# Evaluation of the low-lying energy spectrum of magnetic Keplerate molecules with DMRG

Matthias Exler* and Jürgen Schnack†
*Universität Osnabrück, Fachbereich Physik, D-49069 Osnabrück*
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We apply the density-matrix renormalization group technique to magnetic molecules in order to evaluate the low-lying energy spectrum. In particular, we investigate the giant Keplerate molecule $\{Mo_{72}Fe_{30}\}$,[1] 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.[2] 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 Ref. 3.

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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, 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 $6^{30}$, which is beyond the power of any computer.

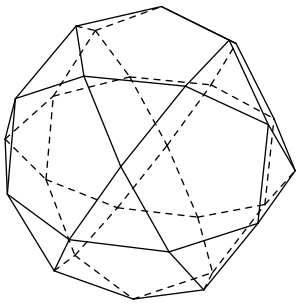

FIG. 1: Three-dimensional model of $\{Mo_{72}Fe_{30}\}$: the vertices mark the sites of the $Fe^{3+}$ ions (spin 5/2), and the lines denote nearest-neighbor interactions.

Many attempts have been undertaken in order to approximate the energy eigenvalue spectrum of large magnetic systems. Among these the Density Matrix Renormalization Group technique (DMRG)[5] 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.[8,9,10] It is as well a powerful tool for studying $T = 0$ quantum phase transitions,[11] as 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".[14,15,16,17] 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 article is twofold. We show that DMRG can be used in order to approximate the low-lying energy levels of magnetic macromolecules like $\{Mo_{72}Fe_{30}\}$, 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] became 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 ba-

sis states. The size $m$ of the truncated block Hilbert space is a major input parameter of the method and to a large extent determines its accuracy. The block basis states are derived from a twice as large system – superblock – by first diagonalizing the Hamiltonian on the superblock, then building a reduced density matrix from the superblock ground state, and finally diagonalizing the reduced density matrix.

DMRG is best suited for chain-like structures. Many accurate results have been achieved by applying DMRG to various (quasi-)one-dimensional systems.[8,9,10] 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 and open boundary conditions[19].

In order to apply DMRG calculations to 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 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.

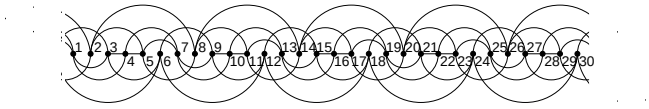


FIG. 2: One-dimensional projection of the icosidodecahedron: the lines represent interactions.

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

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

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

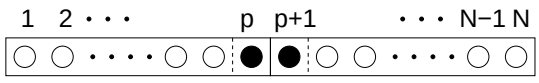


FIG. 3: Block setup for second part of DMRG algorithm ("sweeping"): The whole system of $N$ spins constitutes the superblock. The spins $\{1, 2, \ldots, p\}$ belong to the left block, the other spins $\{p+1, \ldots, N\}$ to the right block.

We use a block algorithm similar to the setup in White's original paper.[5] Two blocks are connected via two single spin sites, these four parts form the superblock, see Fig. 3. The Hamiltonian for the superblock can be written as

$$\underset{\sim}{H}^{\mathrm{SB}} = \underset{\sim}{H}^{\mathrm{l}} + \underset{\sim}{H}^{\mathrm{r}} + (-2) \sum_{i=1}^{p} \sum_{j=p+1}^{N} J_{ij}\ \underset{\sim}{\vec{S}}_i \cdot \underset{\sim}{\vec{S}}_j \quad , \qquad (2)$$

where $\underset{\sim}{H}^{l}$ and $\underset{\sim}{H}^{r}$ represent the Hamiltonians for the left and right block including the respective single spin. These Hamiltonians include the interactions inside the respective blocks, therefore the third term in (2) describes the interactions of the spins belonging to the left block with those of the right block.

In our implementation we have to keep track of the operators $\underset{\sim}{S}_i^+$ and $\underset{\sim}{S}_i^z$ (in matrix representation) for all sites $i$. In the case of a system with pure nearest-neighbor interaction one would have to keep only the operators for sites at the borders of the blocks. Because of the long-range interactions, the 2D-DMRG approach consumes more memory and the calculation of the Hamiltonian takes more time.

The algorithm consists of two steps. During the first step the superblock grows with each iteration by two sites until the final length of the system is reached. The second step is an implementation of White's sweep-algorithm.[5] While the superblock is kept at its maximum length, in each iteration the left block grows by one site whereas the right block is shortened by one site. When the right block reaches the size of two sites, the direction of the sweep is turned, and the right block grows in the next iterations. One performs a number of sweeps until the desired property, in our case the ground state energy, converges.

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 diagonalization is possible and was carried out by J. Richter.[2,21] We use these results to analyze the principle feasibility and the accuracy of the method.

The DMRG calculations were implemented using the enumeration of the spin sites as shown in Figs. 2 and 4.

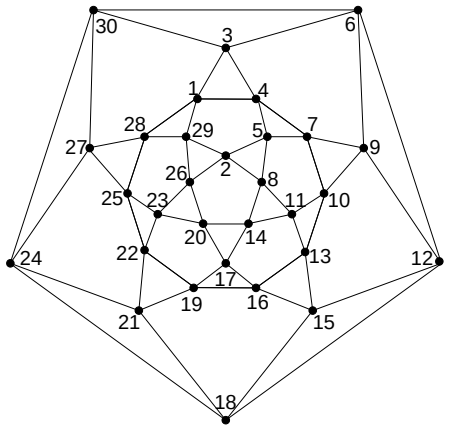


FIG. 4: Two-dimensional projection of the icosidodecahedron, the site numbers are those used in our DMRG algorithm.

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. 4, is rotationally symmetric with a five-fold symmetry corresponding to the five-fold symmetry of the central pentagon. The sites 1 to 6 form the unit cell.

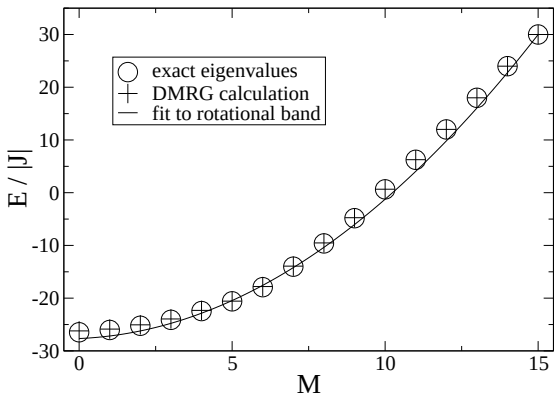


FIG. 5: Eigenvalues and lowest rotational band of the $s = 1/2$ icosidodecahedron.

In Fig. 5 our DMRG results (crosses) are compared to the energy eigenvalues (circles) determined numerically by J. Richter with a Lanczos method.[2,21] We find very good agreement of both sequences, with a maximal relative error of about 1%. Although we don't achieve the high accuracy of one-dimensional calculations (often better than $10^{-6}$), the result demonstrates that DMRG is applicable to finite 2D spin systems.

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.

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

Since the DMRG technique has proven applicable for the $s = \frac{1}{2}$ 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 states energies of the sub-spaces $\mathcal{H}(S)$ 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 sub-lattices. The most prominent example are bipartite rings or chains which consist of two sub-lattices with opposite sub-lattice magnetization. In the case of $\{Mo_{72}Fe_{30}\}$ the spin system is decomposable into three sub-lattices with sub-lattice 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

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

where $\underset{\sim}{\vec{S}}$ is the total spin operator and the others are sub-lattice 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 $\underset{\sim}{H}_{\text{approx}}$ as a function of $S$ form a rotational band by construction

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

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 $\mathcal{H}(M)$ sub-spaces. These states are equivalent to the ground states of the sub-spaces $\mathcal{H}(S)$ with $S = M$. The proof for this property rests on the monotonous increase of the sequence $E(M)$ with $M$ for $0 \le M \le Ns$.

Fig. 6 shows our results and a fit to the lowest rotational band. We find a good agreement between our

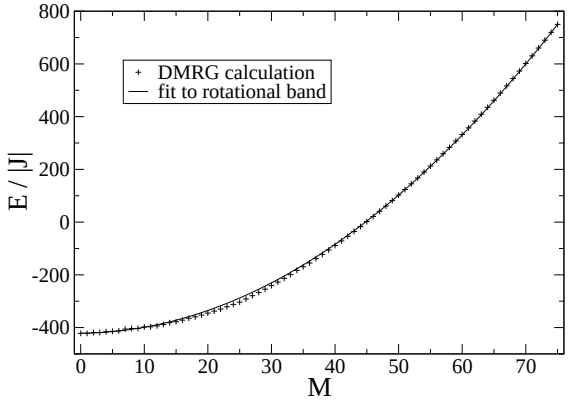


FIG. 6: DMRG eigenvalues and lowest rotational band of the $s = 5/2$ icosidodecahedron.

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 as shown in section III for a fictitious magnetic molecule of 30 spins $s = 1/2$ and icosidodecahedral structure. 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 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.

The present calculations were carried out keeping $m = 60$ block states, which means that the calculation time for one ground state is about a day on a standard PC, and there are 76 $\mathcal{H}(M)$ ground states ($M = 0, 1, \ldots, 75$) in $\{Mo_{72}Fe_{30}\}$. For a more accurate calculation one would have to use more powerful machines and more computer time both allowing higher values for $m$ and therefore leading to a better accuracy.

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* Electronic address: matexler@uos.de
† Electronic address: jschnack@uos.de

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