in equations (11-17).

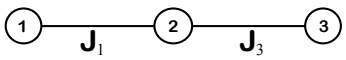

Figure 2. Three spin linear cluster.

3. Conclusion

Starting from an effective spin Hamiltonian, we have investigated the magnetic properties of a spin cluster. Using a spin coupling scheme and Wigner-Eckart theorem we computed exactly the energy levels, the free energy, and the magnetic susceptibility. These findings are useful for large systems made of weakly interacting small clusters (e.g. three-spin clusters), in which the system's magnetic susceptibility is that found in eq.17 times the total number of clusters. Moreover these findings form a good basis to treat approximately complex Heisenberg systems of many interacting degrees of freedom. In this case, the small cluster encompasses the short range effects and the spin operators outside the cluster are approximately replaced by their expectation values. The resulting reduced and more manageable problem is similar to the one studied here, and is solved in a self-consistent way.

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