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2001 J. Phys. A: Math. Gen. 34 1611

(http://iopscience.iop.org/0305-4470/34/8/308)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS A: MATHEMATICAL AND GENERAL

J. Phys. A: Math. Gen. **34** (2001) 1611–1627 www.iop.org/Journals/ja PII: S0305-4470(01)16416-4

The irregular tetrahedron of classical and quantum spins subjected to a magnetic field

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Received 15 August 2000

Abstract

We obtain analytical expressions for the total magnetic moment and the static spin correlation functions of the classical Heisenberg model for an irregular tetrahedron array of spins that interact via two different exchange interactions and that are subject to a uniform magnetic field of arbitrary strength. This system provides a useful theoretical framework for calculating the magnetic properties of several recently synthesized molecular magnets. The tetrahedron systems, each considered for antiferromagnetic exchange, are of particular interest since they exhibit frustrated spin ordering for sufficiently low temperatures and weak magnetic fields. We compare the results with the corresponding irregular tetrahedron of quantum spins for several quantum spin values.

PACS numbers: 7510H, 7550X

1. Introduction

In recent years there has been a surge of interest in the magnetic properties of synthesized molecular clusters [1, 2] containing relatively small numbers of paramagnetic ions. With the ability to control the placement of magnetic moments of diverse species within stable molecular structures, one can test basic theories of magnetism and explore the design of novel systems that offer the prospect of useful applications [3, 4]. A common feature of these organic-based molecular magnets is that intermolecular magnetic interactions are extremely weak compared with those within individual molecules, i.e. a bulk sample can be described in terms of independent individual molecular magnets.

As examples of molecular magnets with ultra-small numbers of embedded paramagnetic ions we mention the dimer system [5] consisting of two Fe^{3+} ions (spin $S = \frac{5}{2}$), a nearly equilateral triangular array [6] of V^{4+} ions (total spin $j = \frac{7}{2}$), a nearly square array [7] of Nd^{3+} ions (total spin $j = \frac{9}{2}$), a regular tetrahedron array [8] of Cr^{3+} ions (spin $S = \frac{3}{2}$) and an irregular tetrahedron array [9] of Fe^{3+} ions (spin $S = \frac{5}{2}$). Also noteworthy is the pyrochlore antiferromagnet $Tb_2Ti_2O_7$, although distinct from the class of organic molecules yet sharing the feature that the Tb^{3+} ions (total spin $j = 6$) reside on a network of very weakly coupled tetrahedra [10].

This paper has been motivated by the rapid experimental developments in the synthesis of molecular magnets with ultra-small numbers of strongly interacting moments. It is perhaps surprising that for high-spin moments the calculation of equilibrium magnetic properties for arbitrary temperatures and magnetic field strengths presents a serious challenge. One might expect that the determination of the partition function for a few-spin system would be a relatively simple task. To put this matter in perspective, it should be recalled that for a finite open chain of *classical* spins which interact with nearest-neighbour (NN) isotropic Heisenberg exchange, the partition function has been evaluated only in the absence of an external magnetic field [11]. For the related system, where the linear chain is closed so as to form a 'Heisenberg ring', the calculation of the partition function and the equilibrium spin correlation function is extremely involved. Exact, unwieldy infinite-series expansions of these quantities were successfully derived [12] many years ago, but only for zero applied field. With the introduction of an external magnetic field the analytic calculation of the partition function has been an intractable problem even for small numbers of interacting moments[1].

The purpose of this paper is to provide the full magnetic equation of state (molecular magnetic moment) and spin correlation functions, versus temperature and applied magnetic field, for a specific molecular magnet consisting of an irregular tetrahedron array of spins where three spins are placed in a ring and are coupled with a given exchange interaction, J while the fourth spin of the tetrahedron is coupled with a different exchange interaction J' to the remaining three spins. The whole cluster of spins is then subjected to an external magnetic field. In more experimental terms, we calculate quantities that are directly related to the temperature and applied field-dependent magnetization.

This system mirrors some of the synthetic molecular magnets cited above and the results also apply to the regular tetrahedron and regular triangle of spins, which are special cases of this general model and are of special interest in their own right because such systems [6, 10] exhibit frustrated order at sufficiently low temperatures and weak magnetic fields.

In section 2 we summarize several basic formulae for a general system of N classical spins coupled by two different exchange interactions and subjected to a magnetic field. In section 3 we describe the analogous quantum system with individual quantum spins S and make the correspondence between the classical and quantum models. In section 4 we illustrate our method for evaluating the partition function for the irregular tetrahedron of classical spins in the presence of an external magnetic field. In section 5 we comment briefly on the results that apply to the ground state configuration of the spins for an arbitrary value of the magnetic field. In section 6 we describe the main results for the irregular tetrahedron of classical spins that apply to any value of temperature and magnetic field and compare them with the corresponding exact results for the irregular tetrahedron of quantum spins for increasing value of quantum spin S. In section 7 we show the formulae that apply to a general temperature in the absence of an external magnetic field and finally in section 8 we summarize the results and comment briefly on the obstacles to extending the present calculations to larger arrays of spins, while noting several larger systems that can be dealt with successfully.

2. General formulae for the classical model

For a general system consisting of N classical spins coupled by two different exchange interaction values J and J' and subjected to a uniform external magnetic field $\vec{B}$ the Hamiltonian

[1] A numerical method for calculating equilibrium quantities such as the partition function and equal-time spin correlation functions has been given in [13].

is written as

$$H_N(J, J', B) = H_N(J, J') - \mu \vec{B} \cdot \sum_{i=1}^{N} \vec{S}_i \tag{1}$$

where $H_N(J, J')$ is the zero-field Hamiltonian.

The direction of $\vec{B}$ serves to define the z (polar) axis, μ (> 0) is the gyromagnetic ratio and the spins $\vec{S}_i$ are classical unit vectors whose orientation is specified by the polar and azimuthal angles θ_i and φ_i.

The partition function for an arbitrary magnetic field is given by

$$Z_N(J, J', B) = \int \cdots \int \prod_{i=1}^{N} \mathrm{d}\Omega_i \exp\left[-\beta H_N(J, J', B)\right] \tag{2}$$

where $\mathrm{d}\Omega_i = \mathrm{d}\theta_i \sin(\theta_i)\, \mathrm{d}\varphi_i$ is an element of solid angle extended from 0 to π and 0 to 2π, respectively, $\beta = 1/(k_B T)$, k_B is the Boltzmann constant and T is the absolute temperature of the system.

The total magnetic moment induced by the magnetic field is given by

$$\langle M_z\rangle(B) = \mu \sum_{i=1}^{N} \langle S_{iz}\rangle = \frac{1}{\beta}\frac{\partial}{\partial B} \ln Z_N(J, J', B) \tag{3}$$

and the expression for the total susceptibility $\chi_N(T, B) = \frac{\partial}{\partial B}\langle M_z\rangle(B)$ is provided by the fluctuation relation in the form

$$\chi_N(T, B) = \mu^2 \beta \sum_{i=1}^{N} \sum_{j=1}^{N} \left[\langle S_{iz} S_{jz}\rangle - \langle S_{iz}\rangle\langle S_{jz}\rangle\right]. \tag{4}$$

In the zero-field limit we have $\langle S_{iz} S_{jz}\rangle = \frac{1}{3}\langle \vec{S}_i \cdot \vec{S}_j\rangle$ and $\langle S_{iz}\rangle = 0$ so the zero-field susceptibility per spin $\chi_N(T, B = 0)/N$ may be written as

$$\frac{\chi_N(T, B = 0)}{N} = \tfrac{1}{3}\mu^2 \beta \tilde{\chi}_N(T) \tag{5}$$

in terms of a reduced susceptibility $\tilde{\chi}_N(T)$ given by

$$\tilde{\chi}_N(T) = 1 + \frac{2}{N} \sum_{i>j}^{N} \langle \vec{S}_i \cdot \vec{S}_j\rangle. \tag{6}$$

In the high-temperature limit all of the correlation functions $\langle \vec{S}_i \cdot \vec{S}_j\rangle$ vanish for $i > j$ and as a result equation (5) correctly reduces to Curie's law.

3. The quantum model

The Hamiltonian of equation (1) provides the classical counterpart to the quantum Heisenberg model,

$$\hat{H}_N(J_S, J'_S, B) = \hat{H}_N(J_S, J'_S) - g\mu_B \vec{B} \cdot \sum_{i=1}^{N} \hat{\vec{S}}_i \tag{7}$$

of atomic ion spins S (expressed in units of $\hbar$) with two different exchange interactions, J_S and J'_S. (Here and later in the text the caret symbol will be used for quantum operators.) The correspondence to the classical Heisenberg model is achieved by rescaling all quantum spin operators by the factor $\sqrt{S(S+1)}$. It thus follows that $J = S(S+1)J_S$, $J' = S(S+1)J'_S$ and the quantity μ in equation (1) is given by $\mu = (g\mu_B)\sqrt{S(S+1)}$, where g is the Landé g-factor for the given ion and μ_B is the Bohr magneton. In subsequent sections of this paper we compare results for the equilibrium magnetization and the spin correlation function for increasing values of S. The results rapidly approach the classical limit for increasing values of the quantum spin S.

4. The irregular tetrahedron of classical spins

The irregular tetrahedron of classical spins consists of $N = 4$ spins where three spins are placed in a ring and are coupled by a non-zero exchange interaction $J \neq 0$ and the fourth spin is coupled with a different exchange interaction J' to the remaining three spins. The whole cluster of spins is then subjected to an external magnetic field $\vec{B}$ and the Hamiltonian that describes this system is written as

$$H(J, J', B) = J(\vec{S}_1 \cdot \vec{S}_2 + \vec{S}_2 \cdot \vec{S}_3 + \vec{S}_3 \cdot \vec{S}_1) + J'\vec{S}_4 \cdot \sum_{i=1}^{3} \vec{S}_i - \mu\vec{B} \cdot \sum_{i=1}^{4} \vec{S}_i. \quad (8)$$

We start by showing that with the introduction of the auxiliary spin vector, $\vec{S}_{123} = \vec{S}_1 + \vec{S}_2 + \vec{S}_3$, the calculation of the partition function $Z(J, J', B)$ can readily be achieved. The success of our method will hinge on the fact that the Hamiltonian may be rewritten in a simpler form as

$$H(J, J', B) = \tfrac{1}{2}J(S_{123}^2 - 3) + J'\vec{S}_4 \cdot \vec{S}_{123} - \mu\vec{B} \cdot (\vec{S}_{123} + \vec{S}_4). \quad (9)$$

As it stands the integral in equation (2) for the irregular tetrahedron of classical spins is eight dimensional, but we note that the value of this integral is left unchanged if we multiply the integrand by the three-dimensional Dirac delta function

$$\delta^{(3)}(\vec{S}_{123} - \vec{S}_1 - \vec{S}_2 - \vec{S}_3) = \int \frac{\mathrm{d}^3 q}{(2\pi)^3} \exp\left[\mathrm{i}\vec{q} \cdot (\vec{S}_{123} - \vec{S}_1 - \vec{S}_2 - \vec{S}_3)\right] \quad (10)$$

and then integrate over the $\vec{S}_{123}$ variable. Although we are now faced with a 14-dimensional integral the subsequent calculations are actually very straightforward. In particular, we exploit the dependence of $H(J, J', B)$ on $\vec{S}_{123}$ and $\vec{S}_4$, rather than the individual unit vectors $\vec{S}_i$ ($i = 1, 2, 3$); the latter appear only in the argument of the exponential of equation (10). The integrations over each of the three pairs of angles θ_i, φ_i ($i = 1, 2, 3$) are now performed trivially. The remaining, ostensibly eight-dimensional integral depends only on $\vec{S}_{123}$, $\vec{q}$ and angles θ_4, φ_4, although in actual fact it is immediately reducible to a one-dimensional integral after performing firstly the integration over the $\vec{q}$ variable, secondly the integration over the angles θ_4, φ_4, and finally the integration over the angular part of the $\vec{S}_{123}$ variable. As a final result we obtain

$$Z(J, J', B) = (4\pi)^4 \exp(\tfrac{3}{2}a) \int_0^3 \mathrm{d}S_{123}\, D(S_{123}) \exp(-\tfrac{1}{2}aS_{123}^2) K(a', b, S_{123}) \quad (11)$$

where

$$K(a', b, S_{123}) = \frac{1}{2}\int_{-1}^{1} \mathrm{d}x \exp(bS_{123}x) \frac{\sinh\left(\sqrt{a'^2 S_{123}^2 - 2a'bS_{123}x + b^2}\right)}{\sqrt{a'^2 S_{123}^2 - 2a'bS_{123}x + b^2}} \quad (12)$$

where we introduce the dimensionless quantities $a = \beta J$, $a' = \beta J'$, $b = \mu\beta B$ and $D(S_{123})$ denotes the integral

$$D(S_{123}) = 4\pi S_{123}^2 \int \frac{\mathrm{d}^3 q}{(2\pi)^3} \exp(\mathrm{i}\vec{q} \cdot \vec{S}_{123}) \left(\frac{\sin q}{q} \right)^3. \tag{13}$$

Now one can readily evaluate the latter integral with the result

$$D(S_{123}) = \begin{cases} \frac{1}{2} S_{123}^2 & 0 \leqslant S_{123} \leqslant 1 \\ \frac{1}{4} S_{123}(3 - S_{123}) & 1 \leqslant S_{123} \leqslant 3 \\ 0 & S_{123} > 3. \end{cases} \tag{14}$$

Note that $D(S_{123})$ is continuous at the merger points $S_{123} = 1$ and 3, but its derivative is discontinuous at these points. As expected, contributions to the partition function can only arise from values of S_{123} in the interval $(0, 3)$; hence $D(S_{123})$ must necessarily vanish for $S_{123} > 3$, and the upper limit in equation (11) reflects this fact.

One can evaluate $K(a', b, S_{123})$ in closed form and the final result is

$$\begin{aligned} K(a', b, S_{123}) = {} & \frac{\exp(\frac{1}{2}a'(1 + S_{123}^2))}{4a' S_{123}} \frac{\exp(b^2/2a')}{b} \sqrt{\frac{\pi a'}{2}} \left(\operatorname{erf}\left[\sqrt{\frac{a'}{2}}(S_{123} - 1) + \frac{b}{\sqrt{2a'}} \right] \right. \\ & - \operatorname{erf}\left[\sqrt{\frac{a'}{2}}(S_{123} - 1) - \frac{b}{\sqrt{2a'}} \right] - \operatorname{erf}\left[\sqrt{\frac{a'}{2}}(S_{123} + 1) + \frac{b}{\sqrt{2a'}} \right] \\ & \left. + \operatorname{erf}\left[\sqrt{\frac{a'}{2}}(S_{123} + 1) - \frac{b}{\sqrt{2a'}} \right] \right) \end{aligned} \tag{15}$$

where $\operatorname{erf}(z)$ denotes the familiar error function (see, for example, chapter 7 of [14]), which is defined for any value of the complex variable z. The properties of this function which are useful in the present setting, including its connection with the confluent hypergeometric function, and its asymptotic properties for large real and large imaginary argument, are listed in the appendix.

In the zero-field limit ($b \to 0$) one obtains the result

$$K(a', b = 0, S_{123}) = \frac{\sinh(a' S_{123})}{(a' S_{123})} \tag{16}$$

noting that this function is even with respect to a'.

5. $T = 0$, general B

Before proceeding to extract physical results from equation (11), we consider the limiting case of zero temperature, $T = 0$ K and arbitrary magnetic field B. For given B, the ground state configuration of the spins depends very much on the sign and relative magnitude of J and J'. If one obtains the minimum energy, $E_0(J, J', B)$ for the irregular tetrahedron of classical spins, then the zero-temperature equilibrium spin correlation functions for a general B are given by $\langle \vec{S}_1 \cdot \vec{S}_2 \rangle (T = 0) = \frac{1}{3} \frac{\partial E_0(J,J',B)}{\partial J}$ and $\langle \vec{S}_4 \cdot \vec{S}_1 \rangle (T = 0) = \frac{1}{3} \frac{\partial E_0(J,J',B)}{\partial J'}$, while the total magnetization due to the magnetic field is given by $\langle M_z \rangle (T = 0) = -\frac{\partial E_0(J,J',B)}{\partial B}$.

5.1. $J > 0$, $J' \geqslant 0$

The most complex case arises when the irregular tetrahedron of classical spins is subjected to a magnetic field and the spins are coupled through AF exchange interactions, $J = |J| > 0$ and $J' = |J'| \geqslant 0$. Since both exchange interactions are AF, the ground state configuration of the spins depends strongly on the relative strength between $|J'/J|$ and $\mu B/|J|$. Without giving the details we found that the ground state spin correlation between the spins placed in the ring that are coupled through J is given by

$$\langle \vec{S}_1 \cdot \vec{S}_2 \rangle (T = 0) = \begin{cases} \frac{1}{6}\left[\left(\left|\frac{J'}{J}\right| - \frac{\mu B}{|J|}\right)^2 - 3\right] & 0 \leqslant \left|\frac{J'}{J}\right| \leqslant 1 \quad \frac{\mu B}{|J|} \leqslant \left|\frac{J'}{J}\right| \\ \frac{1}{6}\left[\left(\frac{\mu B}{|J|} - \left|\frac{J'}{J}\right|\right)^2 - 3\right] & 0 \leqslant \left|\frac{J'}{J}\right| \leqslant 1 \quad 0 < \left(\frac{\mu B}{|J|} - \left|\frac{J'}{J}\right|\right) \leqslant 3 \\ 1 & 0 \leqslant \left|\frac{J'}{J}\right| \leqslant 1 \quad 3 < \left(\frac{\mu B}{|J|} - \left|\frac{J'}{J}\right|\right) < \infty \\ \frac{1}{6}\left[\left(\frac{\mu B}{|J|} + \left|\frac{J'}{J}\right|\right)^2 - 3\right] & 1 < \left|\frac{J'}{J}\right| < \infty \quad \left(\frac{\mu B}{|J|} + \left|\frac{J'}{J}\right|\right) \leqslant 3 \\ 1 & 1 < \left|\frac{J'}{J}\right| < \infty \quad 3 < \left(\frac{\mu B}{|J|} + \left|\frac{J'}{J}\right|\right) \leqslant 3\left|\frac{J'}{J}\right| \\ 1 & 1 < \left|\frac{J'}{J}\right| < \infty \quad 3\left|\frac{J'}{J}\right| \leqslant \left(\frac{\mu B}{|J|} + \left|\frac{J'}{J}\right|\right) \leqslant 5\left|\frac{J'}{J}\right| \\ 1 & 1 < \left|\frac{J'}{J}\right| < \infty \quad 5\left|\frac{J'}{J}\right| \leqslant \left(\frac{\mu B}{|J|} + \left|\frac{J'}{J}\right|\right) < \infty. \end{cases} \tag{17}$$

The ground state spin correlation between the fourth spin and each of the remaining three spins on the ring is given by

$$\langle \vec{S}_4 \cdot \vec{S}_1 \rangle (T = 0) = \begin{cases} -\frac{1}{3}\left[\left|\frac{J'}{J}\right| - \frac{\mu B}{|J|}\right] & 0 \leqslant \left|\frac{J'}{J}\right| \leqslant 1 \quad \frac{\mu B}{|J|} \leqslant \left|\frac{J'}{J}\right| \\ \frac{1}{3}\left[\frac{\mu B}{|J|} - \left|\frac{J'}{J}\right|\right], & 0 \leqslant \left|\frac{J'}{J}\right| \leqslant 1 \quad 0 < \left(\frac{\mu B}{|J|} - \left|\frac{J'}{J}\right|\right) \leqslant 3 \\ 1 & 0 \leqslant \left|\frac{J'}{J}\right| \leqslant 1 \quad 3 < \left(\frac{\mu B}{|J|} - \left|\frac{J'}{J}\right|\right) < \infty \\ -\frac{1}{3}\left[\frac{\mu B}{|J|} + \left|\frac{J'}{J}\right|\right] & 1 < \left|\frac{J'}{J}\right| < \infty \quad \left(\frac{\mu B}{|J|} + \left|\frac{J'}{J}\right|\right) \leqslant 3 \\ -1 & 1 < \left|\frac{J'}{J}\right| < \infty \quad 3 < \left(\frac{\mu B}{|J|} + \left|\frac{J'}{J}\right|\right) \leqslant 3\left|\frac{J'}{J}\right| \\ \frac{1}{6}\left[\left(\frac{\mu B}{|J|}\right)^2 \Big/ \left(\left|\frac{J'}{J}\right|\right)^2 - 10\right] & 1 < \left|\frac{J'}{J}\right| < \infty \quad 3\left|\frac{J'}{J}\right| \leqslant \left(\frac{\mu B}{|J|} + \left|\frac{J'}{J}\right|\right) \leqslant 5\left|\frac{J'}{J}\right| \\ 1 & 1 < \left|\frac{J'}{J}\right| < \infty \quad 5\left|\frac{J'}{J}\right| \leqslant \left(\frac{\mu B}{|J|} + \left|\frac{J'}{J}\right|\right) < \infty. \end{cases} \tag{18}$$

The whole picture of the ground state configuration of the spins is completed by giving the total ground state magnetization induced by the magnetic field,

$$\frac{\langle M_z\rangle(T=0)}{\mu} = \begin{cases} 1+\dfrac{\mu B}{|J|}-\left|\dfrac{J'}{J}\right| & 0\leqslant\left|\dfrac{J'}{J}\right|\leqslant 1 \quad \dfrac{\mu B}{|J|}\leqslant\left|\dfrac{J'}{J}\right| \\ 1+\dfrac{\mu B}{|J|}-\left|\dfrac{J'}{J}\right| & 0\leqslant\left|\dfrac{J'}{J}\right|\leqslant 1 \quad 0<\left(\dfrac{\mu B}{|J|}-\left|\dfrac{J'}{J}\right|\right)\leqslant 3 \\ 4 & 0\leqslant\left|\dfrac{J'}{J}\right|\leqslant 1 \quad 3<\left(\dfrac{\mu B}{|J|}-\left|\dfrac{J'}{J}\right|\right)<\infty \\ \dfrac{\mu B}{|J|}+\left|\dfrac{J'}{J}\right|-1 & 1<\left|\dfrac{J'}{J}\right|<\infty \quad \left(\dfrac{\mu B}{|J|}+\left|\dfrac{J'}{J}\right|\right)\leqslant 3 \\ 2 & 1<\left|\dfrac{J'}{J}\right|<\infty \quad 3<\left(\dfrac{\mu B}{|J|}+\left|\dfrac{J'}{J}\right|\right)\leqslant 3\left|\dfrac{J'}{J}\right| \\ \left(\dfrac{\mu B}{|J|}\right)\Big/\left(\left|\dfrac{J'}{J}\right|\right) & 1<\left|\dfrac{J'}{J}\right|<\infty \quad 3\left|\dfrac{J'}{J}\right|\leqslant\left(\dfrac{\mu B}{|J|}+\left|\dfrac{J'}{J}\right|\right)\leqslant 5\left|\dfrac{J'}{J}\right| \\ 4 & 1<\left|\dfrac{J'}{J}\right|<\infty \quad 5\left|\dfrac{J'}{J}\right|\leqslant\left(\dfrac{\mu B}{|J|}+\left|\dfrac{J'}{J}\right|\right)<\infty. \end{cases} \tag{19}$$

5.2. $J>0,\ J'\leqslant 0$

When the exchange interactions between the spins of the irregular tetrahedron subjected to the magnetic field are such that $J=|J|>0$ and $J'=-|J'|\leqslant 0$, the ground state spin correlation functions between the spins of the ring coupled through J is given by

$$\langle\vec{S}_1\cdot\vec{S}_2\rangle(T=0) = \begin{cases} \dfrac{1}{6}\left[\left(\left|\dfrac{J'}{J}\right|+\dfrac{\mu B}{|J|}\right)^2-3\right] & 0\leqslant\left(\dfrac{\mu B}{|J|}+\left|\dfrac{J'}{J}\right|\right)\leqslant 3 \\ 1 & 3<\left(\dfrac{\mu B}{|J|}+\left|\dfrac{J'}{J}\right|\right)<\infty. \end{cases} \tag{20}$$

The ground state spin correlation between the fourth spin and each of the remaining spins on the ring is given by

$$\langle\vec{S}_4\cdot\vec{S}_1\rangle(T=0) = \begin{cases} \dfrac{1}{3}\left[\left|\dfrac{J'}{J}\right|+\dfrac{\mu B}{|J|}\right] & 0\leqslant\left(\dfrac{\mu B}{|J|}+\left|\dfrac{J'}{J}\right|\right)\leqslant 3 \\ 1 & 3<\left(\dfrac{\mu B}{|J|}+\left|\dfrac{J'}{J}\right|\right)<\infty. \end{cases} \tag{21}$$

The total ground state magnetization induced by the magnetic field is given by

$$\frac{\langle M_z\rangle(T=0)}{\mu} = \begin{cases} 1+\dfrac{\mu B}{|J|}+\left|\dfrac{J'}{J}\right| & 0\leqslant\left(\dfrac{\mu B}{|J|}+\left|\dfrac{J'}{J}\right|\right)\leqslant 3 \\ 4 & 3<\left(\dfrac{\mu B}{|J|}+\left|\dfrac{J'}{J}\right|\right)<\infty. \end{cases} \tag{22}$$

5.3. $J<0,\ J'\geqslant 0$

When the exchange interactions between the spins of the irregular tetrahedron subjected to the magnetic field are such that $J=-|J|<0$ and $J'=|J'|\geqslant 0$, the ground state spin correlation function between the spins of the ring that interact with exchange J with each other is given by

$$\langle \vec{S}_1 \cdot \vec{S}_2 \rangle (T=0) = \begin{cases} 1 & 0 \leqslant \dfrac{\mu B}{|J|} \leqslant 2\left|\dfrac{J'}{J}\right| \\ 1 & 2\left|\dfrac{J'}{J}\right| < \dfrac{\mu B}{|J|} \leqslant 4\left|\dfrac{J'}{J}\right| \\ 1 & 4\left|\dfrac{J'}{J}\right| < \dfrac{\mu B}{|J|} < \infty. \end{cases} \tag{23}$$

The ground state spin correlation between the fourth spin and each of the remaining three spins on the ring is given by

$$\langle \vec{S}_4 \cdot \vec{S}_1 \rangle (T=0) = \begin{cases} -1 & 0 \leqslant \dfrac{\mu B}{|J|} \leqslant 2\left|\dfrac{J'}{J}\right| \\ \dfrac{1}{6}\left[\left(\dfrac{\mu B}{|J|}\right)^2 \Big/ \left(\left|\dfrac{J'}{J}\right|\right)^2 - 10\right] & 2\left|\dfrac{J'}{J}\right| < \dfrac{\mu B}{|J|} \leqslant 4\left|\dfrac{J'}{J}\right| \\ 1 & 4\left|\dfrac{J'}{J}\right| < \dfrac{\mu B}{|J|} < \infty. \end{cases} \tag{24}$$

The total ground state magnetization induced by the magnetic field is given by

$$\frac{\langle M_z \rangle (T=0)}{\mu} = \begin{cases} 2 & 0 \leqslant \dfrac{\mu B}{|J|} \leqslant 2\left|\dfrac{J'}{J}\right| \\ \left(\dfrac{\mu B}{|J|}\right) \Big/ \left(\left|\dfrac{J'}{J}\right|\right) & 2\left|\dfrac{J'}{J}\right| < \dfrac{\mu B}{|J|} \leqslant 4\left|\dfrac{J'}{J}\right| \\ 4 & 4\left|\dfrac{J'}{J}\right| < \dfrac{\mu B}{|J|} < \infty. \end{cases} \tag{25}$$

5.4. $J < 0$, $J' \leqslant 0$

The simplest case is that when the irregular tetrahedron of classical spins is subjected to a magnetic field and the spins interact with F exchange, $J = -|J| < 0$ and $J' = -|J'| \leqslant 0$. Since the two exchange interactions are F, the ground state configuration of the spins is one where all spins are collinear to the magnetic field for any value of the magnetic field. So for any $0 \leqslant \left|\frac{J'}{J}\right| < \infty$ and $0 \leqslant \frac{\mu B}{|J|} < \infty$ the ground state spin correlation functions are

$$\langle \vec{S}_1 \cdot \vec{S}_2 \rangle (T=0) = 1 \tag{26}$$

$$\langle \vec{S}_4 \cdot \vec{S}_1 \rangle (T=0) = 1 \tag{27}$$

and the total ground state magnetization is

$$\frac{\langle M_z \rangle (T=0)}{\mu} = 4. \tag{28}$$

6. General T, general B

Due to the symmetry of the system, the spin correlation function between any pair of spins coupled through J will be given from $\langle \vec{S}_1 \cdot \vec{S}_2 \rangle (B) = \langle \vec{S}_2 \cdot \vec{S}_3 \rangle (B) = \langle \vec{S}_3 \cdot \vec{S}_1 \rangle (B) = -\frac{1}{3\beta}\frac{\partial}{\partial J} \ln Z(J, J', B)$, and for the same reason the spin correlation function between the fourth spin and any of the other three spins is obtained from $\langle\vec{S}_4 \cdot \vec{S}_1\rangle(B) = \langle\vec{S}_4 \cdot \vec{S}_2\rangle(B) = \langle\vec{S}_4 \cdot \vec{S}_3\rangle(B) = -\frac{1}{3\beta}\frac{\partial}{\partial J'} \ln Z(J, J', B)$. The total magnetization due to the magnetic field may be found from the standard formula $\frac{\langle M_z\rangle(B)}{\mu} = \frac{1}{\mu\beta}\frac{\partial}{\partial B} \ln Z(J, J', B)$. Following these steps one finds that

$$\langle\vec{S}_1 \cdot \vec{S}_2\rangle(B) = -\frac{1}{2} + \frac{1}{6}\frac{\int_0^3 \mathrm{d}S_{123}\, D(S_{123}) S_{123}^2 \exp(-\frac{1}{2}aS_{123}^2) K(a', b, S_{123})}{\int_0^3 \mathrm{d}S_{123}\, D(S_{123}) \exp(-\frac{1}{2}aS_{123}^2) K(a', b, S_{123})}. \tag{29}$$

One can certainly evaluates the integrals appearing in equation (29) and in other similar expressions in closed form, although for all practical purposes the above one-dimensional integral form is much more transparent.

The calculation of the other spin correlation function and the total magnetization is much more complicated, but as a first convenient step it may suffice to write

$$\langle\vec{S}_4 \cdot \vec{S}_1\rangle(B) = -\frac{1}{3}\frac{\int_0^3 \mathrm{d}S_{123}\, D(S_{123}) \exp(-\frac{1}{2}aS_{123}^2) \frac{\partial}{\partial a'} K(a', b, S_{123})}{\int_0^3 \mathrm{d}S_{123}\, D(S_{123}) \exp(-\frac{1}{2}aS_{123}^2) K(a', b, S_{123})} \tag{30}$$

and

$$\frac{\langle M_z\rangle(B)}{\mu} = \frac{\int_0^3 \mathrm{d}S_{123}\, D(S_{123}) \exp(-\frac{1}{2}aS_{123}^2) \frac{\partial}{\partial b} K(a', b, S_{123})}{\int_0^3 \mathrm{d}S_{123}\, D(S_{123}) \exp(-\frac{1}{2}aS_{123}^2) K(a', b, S_{123})}. \tag{31}$$

The analytic calculation of $\frac{\partial}{\partial a'} K(a', b, S_{123})$ and $\frac{\partial}{\partial b} K(a', b, S_{123})$ is very lengthy, so it is preferable to use standard numerical integration methods instead of performing such a tedious analytic integration, although we were also able to obtain the analytic expressions for these terms.

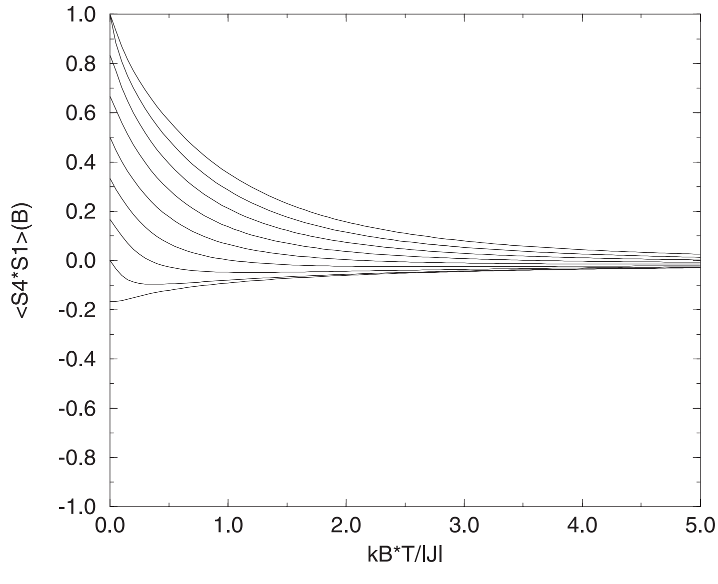

Figure 1. For the irregular tetrahedron of classical spins with AF exchange interaction, $J = |J| > 0$ and $J' = |J'| \geqslant 0$ we plot the spin correlation function $\langle\vec{S}_4 \cdot \vec{S}_1\rangle(B)$ as a function of the dimensionless parameter $k_B T/|J|$ for $|J'|/|J| = 0.5$ and several values of the magnetic field. The curves shown are for $\mu B/|J| = 0.0$ (lowest curve), 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5 and 4.0 (highest curve).

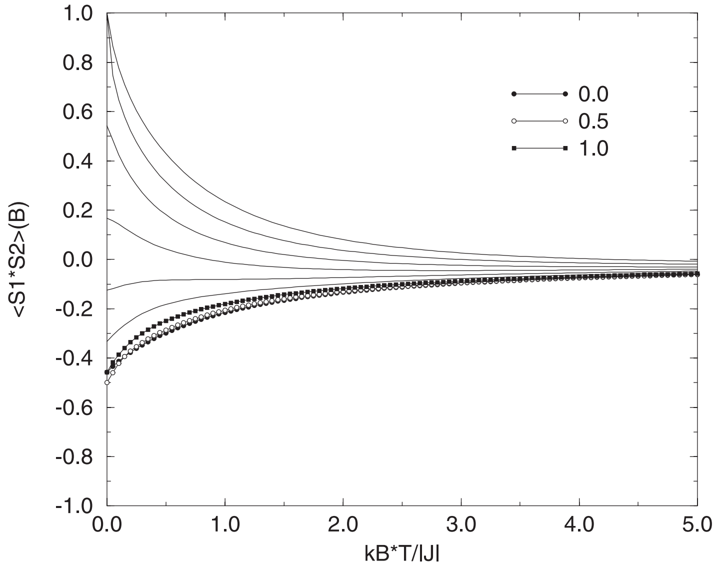

Figure 2. For the irregular tetrahedron of classical spins with AF exchange interaction, $J = |J| > 0$ and $J' = |J'| \geqslant 0$ we plot the spin correlation function $\langle \vec{S}_1 \cdot \vec{S}_2 \rangle (B)$ as a function of the dimensionless parameter $k_B T/|J|$ for $|J'|/|J| = 0.5$ and several values of the magnetic field. The curves shown are for $\mu B/|J| = 0.0$ (full circle), 0.5 (open circle), 1.0 (full square), 1.5 (lowest full curve), 2.0, 2.5, 3.0, 3.5 and 4.0 (highest full curve).

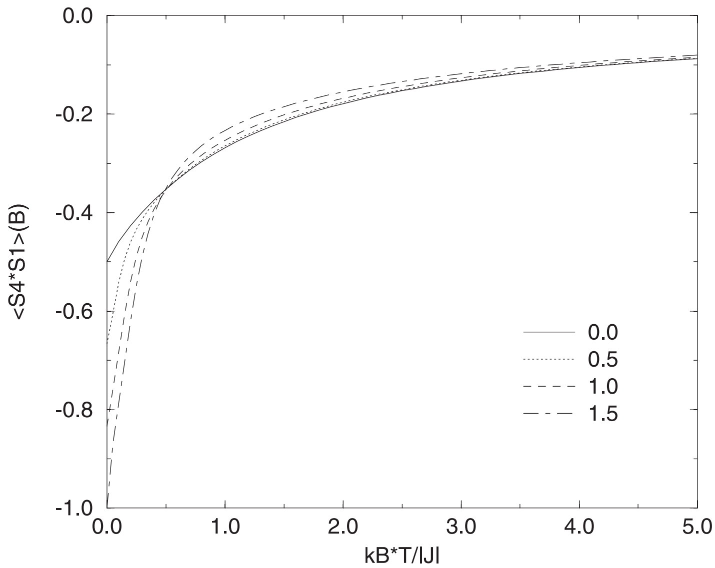

Figure 3. For the irregular tetrahedron of classical spins with AF exchange interaction, $J = |J| > 0$ and $J' = |J'| \geqslant 0$ we plot the spin correlation function $\langle \vec{S}_4 \cdot \vec{S}_1 \rangle (B)$ as a function of the dimensionless parameter $k_B T/|J|$ for $|J'|/|J| = 1.5$ and different values of the magnetic field. The curves shown are for $\mu B/|J| = 0.0$ (full), 0.5 (dotted), 1.0 (broken) and 1.5 (chain).

In the following we focus our attention on the most interesting and complex case of the irregular tetrahedron of classical spins with AF exchange interaction, $J = |J| > 0$ and

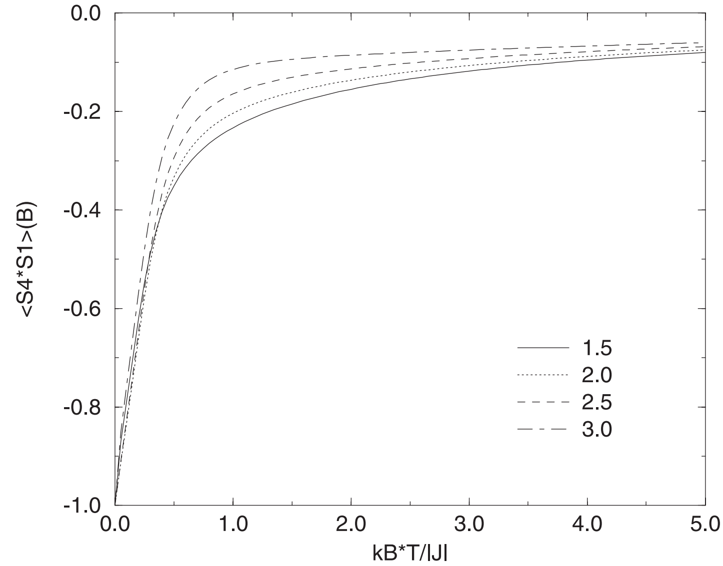

Figure 4. For the irregular tetrahedron of classical spins with AF exchange interaction, $J = |J| > 0$ and $J' = |J'| \geqslant 0$ we plot the spin correlation function $\langle \vec{S}_4 \cdot \vec{S}_1 \rangle (B)$ as a function of the dimensionless parameter $k_B T/|J|$ for $|J'|/|J| = 1.5$ and different values of the magnetic field. The curves shown are for $\mu B/|J| = 1.5$ (full), 2.0 (dotted), 2.5 (broken) and 3.0 (chain).

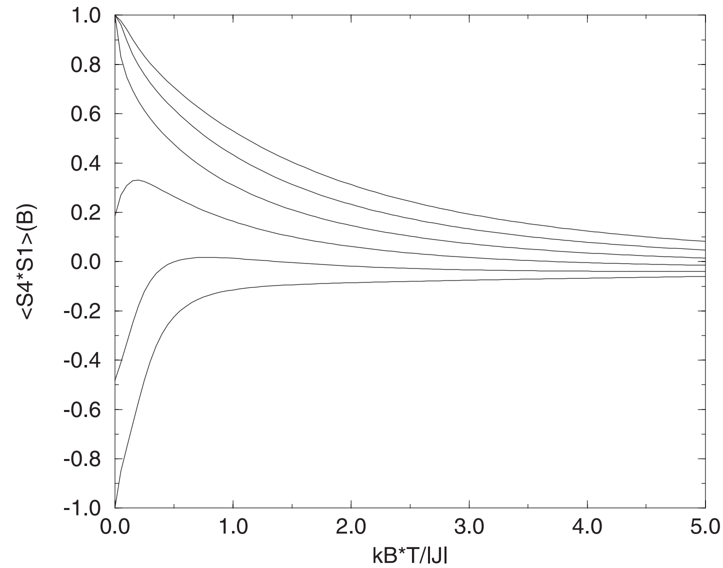

Figure 5. For the irregular tetrahedron of classical spins with AF exchange interaction, $J = |J| > 0$ and $J' = |J'| \geqslant 0$ we plot the spin correlation function $\langle \vec{S}_4 \cdot \vec{S}_1 \rangle (B)$ as a function of the dimensionless parameter $k_B T/|J|$ for $|J'|/|J| = 1.5$ and different values of the magnetic field. The curves shown are for $\mu B/|J| = 3.0$ (lowest curve), 4.0, 5.0, 6.0, 7.0 and 8.0 (highest curve).

$J' = |J'| \geqslant 0$ subjected to an external magnetic field $\vec{B}$, without giving any specific results for the cases where at least one exchange is F.

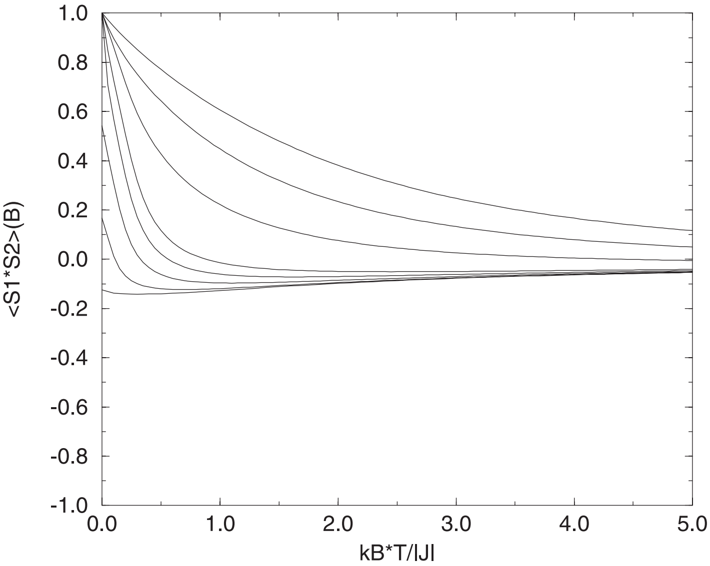

Figure 6. For the irregular tetrahedron of classical spins with AF exchange interaction, $J = |J| > 0$ and $J' = |J'| \geqslant 0$ we plot the spin correlation function $\langle \vec{S}_1 \cdot \vec{S}_2 \rangle(B)$ as a function of the dimensionless parameter $k_B T/|J|$ for $|J'|/|J| = 1.5$ and several values of the magnetic field. The curves shown are for $\mu B/|J| = 0.0$ (lowest curve), 0.5, 1.0, 1.5, 2.0, 4.0, 6.0 and 8.0 (highest curve).

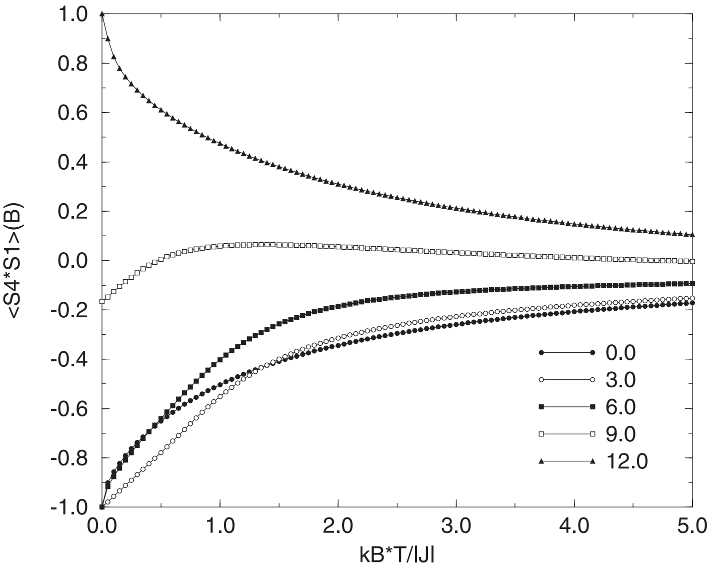

Figure 7. For the irregular tetrahedron of classical spins with AF exchange interaction, $J = |J| > 0$ and $J' = |J'| \geqslant 0$ we plot the spin correlation function $\langle \vec{S}_4 \cdot \vec{S}_1 \rangle(B)$ as a function of the dimensionless parameter $k_B T/|J|$ for $|J'|/|J| = 3.0$ and several values of the magnetic field. The curves shown are for $\mu B/|J| = 0.0$ (full circle), 3.0 (open circle), 6.0 (full square), 9.0 (opaque square) and 12.0 (full triangle).

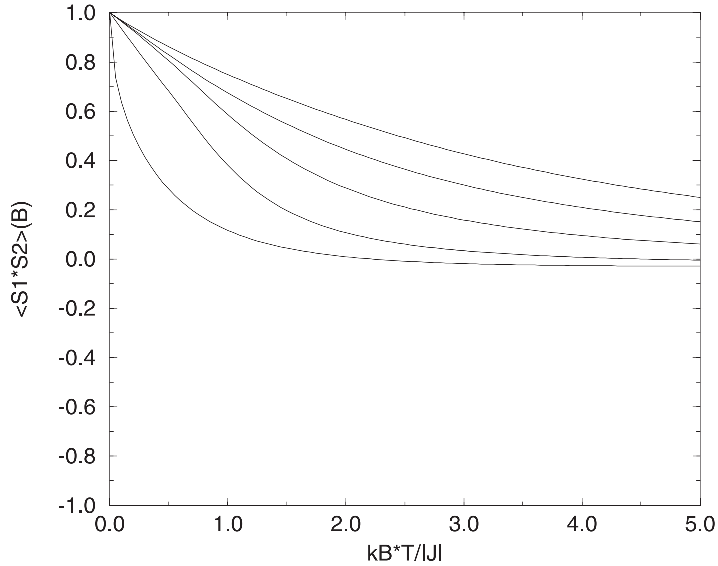

Figure 8. For the irregular tetrahedron of classical spins with AF exchange interaction, $J = |J| > 0$ and $J' = |J'| \geqslant 0$ we plot the spin correlation function $\langle \vec{S}_1 \cdot \vec{S}_2 \rangle(B)$ as a function of the dimensionless parameter $k_B T/|J|$ for $|J'|/|J| = 3.0$ and several values of the magnetic field. The curves shown are for $\mu B/|J| = 0.0$ (lowest curve), 3.0, 6.0, 9.0 and 12.0 (highest curve).

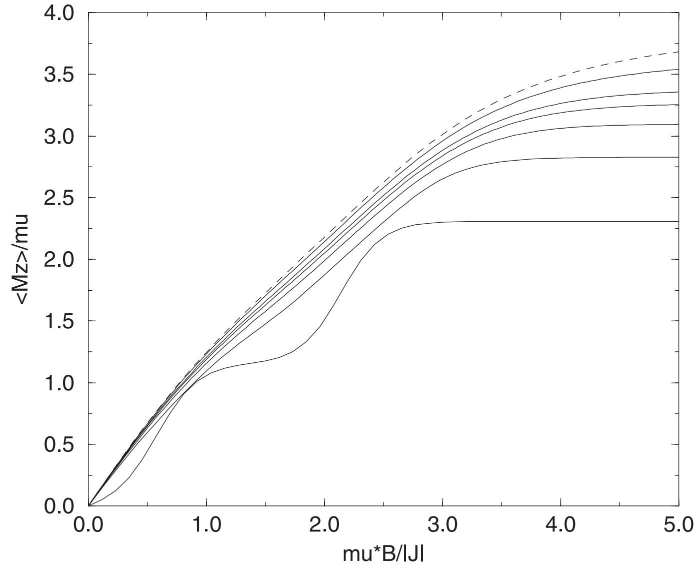

Figure 9. Field-induced total magnetic moment in units of $\mu = g\mu_B\sqrt{S(S+1)}$ as a function of $\mu B/J$ for the irregular tetrahedron of quantum spin-S particles with AF exchange interaction ($J_S = |J_S| > 0$, $J'_S = |J'_S| \geqslant 0$) and $|J'_S|/|J_S| = |J'|/|J| = 0.5$, where $J = S(S+1)J_S$ and $J' = S(S+1)J'_S$. For a very low reduced temperature, $k_B T/|J| = 0.2$, the curves shown are for $S = \frac{1}{2}$ (lowest curve), 1, $\frac{3}{2}$, 2, $\frac{5}{2}$, $\frac{9}{2}$ and for the classical model (broken curve).

In figure 1 we display our results for $\langle\vec{S}_4 \cdot \vec{S}_1\rangle(B)$ as a function of the dimensionless parameter $k_BT/|J|$ for several values of $\mu B/|J|$ and for $|J'|/|J| = 0.5$. In figure 2 we display our results for $\langle\vec{S}_1 \cdot \vec{S}_2\rangle(B)$ as a function of the dimensionless parameter $k_BT/|J|$ for several values of $\mu B/|J|$ and for $|J'|/|J| = 0.5$. In both cases the results derived in the previous section for $T = 0$ K are also included.

The case when $|J'|/|J| = 1.5$ is more complicated than the previous case. In figure 3 we show our results for $\langle\vec{S}_4 \cdot \vec{S}_1\rangle(B)$ as a function of the dimensionless parameter $k_BT/|J|$ for $\mu B/|J| = 0.0, 0.5, 1.0$ and 1.5, and for $|J'|/|J| = 1.5$. As shown in figure 4 for values of the magnetic field in the range $1.5 \leqslant \mu B/|J| \leqslant 3$ the fourth spin is always antiparallel to the other three spins at $T = 0$ K. For increasing values of the magnetic field, as shown in figure 5, the spin correlation $\langle\vec{S}_4 \cdot \vec{S}_1\rangle(B)$ gradually increases, until it becomes 1.0 at $T = 0$ K for $\mu B/|J| \geqslant 6$. In figure 6 we display our results for $\langle\vec{S}_1 \cdot \vec{S}_2\rangle(B)$ as a function of the dimensionless parameter $k_BT/|J|$ for several values of $\mu B/|J|$ and for $|J'|/|J| = 1.5$.

In figure 7 we give our results for $\langle\vec{S}_4 \cdot \vec{S}_1\rangle(B)$ as a function of the dimensionless parameter $k_BT/|J|$ for several values of $\mu B/|J|$ and for $|J'|/|J| = 3.0$ and in figure 8 we give our results for $\langle\vec{S}_1 \cdot \vec{S}_2\rangle(B)$ as a function of the dimensionless parameter $k_BT/|J|$ for several values of $\mu B/|J|$ and for $|J'|/|J| = 3.0$.

For relatively small values of the quantum spin S, exact numerical results can be obtained using standard diagonalization methods. In figure 9 we show the total magnetic moment in units of $\mu = g\mu_B\sqrt{S(S+1)}$ versus $\mu B/|J|$, for the irregular tetrahedron of quantum spins with AF exchange interaction, $J_S = |J_S| > 0$, $J'_S = |J'_S| \geqslant 0$, where $J = S(S+1)J_S$, $J' = S(S+1)J'_S$ and $|J'_S|/|J_S| = |J'|/|J| = 0.5$. We consider a very low dimensionless temperature, $k_BT/|J| = 0.2$. The full curves shown are for the quantum spin $S = \frac{1}{2}$ (lowest curve), 1, $\frac{3}{2}$, 2, $\frac{5}{2}$ and $\frac{9}{2}$. The broken curve is the corresponding result for the model of classical spins. For increasing values of S the curves rapidly converge to the classical curve, although one notes that for lower values of temperature we need higher values of S in order to achieve a good convergence to the classical result.

7. General T, $B = 0$

In the limit of zero magnetic field ($b \to 0$) we find that

$$\lim_{b\to 0} \frac{\partial}{\partial a'} K(a', b, S_{123}) = \frac{1}{a'}\left[\cosh(a'S_{123}) - \frac{\sinh(a'S_{123})}{a'S_{123}}\right] \tag{32}$$

and

$$\lim_{b\to 0} \frac{\partial}{\partial b} K(a', b, S_{123}) = S_{123}\frac{\sinh(a'S_{123})}{2a'S_{123}} - \frac{1}{2a'S_{123}}\left[\cosh(a'S_{123}) - \frac{\sinh(a'S_{123})}{a'S_{123}}\right]. \tag{33}$$

As a consequence of these results, the zero-field spin correlation functions for the irregular tetrahedron clusters are given by

$$\langle\vec{S}_1 \cdot \vec{S}_2\rangle(B = 0) = -\frac{1}{2} + \frac{1}{6}\frac{\int_0^3 \mathrm{d}S_{123}\, S_{123}^2 D(S_{123}) \exp(-\frac{1}{2}aS_{123}^2)\sinh(a'S_{123})/(a'S_{123})}{\int_0^3 \mathrm{d}S_{123}\, D(S_{123}) \exp(-\frac{1}{2}aS_{123}^2)\sinh(a'S_{123})/(a'S_{123})} \tag{34}$$

and

$$\langle\vec{S}_4 \cdot \vec{S}_1\rangle(B = 0) = \frac{1}{3a'} - \frac{1}{3a'}\frac{\int_0^3 \mathrm{d}S_{123}\, D(S_{123}) \exp(-\frac{1}{2}aS_{123}^2) \cosh(a'S_{123})}{\int_0^3 \mathrm{d}S_{123}\, D(S_{123}) \exp(-\frac{1}{2}aS_{123}^2)\sinh(a'S_{123})/(a'S_{123})}. \tag{35}$$

For $J' = 0$ one notes that $\langle \vec{S}_1 \cdot \vec{S}_2 \rangle (B = 0)$ recovers the corresponding result for the ring of three spins in the absence of the magnetic field, while $\langle \vec{S}_4 \cdot \vec{S}_1 \rangle (B = 0) \equiv 0$ for any value of parameter a.

The case when $J' = J$ $(a' = a)$ is interesting too because it corresponds to the regular tetrahedron cluster of four spins coupled with the same exchange interaction J as in the Cr4 structure [8]. We verified that in this case the spin correlation functions between any pair of spins are the same, $\langle \vec{S}_1 \cdot \vec{S}_2 \rangle (B = 0) = \langle \vec{S}_4 \cdot \vec{S}_1 \rangle (B = 0)$, and are given by

$$\langle \vec{S}_1 \cdot \vec{S}_2 \rangle (B = 0) = -\frac{1}{3} + \frac{1}{4a} + \frac{1}{12a} \times \frac{4\exp(-2a) - \exp(-8a) - 3}{\sqrt{8\pi a}\left[2\,\mathrm{erf}(\sqrt{2a}) - \mathrm{erf}(\sqrt{8a})\right] + 4\exp(-2a) - \exp(-8a) - 3}. \tag{36}$$

From the expression for the zero-field spin correlation function, one can easily compute the reduced zero-field susceptibility per spin for the irregular classical tetrahedron system which is given by $\tilde{\chi}_N(T) = 1 + \frac{3}{2}[\langle \vec{S}_1 \cdot \vec{S}_2 \rangle (B = 0) + \langle \vec{S}_4 \cdot \vec{S}_1 \rangle (B = 0)]$.

8. Summary

In this paper we have studied in detail the properties of a classical Heisenberg magnetic system consisting of an irregular tetrahedron array of spins that interact with each other through two different exchange interactions and are subjected to a uniform external magnetic field. By using a method which introduces auxiliary spin variables into the defining expression for the partition function, we obtained the exact analytical formulae for the magnetic moment induced by the external magnetic field for arbitrary temperature (i.e. the complete magnetic equation of state), as well as the field and temperature dependence of the spin correlation functions. The results also apply to systems of spins with the regular triangle and regular tetrahedron geometries. We succeeded in expressing the partition function, the total magnetic moment, and the spin correlation function as one-dimensional integrals, a representation which is particularly convenient for the purpose of extracting highly accurate numerical values, figures, etc.

In the special case of the irregular tetrahedron with both exchange interactions being AF and when $|J'|/|J| = 0.5$, we gave detailed comparisons between our results for the classical spins and the corresponding quantum system of individual spins $S = \frac{1}{2}, 1, \frac{3}{2}, \ldots$. The reader can correctly anticipate that as the individual spin quantum number S increases, the rapid changes at low temperatures of the magnetic moment versus the applied magnetic field rapidly wash out. For increasing S the eigenvalue spectrum proliferates, becoming continuous in the large-S limit, and the magnetic moment is a slowly varying function of the applied field.

Despite the smallness of the system we have considered, this study is timely for there is considerable experimental activity at present devoted to the synthesis and physical analysis of large organic molecules in which are embedded a very small number of paramagnetic ions, with the geometries of an irregular tetrahedron, regular tetrahedron and regular triangle.

A very common choice [9] of paramagnetic ion is Fe^{3+} which has spin $S = \frac{5}{2}$ and for which the present results are directly applicable, except for sufficiently low temperatures. The complex known as Fe4 is well described [9] by such a model. As we illustrated in this work, when all exchange interactions between spins are AF, it turns out that the magnetic frustration of this system is a very intricate function of temperature, magnetic field and the ratio of the two exchange interactions.

What are the prospects for succeeding in generalizing this paper to larger arrays of interacting Heisenberg spins, including more complicated geometries? For specialized geometries and interactions, generalizations of the present methods are indeed possible. One example is that of an array of five spins positioned at the vertices of a regular hexagon. A second example is that of an array of six spins positioned at the vertices of a regular octahedron.

A third example is that of an arbitrary number, N, of spins which interact with all others via a common isotropic exchange constant. This is the isotropic classical Heisenberg analogue of the well known Kittel–Shore model [15] which involves interacting Ising spins.

Whereas in the past these and other small systems might have been considered as appropriate 'recreational' projects for mathematical physicists, because of the dramatic recent advances in synthesis chemistry these models are currently of considerable experimental importance.

Appendix

For convenience we list here several formulae for the error function $\mathrm{erf}(z)$, which are useful to this paper. For any complex variable z this function is defined by

$$\mathrm{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z \mathrm{d}t\, \mathrm{e}^{-t^2}. \tag{A1}$$

Note that $\mathrm{erf}(-z) = -\,\mathrm{erf}(z)$ and its Taylor expansion,

$$\mathrm{erf}(z) = \frac{2}{\sqrt{\pi}} \sum_{n=0}^{\infty} \frac{(-1)^n z^{2n+1}}{n!(2n+1)} \tag{A2}$$

converges for all finite z. The relation

$$\mathrm{erf}(z) = \frac{2z}{\sqrt{\pi}} M(\tfrac{1}{2}, \tfrac{3}{2}, -z^2) = \frac{2z}{\sqrt{\pi}} \exp(-z^2) M(1, \tfrac{3}{2}, z^2) \tag{A3}$$

proves to be very helpful, where

$$M(a, b, z) = \sum_{n=0}^{\infty} \frac{(a)_n z^n}{(b)_n n!} \tag{A4}$$

denotes the confluent hypergeometric function, $(a)_0 = 1$, and $(a)_n = a(a+1)(a+2)\cdots(a+n-1)$ for $n \geqslant 1$. With the aid of equation (A3) one can establish the following two asymptotic formulae that are of importance in the main text for investigating the low-temperature properties of the spin systems. If x denotes a real positive variable, we have for the $x \gg 1$ regime

$$\mathrm{erf}(x) \sim 1 - \frac{1}{\sqrt{\pi}} \frac{\exp(-x^2)}{x} \left[1 - \frac{1}{2x^2} + \mathrm{O}\left(\frac{1}{x^4}\right)\right] \tag{A5}$$

and

$$\mathrm{erf}(\mathrm{i}x) \sim \frac{\mathrm{i}}{\sqrt{\pi}} \frac{\exp(x^2)}{x} \left[1 + \frac{1}{2x^2} + \mathrm{O}\left(\frac{1}{x^4}\right)\right] \tag{A6}$$

where $\mathrm{i} = \sqrt{-1}$.

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