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Magnetic Properties of Small Molecular Clusters

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Abstract. There has been a great deal of interest over the last two decades on the magnetic properties of small synthesized molecular clusters containing a finite number of magnetic ions whose positions define a three-dimensional regular structure. In many cases such molecular clusters incorporate large-spin ions whose magnetic interactions can be well described in terms of classical Heisenberg spins. In this work we calculate exactly the magnetic properties of small molecular clusters described by a classical Heisenberg model of an arbitrary number of spins all coupled equally to each other and subject to a uniform external magnetic field. We solve the problem by employing a simple mathematical approach whose idea is the introduction of auxiliary spin variables into the defining expression of the partition function. The model can be directly applied to understand the magnetic properties of recently synthesized small molecular clusters that contain a finite number of large-spin magnetic ions.

1. Introduction

There has been a great deal of interest over the last two decades on the magnetic properties of small synthesized molecular clusters containing a very small number (in some cases as few as four) magnetic ions [1, 2]. The interest in molecular magnetic systems stems not only from their basic properties, but also because of their potential applications. In most cases the positions of the magnetic ions are uniformly spaced. For instance, the “ferric wheel” \( \text{Fe}^{10} \) molecule defines a nearly 2-dimensional ring structure [3] and its magnetic properties originate from the ten paramagnetic \( \text{Fe}^{3+} \) ions, each of spin \( S = 5/2 \), which interact with nearest-neighbor antiferromagnetic (AF) isotropic Heisenberg spin exchange. In fact, because of the large value of \( S \) it turns out that the measured magnetic susceptibility can be reproduced to very high accuracy [4], for temperatures above \( 40 \, \text{K} \), by using the classical Heisenberg model for a ring of spins, which incorporates an exchange interaction between classical unit vectors. The \( \text{Fe}^{10} \) molecule thus serves as a prototype of what we refer to as a classical Heisenberg system.

Other molecules incorporate paramagnetic ions whose positions define a 3-dimensional structure and they cannot be described as Heisenberg rings. Simplest examples of this type are the molecules \( \text{Fe}^{4} \) and \( \text{Cr}^{4} \), which feature four \( \text{Fe}^{3+} \) ions [5] and four \( \text{Cr}^{3+} \) ions [6] \( (S = 3/2) \), respectively, which occupy the vertices of a tetrahedron embedded in the molecule. The \( \text{Cr}^{4} \) molecule is very interesting in its own because is one of the few compounds which exhibits intra-molecular ferromagnetic (F) coupling. Numerous other examples of molecules featuring paramagnetic ions that define a 3-dimensional structure could be cited [7, 8].

Only on very special cases such as a finite open chain of \( N \) classical Heisenberg spins in zero magnetic field [9] or a closed ring of \( N \) classical Heisenberg spins in zero magnetic field [10]...
the partition function can be readily evaluated. However, no exact expressions for the partition function for the above chain or ring spin models can be obtained in presence of an external magnetic field at an arbitrary $N$.

The tetrahedron-shaped molecules $Cr4$ and $Fe4$ are among the simplest cases which cannot be described in terms of rings or chains of spins, therefore, a different model must be adopted [11]. The simplest general model to represent such cases would be a system consisting of an arbitrary number of spins with all spins coupled equally to each other. In this paper we adopt this model and derive analytic expressions, in the form of 1-dimensional integrals, for the partition function and the magnetic equation of state for the classical Heisenberg model of $N$ spins in an external magnetic field with all spins coupled equally to each other by isotropic exchange interactions.

The current analytic results, apart from any intrinsic interest, can provide useful benchmarks to gauge numerical methods for calculating the magnetic equation of state and can be directly applied to small molecular clusters featuring a small number of high-spin magnetic ions, new examples of which continue to be synthesized.

2. Theory and results
We consider a model of arbitrary $N(\geq 2)$ classical spins whose interactions are described by a classical Heisenberg Hamiltonian with all spins coupled equally to each other. The spins are also subject to a uniform external magnetic field $\vec{B}$ and we write the Hamiltonian of the system as

$$H_N(B,J) = J \sum_{i<j} \vec{S}_i \cdot \vec{S}_j - \gamma \vec{B} \cdot \sum_{i=1}^{N} \vec{S}_i.$$  

(1)

The direction of $\vec{B}$ serves to define the z (polar) axis, the spins $\vec{S}_i$ are classical unit vectors whose orientations are specified by two angles, $\theta_i$ and $\varphi_i$. All spins are coupled equally with a coupling constant $J$ which can be either AF, $J = |J| > 0$ or F, $J = -|J| < 0$ and $\gamma (> 0)$ is the gyromagnetic ratio. For an arbitrary value of the magnetic field, $B$, the partition function is given by

$$Z_N(B,J,T) = \int \cdots \int d\Omega_i \exp \left[ -\beta H_N(B,J) \right],$$  

(2)

where $d\Omega_i = d\theta_i \sin \theta_i d\varphi_i$ is an element of solid angle, the angles $\theta_i$ and $\varphi_i$ extend from 0 to $\pi$ and 0 to $2\pi$, respectively, $\beta = 1/(k_B T)$, $k_B$ is the Boltzmann’s constant and $T$ is the absolute temperature of the system. All other quantities such as magnetic moment, zero- or nonzero-magnetic field susceptibility and so on, can be calculated from the partition function. For example, the total magnetic moment induced by the magnetic field is given by

$$\langle M_z \rangle (B) = \gamma \sum_{i=1}^{N} \langle S_{iz} \rangle = \frac{1}{\beta} \frac{\partial}{\partial B} \ln Z_N(B,J,T).$$  

(3)

As it stands, the expression for $Z_N(B,J,T)$ involves the evaluation of a $2N$-dimensional integral. The first step toward the exact calculation of the partition function, is to note that $H_N(B,J)$ may be rewritten solely in terms of the total spin vector, $\vec{S} = \sum_{i=1}^{N} \vec{S}_i$ as:

$$H_N(B,J) = \frac{J}{2} \left( \vec{S}^2 - N \right) - \gamma \vec{B} \cdot \vec{S}.$$  

(4)

The second step is to multiply the integral in Eq.(2) by 1 = $\int d^3 S \delta^{(3)}(\vec{S} - \sum_{i=1}^{N} \vec{S}_i)$ (thus leave it unchanged) and then write $\delta^{(3)}(\vec{S} - \sum_{i=1}^{N} \vec{S}_i) = \int \frac{dk}{(2\pi)^3} \exp \left[ ik \cdot \left( \vec{S} - \sum_{i=1}^{N} \vec{S}_i \right) \right]$ where we used a standard expression for the Dirac delta function [12]. Although we are now faced with a
Figure 1. Function $D_N(S)$ for several $N$ as a function of the magnitude of the total spin, $S$. For a given number $N$ of spins this function is nonzero and continuous within the interval $0 \leq S \leq N$ and vanishes elsewhere.

Figure 2. Magnetic moment per spin in units of $\gamma$ plotted as a function of the dimensionless variable, $\gamma B/|J|$ for two values of $k_B T/|J|$. In all cases we consider an AF coupling between $N = 2, 3$ and 4 classical spins.

$(2N + 6)$-dimensional integral the subsequent calculations are actually straightforward with the final result:

$$Z_N(B, J, T) = (4\pi)^N \exp\left(\frac{N}{2}a\right) \int_0^N dS D_N(S) \exp\left(-\frac{a}{2}S^2\right) \frac{\sinh(bS)}{bS},$$

where $a = \beta J$ and $b = \gamma \beta B$ are dimensionless quantities, and $D_N(S)$ is a function given by

$$D_N(S) = 4\pi S^2 \int \frac{d^3k}{(2\pi)^3} \exp(i\vec{k} \cdot \vec{S}) \left[\frac{\sin(k)}{k}\right]^N.$$  

One can evaluate $D_N(S)$ for any given $N$, although several general properties can be easily anticipated. As expected for the case of $N$ unit spins, contributions to $Z_N(B, J, T)$ can only arise for $0 \leq S \leq N$ values. Hence $D_N(S)$ must necessarily vanish for $S > N$, and the upper limit in Eq.(5) reflects this fact. Additionally, since $Z_N(B = 0, J = 0, T) = (4\pi)^N$, we can immediately see that for any given $N$ the function $D_N(S)$ satisfies the following constrain that we refer to as a normalization condition:

$$\int_0^N dS D_N(S) = 1.$$  

It is straightforward to calculate $D_N(S)$ if $N$ is not too large. Some results are shown in Figure 1 where we plot $D_N(S)$ as a function of $S$ for several $N$. For a large number of spins ($N \gg 1$), the exact calculation of $D_N(S)$ becomes time-consuming. In this case, one may use the formula [13]

$$\lim_{N \to \infty} \left[\frac{\sin(k)}{k}\right]^N = \exp(-N \frac{k^2}{4})$$

to approximate $D_{N \gg 1}(S) \approx 4\pi S^2 \cdot \exp(-\frac{a}{2}S^2) / (2\pi N)^{3/2}$. Note that, despite the approximation, $D_{N \gg 1}(S)$ still satisfies the normalization condition in Eq.(7). The total magnetic moment induced by the magnetic field is calculated via Eq.(3) and one finds

$$\langle M_z \rangle(B) = -\frac{1}{b} + \frac{1}{b} \int_0^N dS D_N(S) \exp(-\frac{a}{2}S^2) \cos(bS) - \frac{a}{2} S^2 \sinh(bS) / (bS).$$
We use this formula to calculate the magnetization of small molecular clusters containing \( N = 2, 3 \) and 4 spins. The results for the magnetic moment per spin, \( \langle M_z \rangle / (N \gamma) \) in units of \( \gamma \) as a function of \( b/|a| = \gamma B/|J| \) for two values of the dimensionless temperature, \( k_B T/|J| \) and for AF coupling between the spins are shown in Figure 2.

3. Conclusion
In this work we calculated exactly the magnetic properties of small molecular clusters described by a classical Heisenberg model of an arbitrary number of spins all coupled equally to each other and subject to a uniform external magnetic field. The statistical problem of this specific model was solved exactly by introducing auxiliary spin variables into the defining expression of the partition function. This model can be directly applied to understand the magnetic properties of recently synthesized small molecular clusters that contain a finite number of large-spin magnetic ions. The partition function, total magnetic moment and other related quantities are obtained as a simple 1-dimensional integral expressions that depends only on the total spin variable \( S \). One needs only to compute the function \( D_N(S) \) in order to obtain the partition function. The function \( D_N(S) \) depends on the number \( N \) of spins, is nonzero for \( 0 \leq S \leq N \) and within this interval is a piecewise function continuous at the merger points, but its first derivative is not always continuous at these points. We also found that \( D_N(S) \) satisfies a constrain given by Eq.(7). Since the exact calculation of \( D_N(S) \) for \( N \gg 1 \) is time-consuming, we derived an approximated expression, \( D_{N\gg1}(S) \) which can be used instead of the exact function.

Although this model may be too artificial to describe systems with a large number of spins, it is fairly realistic for several synthesized molecular magnetic clusters with few spins. Of great physical interest is the case of \( N = 4 \) spins, a model which corresponds to the recently synthesized \( Fe_4 \) and \( Cr_4 \) molecular magnets, consisting of four ions which occupy the vertices of a tetrahedron and interact equally with each other [5, 6]. This was our main motivation to adopt the “equal coupling” model and calculate explicitely the partition function and total magnetic moment for small clusters with \( N = 2, 3 \) and 4 spins. In particular, for AF exchange between \( N = 4 \) spins, as in the \( Fe_4 \) magnetic cluster case, we observed typical geometric/magnetic frustration behavior. We found that at \( T = 0 \), each spin forms an angle of \( \arccos(-1/3) \) with the other three spins as to maximally avoid each other due to the presence of the AF coupling.

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