Trends in phenomenological modeling of molecular nanomagnets[*]

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Abstract. The non-perturbative approaches have become important tools in simulations of molecular nanomagnets. Here the direct, numerically exact diagonalization and quantum transfer matrix (QTM) techniques, applicable to Heisenberg spin systems modeling molecular-based rings, are described. The models include the single-ion anisotropy, alternating nearest-neighbor bilinear exchange coupling and the biquadratic term. We present results obtained for two molecules: Cr_8 and Ni_{12}.

Key words: molecular nanomagnet, quantum transfer matrix, exact diagonalization, Heisenberg Hamiltonian

1 Introduction

Molecular clusters composed out of transition-metal ions and shielded from each other by a shell of organic ligands act as individual quantum nanomagnets. The quantum microscopic properties of such molecules can be then observed on a macroscopic scale. This makes them very interesting objects of theoretical and experimental investigation. Their envisaged practical applications in a future quantum computer [1] or as storage devises have stimulated the development of efficient theoretical tools. Phenomenological modeling of such molecules is based on the assumption that the intercluster interactions are negligible and the properties of a system are determined by strong intracluster exchange interactions. In the first approximation a pure Heisenberg Hamiltonian is used. However, the experimental findings indicate more complex interactions, suggesting inclusion

of alternating couplings, single-ion anisotropy, second neighbors interactions or exchange anisotropy. A standard approach to these, more complex Hamiltonians is based on perturbative techniques [2], which however have natural limitations. In this paper we present two numerically exact non-perturbative methods applied to molecular rings: exact diagonalization and quantum transfer matrix technique.

2 Spin models

To model the molecular rings we use the following quantum spin ($s = 3/2$ for Cr_8 and $s = 1$ for Ni_{12}) Hamiltonian:

$$\mathcal{H} = \sum_{j=1}^{n/2} \left(J^o \mathbf{s}_{2j-1} \cdot \mathbf{s}_{2j} + J^e \mathbf{s}_{2j} \cdot \mathbf{s}_{2j+1} \right)$$
$$+ \sum_{j=1}^{n} \left(D(s_j^z)^2 + g\mu_B B \left(s_j^x \sin\theta + s_j^z \cos\theta \right) \right) , \tag{1}$$

where $J^{o,e}$ are nearest-neighbor exchange integrals for 'odd' and 'even' pairs, respectively, n is the number of sites D is the (site-independent) single-ion anisotropy, B is the external magnetic field applied in the $x - z$ plane and forming an angle θ with the z axis. g is the corresponding Landé factor and μ_B stands for Bohr magneton. We assume periodic boundary conditions ($j + 8 \equiv j$). We calculate first the free energy

$$F = -k_B T \ln Z , \quad Z = \mathrm{Tr} e^{-\beta\mathcal{H}} , \tag{2}$$

and then by numerical differentiation obtain the following thermodynamic quantities

$$C = -T \left(\frac{\partial^2 F}{\partial T^2} \right)_B , \quad \chi = - \left(\frac{\partial^2 F}{\partial B^2} \right)_T . \tag{3}$$

the magnetic torque is calculated with the help of the formula:

$$\tau = -g\mu_B \left(\langle S^x \rangle \cos\theta - \langle S^z \rangle \sin\theta \right) \tag{4}$$

where $\langle S^x \rangle$ and $\langle S^z \rangle$ are the thermal averages of the total spin components.

3 Numerical methods

In exact diagonalization only non-alternating couplings are taken into account. The diagonalization is done numerically and exploits the symmetries of the Hamiltonian, which is invariant with respect to the renumbering of sites

$$(1, \, 2, \, \ldots , \, N-1, \, N) \rightarrow (2, \, 3, \, \ldots , \, N, \, 1) \tag{5}$$

generated by the shift operator

$$\mathcal{P} \equiv \sum_{s_1^z} \cdots \sum_{s_N^z} \mid s_2^z \ldots s_N^z s_1^z \rangle \langle s_1^z s_2^z \ldots s_N^z \mid , \tag{6}$$

and the mirror reflection corresponding to the transformation:

$$(1, \, 2, \, \ldots \, , \, N-1, \, N) \to (N, \, N-1, \, \ldots \, , \, 2, \, 1) \, . \tag{7}$$

As a result the eigenstates of the Hamiltonian obtained are classified by three quantum numbers (S^z, k, r), where $-ns \le S^z \le ns$ is the z component of total spin, $0 \le k \le n/2$ corresponds to translational invariance and $r = \pm 1$ is related to mirror reflection.

The quantum transfer matrix technique applies the Trotter formula to the exponent of the Hamiltonian (1) expressed as a sum of two non-commuting Hamiltonians $\mathcal{H}^o$ and $\mathcal{H}^e$. Then the partition function can be written as:

$$Z = \lim_{m \to \infty} Z_m = \lim_{m \to \infty} \mathrm{Tr} \left(e^{-\frac{\beta}{m} \mathcal{H}^o} e^{-\frac{\beta}{m} \mathcal{H}^e} \right)^m . \tag{8}$$

The symmetries of the $\mathcal{H}^o$ and $\mathcal{H}^e$ allow us to express Z_m with the help of a single sparse matrix V and the shift operators $\mathcal{P}$, $\mathcal{P}^\dagger$

$$Z_m = \mathrm{Tr} \left[\left(V \mathcal{P}^\dagger \mathcal{P}^\dagger \right)^{n/2} \mathcal{P}^\dagger \left(V \mathcal{P}^\dagger \mathcal{P}^\dagger \right)^{n/2} \mathcal{P} \right]^m . \tag{9}$$

The trace in (9) is calculated over 4^8 dimensional spin space. The thermodynamic quantities are calculated for different values of m and then extrapolated to $m \to \infty$

4   Results and conclusions

The exact diagonalization technique is applied to the 12 $s = 1$ spin ring. The energy levels are calculated as a function of the anisotropy D for $B = 0$ and as a function of the magnetic field B aligned with the z axis for a fixed value of D. As expected, with increasing magnetic field the magnetisation in the ground state changes discontinuously from 0 to -4 with characteristic unit steps at crossing fields. Yet for higher fields the energy levels with magnetisation -5 and -6 never become the ground state since they have been 'crossed' before by the level with the magnetisation equal to -7.

Using the quantum transfer matrix technique the susceptibility and the specific heat were calculated for a wide range of temperatures. Both these quantities appear insensitive to the bond alternation as long as the mean value of the couplings $\bar{J}$ is fixed and the alternation $\Delta J = |J^o - J^e| > 0.4\bar{J}$. We have also obtained results for the magnetic torque in low temperatures (see fig. 2).

The exact diagonalization and quantum transfer matrix technique give highly precise reliable results also for more complex systems for which the perturbative methods are usually used. A comparison of the quantum transfer matrix results, especially those obtained for the torque with the exact diagonalization should shed more light on the problem of S-mixing in molecular rings.
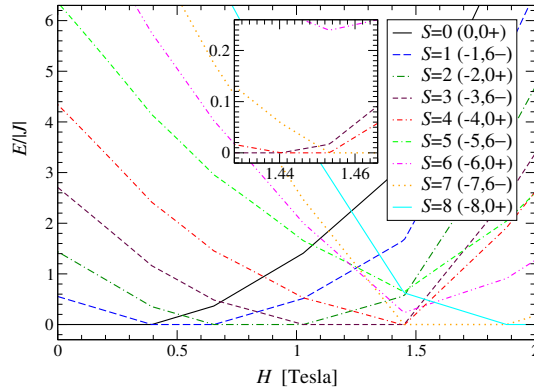
Fig. 1. The field-dependence of the lowest-lying states ($M = -S$) relative to the ground state energy for the antiferromagnetic ring of 12 spins $s = 1$ at the anisotropy $D/|J| = -0.1$
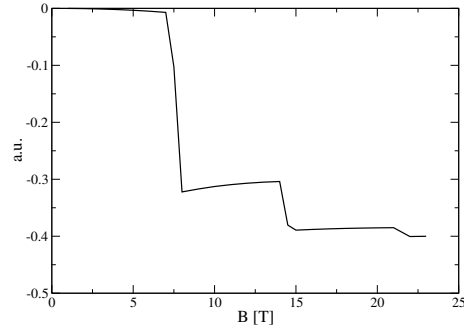

Fig. 2. The magnetic torque of Cr_8, for $T = 50$mK and $\theta = 6°$

References

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