Magnetocaloric properties of magnetic molecules studied with the finite temperature Lanczos method

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Introduction

The very interesting magnetic properties of large (frustrated) magnetic molecules are often hardly accessible due to the prohibitive size of the related Hilbert spaces. The finite-temperature Lanczos method (FTLM) is able to treat spin systems for Hilbert space sizes of up to approximately 10^{10}. Here we first demonstrate for exactly solvable systems that the method is indeed accurate. Then we discuss the thermal properties of heterometallic gadolinium containing magnetic molecules.
Gadolinium containing compounds appear to be advantageous for magnetic refridgeration at very low temperatures since the Gd spin is very large ($s = 7/2$) and the exchange interaction rather weak. This means that one can sweep a large density of magnetic levels with moderate fields.

Finite-temperature Lanczos method

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

$$Z(T,B) = \sum_{\nu} \langle\, \nu \,|\, e^{-\beta \underset{\sim}{H}} \,|\, \nu \,\rangle \,. \qquad (1)$$

Here $\{\ |\nu\rangle\}$ denotes an orthonormal basis of the respective Hilbert space. Following the ideas of Refs. [1] the unknown matrix elements are approximated as

$$\langle\, \nu \,|\, e^{-\beta \underset{\sim}{H}} \,|\, \nu \,\rangle \approx \sum_{n=1}^{N_L} \langle\, \nu \,|\, n(\nu) \,\rangle e^{-\beta \epsilon_n^{(\nu)}} \langle\, n(\nu) \,|\, \nu \,\rangle \,, (2)$$

where $|\, n(\nu) \,\rangle$ is the n-th Lanczos eigenvector starting from $|\, \nu \,\rangle$ as the initial vector of a Lanczos iteration. $\epsilon_n^{(\nu)}$ denotes the associated n-th Lanczos energy eigenvalue. The number of Lanczos steps is chosen as N_L. In addition, the complete and thus very large sum over all states $|\, \nu \,\rangle$ is replaced by a summation over a subset of R random vectors. Altogether this yields for the partition function

$$Z(T,B) \approx \frac{\dim(\mathcal{H})}{R} \sum_{\nu=1}^{R} \sum_{n=1}^{N_L} e^{-\beta \epsilon_n^{(\nu)}} |\langle\, n(\nu) \,|\, \nu \,\rangle|^2 \,. (3)$$

Although this already sketches the general idea, it will always improve the accuracy if symmetries are taken into account as in the following formulation

$$Z(T,B) \approx \sum_{\Gamma} \frac{\dim(\mathcal{H}(\Gamma))}{R_\Gamma} \sum_{\nu=1}^{R_\Gamma} \sum_{n=1}^{N_L} \times e^{-\beta \epsilon_n^{(\nu,\Gamma)}} |\langle\, n(\nu,\Gamma) \,|\, \nu,\Gamma \,\rangle|^2 \,. \qquad (4)$$

Here Γ labels the irreducible representations of the employed symmetry group. The full Hilbert space is decomposed into mutually orthogonal subspaces $\mathcal{H}(\Gamma)$. An observable would then be calculated as

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

The quality of Eq. (5) can be improved by smmetrizing the last line.

Throughout this investigation the complete Hamiltonian of the spin system is given by the Heisenberg and the Zeeman term, i. e.

$$\underset{\sim}{H} = -2 \sum_{i<j} J_{ij} \vec{\underset{\sim}{s}}_i \cdot \vec{\underset{\sim}{s}}_j + g\,\mu_B\,B \sum_i \underset{\sim}{s}_i^z \,. \qquad (6)$$

J_{ij} is the antiferromagnetic exchange parameter between spins at sites i and j.

Accuracy of the method

Before using the finite-temperature Lanczos method for advanced calculations we investigate its accuracy by comparing to exactly known systems, in this case the antiferromagnetic cuboctahedron as well as the antiferromagnetic icosahedron with $s = 3/2$, i.e. Hilbert space dimension 16,777,216 [2, 3]

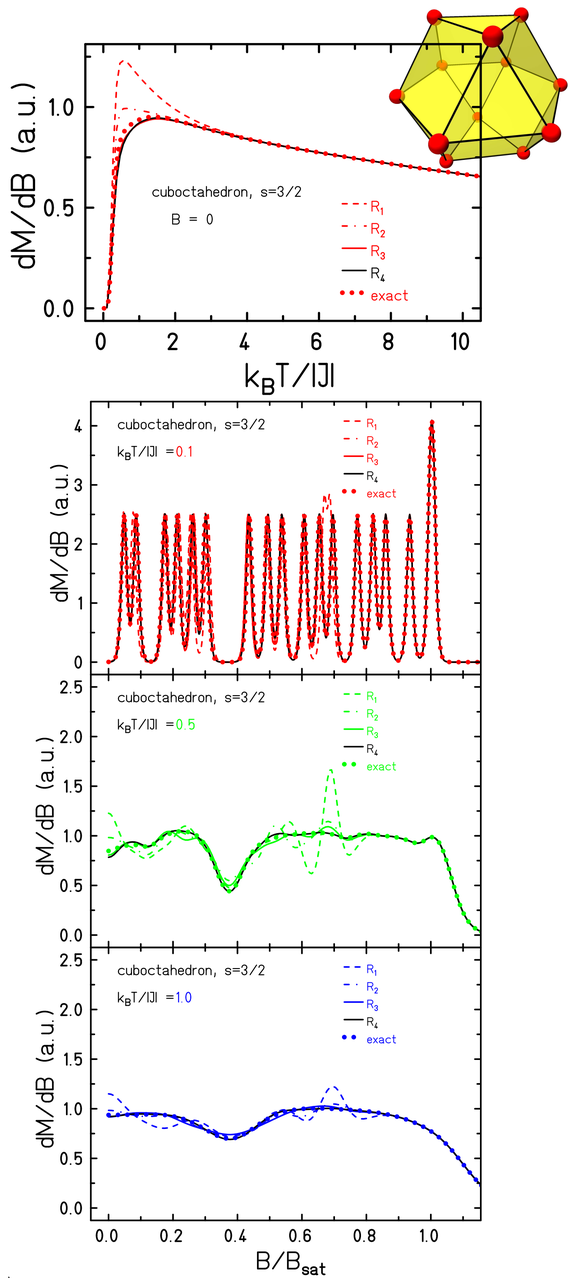

Figure 1 Cuboctahedron for $R_1 = 1, R_2 = 5, R_3 = 20, R_4 = 100$ and $N_L = 100$.

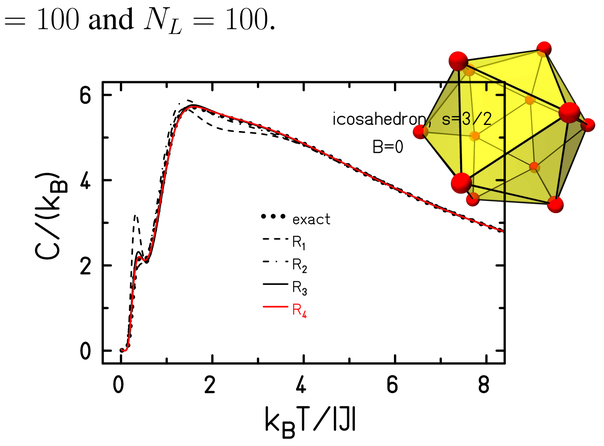

Figure 2 Icosahedron for $R_1 = 1, R_2 = 5, R_3 = 20, R_4 = 100$ and $N_L = 100$.

The very positive experience is that even for large problems the number of random starting vectors as well as the number of Lanczos steps can be chosen rather small, e.g. $R \approx 20, N_L \approx 100$.

Numerical details

We employ openMP parallelization. In order not to store the Hamiltonian matrix – not even the non-zero elements – we evaluate all matrix elements *on the fly*. For this purpose we developed an analytic coding of product basis states in subspaces $\mathcal{H}(M)$ [4]. The basis coding has been extended to mixed spin systems (Master's thesis of Chr. Heesing).
Calculations are done at the LRZ Garching as well as on a Bielefeld based 128 cores machine.

Gd_4M_8

Here we investigate a family of compounds with the chemical formula Gd_4M_8 [5].

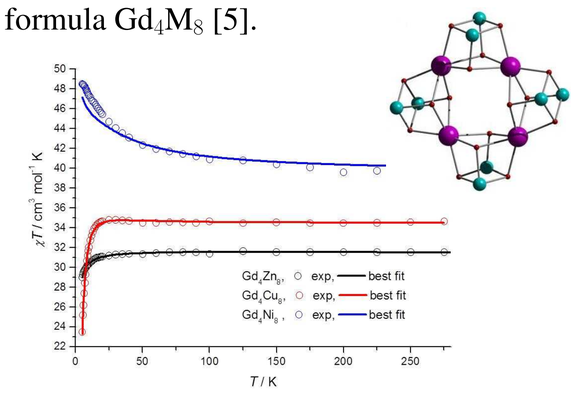

Figure 3 Susceptibility of various Gd_4M_8 compounds: experimental data are given by symbols, theoretical calculations by solid curves [5].

The magnetic observables of the Gd_4M_8 compounds have been evaluated by the FTLM with $R = 20$ and $N_L \approx 100$. The Hilbert space size of Gd_4Ni_8 is a moderate 26,873,856. Differences between theory and experiment stem from neglecting the single-ion anisotropy of the nickel ions as well as from assuming the same spectroscopic splitting factor $g = 2$ for all ions. Current developments aim at the extension of the FTLM towards anisotropic Hamiltonians and g-matrices with all the necessary extensions such as powder averaging (Ph.D. thesis of O. Wendland).

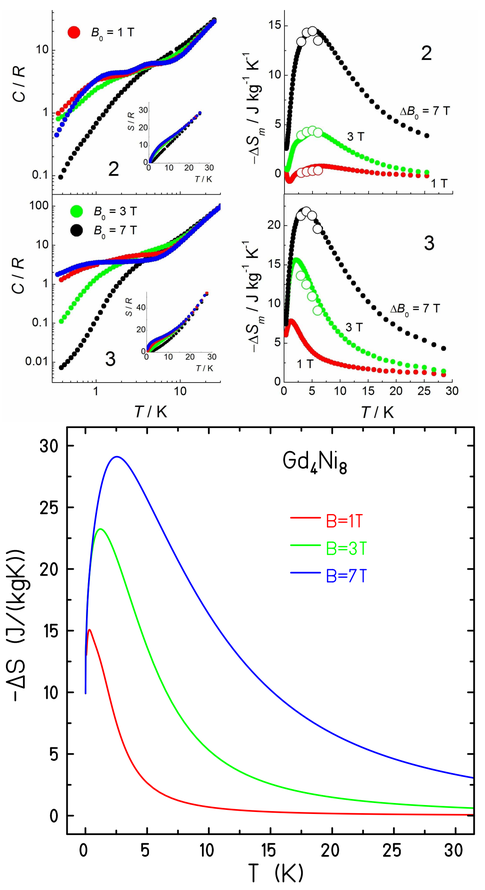

Figure 4 Experimental heat capacity (top left) and $S(T,B) - S(T,B=0)$ (top right) for Gd_4Cu_8 and Gd_4Ni_8 as well as theoretical entropy changes for Gd_4Ni_8 (bottom).

References

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