Low-field susceptibility of classical Heisenberg chains with arbitrary and different nearest-neighbour exchange

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Abstract. Interest in molecular magnets continues to grow, offering a link between the atomic and nanoscale properties. The classical Heisenberg model has been effective in modelling exchange interactions in such systems. In this, the magnetization and susceptibility are calculated through the partition function, where the Hamiltonian contains both Zeeman and exchange energy. For an ensemble of N spins, this requires integrals in $2N$ dimensions. For two, three and four spin nearest neighbour chains these integrals reduce to sums of known functions. For the case of the three and four spin chains, the sums are equivalent to results of Joyce. Expanding these sums, the effect of the exchange on the linear susceptibility appears as Langevin functions with exchange term arguments. These expressions are generalised here to describe an N spin nearest neighbour chain, where the exchange between each pair of nearest neighbours is different and arbitrary. For a common exchange constant, this reduces to the result of Fisher. The high temperature expansion of the Langevin functions for the different exchange constants, leads to agreement with the appropriate high temperature quantum formula of Schmidt et al., when the spin number is large. Simulations are presented for open linear chains of three, four and five spins with up to four different exchange constants, illustrating how the exchange constants can be retrieved successfully.

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1. Introduction

Molecular magnets are typified by relatively small numbers of paramagnetic spins which interact intramolecularly via exchange forces, and where the intermolecular dipole-dipole interaction can be ignored. They are of interest as model magnetic systems, where basic understanding of exchange can be studied, as well as offering promise as novel materials [1, 2, 3], with the possibility of applications in areas including material science, biomedicine and quantum computing - see [4] and references therein. For a recent survey and discussion of theoretical and experimental aspects of magnetic molecules the reader is referred to an article by Luban [5]. From a theoretical point of view, where the spin number is large, the classical Heisenberg model has proved useful. Notably, Fisher [6], Joyce [7] and Blume et al. [8] advanced this model. More recently, with the progress in molecular magnet synthesis, theoretical interest has been revived [9, 10, 11, 12]. Of interest to many of these authors are descriptions of the susceptibility of such magnetic systems where two or more different exchange constants are involved [9, 11, 12]. Significantly, Luban et al. [13] have applied the high-temperature quantum expansion for the low-field susceptibility of Schmidt et al. [11] to obtain from experiment, values for a system with four different exchange parameters, without recourse to diagonalizing large quantum Hamiltonians. With this interest in mind, here we present a classical, low-field susceptibility formula for an open chain of N spins, with arbitrary and different exchange between each pair of nearest neighbours. Using a result due to Gegenbauer [14], the authors [15] have been able to re-derive, in a simple manner, the results of Joyce for open classical Heisenberg spin chains where the partition functions are expressed as sums of known functions, and also to obtain some new results. Expanding these sums, it is possible to obtain analytic expressions for the magnetisation to terms linear in the applied field, corresponding to the linear susceptibility. (In addition, if required, the non-linear susceptibility can be obtained by taking non-linear terms in the magnetisation [15, 16]). The effect of the exchange on the linear susceptibility is expressed in terms of Langevin functions with exchange term arguments. Furthermore by considering the source of each of these terms, it is possible, from the finite cases, to infer a structure for a chain of any number of spins (the N-chain) which is in agreement with a result obtainable from Joyce [7] for a four spin chain. The formula shows the expected asymptotic behaviour for small and large exchange, and for equal exchange, the result of Fisher [6, 9] is recovered. It is consistent within the approach of Takahashi [17] for dimerized classical chains and with that of Furasaki et al. [18] for equal exchange but random sign. It is also in agreement with the appropriate high-temperature expansion resulting from Schmidt et al. [11] for the limit of large spin number. Following Schmidt et al., simulations are performed to illustrate the usefulness of this formula. Within these simulations, open linear chains containing up to five spins, with four different exchange constants, have been considered. The temperature dependence of the low-field susceptibility has been calculated using this formula and noise has been added. The same formula has then been fitted over

the temperature range 50K–300K, in order to show that up to four different exchange constants can be retrieved. Further calculations and simulations might be performed with reference to diagonalizing the Hamiltonian as performed by Luban et al. [13], with a view to outlining the differences between quantum and classical Heisenberg models as dealt with recently by Engelhardt et al. [19].

2. Classical Heisenberg Model for 2-spin and 3-spin chains

The Hamiltonian for two interacting spins contains the isotropic classical Heisenberg exchange and Zeeman (external field) terms

$$\mathcal{H}_{2-\text{spin}} = -J_c \ \vec{e}_1 \cdot \vec{e}_2 - \mu_0 m \vec{H} \cdot (\vec{e}_1 + \vec{e}_2) \tag{1}$$

where $\vec{H}$ is the external magnetic field vector, $\vec{e}_i$ represents the unit vector of each classical spin, μ_0 is the permeability of free space, and where the classical values for the exchange parameter J_c and classical magnetic moment m are taken as [20]

$$J_c = Js\,(s+1)\,,\ m = g\mu_B\sqrt{s\,(s+1)} \quad . \tag{2}$$

Here J is the exchange constant where we take $J > 0$ for ferromagnetic and $J < 0$ for anti-ferromagnetic exchange, g is the Landé spectroscopic splitting factor, μ_B is the Bohr magneton, and s is the spin number. From Ref. [15] the classical partition function for two spins can be written as a sum of known functions

$$Z_{2-\text{spin}} = \sum_{n=0}^{\infty} (2n+1)\, i_n\,(\xi)^2\, i_n\,(K) \tag{3}$$

where $K = J_c/kT$, $\xi = \mu_0 mH/kT$, k is Boltzmann's constant, T is absolute temperature, and the functions $i_n\,(x)$ are [7, 9, 21]

$$i_n\,(x) = \sqrt{\frac{\pi}{2x}} I_{n+\frac{1}{2}}\,(x) \tag{4}$$

where $I_{n+\frac{1}{2}}\,(x)$ are the modified spherical Bessel functions of the first kind [22]. It is worth noting that $i_0\,(x) = \sinh\,(x)/x$ and $i_1\,(x) = \cosh\,(x)/x - \sinh\,(x)/x$ so that $i_1\,(x)/i_0\,(x) = \coth\,(x) - 1/x = L\,(x)$, the Langevin function. In this sum, each $i_n\,(\xi)$ is due to the field acting on each spin and $i_n\,(K)$) is due to the single exchange interaction. The magnetisation can be obtained from

$$M = \frac{Nm}{V}\frac{1}{N}\frac{\partial Z}{\partial \xi} \tag{5}$$

where V is the sample volume and N is the number of spin sites. Expanding the magnetisation to the first order in ξ leads to the low-field susceptibility per spin site

$$\chi_{2-\text{spin}} = \chi_0\,(1 + L\,(K)) \tag{6}$$

where the zero-exchange linear susceptibility per spin site is given by

$$\chi_0 = \frac{\mu_0 m^2}{3kTV} \tag{7}$$

This agrees with previous results [9] and for zero exchange the Curie law is recovered. The Hamiltonian for a three spin chain with two different exchange constants is

$$\mathcal{H}_{3-\text{spin}} = -J_{c_{1,2}}\ \vec{e}_1 \cdot \vec{e}_2 - J_{c_{2,3}}\ \vec{e}_2 \cdot \vec{e}_3 - \mu_0 m\vec{H} \cdot (\vec{e}_1 + \vec{e}_2 + \vec{e}_3) \tag{8}$$

where $J_{c_{1,2}}$ and $J_{c_{2,3}}$ are the exchange constants between spins 1 and 2, and spins 2 and 3, respectively. From Ref. [15] the classical partition function for the three spin chain can be written as

$$Z_{3-\text{spin}} = \sum_{l=0}^{\infty}\sum_{m=0}^{\infty}\sum_{n=0}^{\infty}(2n+1)(2m+1)(2l+1)\begin{pmatrix} n & m & l \\ 0 & 0 & 0 \end{pmatrix}^2 \times$$
$$i_n(\xi)\, i_m(\xi)\, i_l(\xi)\, i_n(K_{1,2})\, i_m(K_{2,3}) \tag{9}$$

where $K_{1,2} = J_{c_{1,2}}/kT$ and $K_{2,3} = J_{c_{2,3}}/kT$. Here, each of the three terms $i_n(\xi)$, $i_m(\xi)$ and $i_l(\xi)$ is due to the field acting on each spin and the two terms $i_n(K_{1,2})$ and $i_m(K_{1,2})$ are due to the two exchange interactions. The coefficient includes the Wigner $3j$ symbol which occurs in angular momentum problems, and can be readily calculated for small values [23]. This is of the same form as that of Joyce [7] for a cluster treated via a Bethe-Peierls-Weiss approximation. Again, expanding to the first order in ξ leads to the low-field susceptibility per spin site

$$\chi_{3-\text{spin}} = \chi_0\left(1 + \frac{2}{3}\left[L(K_{1,2}) + L(K_{2,3}) + L(K_{1,2})\,L(K_{2,3})\right]\right) \tag{10}$$

and again for zero exchange the Curie law is recovered.

3. Extension to an N-spin chain

The terms in Eqs. 6 and 10 can be interpreted as follows: The single term(s) $L(K_{i,i+1})$ are due to nearest-neighbour exchange interactions. The product term in the case of three spins is due to next-nearest-neighbours spin correlations, in this case from spin 1 to spin 3 via spin 2. This can be extended to four spins where

$$\chi_{4-\text{spin}} = \chi_0\left(1 + \frac{2}{4}\begin{bmatrix} L(K_{1,2}) \\ +L(K_{2,3}) \\ +L(K_{3,4}) \\ +L(K_{1,2})\,L(K_{2,3}) \\ +L(K_{2,3})\,L(K_{3,4}) \\ +L(K_{1,2})\,L(K_{2,3})\,L(K_{3,4}) \end{bmatrix}\right) \tag{11}$$

This result is also obtainable from the expansion for four spins [7, 15]. From an examination of the structure it is possible to deduce an N-spin structure for the susceptibility. Thus,for an N-spin chain with nearest-neighbour exchange we can write

$$\chi_{N-\text{spin}} = \chi_0\left(1 + \frac{2}{N}\sum_{k=1}^{N-1}\sum_{j=1}^{N-k}\prod_{i=0}^{k-1}L(K_{j+i,j+1+i})\right). \tag{12}$$

Where the exchange between each pair is taken as equal this simplifies to

$$\chi_{N-\mathrm{spin}} = \chi_0 \left(1 + \frac{2}{N} \sum_{k=1}^{N-1} (N-k)\, L\left(K\right)^k \right). \tag{13}$$

Using the arithmetico-geometric progression (Eq. 0.112 of [24]) for the above series, we can write for N spins

$$\chi_{N-\mathrm{spin}} = \chi_0 \left(\frac{1+L\left(K\right)}{1-L\left(K\right)} - \frac{2L\left(K\right)}{N} \frac{1-L\left(K\right)^N}{\left(1-L\left(K\right)\right)^2} \right) \tag{14}$$

which is the zero-field susceptibility formula of Fisher [6, 9] for an open chain of N spins with equal classical Heisenberg exchange acting between them. It is worth noting that this expression for the susceptibility is consistent with that resulting from the zero-field fluctuation relation [12]

$$\chi_{N-\mathrm{spin}} = \chi_0 \left(1 + \frac{2}{N} \sum_{i>j}^{N} \langle \vec{e}_i \cdot \vec{e}_j \rangle \right) \tag{15}$$

where Fisher's two spin correlation function result for open ended chains, with equal exchange along the chain [6, 9, 20],

$$\langle \vec{e}_i \cdot \vec{e}_{i+n} \rangle = L\left(K\right)^n \tag{16}$$

is a special case.

4. Comparison with finite spin quantum spin models

Schmidt et al. [11] presented exact analytical expressions for the high temperature expansion for finite quantum Heisenberg spin systems with different exchange between nearest neighbour spins. These were employed by Luban et al. [13] for cubane-type magnetic molecule $\{Cr_8\}$ with four different exchange constants. Employing the generic formula of Schmidt et al. to a three spin chain as considered here leads to

$$\chi_{3-\mathrm{spin}} = \chi_0 \left(1 + \frac{2}{3} \left[\frac{K_{1,2}}{3} + \frac{K_{2,3}}{3} + \frac{K_{1,2}K_{2,3}}{9} - \frac{3}{4s\left(s+1\right)} \left[\left(\frac{K_{1,2}}{3} \right)^2 + \left(\frac{K_{2,3}}{3} \right)^2 \right] \right] \right). \tag{17}$$

This is in agreement with a low exchange (high-temperature) expansion of Eq. 10, where the low value approximation $L\left(x\right) \cong x/3$ is taken, but includes a quantum correction term, which vanishes for very large spin number. An empirical hybrid of these would be

$$\chi_{3-\mathrm{spin}} = \chi_0 \left(1 + \frac{2}{3} \left[L\left(K_{1,2}\right) + L\left(K_{2,3}\right) + L\left(K_{1,2}\right) L\left(K_{2,3}\right) - \frac{3}{4s\left(s+1\right)} \left[L\left(K_{1,2}\right)^2 + L\left(K_{2,3}\right)^2 \right] \right] \right) \tag{18}$$

which would agree with both Schmidt high temperature quantum result and the all temperature classical result (for infinite spin number). Calculations similar to those of Schmidt et al., where the high temperature data generated by diagonalizing the Hamiltonian were fitted to a polynomial and related to the formulae of Schmidt et al. might be repeated for the full temperature range, using the various formulae above. Furthermore the N spin classical susceptibility formulae should be of use in studies such that of Engelhardt et al. [19] which aim to distinguish between quantum and classical effects.

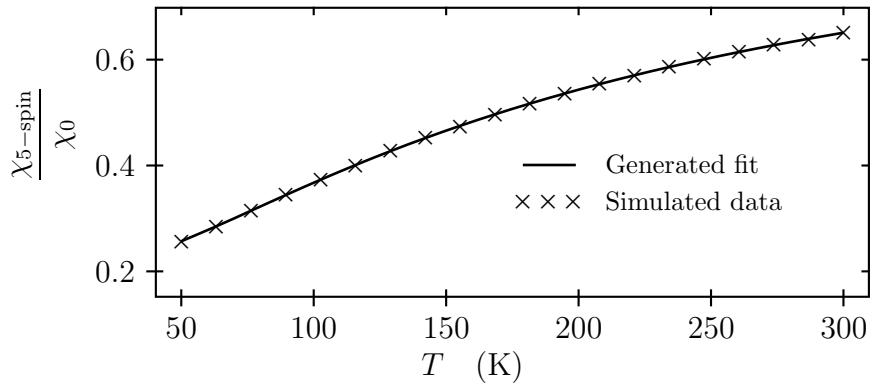

Figure 1. Data generated using exchange parameter values $J_{c_{i,i+1}}/k$, for a 5-spin chain ($i = 1...4$) $\{-135\text{K}, -200\text{K}, -300\text{K}, -380\text{K}\}$ with white noise added. Parameter estimates resulting from the constrained non-linear fit are $\{-133\text{K}, -205\text{K}, -316\text{K}, -366\text{K}\}$ which are accurate to within 5.4% of the true parameter values. (The vertical axis is effectively normalised χT).

5. Simulations for classical spin chains

Following Schmidt et al., we exclude factors such as diagmagnetic contribultions and look exclusively at how accurately exchange parameters may be estimated from simulated susceptibility data. For N-spin chain up to length $N = 5$ theoretical susceptibility data were generated and white noise added. The signal-to-noise ratio is approximately 0.25×10^{-3}. Then, using Maple's sequential quadratic programming (SQP) routine to perform a constrained non-linear fitting of Eq. 12 to the generated data, it was possible retrieve estimates for the exchange parameters. In the case of the 3-spin chain and the 4-spin chain, estimates for the respective two and three exchange parameters are readily obtained. For the 5-spin chain, in order to achieve reliable convergence and so obtain reasonable estimates for the four exchange parameters, constraints specifying the sign of the exchange parameters were incorporated into the fitting procedure. As discussed by Schmidt et al., this requires additional magneto-chemical information in order to generate estimates for the exchange parameters. The fits were performed in the temperature range 50K–300K and the case of the 5-spin chain is presented in Fig. 1 with the chosen and retrieved exchange values. The low temperature range has been avoided, where in experiments quantum effects lead to disagreement with the classical model. For the 4-spin chain the linear co-dependence of the parameters is illustrated in Fig. 2, by the rod-like pattern in the 3-D plot for repeated simulations, consistent with the line-like pattern observable in Fig. 4 of Schmidt et al. for the case of two linear co-dependent exchange parameters.

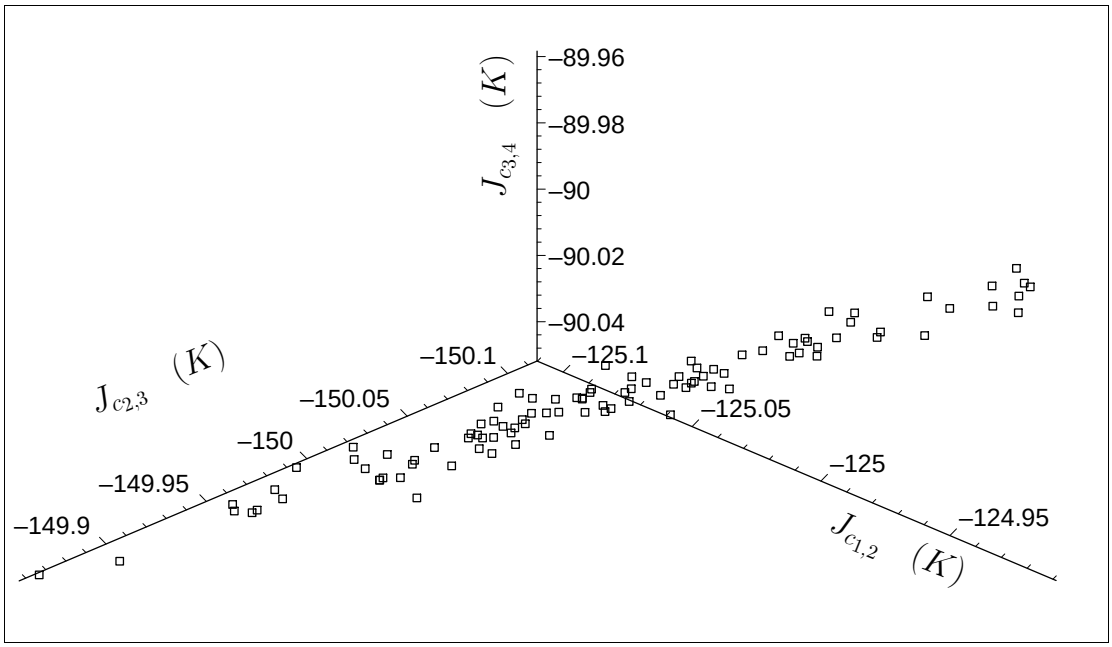

Figure 2. Repeated simulation of fitting to susceptibility data generated for the 4-spin chain using exchange parameter values $\{-150\text{K}, -125\text{K}, -90\text{K}\}$. The linear co-dependence is illustrated by the rod-like structure.

6. Conclusions

Here we present a classical, low-field susceptibility formula for an open chain of N spins, with arbitrary and different exchange between each pair of nearest neighbours. Within this formula, the exchange parameters appear as arguments in Langevin functions. The formula shows the expected asymptotic behaviour for small and large exchange and for equal exchange, the result of Fisher [6, 9] is recovered. It is also in agreement with the appropriate high-temperature expansion resulting from Schmidt et al. [11] for the limit of large spin number. Simulations demonstrate that it is possible to retrieve up to four different exchange constants using this formula.

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