



Advanced quantum methods for the largest magnetic molecules

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ARTICLE INFO

Article history:

Available online 23 January 2013

Keywords:

Molecular magnetism
Finite Temperature Lanczos Method
Quantum Monte Carlo
DMRG

ABSTRACT

We discuss modern numerical methods for quantum spin systems and their application to magnetic molecules.

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1. Introduction

The knowledge of the energy eigenvalues and eigenstates of small magnetic systems such as magnetic molecules is indispensable for a complete understanding of their spectroscopic, dynamic, and thermodynamic properties. In this respect the numerical exact diagonalization of the appropriate quantum Hamiltonian is the method of choice. Nevertheless, such an attempt is very often severely restricted due to the huge dimension of the underlying Hilbert space. For a magnetic system of N spins of spin quantum number s the dimension is $(2s + 1)^N$ which grows exponentially with N .

Group theoretical methods can help to ease this numerical problem. Along these lines much effort has been put into the development of an efficient numerical diagonalization technique of the Heisenberg model

$$H_{\text{Heisenberg}} = -2 \sum_{i < j} J_{ij} \mathbf{s}(i) \cdot \mathbf{s}(j) \quad (1)$$

using irreducible tensor operators and thus employing SU(2) symmetry of angular momenta [1–6]. A combination of this meanwhile well established technique with point-group symmetries could be developed over the past years, first for those point-group symmetries that are compatible with the spin coupling scheme, i.e. avoid complicated basis transforms between different coupling schemes [7–10], later also for general point groups [11–13]. Nevertheless, if the dimension of the largest Hilbert subspace exceeds about 10^5 complete numerically exact diagonalization is no longer possible with current computers and programs.

Fortunately, a few very accurate approximations have been developed that can be applied to quantum spin systems. In this arti-

cle we are going to discuss the Finite Temperature Lanczos Method (FTLM), the Density Matrix Renormalization Group (DMRG) and its dynamical variant as well as Quantum Monte Carlo (QMC).

For problems with Hilbert space dimensions of up to roughly 10^{10} – the Finite Temperature Lanczos Method (FTLM) provides a very accurate and astonishingly easy to program method [14,15]. In recent publications we demonstrated that this method is indeed capable of evaluating thermodynamic observables for magnetic molecules with an accuracy that is nearly indistinguishable from exact results [16–18]. So far we encountered only one problem where achieving a satisfying accuracy posed a problem – the $\text{Fe}_{10}^{\text{III}}$ ferric wheel [19]. Mathematically this method relies on the idea of trace estimators [20]; it is not restricted to spin systems and for instance also applied in quantum chemistry [21,22].

The Density Matrix Renormalization Group (DMRG) method is a variational method that approximates the true eigenstates by so-called matrix-product states [23–26]. These states are iteratively constructed, thus the method allows to treat the full Heisenberg Hamiltonian but in a reduced Hilbert space. The Hilbert space is truncated in a controlled way and the accuracy of the method can be estimated with the help of a truncation error. In the field of molecular magnetism DMRG has been applied for instance to the Heisenberg icosidodecahedron with $s = 5/2$ [27,28], i.e. a model of the $\{\text{Mo}_{72}\text{Fe}_{30}\}$ Keplerate [29,30].

DMRG can be extended in order to evaluate transition matrix elements. This variant is called Dynamical DMRG (DDMRG); it aims at the calculation of dynamical correlation functions as needed for the description of Inelastic Neutron Scattering cross sections [31,32]. In a recent article we could show that DDMRG is able to model INS spectra of the very large magnetic ring molecule Fe_{18} with unprecedented accuracy and thus allows to determine model parameters which would be impossible using only observables such as susceptibility [33]. This extension is not discussed in this article.

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Finally we would like to provide examples for the application of Quantum Monte Carlo (QMC) [34–36] to magnetic molecules. This approximate method which works accurately only for non-frustrated quantum spin systems [37], has already been applied to several molecular systems by Engelhardt and Luban [38–41]. Larry Engelhardt also provides a very popular program – FIT-MART – with which one can deduce Heisenberg exchange parameters from susceptibility data [42].

Some of the discussed methods are freely available as program packages. Besides FIT-MART the program MAGPACK [43] can be used for complete diagonalization. Approximate methods such as DMRG and QMC are provided by the ALPS package [44–46].

The article is organized as follows. In Section 2 the Finite-Temperature Lanczos Method is introduced. Section 3 discusses the application of Quantum Monte Carlo, and Section 4 briefly introduces to the Density Matrix Renormalization Group.

2. Application of the Finite-Temperature Lanczos Method to giant gadolinium clusters

In a recent publication heterometallic cluster complexes $\{\text{Ln}_{12}\text{Mo}_4\}$ featuring a Ln_{12} core that has the structure of a distorted truncated tetrahedron, see Fig. 1, were reported [47]. The experimental magnetic studies of the $\{\text{Gd}_{12}\text{Mo}_4\}$ were accompanied on the theoretical side by calculations that replaced the Gd spin of $s = 7/2$ by fictitious spins $s = 5/2$ since otherwise the calculation would not have been feasible in a reasonable time (of several weeks [sic!]). Now, after a few months, the calculations using the Finite-Temperature Lanczos Method for $N = 12$ spins $s = 7/2$ are completed. Before presenting the results a short reminder of the method shall be given which in detail is explained elsewhere [14–16].

For the evaluation of thermodynamic properties in the canonical ensemble the exact partition function Z depending on temperature T and magnetic field B is given by

$$Z(T, B) = \sum_{|v\rangle} \langle v | e^{-\beta H} | v \rangle. \quad (2)$$

Here $\{|v\rangle\}$ denotes an orthonormal basis of the respective Hilbert space. Following the ideas of Refs. [14,15] the unknown matrix elements are approximated as

$$\langle v | e^{-\beta H} | v \rangle \approx \sum_{n=1}^{N_L} \langle v | n(v) \rangle e^{-\beta \epsilon_n^{(v)}} \langle n(v) | v \rangle, \quad (3)$$

which yields for the partition function

$$Z(T, B) \approx \frac{\dim(\mathcal{H})}{R} \sum_{v=1}^R \sum_{n=1}^{N_L} e^{-\beta \epsilon_n^{(v)}} |\langle n(v) | v \rangle|^2. \quad (4)$$

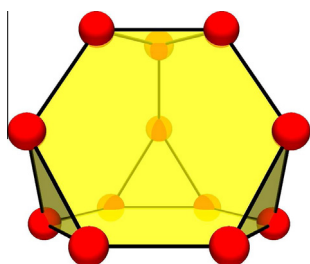


Fig. 1. The core structure of $\{\text{Gd}_{12}\text{Mo}_4\}$ is a truncated tetrahedron. The bullets represent the 12 spin sites and the edges correspond to the 18 exchange interactions between nearest-neighbor spins. The exchange inside the four triangles is named J_1 , between triangles J_2 .

For this procedure $|v\rangle$ is taken as the initial vector of a Lanczos iteration. This iteration consists of N_L Lanczos steps, which span a respective Krylow space, in which the Hamiltonian is diagonalized. This yields the N_L Lanczos eigenvectors $|n(v)\rangle$ as well as the associated Lanczos energy eigenvalues $\epsilon_n^{(v)}$. They are enumerated by $n = 1, \dots, N_L$. The number of Lanczos steps N_L is a parameter of the approximation; $N_L \approx 100$ is usually a good value. In addition, the complete and thus very large sum over all states $|v\rangle$ is replaced by a summation over a subset of R random vectors, where R is the second parameter of the method. For many cases R can be rather small, e.g. $R \approx 20$, whereas for other systems convergence is achieved only for $R \approx 100$. An observable would then be calculated as

$$O(T, B) \approx \frac{1}{Z(T, B)} \sum_{\Gamma} \frac{\dim(\mathcal{H}(\Gamma))}{R_{\Gamma}} \sum_{v=1}^{R_{\Gamma}} \sum_{n=1}^{N_L} e^{-\beta \epsilon_n^{(v, \Gamma)}} \times \langle n(v, \Gamma) | Q | v, \Gamma \rangle \langle v, \Gamma | n(v, \Gamma) \rangle. \quad (5)$$

Here Γ labels the irreducible representations of a symmetry group that can be used to split the Hilbert space into subspaces $\mathcal{H}(\Gamma)$ in order to increase the accuracy. In the following calculations we decomposed the Hilbert space according to the total magnetic quantum number M .

The magnetization of $\{\text{Gd}_{12}\text{Mo}_4\}$ was evaluated for four different parameter sets. Since the total dimension is a staggering $(2s+1)^N = 68,719,476,736$ and even the dimension of the largest Hilbert subspace with $M = 0$ is still 3,409,213,016, the calculations needed about a quarter of a year on a supercomputer. As Fig. 2 shows, the exchange interactions are antiferromagnetic and of the order of -0.05 K. Since they are so small, the experimental data, taken from [47], is not sufficient to disentangle between scenarios where the interactions J_1 between spins within triangles and J_2 between triangles are the same or different. A scenario where only interactions between triangles bind the spins into dimers can be excluded, but a scenario where the system would consist of uncoupled triangles cannot be excluded.

Fig. 3 displays the magnetocaloric behavior for a coupling scheme with $J_1 = J_2 = -0.05$ K. The l.h.s. shows a set of isentropes, i.e. curves which the system would follow when the magnetic field is reduced in an adiabatic process. The figure on the r.h.s. shows the isothermal entropy changes for field sweeps from $B = (1, 2, 7)$ T, respectively, to $B = 0$. The entropy differences are rather large at low temperature as expected for a weakly couple gadolinium system.

3. Quantum Monte Carlo

Quantum Monte Carlo (QMC) [34–36] is a very powerful method for non-frustrated, i.e. bipartite quantum spin systems. For a discussion of frustration see, e.g. [48]. The method can easily deal with up to 100 or more spins. In the field of molecule-based magnetism it is applied to several spin systems, e.g. homo- and heterometallic rings [38–41] as well as to a one-dimensional spin tube [49]. In the latter publication the heat capacity of a system of $N = 100$ spins with $s = 3/2$ was calculated with the help of QMC.

Again the idea is to approximate the partition function. This time the partition function is chopped (sliced) in the sense that the exponential is written as a product of m exponentials with exponents divided by m (Trotter–Suzuki decomposition [50–52]). For $m \rightarrow \infty$ the exponential can be written as a product of the exponentials of the (even non-commuting) parts of the Hamiltonian. One can as well linearize the exponential for large enough m . In any case, the multi-index sum is evaluated in a Monte-Carlo fashion as sketched in the equations below:

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