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Evaluation of the low-lying energy spectrum of magnetic Keplerate molecules using the density-matrix renormalization group technique

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We apply the density-matrix renormalization-group (DMRG) technique to magnetic molecules in order to evaluate the low-lying energy spectrum. In particular, we investigate the giant Keplerate molecule $\{Mo_{72}Fe_{30}\}$ [A. Müller *et al.* Angew Chem. Int. Ed. Engl. **38**, 3238 (1999)], where 30 Fe^{3+} ions (spins 5/2) occupy the sites of an icosidodecahedron and interact via nearest-neighbor antiferromagnetic Heisenberg exchange. The aim of our investigation is to verify the applicability and feasibility of DMRG calculations for complex magnetic molecules. To this end we first use a fictitious molecule with the same structure as $\{Mo_{72}Fe_{30}\}$ but with spins 1/2 as a test system. Here we investigate the accuracy of our DMRG implementation in comparison to numerically exact results [J. Schnack *et al.*, Eur. Phys. J. B **24**, 475 (2001)]. Then we apply the algorithm to $\{Mo_{72}Fe_{30}\}$ and calculate an approximation of the lowest-energy levels in the subspaces of total magnetic quantum number. The results prove the existence of a lowest rotational band, which was predicted in J. Schnack *et al.*, Europhys. Lett. **56**, 863 (2001).

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I. INTRODUCTION

The rapid progress in polyoxometalate chemistry generates larger and larger magnetic molecules. The most prominent example of recent times is the molecular magnet $\{Mo_{72}Fe_{30}\}$, where 30 Fe^{3+} paramagnetic ions (spin 5/2) occupy the sites of an icosidodecahedron, see Fig. 1, and interact via isotropic nearest-neighbor antiferromagnetic Heisenberg exchange.[1,4] Whereas the statistical and dynamical properties of smaller molecules can be evaluated by numerically exact diagonalization,[2] the huge dimension of the Hilbert space of magnetic macromolecules prohibits such attempts. In the case of $\{Mo_{72}Fe_{30}\}$ this dimension amounts to $6^{30} \approx 10^{23}$, which is beyond the power of any computer.

Many attempts have been undertaken in order to approximate the energy eigenvalue spectrum of large magnetic systems. Among these the density-matrix renormalization-group[5] (DMRG) technique is one of the most powerful, at least in the field of one-dimensional spin systems, where, for instance, questions concerning Haldane's conjecture[6,7] could be answered with great accuracy.[8–10] It is as well a powerful tool for studying $T=0$ quantum phase transitions,[11] since it delivers accurate results for ground states. The DMRG method was also applied to spin rings—"ferric wheels"—which are quasi-one-dimensional magnetic molecules.[12] Here the aim was to evaluate low-lying magnetic levels and the related low-temperature spin dynamics in order to understand macroscopic quantum coherent phenomena.

Another method of approximating the energy spectrum is stimulated by the observation that in many Heisenberg spin systems the low-lying energy levels $E_{\min}(S)$ form a rotational band,[13] i.e., they depend approximately quadratically on the total spin quantum number S. Experimentally this property has been described as "following the Landé interval rule."[14–17] For spin ring systems the low-energy spectrum consists of a sequence of rotational bands, which allows to address questions of spin tunneling and other transitions without diagonalizing the full Hamiltonian.[18]

The purpose of this paper is twofold. We show that DMRG can be used in order to approximate the low-lying energy levels of magnetic macromolecules such as $\{Mo_{72}Fe_{30}\}$, and we prove numerically that the lowest levels as a function of total spin S form indeed a rotational band. The latter observation strengthens the predictions made in Ref. 3.

II. DMRG TECHNIQUE

The DMRG technique[5] has become one of the standard numerical methods for quantum lattice calculations in recent years.[19] Its basic idea is the reduction of Hilbert space while focusing on the accuracy of a target state. For this purpose the system is divided into subunits—blocks—which are represented by reduced sets of basis states. The dimension m of the truncated block Hilbert space is a major input parameter of the method and to a large extent determines its accuracy.

DMRG is best suited for chainlike structures. Many accu-

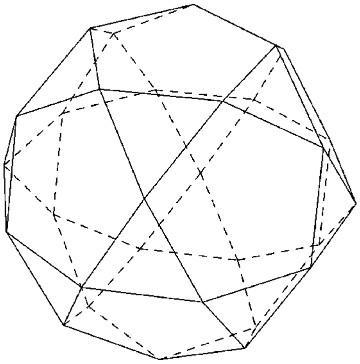

FIG. 1. Three-dimensional model of $\{Mo_{72}Fe_{30}\}$: the vertices mark the sites of the Fe^{3+} ions (spin 5/2), and the lines denote nearest-neighbor interactions.

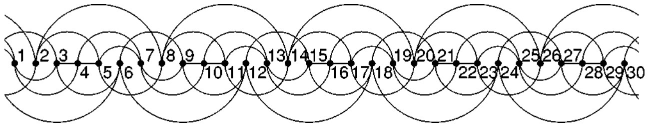

FIG. 2. One-dimensional projection of the icosidodecahedron: the lines represent interactions.

rate results have been achieved by applying DMRG to various (quasi-) one-dimensional systems.[8–10] The best results were found for the limit of infinite chains with open boundary conditions. It is commonly accepted that DMRG reaches maximum accuracy when it is applied to systems with a small number of interactions between the blocks, e.g., systems with only nearest-neighbor interaction.[19]

In order to carry out DMRG calculations for two-dimensional systems a mapping onto a one-dimensional structure was proposed.[19] We adopt this idea and derive a simple DMRG algorithm for two-dimensional (2D) spin systems in the Heisenberg model.[20] Since the spin array consists of a countable number of spins, any arbitrary numbering is already a mapping onto a one-dimensional structure. However, even if the original system had only nearest-neighbor exchange, the new one-dimensional system has many long-range interactions depending on the way the spins are enumerated, see, e.g., Fig. 2. Therefore, a numbering which minimizes long-range interactions is preferable.

The Hamiltonian of the Heisenberg model, which is appropriate for the investigated magnetic molecules, can be written as

$$\underset{\sim}{H} = -\sum_{i\neq j} J_{ij}\ \underset{\sim}{\vec{S}}_i\cdot\underset{\sim}{\vec{S}}_j = -2\sum_{i>j} J_{ij}\ \underset{\sim}{\vec{S}}_i\cdot\underset{\sim}{\vec{S}}_j, \qquad (1)$$

where J_{ij} is the interaction matrix and $\underset{\sim}{\vec{S}}_i$ are the spin operators at the sites i.

We use a block algorithm (including the sweeps) similar to the setup in White's original paper.[5] Two blocks are connected via two single spin sites, and these four parts form the superblock.

The Hamiltonian is invariant under rotations in spin space. Therefore the total magnetic quantum number M is a good quantum number and we can perform our calculation in each orthogonal subspace $\mathcal{H}(M)$ separately.

III. ACCURACY OF THE METHOD

Since it is difficult to predict the accuracy of a DMRG calculation, we apply our implementation to an exactly diagonalizable system first. The most realistic test system for the use of DMRG for $\{Mo_{72}Fe_{30}\}$ is the icosidodecahedron with spins $s=1/2$. This fictitious molecule, which possibly may be synthesized with vanadium ions instead of iron ions, has the same structure as $\{Mo_{72}Fe_{30}\}$, but the smaller spin quantum number reduces the dimension of the Hilbert space significantly. Therefore a numerically exact determination of low-lying levels using a Lanczos method is possible and was carried out by Richter, Schulenburg, and co-workers.[2,21] We use these results to analyze the principle feasibility and the accuracy of the method.

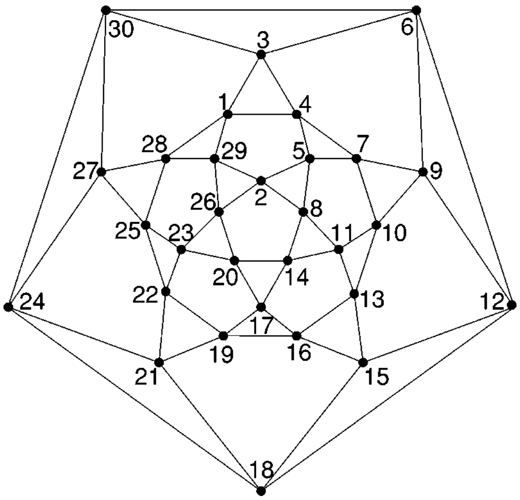

FIG. 3. Two-dimensional projection of the icosidodecahedron; the site numbers are those used in our DMRG algorithm.

The DMRG calculations were implemented using the enumeration of the spin sites as shown in Figs. 2 and 3. We choose this enumeration because it minimizes the average interaction length between two sites. The interaction length on the chain is measured as the distance $|j-i|$ of the two interacting sites i and j. The DMRG method favors systems with a minimal number of interactions between the blocks. Therefore, a short average interaction length helps to reduce the number of interblock interactions. With our enumeration we get an average length of 3 between two interacting sites. However, the choice is not unique because of the various symmetries of the system. Our choice, Fig. 3, is rotationally symmetric with a fivefold symmetry corresponding to the fivefold symmetry of the central pentagon. The sites 1–6 form the unit cell.

In Fig. 4 our DMRG results (crosses) are compared to the energy eigenvalues (circles) determined numerically with a Lanczos method.[2,21] We find very good agreement of both sequences, with a maximal relative error of less than 1%. Although we don't achieve the high accuracy of one-dimensional calculations (often with a relative error of the order of 10^{-6}), the result demonstrates that DMRG is applicable to finite 2D spin systems.

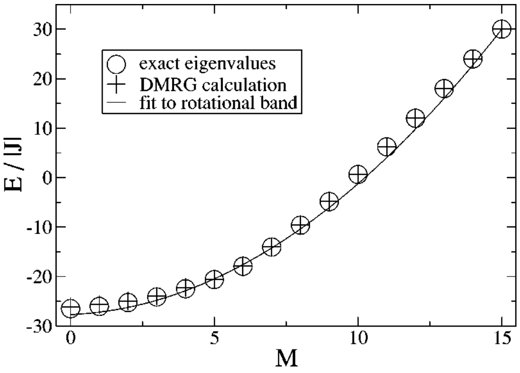

FIG. 4. Eigenvalues and lowest rotational band of the $s=1/2$ icosidodecahedron.

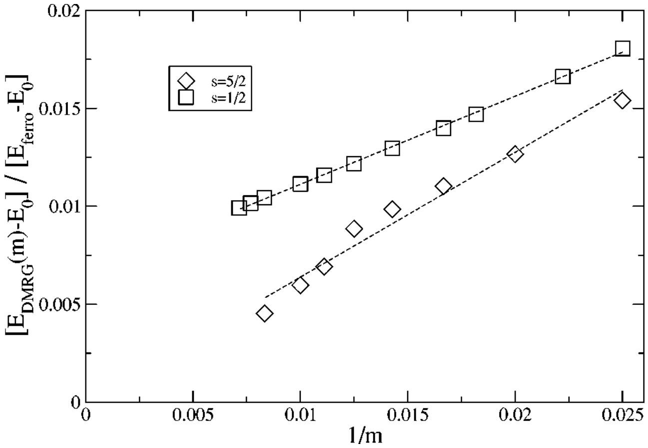

FIG. 5. Dependence of the approximate ground-state energy on the DMRG parameter m. E_0 is the true ground-state energy in the case $s=1/2$ and the extrapolated one for $s=5/2$.

Our results were obtained keeping $m=60$ states per block. The number of states could easily be increased for the $s=1/2$ case, but we wanted to have a prediction for $\{Mo_{72}Fe_{30}\}$, where m is limited by the available computer resources because of the much larger spin $s=5/2$. The number of sweeps ranged from 5 to 20 depending on how quickly the algorithm ran into oscillations with no further improvement of accuracy. This oscillatory behavior of the sweep algorithm is described in Ref. 19.

We also investigated the behavior of the accuracy of our DMRG energies when varying the value of m. Unfortunately, we found a very weak convergence of the relative error with increasing m. In our calculations, the error relative to the width of the spectrum

$$\epsilon(m)=\frac{E_{\mathrm{DMRG}}(m)-E_0}{|E_0^{\mathrm{AF}}-E_0^{\mathrm{F}}|} \tag{2}$$

is approximately proportional to $1/m$ (see Fig. 5). Unfortunately, such weak convergence is characteristic for two-dimensional systems in contrast to one-dimensional chain structures, where the relative error of the approximate energy was reported to decay exponentially with m.[5] Nevertheless, the extrapolated ground-state energy for $s=1/2$ deviates only by $\epsilon=0.7\%$ from the ground-state energy determined with a Lanczos algorithm.

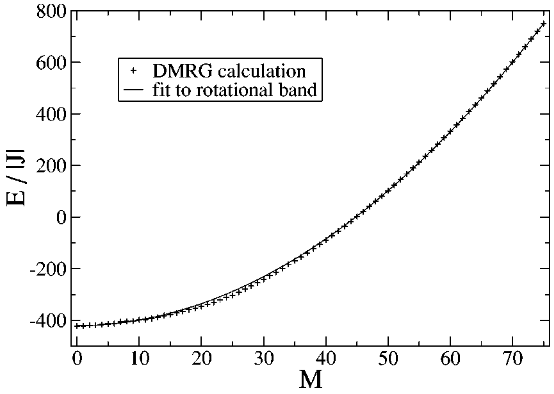

FIG. 6. DMRG eigenvalues and lowest rotational band of the $s=5/2$ icosidodecahedron; $m=60$ was used except for the lowest and first exited levels which were calculated with $m=120$.

IV. ROTATIONAL BAND IN $\{Mo_{72}Fe_{30}\}$

Since the DMRG technique has proven applicable for the $s=1/2$ case of the icosidodecahedron, we use our algorithm to approximate energy eigenvalues of the magnetic Keplerate molecule $\{Mo_{72}Fe_{30}\}$. In Ref. 3 it was predicted that the low-lying energy eigenstates of $\{Mo_{72}Fe_{30}\}$ form "rotational bands," i.e., the sequence of ground-state energies of the subspaces $\mathcal{H}(S)$ is expected to have a quadratic dependence on the total spin quantum number S. A spectrum with rotational bands usually arises in antiferromagnets if the spin system can be divided into sublattices. The most prominent example is bipartite rings or chains which consist of two sublattices with opposite sublattice magnetization. In the case of $\{Mo_{72}Fe_{30}\}$ the spin system is decomposable into three sublattices with sublattice spin quantum numbers S_A, S_B, and S_C.[3,13] Then the low-lying spectrum can be described by an approximate Hamilton operator

$$\underset{\sim}{H}_{\mathrm{approx}}=-J\frac{D}{N}[\underset{\sim}{\vec{S}}^2-\gamma(\underset{\sim}{\vec{S}}_A^2+\underset{\sim}{\vec{S}}_B^2+\underset{\sim}{\vec{S}}_C^2)], \tag{3}$$

where $\underset{\sim}{\vec{S}}$ is the total spin operator and the others are sublattice spin operators. At least in the case of bipartite systems this approximation has turned out to be a very good one.[13,18]

The minimal-energy eigenvalues of $\underset{\sim}{H}_{\mathrm{approx}}$ as a function of S form a rotational band by construction,

$$E_{\mathrm{min}}(S)=-J\frac{D}{N}S(S+1)+E_a. \tag{4}$$

We use the DMRG method to approximate the lowest-energy eigenvalues of the full Hamiltonian (1) and compare them to those predicted by the rotational band hypothesis (4). In our calculation we obtain energy levels for the ground states of $\mathcal{H}(M)$ subspaces. These states are equivalent to the ground states of the subspaces $\mathcal{H}(S)$ with $S=M$. The proof for this property rests on the monotonous increase of the sequence $E(M)$ with M for $0\leqslant M\leqslant Ns$.

Figure 6 shows our results and a fit to the lowest rotational band. Assuming the same dependence on m as in the $s=1/2$ case, the relative error (2) of our DMRG data should also be less than 1%. We find good agreement between our DMRG data and the predicted quadratic dependence. From the fit of our data we obtain $D=6.17$ and $\gamma=1.05$. These values are very close to the values $D=6.23$ and $\gamma=1.07$ given in Ref. 3, which were inferred from magnetization measurements.

V. SUMMARY

The major result of our investigation is that the DMRG approach delivers acceptable results for 2D systems. Therefore, we assume that our numerical approximation of low-lying energy levels for $\{Mo_{72}Fe_{30}\}$ is reliable. Thus, we have obtained good confidence that the prediction of a lowest rotational band made in Ref. 3 is justified. The lowest band of $\{Mo_{72}Fe_{30}\}$ indeed has a parabolic dependence on S. It remains the task of forthcoming investigations to determine whether also the higher-lying rotational bands appear with the same distinctness or whether they are scattered due to the strong frustration effects. In any case such calculations demand much higher precision and thus numerical effort.

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