Large-scale simulations of the finite-temperature properties of the molecular assemblies Mn6 and Ni12

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Abstract

The numerical transfer-matrix approach and the exact diagonalization technique are worked out for the isotropic Heisenberg model with the uniform and alternating spin variables within the ring geometry. They are applied in large-scale simulations to the above cyclic organometallic clusters Mn6 (i.e. [Mn(hfac)2NITPh]6) and Ni12 (i.e. Ni12(O2CMe)12(chp)12(H2O)6(THF)6) in order to quantitatively model their magnetic properties. For the Ni12 complex new experimental data are also reported. The microscopic spin model parameters for both molecules are obtained from a fit of the theoretical curves to the experimental results. © 2002 Elsevier Science B.V. All rights reserved.

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The synthesis of polynuclear metal complexes with oxygen atom bridges has resulted in a series of new molecules with unusual geometric symmetries and patterns [1]. Their magnetic properties, associated with a large number of interacting paramagnetic centers in a single aggregate, have significantly stimulated the research effort with the prospect of theoretical and technological applications [2–4]. They set the low-size limit for magnetic nanoparticles, may display magnetic quantum tunneling [1] and quantum-size effects in the thermodynamic properties [5].

Molecular aggregates are complex organometallic systems difficult to approach by first-principle methods. The usual way to characterize molecular magnets is to model them in terms of spin Hamiltonians. However, characterization of the polynuclear magnetic clusters, even in terms of the spin models, remains a challenging task [6,7] and the role of numerical simulations is very important in this field [8]. Using our modeling approach and an effective parallelization technique, our simulations turn out time consuming and exceeded 104 CPU hours on supercomputing platforms Cray J90 and Cray T3E.

The aim of this paper is to improve the diagonalization technique and to adapt the quantum trans-
fer-matrix (QTM) technique so that the high
certainty rings as large as \([\text{Mn(hfac)}_2\text{NITPh}]_6\) and
\(\text{Ni}_{12}(\text{O}_2\text{CMe})_{12}(\text{chp})_{12}(\text{H}_2\text{O})_6(\text{THF})_6\) could be quantita-
tively characterized as far as their thermodynamic
properties are concerned. The complexes are referred
to as the supramolecular clusters \(\text{Mn}_6\) and \(\text{Ni}_{12}\). Their
common feature is the unusual spin \(S = 12\) ground
state, one of the highest spin multiplicity states ob-
served for molecular species [2–4]. They belong to the
intensively studied class of the cyclic clusters [9,10].

To characterize the finite-temperature properties
of \(\text{Mn}_6\) and \(\text{Ni}_{12}\), we consider the rings within the
framework of the isotropic spin model Hamiltonian
\[
\mathcal{H} = - \sum_{i=1}^{N} \left( J S_i \cdot S_{i+1} + g \mu_B B S_i^z \right),
\]
where \(J\) denotes the nearest-neighbor interaction con-
tant (positive for the ferromagnetic coupling), \(B\) is
the external magnetic field, \(g\) is the corresponding gy-
romagnetic ratio and \(N\) stands for the number of sites
in the ring \((N + 1 \to 1)\). The spin value \(S_i\) may be uni-
form or non-uniform. For the \(\text{Ni}_{12}\) molecule \(S = 1\) and
for the \(\text{Mn}_6\) cluster \(S = \frac{5}{2}\) for odd and \(S = \frac{5}{2}\) for even
site \(i\).

The advantages of the quantum transfer-matrix
(QTM) simulation method have been demonstrated for
the macroscopic Haldane-gap [11] and molecular-
based [12] magnetic chains. The results are not subject
to any statistical or systematic errors and the macro-
scopic limit can be directly evaluated from the largest
eigenvalue of the transfer matrix.

To outline the method for the non-uniform ring, we
express Hamiltonian (1) as a sum \(\sum_{i=1}^{N} \mathcal{H}_{i,i+1}\) of the
spin-pair operators \(\mathcal{H}_{i,i+1}\), where
\[
\mathcal{H}_{i,i+1} = - \left[ J S_i \cdot S_{i+1} + \frac{1}{2} g \mu_B B (S_i^z + S_{i+1}^z) \right].
\]

In the checker-board decomposition we divide the
Hamiltonian (1) into two non-commuting parts \(\mathcal{H} = \mathcal{H}^{\text{odd}} + \mathcal{H}^{\text{even}}\), each part defined by the commuting
spin-pair operators \(\mathcal{H}_{i,i+1}\). Then the series of the clas-
tsical approximants of the quantum thermal values can
be found, using the general Suzuki–Trotter formula. The
partition function \(Z\) is calculated from the approxi-

\[
Z_m = \text{Tr} \left[ \prod_{i=1}^{N/2} \mathcal{V}_{2i-1,2i} \prod_{i=1}^{N/2} \mathcal{V}_{2i,2i+1} \right]^m,
\]
in the limit \(m \to \infty\), where
\[
\mathcal{V}_{i,i+1} = e^{-\beta \mathcal{H}_{i,i+1}/m}, \quad i = 1, 2, \ldots, N.
\]

To perform the trace operation, we define a unitary
shift operator \(\mathcal{D}\)
\[
\mathcal{D} = \prod_{s_i^z \in \{1, -1\}} \sum_{s_i^z} |s_1^z \ldots s_N^z)^N/(s_1^z s_2^z \ldots s_N^z)\rangle,
\]
where \(s_i^z\) is the eigenvalue of the \(z\) component of
the spin operator \(S_i\). Using Eq. (3), we may express
operators \(\mathcal{V}_{i,i+1}\) \((i = 1, 2, \ldots, N)\) in terms of the
operators \(\mathcal{V}_{1,2}\) and \(\mathcal{V}_{2,3}\) so that the \(m\)th classical
approximant of the partition function amounts to
\[
Z_m = \text{Tr}(\mathcal{W}_1 \mathcal{W}_2)^m,
\]
where
\[
\mathcal{W}_i = (\mathcal{V}_{i,i+1}\mathcal{D}^+)^{N/2}, \quad i = 1, 2.
\]

The numerical implementation of (4) is based on
two global transfer operators \(\mathcal{W}_i\) \((i = 1, 2)\) expressed by
the sparse matrices defined by the operators \(\mathcal{V}_{i,i+1}\)
\((i = 1, 2)\). The thermodynamic functions are related to
the free energy \(F = -k_B T \ln Z\) and the zero-field
susceptibility is given as its second derivative with
respect to the field.

To accomplish the exact numerical diagonalization of
Hamiltonian (1) in the case of the uniform spin vari-
able \(S = 1\) and \(N = 12\) (appropriate for \(\text{Ni}_{12}\)), we pro-
do as follows. The Hilbert space of states of an \(N\)-site
ring is a direct product of single spin spaces, there-
fore the base states can be labeled by the \(N\)-tuple of
the eigenvalues of the \(z\) component of the single spin
operator \(|s_1^z \ldots s_N^z\rangle = |s_1^z\rangle \ldots |s_N^z\rangle\). The \(z\)-component
of the total spin \(S_z\) commutes with the Hamiltonian
\(\mathcal{H}\) and we can operate separately in subspaces char-
acterized by the eigenvalues \(S_z = \sum_{i=1}^{N} s_i^z\) of this
operator. In our case \(-N \leq S_z \leq N\) and the diagonaliza-
tion problem is factored into \(2N + 1\) smaller problems.

Both the Hamiltonian and the \(z\) component of the
total spin \(S_z\) are invariant with respect to the following
re-numbering of sites
\[
(1, 2, \ldots, N - 1, N) \to (2, 3, \ldots, N, 1) \to \cdots \to (N, 1, \ldots, N - 2, N - 1).
\]

This re-numbering can be represented by the shift
operator
\[
\mathcal{P} = \prod_{s_i^z \in \{1, -1\}} \sum_{s_i^z} |s_1^z \ldots s_N^z)^N/(s_1^z s_2^z \ldots s_N^z)\rangle,
\]
which is a unitary operator commuting with $\mathcal{H}$ and $S_z$. The eigenvalues of $\mathcal{P}$ are the $N$-order roots of 1 and the corresponding eigenvectors are complex linear combinations of base vectors. As the Hamiltonian elements between eigenvectors of $\mathcal{P}$ belonging to different eigenvalues are zero, the matrix representation of (1) in the large invariant subspace of $S_z$ can be further split into $N$ smaller blocks.

We consider the real symmetry operator $\mathcal{K} = \frac{1}{2}(\mathcal{P} + \mathcal{P}^\dagger)$, whose eigenvalues are $\lambda_k = \cos(2\pi k/N)$, where $k = 0, \ldots, [(N-1)/2]$. The invariant subspaces of $\mathcal{K}$ are sums of invariant subspaces of $\mathcal{P}$ belonging to conjugate eigenvalues, but they can be further split by including in our analysis one more symmetry operator $R$ (mirror reflection) corresponding to the following renumbering of sites

$$(1, 2, \ldots, N-1, N) \rightarrow (N, N-1, \ldots, 2, 1).$$

The operator $R$ commutes with $\mathcal{K}$ (although not with $\mathcal{P}$) and has eigenvalues $R = \pm 1$. Apart from the particular subspaces $k = 0$ and $k = N/2$ ($N$ even), where $\mathcal{K}$ and $\mathcal{P}$ coincide and $R$ decreases to the identity operator $I$ or $-I$, the mirror symmetry yields a further splitting of matrices into two blocks of equal dimensions. In this way, each subspace belonging to a given value of $S_z$, except $S_z = \pm N$ which are one-dimensional, is split in to exactly $N$ invariant orthogonal real subspaces classified according to $k$ and $R$. It turns out that the dimensions of subspaces belonging to the same value of $S_z$ are nearly (in some cases exactly) equal, which is the best one could hope for from the viewpoint of computational complexity. The largest invariant subspace corresponds to $S_z = 0$, $k = 1$ (and $R = 1$) and has a dimension of 6166. As a result, our procedure has led to matrices smaller than known before. The diagonalization task for matrices of that order is tractable on a supercomputer and the whole spectrum of the Hamiltonian can be ‘exactly’ calculated.

The calculation of the zero-field susceptibility is much simplified by the fact that it depends only on the zero-field energy eigenvalues.

$$T \chi_{\text{mol}} = R(g \mu_B / k_B)^2 \langle S_z^2 \rangle / \hbar \omega.$$  \hfill (5)

The QTM approach is applied to calculate the susceptibility of the Mn$_6$ molecule which can be considered as a ring consisting of $n = 6$ spin pairs $S_A = \frac{1}{2}$, $S_B = \frac{1}{2}$, where $n = N/2$. To save supercomputer time, for temperatures higher than $k_B T / J = 0.05$, we have performed our simulations only up to $n = 5$ pairs. Then we have extrapolated the estimates of the zero-field susceptibility to $n = 6$ which corresponds to Mn$_6$.

The measured susceptibility of Mn$_6$ [4] in terms of the correlation function $\langle S_z^2 \rangle$ given in Eq. (5) is drawn for the formula unit as a function of the reduced temperature $k_B T / J$ in Fig. 1 by small circles. Having fixed $g = 2$ due to the negligible spin-orbit coupling for Mn ions, the best fit has been found for the isotropic parameter $|J| / k_B = 350 \pm 10$ K which is consistent with the existing qualitative estimates [2,4]. In Fig. 1, our findings are plotted by the open circles with the error bars if they exceed the size of the symbol. Our ‘exact’ estimate obtained for $n = 6$ within extrapolations at $k_B T / J = 0.05$ is also depicted by the large full circle in Fig. 1.

To describe the magnetic behavior of Ni$_{12}$, we have fully diagonalized the isotropic Hamiltonian (1) for the spin value $S = 1$ and the number of sites $N = 12$, and we have supplemented the existing measurements of the effective magnetic moment [3] towards lower temperatures down to 1.6 K in an applied field of 0.098 T, using a Metronique Ingegnerie SQUID. We
Fig. 2. The behavior of the correlation function $\langle S_z^2 \rangle$ for the molecule Ni$_{12}$ as a function of the reduced temperature $k_B T / J$. The new experimental data are plotted by the open circles and the previous ones by the full circles. Our theoretical estimates are drawn by the full line.

plot these new results as the correlation function $\langle S_z^2 \rangle$ for the formula unit together with the former ones properly transformed [3] in Fig. 2, using the full and open circles, respectively. The curve drawn by the full line in Fig. 2 represents the best fit obtained for the following model parameters

$$J/k_B = 8.5 \pm 0.5 \text{ K}, \quad g = 2.23 \pm 0.01.$$  

The theoretical predictions very well interpolate the corresponding measured values.

As far as the two lowest levels are concerned, we have found that the ground state corresponds to $S = 12$ and is separated from the first excited 46-fold degenerated state by the distance $\Delta E = 0.2680$ in units of $J$ which amounts to 2.278 K. The highest energy value with reverse sign corresponds to the ground state energy of the antiferromagnetic model. Our results for $N \leq 8$ coincide with those quoted in Table 1 of Blöte [13]. Taking into account the terms with $N > 8$, our conservative estimate of the ground state energy of the macroscopic chain ($N \to \infty$) $2E_0/J = 2.804(3)$ is consistent with the corresponding value found by Blöte [13].

References