Heisenberg exchange parameters of molecular magnets from the high-temperature susceptibility expansion

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Abstract

We provide exact analytical expressions for the magnetic susceptibility function in the high temperature expansion for finite Heisenberg spin systems with an arbitrary coupling matrix, arbitrary single-spin quantum number, and arbitrary number of spins. The results can be used to determine unknown exchange parameters from zero-field magnetic susceptibility measurements without diagonalizing the system Hamiltonian. We demonstrate the possibility of reconstructing the exchange parameters from simulated data for two specific model systems. We examine the accuracy and stability of the proposed method.
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I. INTRODUCTION AND SUMMARY

Due to advances of synthesis methods in coordination chemistry[1,2] and, especially, in polyoxometalate chemistry,[3–6] the field of molecular magnets has undergone rapid progress in recent years. To date each of the identical molecular magnets contains as few as two and up to several dozens of paramagnetic ions ("spins"). The largest paramagnetic molecule synthesized, the polyoxometalate[4] $\{Mo_{72}Fe_{30}\}$ contains 30 iron ions of spin $s = 5/2$. Although these materials are synthesized as macroscopic samples, i.e. crystals or powders, the intermolecular magnetic interactions are generally utterly negligible as compared to the intramolecular interactions. Therefore, measurements of their magnetic properties reflect mainly ensemble properties of single molecules. It appears that in most cases the magnetic properties of these molecules are rather well described by the Heisenberg model with possibly small anisotropy corrections.[7–11]

In order to calculate from first principles the energy spectrum and the magnetic properties it is essential to accurately determine the exchange parameters, as these measure the strength of the two-spin interactions. The usual procedure consists of the following steps: diagonalization of the system Hamiltonian for an arbitrary choice of exchange parameters;

calculation of the partition function and a quantity, such as the magnetization, which can be compared to experimental data; variation of the exchange parameters so as to achieve an optimal fit between the experimental and theoretical data. This can be a rather straightforward task for simple configurations such as small spin rings with a single nearest-neighbor coupling. However, for more complicated systems, for example where two or more exchange parameters may be needed it may be impractical to perform such calculations for different trial choices of the parameters, even if one is guided by chemical and structural information. Worse yet, for large spin systems, where in practice the Hamiltonian cannot be diagonalized, it may even be impossible to fix the exchange parameters, since one cannot calculate the weak-field susceptibility over the full tempearature range, for comparison with experiment.

In this article we explore the possibility of determining the exchange parameters of Heisenberg molecular magnets using the exactly calculable first three terms of the high-temperature expansion of the zero-field susceptibilty $\chi(\beta)$, in powers of β. In comparison to earlier work[12,13] exact results are derived here for these three coefficients, for arbitrary coupling, arbitrary single-spin quantum number, and an arbitrary number of spins. The procedure we explore here opens up the possibility of treating large systems where the Hamiltonian can no longer be diagonalized. We also outline the necessary algorithms for calculating additional terms of the high-temperature expansion, but these would require computer algebra methods.

Deducing exchange parameters from experimental susceptibility data of course presumes that one possesses accurate estimates of the number of paramagnetic ions, the spectroscopic splitting factor(s), diamagnetic contributions, temperature-independent paramagnetism, etc. We do not consider these issues here; instead we concentrate on the question, with what accuracy exchange parameters can be deduced using theoretical susceptibility data, for a Heisenberg molecular magnet, limited to the high-temperature regime. We do not want to mix questions about the accuracy of the method with uncertainties in experimental data which are of different origin.

This article is organized as follows. After recalling basic definitions in Sec. II we derive the trace formulae which are necessary for the high-temperature expansion in Sec. III. These results are summarized in Sec. IV and related to the expansion coefficients of the Taylor series of $\chi(\beta)$. The accuracy and stability of the proposed method are illustrated for two selected model systems in Sec. V. We briefly summarize our findings in Sec. VI.

II. DEFINITIONS

For the following investigations we assume that the spin system under consideration is well described by the following general bilinear Heisenberg Hamilton operator

$$\underset{\sim}{H}_0 \equiv \sum_{\mu<\nu} J_{\mu\nu} \underset{\sim}{\vec{s}}_\mu \cdot \underset{\sim}{\vec{s}}_\nu = \sum_{\mu<\nu} J_{\mu\nu} \sum_{i=1}^{3} \underset{\sim}{s}_\mu^{(i)} \underset{\sim}{s}_\nu^{(i)} \ . \tag{1}$$

The exchange parameters $J_{\mu\nu}$ are given in units of energy, with $J_{\mu\nu} < 0$ resulting in ferromagnetic, $J_{\mu\nu} > 0$ in antiferromagnetic coupling. $\underset{\sim}{\vec{s}}_\mu$ are the dimensionless single-particle spin operators and $\underset{\sim}{s}_\mu^{(i)}$ denotes the spin components $i \in \{1,2,3\} \equiv \{x,y,z\}$ of the spin

at site μ. The interaction with the magnetic field is taken into account by including the Zeeman term

$$\underset{\sim}{H} \equiv \underset{\sim}{H}_0 + g\mu_B B \underset{\sim}{S}^{(3)} \ , \tag{2}$$

where $\underset{\sim}{S}^{(3)}$ is the z-component of the total spin operator, and g is the spectroscopic splitting factor. For simplicity we are supposing that all of the paramagnetic ions possess the same value of g. The present results can be easily generalized to cases where several different paramagnetic species are present. As usual the magnetisation is defined as

$$\mathcal{M} = -\frac{1}{Z} \operatorname{Tr}\left\{ g\mu_B \underset{\sim}{S}^{(3)} \, \mathrm{e}^{-\beta \underset{\sim}{H}} \right\} \ , \ Z = \operatorname{Tr}\left\{ \exp(-\beta \underset{\sim}{H}) \right\} \ , \tag{3}$$

Z being the partition function. Accordingly the zero-field magnetic susceptibility is

$$\chi_0 = \left(\frac{\partial \mathcal{M}}{\partial B} \right)_{B=0} = \beta (g\mu_B)^2 \frac{\operatorname{Tr}\left\{ \underset{\sim}{S}^{(3)2} \exp(-\beta \underset{\sim}{H}_0) \right\}}{\operatorname{Tr}\left\{ \exp(-\beta \underset{\sim}{H}_0) \right\}} \ . \tag{4}$$

The susceptibility may be renormalised by division of $(g\mu_B)^2$

$$\hat{\chi}(\beta) \equiv \frac{\chi_0(\beta)}{(g\mu_B)^2} \ . \tag{5}$$

A Taylor expansion of $\hat{\chi}$ in powers of β, starting from (4), yields after some calculations

$$\begin{aligned} \hat{\chi}(\beta) = \sum_{n=1}^{\infty} c_n \beta^n = \frac{\mu_0}{t_0}\beta - \frac{\mu_1}{t_0}\beta^2 + \left(-\frac{t_2\mu_0}{2t_0^2} + \frac{\mu_2}{2t_0} \right) \beta^3 \\ + \left(\frac{t_3\mu_0}{6t_0^2} + \frac{t_2\mu_1}{2t_0^2} - \frac{\mu_3}{6t_0} \right) \beta^4 \\ + \left(\mu_0 \left(\frac{t_2^2}{4t_0^3} - \frac{t_4}{24t_0^2} \right) - \frac{t_3\mu_1}{6t_0^2} - \frac{t_2\mu_2}{4t_0^2} + \frac{\mu_4}{24t_0} \right) \beta^5 \\ + \dots \ , \end{aligned} \tag{6}$$

where

$$t_n \equiv \operatorname{Tr}\left\{ \underset{\sim}{H}_0^n \right\} \ , \quad \mu_n \equiv \operatorname{Tr}\left\{ \underset{\sim}{H}_0^n \underset{\sim}{S}^{(3)2} \right\} \ , \quad n \in \mathbb{N}, \ . \tag{7}$$

Comparing expansion (6) with a Curie-Weiss law

$$\hat{\chi}_{CW}(\beta) = \frac{\hat{C}}{T - T_c} = \hat{C} k_B \beta (1 - k T_c \beta)^{-1} = \hat{C} k_B \beta \left(1 + k_B T_c \beta + (k_B T_c \beta)^2 + \dots \right) \tag{8}$$

yields the known theoretical results[14] for the Curie constant $\hat{C}$ and the Weiss temperature T_c

$$k_B \hat{C} = \frac{\mu_0}{t_0} \quad \text{and} \quad k_B T_c = -\frac{\mu_1}{\mu_0} \ . \tag{9}$$

Generally, the β^3-term of (8) will not coincide with the β^3-term of the rigorous expansion (6). This is due to the fact that the Curie-Weiss law itself is only valid at high temperatures.[15] Thus, the β^3-term of (6) constitutes a first (quantum) correction to the Curie-Weiss law for lower temperatures.

III. TRACE FORMULAE

Expanding the terms occuring in the trace (7)

$$t_n = \mathrm{Tr}\left\{\underset{\sim}{H}_0^n\right\} = \mathrm{Tr}\left\{\sum_{\mu<\nu} J_{\mu\nu} \sum_{i=1}^{3} \underset{\sim}{s}_\mu^{(i)} \underset{\sim}{s}_\nu^{(i)}\right\}^n \tag{10}$$

and using $\mathrm{Tr}(A\otimes B) = (\mathrm{Tr}A)(\mathrm{Tr}B)$ one ends up with terms of the form

$$\mathrm{Tr}(A_1 \ldots A_\ell), A_\nu \in \{\underset{\sim}{s}^{(1)}, \underset{\sim}{s}^{(2)}, \underset{\sim}{s}^{(3)}\} \ . \tag{11}$$

Here the spin operators $\underset{\sim}{s}$ without a site index denote operators operating in the single-spin Hilbert space $\mathbb{C}^{2s+1}$. Let $\ell_i (i = 1, 2, 3)$ denote the number of occurrences of $\underset{\sim}{s}^{(i)}$ in the product $A_1 \ldots A_\ell$. One can easily show that $\mathrm{Tr}(A_1 \ldots A_\ell)$ is non-zero only if all ℓ_i are even or all ℓ_i are odd. We give a list of the simplest cases, where the trace is non-zero:

$$\begin{aligned}
&\ell = 0 : \mathrm{Tr}\{\underset{\sim}{\mathbb{1}}\} = 2s+1, \\
&\ell = 2 : \mathrm{Tr}\left\{\underset{\sim}{s}^{(i)2}\right\} = \sum_{m=-s}^{s} m^2 = \frac{1}{3}s(s+1)(2s+1), \\
&\ell = 3 : \mathrm{Tr}\left\{\underset{\sim}{s}^{(1)}\underset{\sim}{s}^{(2)}\underset{\sim}{s}^{(3)}\right\} = -\mathrm{Tr}\left\{\underset{\sim}{s}^{(3)}\underset{\sim}{s}^{(2)}\underset{\sim}{s}^{(1)}\right\} = \frac{i}{6}s(s+1)(2s+1), \\
&\ell = 4 : \mathrm{Tr}\left\{\underset{\sim}{s}^{(i)4}\right\} = \sum_{m=-s}^{s} m^4 = \frac{1}{15}s(s+1)(2s+1)(3s^2+3s-1), \\
&\ell = 4 : \mathrm{Tr}\left\{\underset{\sim}{s}^{(1)2}\underset{\sim}{s}^{(2)2}\right\} = \frac{1}{30}s(s+1)(2s+1)(2s^2+2s-1) \ .
\end{aligned} \tag{12}$$

Note that there are no $\ell = 1$ cases; hence all traces $\mathrm{Tr}\left\{\underset{\sim}{s}_{\mu_1}^{(i_1)j_1} \ldots \underset{\sim}{s}_{\mu_K}^{(i_K)j_K}\right\}$ vanish if at least for some $k = 1, \ldots, K$ the site index μ_k is different from the other μ_k' and $j_k = 1$, therefore,

$$t_1 = \mathrm{Tr}\left\{\underset{\sim}{H}_0\right\} = 0 \ . \tag{13}$$

From the list (12) we obtain for $n = 2$:

$$\begin{aligned}
t_2 = \mathrm{Tr}\left\{\underset{\sim}{H}_0^2\right\} &= \sum_{\mu<\nu} J_{\mu\nu}^2 \sum_{i=1}^{3} \mathrm{Tr}\left\{\underset{\sim}{s}_\mu^{(i)2} \otimes \underset{\sim}{s}_\nu^{(i)2} \otimes \underset{\sim}{\mathbb{1}}_{N-2}\right\} \\
&= \left(\sum_{\mu<\nu} J_{\mu\nu}^2\right) \frac{1}{3}s^2(s+1)^2(2s+1)^N \ ,
\end{aligned} \tag{14}$$

where $\underset{\sim}{\mathbb{1}}_{N-2}$ denotes the unit operator in the Hilbert space of $N-2$ spins. For $n = 3$ there occur two kinds of non-zero terms:

$$\mathrm{Tr}\left\{\underset{\sim}{s}_\mu^{(1)}\underset{\sim}{s}_\mu^{(2)}\underset{\sim}{s}_\mu^{(3)} \otimes \underset{\sim}{s}_\nu^{(1)}\underset{\sim}{s}_\nu^{(2)}\underset{\sim}{s}_\nu^{(3)} \otimes \underset{\sim}{\mathbb{1}}_{N-2}\right\} \tag{15}$$

and those terms obtained by permutations of $\{1, 2, 3\}$, and

$$\mathrm{Tr}\left\{\underset{\sim}{s}_{\mu}^{(i)2}\otimes\underset{\sim}{s}_{\nu}^{(i)2}\otimes\underset{\sim}{s}_{\kappa}^{(i)2}\otimes\underset{\sim}{\mathbb{1}}_{N-3}\right\}\ , \tag{16}$$

where μ,ν,κ are pairwise distinct and $i=1,2,3$. Consequently we obtain

$$t_3=\mathrm{Tr}\left\{\underset{\sim}{H}_0^3\right\}=T_1+T_2\ , \tag{17}$$

$$\begin{aligned}T_1&=\sum_{\mu<\nu}J_{\mu\nu}^3\,3!(2s+1)^{N-2}\mathrm{Tr}\left\{\underset{\sim}{s}^{(1)}\underset{\sim}{s}^{(2)}\underset{\sim}{s}^{(3)}\right\}^2 \\ &=-\sum_{\mu<\nu}J_{\mu\nu}^3\frac{1}{6}s^2(s+1)^2(2s+1)^N\ ,\end{aligned} \tag{18}$$

$$\begin{aligned}T_2&=3!\left(\sum_{\mu<\nu<\kappa}J_{\mu\nu}J_{\mu\kappa}J_{\nu\kappa}\right)(2s+1)^{N-3}\sum_{i=1}^{3}\mathrm{Tr}\left\{\underset{\sim}{s}^{(i)2}\right\}^3 \\ &=\left(\sum_{\mu<\nu<\kappa}J_{\mu\nu}J_{\mu\kappa}J_{\nu\kappa}\right)\frac{2}{3}s^3(s+1)^3(2s+1)^N\ .\end{aligned} \tag{19}$$

IV. THE TAYLOR EXPANSION OF χ

A. The linear term

For the linear term we just need t_0 and μ_0. t_0 is nothing else than the dimension of the N-spin Hilbert space

$$t_0=\mathrm{Tr}\left\{\underset{\sim}{\mathbb{1}}\right\}=(2s+1)^N\ . \tag{20}$$

For μ_0 we obtain with the help of list (12)

$$\begin{aligned}\mu_0&=\mathrm{Tr}\left\{\underset{\sim}{S}^{(3)2}\right\}=\frac{1}{3}\mathrm{Tr}\left\{\underset{\sim}{\vec{S}}^2\right\} \\ &=\frac{1}{3}\left(\sum_{\nu}\mathrm{Tr}\left\{\underset{\sim}{\vec{s}}_{\nu}^{\,2}\right\}+\sum_{\nu\neq\mu}\mathrm{Tr}\left\{\underset{\sim}{\vec{s}}_{\nu}\cdot\underset{\sim}{\vec{s}}_{\mu}\right\}\right)=\frac{1}{3}Ns(s+1)t_0\ ,\end{aligned} \tag{21}$$

and therefore

$$c_1=\frac{1}{3}Ns(s+1)\ . \tag{22}$$

Hence, combining (9), (20), and (21) we find that the Curie-Weiss constant is given by

$$k_BC\equiv k_B(g\mu_B)^2\hat{C}=(g\mu_B)^2\frac{1}{3}Ns(s+1)\ , \tag{23}$$

which is identical to the mean-field result.[14,15]

B. The β^2-term

For the quadratic term we calculate μ_1 directly

$$\begin{aligned}\mu_1 &= \mathrm{Tr}\left\{\underset{\sim}{H}_0\underset{\sim}{S}^{(3)2}\right\} = \frac{1}{3}\mathrm{Tr}\left\{\underset{\sim}{H}_0\vec{\underset{\sim}{S}}^2\right\} \\ &= \frac{1}{3}\sum_{\mu<\nu,i} J_{\mu\nu}\mathrm{Tr}\left\{\underset{\sim}{s}_\mu^{(i)}\underset{\sim}{s}_\nu^{(i)}\left(2\sum_{\kappa<\lambda,j}(\underset{\sim}{s}_\kappa^{(j)}\underset{\sim}{s}_\lambda^{(j)}) + Ns(s+1)\underset{\sim}{\mathbf{1}}\right)\right\} .\end{aligned} \tag{24}$$

Since $\mathrm{Tr}\{\underset{\sim}{s}_\mu^{(i)}\underset{\sim}{s}_\nu^{(j)}\} = 0$ for $\mu \neq \nu$ the second summand vanishes. According to section III, the first one is only non-zero if $\mu = \kappa, \nu = \lambda, i = j$. Hence

$$\begin{aligned}\mu_1 &= \frac{2}{3}\sum_{\mu<\nu,i} J_{\mu\nu}\mathrm{Tr}\left\{\underset{\sim}{s}_\mu^{(i)2}\underset{\sim}{s}_\nu^{(i)2}\right\} = 2\left(\sum_{\mu<\nu} J_{\mu\nu}\right)\left(\frac{1}{3}s(s+1)\right)^2(2s+1)^N \\ &= \frac{2}{9}\left(\sum_{\mu<\nu} J_{\mu\nu}\right) s^2(s+1)^2 t_0 .\end{aligned} \tag{25}$$

This results in a coefficient

$$c_2 = -\frac{2}{9}\left(\sum_{\mu<\nu} J_{\mu\nu}\right) s^2(s+1)^2 \tag{26}$$

and a Weiss temperature of

$$k_B T_c = -\frac{\mu_1}{\mu_0} = -\frac{2}{3N}s(s+1)\left(\sum_{\mu<\nu} J_{\mu\nu}\right) , \tag{27}$$

which agrees with the mean field result.[14,15]

C. The β^3-term and higher orders

Using the same method the next term can be calculated. The coefficient reads

$$\begin{aligned}c_3 = &\frac{2}{27}s^3(s+1)^3\sum_{\kappa<\lambda<\mu}(J_{\kappa\lambda}J_{\kappa\mu} + J_{\kappa\mu}J_{\lambda\mu} + J_{\kappa\lambda}J_{\lambda\mu}) \\ &-\frac{1}{18}s^2(s+1)^2\sum_{\kappa<\lambda}\left(J_{\kappa\lambda}^2\right) .\end{aligned} \tag{28}$$

Hence c_3 depends not on all exchange parameters but only on a certain combination of the second moments (or correlation coefficients) of the exchange parameters.

It is clear how coefficients of higher orders are to be calculated, although the expressions rapidly become very lengthy. Computer algebra methods would have to be employed to determine and evaluate those expressions.

V. APPLICATIONS

The first two expansion coefficients in the Taylor expansion (6) of the susceptibility in powers of β that involve the exchange parameters are c_2 and c_3. We propose exploiting accurate numerical estimates for c_2 and c_3 to provide information on the exchange parameters. The following version of (6)

$$k_B\,T\,(k_B\,T\hat{\chi}-c_1)=\sum_{n=2}^{\infty}c_n\beta^{n-2}=c_2+c_3\beta+\cdots\ , \tag{29}$$

is especially convenient since we can determine c_2 and c_3 by a least-squares fit between a low degree polynomial in β to measured values of the quantity $k_B\,T\,(k_B\,T\hat{\chi}-c_1)$, compare also Ref. 12. To increase the accuracy of the determined values of c_2 and c_3 it is generally advisable to use a polynomial in β of degree two or higher. In an iterative procedure one could check the extent to which the values of c_2 and c_3 change as higher degree polynomials are used. We remind the reader that we assume that the spectroscopic splitting factor g, which is necessary to obtain function (29), has accurately been determined, e.g. by ESR measurements.

In the following two examples we test the proposed method for two model systems. Starting with given exchange parameters we determine the partition function by exact diagonalization of the Hamiltonian and calculate the susceptibility. Our aim is to extract accurate estimates for the exchange parameters from a limited number of susceptibility data points. We also assess how the method depends on the chosen temperature interval and how robust the method is when the experimental data includes random error.

If the system has two exchange parameters J_1 and J_2 it is obvious from (26) and (28) that c_2 is a linear function of J_1 and J_2 whereas c_3 is a quadratic function of these variables. Hence J_1 and J_2 can be determined by numerically solving a simple non-linear equation once accurate values of c_2 and c_3 are available. In cases where multiple solutions exist additional magneto-chemical information, for instance concerning the sign of the exchange parameters, must be considered.

A similar complication arises for the special class of so-called isospectral spin systems, where the same eigenvalue spectrum is associated with a host of different choices of the exchange parameters.[16] For such systems it is in principle impossible to obtain unique exchange parameters from susceptibility data.

A. Cubic spin array

Our first model system is a spin array where $N = 8$ spins $s = 1$ are located at the vertices of a cube. The spins are assumed to interact via two antiferromagnetic exchange parameters of typical magnitude, $J_1/k_B = 20$ K between nearest neighbors in the top and bottom face and $J_2/k_B = 10$ K connecting the two faces, see Fig. 1. The calculated magnetic susceptibility is shown in Fig. 2 as a thick line. The thin horizontal line corresponds to the high-temperature limiting value of $k_BT\hat{\chi}$ given by the coefficient c_1, see (6) and (22). For the determination of the underlying exchange parameters a restricted set of susceptibility

data is used. This set consists of data taken in steps of 5 K from 150 K to 300 K (crosses in Fig. 2). As already mentioned, not the susceptibility $\hat{\chi}$ itself or $T\hat{\chi}$ are fitted but

$$f(T) = T\left(k_B T\hat{\chi} - c_1\right). \tag{30}$$

The graph of the latter function is shown in Fig. 3. One notes that its dependence on $1/T$ in the relevant temperature interval is already rather linear. Therefore one expects good results using the fitting procedure based on a low degree polynomial. Indeed, approximating $T\left(k_B T\hat{\chi} - c_1\right)$ by a polynomial of third order yields $J_1/k_B = 19.96$ K and $J_2/k_B = 10.09$ K, a result which is not improved by using polynomials of higher degree.

We also investigated how the chosen temperature interval influences the analysis. Including only data between 150 K and 200 K yields exchange parameters which deviate by at most 10 % from the correct values.

Different from our model investigation, experimental data necessarily incorporates random noise. In order to estimate this effect, the determination of the exchange parameters was carried out with a number of modified data sets. For each data set all susceptibility values were allowed to deviate by at most ± 5 % from the correct values. The resulting exchange parameters are shown in Fig. 4, each point corresponding to a different modified data set. It appears that the influence of the fluctuations is different for the two exchange parameters due to the non-linear dependence of J_1 and J_2 on the expansion coefficients c_n.

B. Ring spin array

As a second model system we investigate a ring with $N = 6$ and $s = 5/2$. In order to further quantify the accuracy of the proposed method, we chose two cases, case (a) where the spins are connected only by a nearest-neighbor interaction $J_1/k_B = 20$ K, and case (b) where we have an additional next-nearest-neighbor interaction $J_2/k_B = 10$ K, see Fig. 5. The corresponding values of $T\chi$, again obtained by complete diagonalization of the Hamiltonian, are given in Fig. 6. The thick curve corresponds to case (a) and the dashed curve corresponds to case (b). The thin line again gives the high temperature limit. Data points used for our analysis are depicted by crosses, again within the range between 150 K and 300 K. Note that for this model system the data points deviate from the high temperature behavior much more than in the previous example, i.e. the dependence of $f(T)$ on $1/T$ (Fig. 7) in the above temperature range especially for case (b), is not as linear as it was in the previous example.

The present method is sufficiently robust to provide accurate estimates of the exchange parameters without exploiting any prior information. This is illustrated by using two exchange parameters for case (a) and finding that $J_1/k_B = 20.04$ K and $J_2/k_B = -0.04$ K, which is in very good agreement with the actual exchange parameters in case (a). For case (b) we find $J_1/k_B = 19.33$ K and $J_2/k_B = 10.69$ K, which is not as accurate as in the previous examples. Nevertheless, even in this worst case, using these exchange parameters results in $k_B T\hat{\chi}$ which, when plotted in Fig. 6, is indistinguishable for all temperatures from that for the correct values of J_1 and J_2. Improved exchange parameters might be achievable if measured data for χ is available for higher temperatures, but unfortunately many substances – especially those containing solvent molecules for instance – become structurally unstable at such temperatures.

VI. SUMMARY

In summary, we have provided exact analytical expressions for the first three terms of the high-temperature expansion of the magnetic susceptibility function for Heisenberg spin systems with an arbitrary coupling matrix $J_{\mu\nu}$ and arbitrary intrinsic spins s. The results can be rather easily used in order to determine unknown exchange parameters for molecular magnets from zero-field magnetic susceptibility data with good accuracy, thereby obviating the need for diagonalizing the system Hamiltonian.

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FIGURES

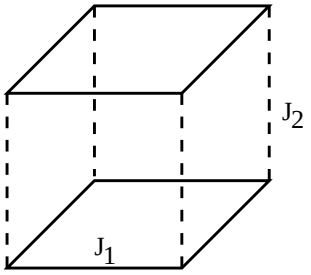

FIG. 1. Structure of a spin cube of $N = 8$ and $s = 1$. The assumed exchange parameters are $J_1/k_B = 20$ K, $J_2/k_B = 10$ K.

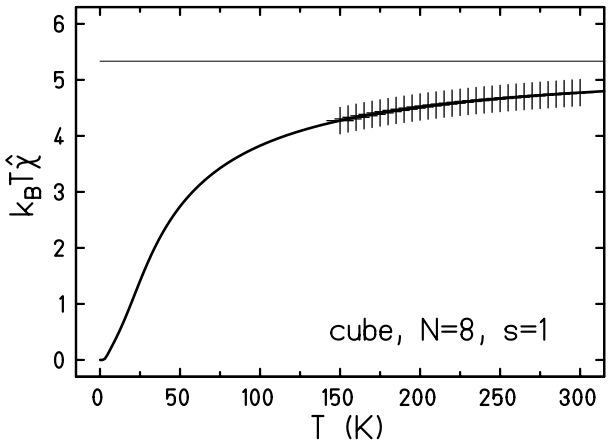

FIG. 2. $k_B T\hat{\chi}$ data (thick line) for the spin cube shown in Fig. 1. The data set used in the calculations is denoted by crosses. The thin line is the high temperature limit.

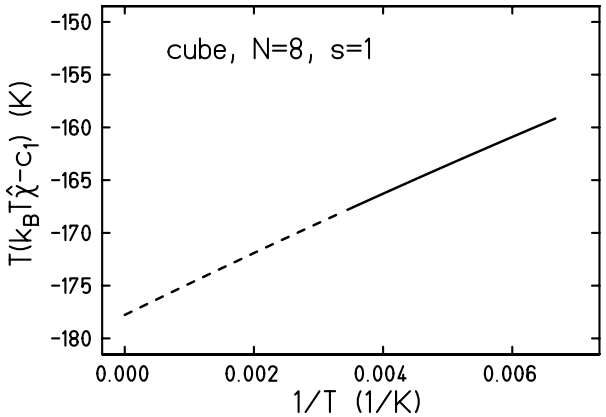

FIG. 3. Functional dependence of $T\,(k_B T\hat{\chi} - c_1)$ on $1/T$ (thick line) for the data set (crosses) shown in Fig. 2. The continuation of this function for higher temperatures is given by the dashed line.

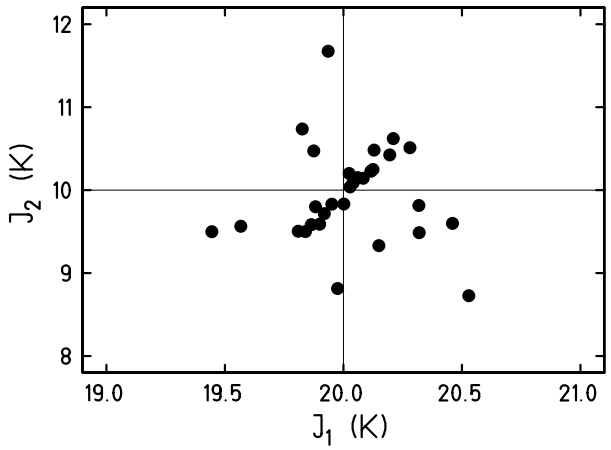

FIG. 4. Distribution of exchange parameters of the spin cube under the assumption that the susceptibility data incorporates random errors at the level of 5 %.

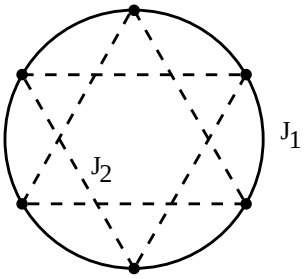

FIG. 5. Structure of a spin ring of $N = 6$ and $s = 5/2$ with nearest-neighbor J_1 and next-nearest-neighbor coupling J_2. The assumed exchange parameters are (a) $J_1/k_B = 20$ K, $J_2 = 0$ and (b) $J_1/k_B = 20$ K, $J_2/k_B = 10$ K.

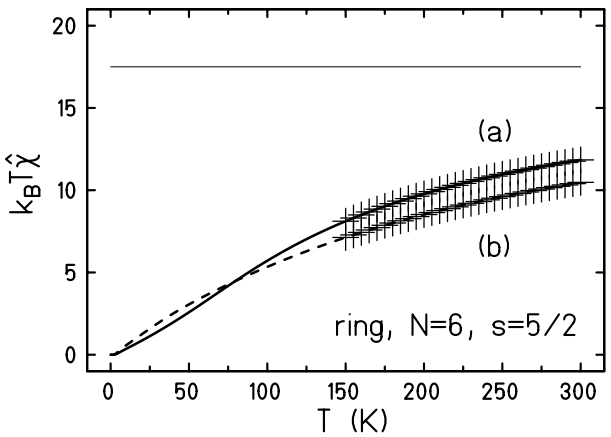

FIG. 6. $k_B T\hat{\chi}$ data for the spin ring introduced in Fig. 5. The thick curve shows case (a) and the dashed curve shows case (b). The thin line corresponds to the high temperature limit. The data sets used in the calculations are depicted by crosses.

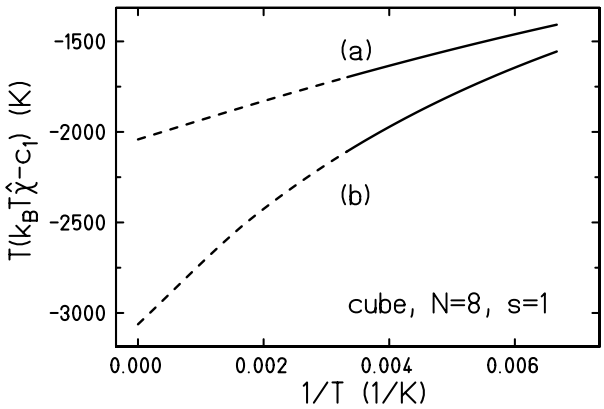

FIG. 7. Functional dependence of $T\,(k_B T\hat{\chi} - c_1)$ on $1/T$ (thick line) for the data set (crosses) shown in Fig. 6. The continuation of these functions for higher temperatures is given by dashed lines.