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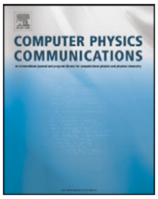

Quantum effects and Haldane gap in magnetic chains with alternating anisotropy axes

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ABSTRACT

The isotropic quantum Heisenberg model with alternating uniaxial anisotropy axes is analyzed numerically by the density-matrix renormalization-group (DMRG) method. In the classical version, the model is applied to describe the magnetic properties of the $S = 2$ zigzag chain containing Mn(III) acetate meso-tetraphenylporphyrin complexes coupled by the phenylphosphinate ligands which transmit antiferromagnetic interactions. Although the tensors representing the uniaxial magnetic anisotropy D and g factors are non-diagonal in the global coordination system, the DMRG approach has been successfully applied to this complex model in the entire temperature region studied. The predictions of our quantum approach are compared to those previously obtained from the classical one and the importance of quantum effects for analysis of the single-crystal susceptibility and magnetization is demonstrated. At low temperatures the magnetization in the field applied along the c direction increases much more slowly than the classical counterpart. The magnetization behavior is very sensitive to temperature. Moreover, the presence of a magnetization jump in the limit $T \to 0$ at the field $H = 3.8$ Tesla can be an indication of the Haldane gap of the order of 10.2 K. The considerable differences are demonstrated for the temperature dependent single-crystal susceptibilities, but surprisingly they disappear after averaging over the three crystallographic directions which has not been reported before.

1. Introduction

A new class of nanomagnets, the so-called single-chain magnets (SCM), has aroused great interest because of their unique properties [1]. These materials are composed of magnetically isolated chains that can be individually magnetized. As purely one-dimensional systems they remain in the paramagnetic state at any temperature. Nevertheless, a combination of a large uniaxial anisotropy and large magnetic interactions between the high-spin magnetic units of the chain promotes long relaxation times and the system can behave as a magnet. Although the SCM materials synthesized hitherto manifest long relaxation times at low temperatures only, various attempts are carried out to remove these limitations. The point is that SCM behavior is not only a feature of ferro- and ferrimagnetics but also of canted antiferromagnetic chains [2]. Moreover, noncollinear anisotropy axes are often found in molecular systems.

The SCM materials are studied theoretically under the assumption that the spins are treated in the classical approximation, taking into account the Ising limit or replacing the spin operators by classical vectors. The latter approach has been adopted [2] for analysis of the SCM compound made of aligned acetate meso-tetraphenylporphyrin complexes of the formula [Mn(TPP)O_2PHPh]-H_2O. At first sight it seems justified to consider the classical limit for the Heisenberg model for the spin $S = 2$ and temperatures not too low when compared with the weak magnetic coupling constant J/k_B (in our units equal to 1.36 K).

This study was undertaken to address the following questions. (a) As the crossover temperature separating the quantum and classical behavior for a given Heisenberg model is unknown, is the assumption of total neglect the role of the quantum effects correct or too far-reaching?; (b) Is the antiferromagnetic $S = 2$ Heisenberg model with noncollinear anisotropy axes a good realization of the Haldane-gap system? Both these questions have not been discussed in the previous paper [2].

So far we have considered the quantum chains [3,4] with rather weak exchange coupling and weak/moderate uniaxial anisotropy with the unique orientation of the easy axis. The analysis based on the DMRG approach has led to significant improvement as far as the modeling of the thermodynamic properties is concerned. In this paper we extend the approach over the model with the anisotropy axes not only tilted from the z direction but also alternating from site to site along the chain.

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2. Model

The $[\mathrm{Mn(TPP)O_2PHPh}]\mathrm{H_2O}$ compound represents systems comprising only one type of spin and one type of exchange interaction, which allows simulation of static and dynamic properties of the system in the whole range of temperatures studied with the use of one model [2]. This compound is considered as the textbook example of SCM. The chain structure is generated by a glide plane resulting in Jahn–Teller elongation axes of the Mn(III) octahedra that alternate along the chain.

Therefore the uniaxial magnetic anisotropy D and g factors enter the model Hamiltonian as the non-diagonal tensors which lead to the following formula:

$$\mathcal{H}=\sum_{i=1}^{L}\left[\sum_{\alpha}JS_i^{\alpha}S_{i+1}^{\alpha}+\sum_{\beta,\gamma}\left(S_i^{\beta}D_i^{\beta\gamma}S_i^{\gamma}+\mu_B H^{\beta}g^{\beta\gamma}S_i^{\gamma}\right)\right],$$

where $S=2$ and L stands for the length of the chain.

The anisotropy tensor $D^{\beta\gamma}$ and the $g^{\beta\gamma}$ factor, where $\alpha,\beta,\gamma=x,y,z$, have been found to be non-diagonal according to the following analysis. It is known [5] that there is such a local system of coordinates, where the $D^{\beta\gamma}$ tensor has only non-zero elements on the diagonal (D_{xy},D_{xy},D_{zz}). At the same time by subtracting and adding the unit matrix multiplied by the factor $Tr(D^{\beta\gamma})/3$ one gets the traceless tensor, again only with non-zero diagonal elements $(D_{\perp},D_{\perp},D_z)$. After elementary modifications it can be presented in the diagonal form: $(0,0,D_z)$. Moreover, the local system of coordinates guarantees that the $g^{\beta\gamma}$ tensor has a diagonal form with elements $(g_{\perp},g_{\perp},g_z)$.

In order to transform the Hamiltonian from the local coordinates to the lab ones the following similarity transformation is necessary: $\mathcal{H}_{lab}=R(\phi)R(\theta)\mathcal{H}'_{loc}R(\theta)^{-1}R(\phi)^{-1}$.

Then both tensors $D^{\beta\gamma}$ and $g^{\beta\gamma}$ take the final form:

$$D=D_z\begin{pmatrix}\cos^2\phi\sin^2\theta & -\cos\phi\sin\phi\sin^2\theta & -\cos\phi\sin\theta\cos\theta\\ -\cos\phi\sin\phi\sin^2\theta & \cos^2\phi\sin^2\theta & \sin\phi\sin\theta\cos\theta\\ -\cos\phi\sin\theta\cos\theta & \sin\phi\sin\theta\cos\theta & \cos^2\theta\end{pmatrix}.$$

$$g=\begin{pmatrix}g_{\perp}\cos^2\theta\cos^2\phi+g_z\cos^2\phi\sin^2\theta+g_{\perp}\sin^2\phi & (g_{\perp}-g_z)\cos\phi\sin^2\theta\sin\phi & (g_{\perp}-g_z)\cos\theta\cos\phi\sin\theta\\ (g_{\perp}-g_z)\cos\phi\sin^2\theta\sin\phi & g_{\perp}\cos^2\phi+(g_{\perp}\cos^2\theta+g_z\sin^2\theta)\sin^2\phi & (-g_{\perp}+g_z)\cos\theta\sin\theta\sin\phi\\ (g_{\perp}-g_z)\cos\theta\cos\phi\sin\theta & (-g_{\perp}+g_z)\cos\theta\sin\theta\sin\phi & g_z\cos^2\theta+g_{\perp}\sin^2\theta\end{pmatrix}.$$

The transformation angles (ϕ,θ) were taken from the data presented in [2]. The non-diagonal tensors demand using the complex matrix representation of the model Hamiltonian which leads to higher computational complexity with respect to our previous papers [3,4].

3. Simulation method

Originally the density-matrix renormalizińion group method (DMRG) has been proposed by White for the ground-state calculations of quantum spin chains [6]. A key problem is to find in a subspace of a given size, much smaller than the original configuration space, optimal basis states in which the Hamiltonian could be expressed. Starting with a small system for which Hamiltonian can be exactly diagonalized, one adds iteratively couples of spins until the allowed (in the computational sense) size is reached. Then further addition of new spins makes one to discard simultaneously the least important states to keep the size of the effective Hamiltonian fixed. This truncation is done through the construction of a reduced density matrix whose eigenstates provide the optimal basis set.

Nishino applied the DMRG idea to truncation of transfer matrices [7] for 2d strips at finite temperature. It is not surprising, since a quantum system in d dimensions can be mapped onto another classical system in $d+1$ [8]. Nishino's formulation of the DMRG for two-dimensional classical systems has paved the way for the study of one-dimensional quantum systems at non-zero temperature [9]. The starting point was the quantum transfer matrix method (QTM) which had been earlier proposed to study thermodynamic properties of quantum spin chains [10–12]. By means of the Trotter–Suzuki decomposition, the partition function of the chain is mapped onto the partition function of the classical 2d system with multi-spin interactions. The partition function of the classical system takes the form of a series of approximants Z_M, where M is called the Trotter number. The higher M, the greater is taken into account quantum nature of the problem. As the dimension of QTM exponentially increases with increasing Trotter number computations of Z_M are feasible for relatively small M which can prevent reliable estimations of the thermodynamic functions in a low-temperature region (see references in [12–14]). To overcome this restriction and cover the entire experimental temperature range, the DMRG approach has been applied [15–18].

In the zero-temperature DMRG method, we extend the quantum Hamiltonian in the real space direction, where the number of basis states is reduced by using the eigenvectors of the density matrix calculated from the ground-state wave function. In the finite-temperature DMRG method, we extend the transfer matrix in the Trotter direction by restricting the basis states using the density matrix calculated from the transfer matrix eigenvector related to the maximum eigenvalue $\lambda_{\max}$ [18]. Contrary to the zero-temperature DMRG method, the transfer matrices to be diagonalized are asymmetric here due to the checkerboard decomposition.

The non-Hermiticity of the transfer matrix and the corresponding density matrices which are constructed from the right and left eigenvectors of the largest eigenvalue of transfer matrix, can result in significant numerical instabilities. It can spoil substantially the convergence of results. This is particularly important when calculations are performed with real algebra. For example, the lack of the biorthogonality between the left and right eigenvectors may affect the density matrix and substantially increase the truncation error. Another problem would be caused by degenerate eigenvalues, for which standard procedures give spurious small imaginary parts. Usually this problem has been solved by using the real and imaginary components of the corresponding complex conjugate eigenvector pairs and discarding the imaginary part of the eigenvalues, which are artifacts of roundoff errors. Fortunately, we were able to overcome these problems by applying complex algebra [3,4], which guaranties the biortogonality of complex eigenvectors.

At each temperature, the free energy of the system per site is obtained from the maximum eigenvalue $\lambda_{\max}$

$$f=-k_BT\ln\lambda_{\max}/2.$$

Various thermodynamical quantities as the internal energy, entropy, specific heat or magnetic susceptibility can be obtained by taking adequate derivatives of the free energy with respect to temperature or magnetic field.