Advanced quantum methods for the largest magnetic molecules

Jürgen Schnack[a,*], Jörg Ummethum[a]

[a] *Dept. of Physics, Bielefeld University, P.O. box 100131, D-33501 Bielefeld, Germany*

Abstract

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

Keywords: Molecular Magnetism, DMRG, Frustration
PACS: 75.50.Xx, 75.10.Jm, 78.70.Nx

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

$$\underset{\sim}{H}_{\mathrm{Heisenberg}} = -2 \sum_{i<j} J_{ij}\, \underset{\sim}{\mathbf{s}}(i) \cdot \underset{\sim}{\mathbf{s}}(j) \tag{1}$$

using irreducible tensor operators and thus employing SU(2) symmetry of angular momenta [1, 2, 3, 4, 5, 6]. A combination of this meanwhile well established technique with point-group symmetries could be developed over the

*corresponding author
Email address: jschnack@uni-bielefeld.de (Jürgen Schnack)

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, 8, 9, 10], later also for general point groups [11, 12, 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 article 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, 17, 18]. So far we encountered only one problem where achieving a satisfying accuracy posed a problem – the Fe^{III}_{10} ferric wheel [19]. Mathematically this methods 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, 24, 25, 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 $Mo_{72}Fe_{30}$ 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.

Finally we would like to provide examples for the application of Quantum Monte Carlo (QMC) [34, 35, 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 Larry Engelhardt [38, 39, 40, 41]. He 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, 45, 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

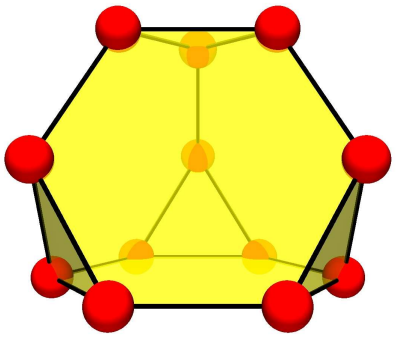

Figure 1: The core structure of $\{Gd_{12}Mo_4\}$ is a truncated tetrahedron. The bullets represent the 12 spin sites and the edges correspond to the 18 exchange interactions between nearest-neighbor spins. The exchange inside the four triangles is named J_1, between triangles J_2.

In a recent publication heterometallic cluster complexes $\{Ln_{12}Mo_4\}$ 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 $\{Gd_{12}Mo_4\}$ 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, 15, 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

$$Z(T,B) \;=\; \sum_{\nu} \langle\, \nu \,|\, e^{-\beta \underset{\sim}{H}} \,|\, \nu \,\rangle \;. \tag{2}$$

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

$$\langle\, \nu \,|\, e^{-\beta \underset{\sim}{H}} \,|\, \nu \,\rangle \;\approx\; \sum_{n=1}^{N_L} \langle\, \nu \,|\, n(\nu) \,\rangle e^{-\beta \epsilon_n^{(\nu)}} \langle\, n(\nu) \,|\, \nu \,\rangle \;, \tag{3}$$

which yields for the partition function

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

For this procedure $|\,\nu\,\rangle$ 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 $|\,n(\nu)\,\rangle$ as well as the associated Lanczos energy eigenvalues $\epsilon_n^{(\nu)}$. They are enumerated by $n = 1, \ldots, N_L$. 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 $|\,\nu\,\rangle$ 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

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

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.

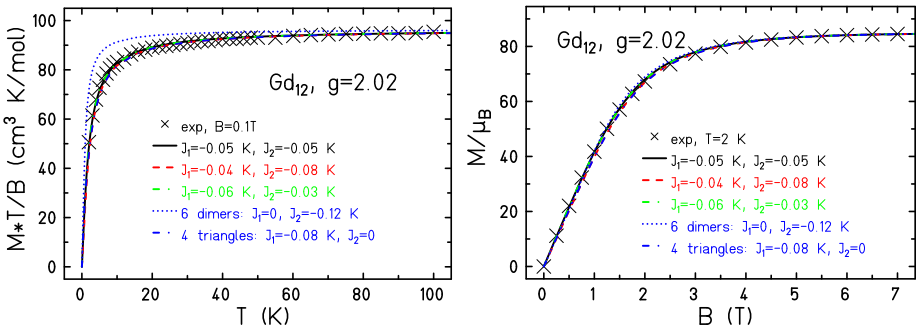

Figure 2: Magnetization of $\{Gd_{12}Mo_4\}$ as function of temperature (l.h.s.) as well as of applied magnetic field (r.h.s.). The experimental data [47] are given as symbols, the theoretical calculations as curves.

The magnetization of $\{Gd_{12}Mo_4\}$ 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.

Figure 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.

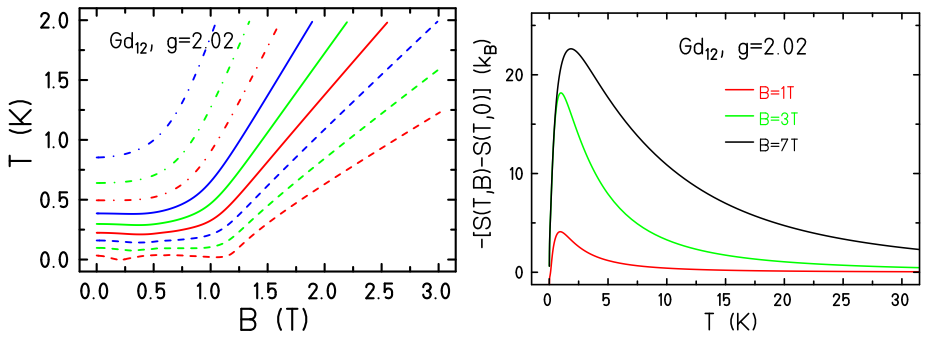

Figure 3: Theoretical magnetic isentropes $\{Gd_{12}Mo_4\}$ as function of temperature and field (l.h.s.) and isothermal entropy change for various starting fields (r.h.s.). The chosen parameters are $J_1 = J_2 = -0.05$ K.

3. Quantum Monte Carlo

Quantum Monte Carlo (QMC) [34, 35, 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 is was applied to several spin systems, e.g. homo- and heterometallic rings [38, 39, 40, 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, 51, 52]). For $m \to \infty$ 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:

$$\begin{aligned} Z(T,B) &= \sum_{\nu} \langle\, \nu \,|\, e^{-\beta \underset{\sim}{H}} \,|\, \nu \,\rangle = \sum_{\nu} \langle\, \nu \,|\, \left[\exp\left\{-\beta \underset{\sim}{H}/m\right\}\right]^m \,|\, \nu \,\rangle \qquad (6) \\ &= \sum_{\nu,\alpha,\gamma,\ldots} \langle\, \nu \,|\, \exp\left\{-\beta \underset{\sim}{H}/m\right\} \,|\, \alpha \,\rangle\langle\, \alpha \,|\, \exp\left\{-\beta \underset{\sim}{H}/m\right\} \,|\, \gamma \,\rangle\langle\, \gamma \,|\, \cdots \\ &\approx \sum_{\nu,\alpha,\gamma,\ldots} \langle\, \nu \,|\, \left\{1 - \beta \underset{\sim}{H}/m\right\} \,|\, \alpha \,\rangle\langle\, \alpha \,|\, \cdots \ . \end{aligned}$$

As an example the magnetic susceptibility of the ten-membered ferric wheel, which was synthesized 18 years ago [53], is presented in Fig. 4. The symbols mark the experimental values [53], the solid curve shows the result of exact diagonalization [13], and the dotted curve shows the result obtained with ALPS QMC using 10^7 steps for equilibration and 10^{10} steps for the Monte-Carlo sampling for each temperature. As one can see the QMC result is indistinguishable from the exact one.

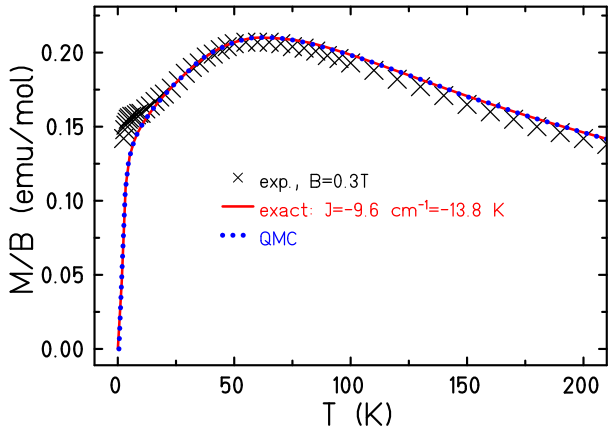

Figure 4: Susceptibility of an antiferromagnetically coupled spin ring with $N = 10$ and $s = 5/2$. The exchange parameter $J = -9.6$ cm^{-1} as well as the susceptibility data are taken from Ref. [53]. The solid curve displays the result of complete matrix diagonalization [13] whereas the dotted curve depicts the QMC result.

4. DMRG results

DMRG is a technically rather involved method. One should however keep in mind that it is a variational method that constructs trial states in a certain way. Being variational means that a lower energy for the trial ground state corresponds to having obtained a better approximation since the energy is bounded from below by the true value (Ritz's variational principle). A maybe helpful (mis-) conception of the idea of the method could be the following: Assume that you want to describe an eight-membered spin chain as depicted in Fig. 5. One starts with a small subsystem of two spins, diagonalizes the Hamiltonian and keeps only the lowest m eigenstates. Then one adds spins sequentially and every time sets up a new basis built of the old kept states and the states representing the added spin, diagonalizes the Hamiltonian and

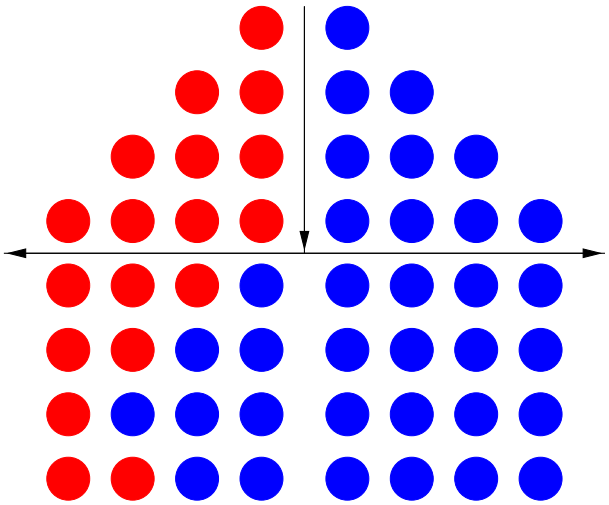

Figure 5: Scheme of DMRG: first the system is iteratively enlarged up to its full size, then a sweep algorithm improves the accuracy further.

again keeps the lowest m states. This idea is brilliant (and called Numerical Renormalization Group), except that it does not work in this naive fashion. Steve White found out, that instead of keeping the lowest m eigenstates of the Hamiltonian it is much better to keep m eigenstates of a reduced density matrix in order to iteratively built up the system and to represent the Hamiltonian [23]. The density matrix is given by the target state, e.g. the ground state $|\,\Psi\,\rangle$, as $\rho = |\,\Psi\,\rangle\langle\,\Psi\,|$ and to reduce it means to trace over a part of the system, i.e. one of the colored parts in Fig. 5. The representation can be further improved by running a so-called sweep algorithm in which the system is subdivided into unequal blocks for which the Hamiltonian is diagonalized and the density matrix calculated.

For the non-expert this seems to be rather obscure, but contrary to several other methods, DMRG is (1) variational, (2) a controlled approximation, i.e. with $m \to \infty$ one approaches the exact result, and (3) offers accuracy estimators in the form of the truncated weight or the entanglement entropy. An extrapolation to the exact result is thus possible by using these measures. Although DMRG is best suited for open one-dimensional chain systems it can be applied to finite-size clusters, too. The resulting convergence, which is exponential in m for one-dimensional chains, is somewhat slower, e.g. like $1/m$ for a spin cluster such as the icosidodecahedron [27].

Here we would like to demonstrate the power of the method by showing

theoretical magnetization curves for another ferric wheel, this time an Fe_{18} ring of $N = 18$ spins with $s = 5/2$ [54]. The dimension of the Hilbert space for this system is about 10^{14} which again renders an exact treatment impossible. The molecule was investigated by means of DMRG and DDMRG [33], the later results were compared to INS data and utilized to fix the parameters of the model.

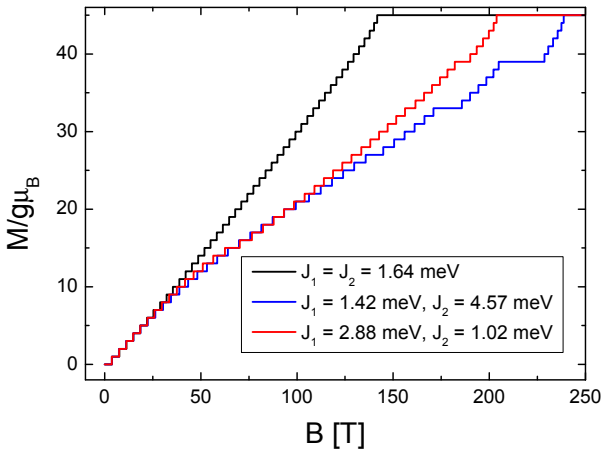

Figure 6: Comparison of the zero-temperature magnetization curves for three different parameter sets as obtained by standard DMRG calculations for the $N = 18$, $s = 5/2$ spin ring. We have kept up to 3000 density matrix eigenstates for the $J_1 = J_2$ model and up to 1200 for the $J_1 \neq J_2$ models. The truncated weights are smaller than 10^{-8}.

In Fig. 6 we present the ($T = 0$) magnetization curves for the three parameterizations discussed in [33]. The results are very interesting. The magnetization curves are virtually identical up to 25 Tesla. The step widths of the magnetization curve for a C_{18}-symmetric ring (single J) are approximately the same for all steps (apart from the very last steps), as would also be the case for the rotational band approximation [55]. The magnetization curves for the other two models (C_6-symmetric: J_1–J_1–J_2) deviate from this behavior. Up to approximately 100 T, the two models with $J_1 \neq J_2$ give very similar magnetization curves and considerable differences appear only at even higher fields. The magnetization curve for $J_1 = 1.42$ meV and $J_2 = 4.57$ meV shows two magnetization plateaus at higher fields. Plateaus in zero-temperature magnetization curves usually emerge in geometrically frustrated spin systems [56]. This system is, however, not geometrically frustrated so that the emergence of a plateau is an interesting effect.

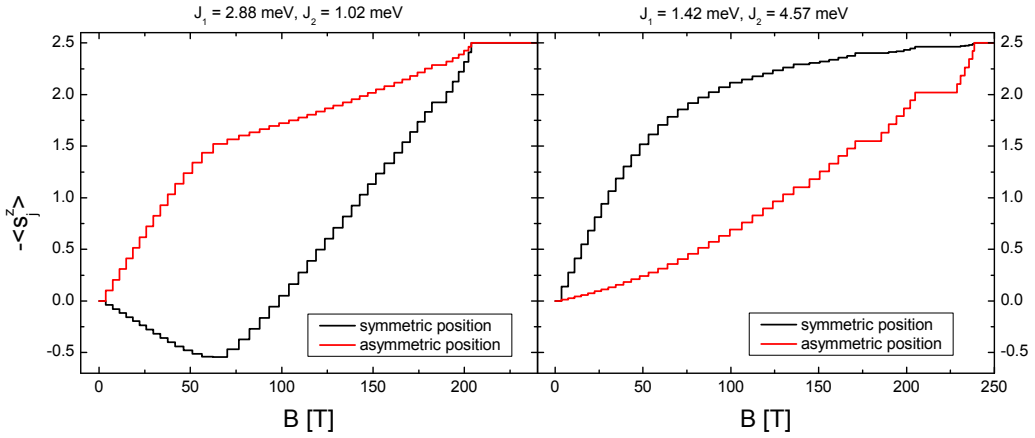

Figure 7: Dependence of the z-component of the local magnetization (which is proportional to $-\langle s_j^z \rangle$) for two different parameter sets as a function of an external magnetic field $\vec{B} = B\vec{e}_z$. The results were obtained using standard DMRG and $T = 0$. The result for the uniform model is not shown because for this model the local moments are simply proportional to the magnetization curve presented in Fig. 6. "Symmetric position" denotes the local magnetization for a spin between two J_1 couplings. Accordingly, "asymmetric position" denotes a spin position between a J_1 and a J_2 coupling.

We have also calculated the local magnetizations for the two models with $J_1 \neq J_2$. Local moments can, e.g., be probed with NMR [57, 58] or XMCD [59]. The local magnetizations for the $J_1 = J_2$ model would simply be proportional to the total magnetization curve. The results are shown in Fig. 7. The calculation demonstrates that the local magnetization of an interacting spin system can deviate substantially from the average and even point into the opposite direction.

Acknowledgment

This work was supported by the German Science Foundation (DFG) through the research group 945. Computing time at the Leibniz Computing Center in Garching is also gratefully acknowledged. Last but not least we like to thank the State of North Rhine-Westphalia and the DFG for financing our local SMP supercomputer as well as the companies BULL and ScaleMP for their support.

References

[1] D. Gatteschi, L. Pardi, Magnetic-properties of high-nuclearity spin clusters - a fast and efficient procedure for the calculation of the energy-levels, Gazz. Chim. Ital. 123 (1993) 231–240.

[2] J. J. Borras-Almenar, J. M. Clemente-Juan, E. Coronado, B. S. Tsukerblat, High-nuclearity magnetic clusters: Generalized spin Hamiltonian and its use for the calculation of the energy levels, bulk magnetic properties, and inelastic neutron scattering spectra, Inorg. Chem. 38 (1999) 6081–6088.

[3] A. Bencini, D. Gatteschi, Electron paramagnetic resonance of exchange coupled systems, Springer, Berlin, Heidelberg, 1990.

[4] B. S. Tsukerblat, Group theory in chemistry and spectroscopy: a simple guide to advanced usage, Dover Publications, Mineola, New York, 2nd edn., 2006.

[5] B. Tsukerblat, Group-theoretical approaches in molecular magnetism: Metal clusters, Inorg. Chim. Acta 361 (2008) 3746–3760.

[6] A. S. Boyarchenkov, I. G. Bostrem, A. S. Ovchinnikov, Quantum magnetization plateau and sign change of the magnetocaloric effect in a ferrimagnetic spin chain., Phys. Rev. B 76 (2007) 224410, doi: 10.1103/PhysRevB.76.224410.

[7] C. Delfs, D. Gatteschi, L. Pardi, R. Sessoli, K. Wieghardt, D. Hanke, Magnetic properties of an octanuclear iron(III) cation, Inorg. Chem. 32 (1993) 3099–3103, doi:10.1021/ic00066a022.

[8] O. Waldmann, Symmetry and energy spectrum of high-nuclearity spin clusters, Phys. Rev. B 61 (2000) 6138.

[9] I. G. Bostrem, A. S. Ovchinnikov, V. E. Sinitsyn, The method of exact diagonalization preserving the total spin and taking the point symmetry of the two-dimensional isotropic Heisenberg magnet into account, Theor. Math. Phys. 149 (2006) 1527–1544.

[10] V. E. Sinitsyn, I. G. Bostrem, A. S. Ovchinnikov, Symmetry adapted finite-cluster solver for quantum Heisenberg model in two dimensions: a

real-space renormalization approach, J. Phys. A-Math. Theor. 40 (2007) 645–668.

[11] R. Schnalle, J. Schnack, Numerically exact and approximate determination of energy eigenvalues for antiferromagnetic molecules using irreducible tensor operators and general point-group symmetries, Phys. Rev. B 79 (2009) 104419, doi:10.1103/PhysRevB.79.104419.

[12] J. Schnack, R. Schnalle, Frustration effects in antiferromagnetic molecules: the cuboctahedron, Polyhedron 28 (2009) 1620–1623, doi:10.1016/j.poly.2008.10.017.

[13] R. Schnalle, J. Schnack, Calculating the energy spectra of magnetic molecules: application of real- and spin-space symmetries, Int. Rev. Phys. Chem. 29 (2010) 403–452, doi:10.1080/0144235X.2010.485755.

[14] J. Jaklic, P. Prelovsek, Lanczos method for the calculation of finite-temperature quantities in correlated systems, Phys. Rev. B 49 (1994) 5065–5068, doi:10.1103/PhysRevB.49.5065.

[15] J. Jaklic, P. Prelovsek, Finite-temperature properties of doped antiferromagnets, Adv. Phys. 49 (2000) 1–92.

[16] J. Schnack, O. Wendland, Properties of highly frustrated magnetic molecules studied by the finite-temperature Lanczos method, Eur. Phys. J. B 78 (2010) 535–541, doi:10.1007/BF01609348.

[17] K. Graham, F. J. Douglas, J. S. Mathieson, S. A. Moggach, J. Schnack, M. Murrie, Cubic assembly of a geometrically frustrated Fe12 spin cluster, Dalton Trans. (2011) –doi:10.1039/C1DT10910C, URL `http://dx.doi.org/10.1039/C1DT10910C`.

[18] T. N. Hooper, J. Schnack, S. Piligkos, M. Evangelisti, E. K. Brechin, The Importance of Being Exchanged: $[Gd_4^{III}M_8^{II}(OH)_8(L)_8(O_2CR)_8]^{4+}$ Clusters for Magnetic Refrigeration, Angew. Chem. Int. Ed. 51 (2012) 4633–4636, doi:10.1002/anie.201200072.

[19] E. Garlatti, private communication, 2012.

[20] M. Hutchinson, A Stochastic Estimator of the Trace of the Influence Matrix for Laplacian Smoothing Splines, Communications in Statistics - Simulation and Computation 18 (3) (1989) 1059–1076, doi: 10.1080/03610918908812806.

[21] U. Manthe, F. Huarte-Larranaga, Partition functions for reaction rate calculations: statistical sampling and MCTDH propagation, Chem. Phys. Lett. 349 (2001) 321 – 328, doi:10.1016/S0009-2614(01)01207-6.

[22] F. Huarte-Larranaga, U. Manthe, Vibrational excitation in the transition state: The $CH_4 + H \rightarrow CH_3 + H_2$ reaction rate constant in an extended temperature interval, J. Chem. Phys. 116 (2002) 2863–2869, doi:10.1063/1.1436307.

[23] S. R. White, Density matrix formulation for quantum renormalization groups, Phys. Rev. Lett. 69 (19) (1992) 2863–2866, doi: 10.1103/PhysRevLett.69.2863.

[24] S. R. White, Density-matrix algorithms for quantum renormalization groups, Phys. Rev. B 48 (1993) 10345.

[25] S. R. White, D. Huse, Numerical renormalization-group study of low-lying eigenstates of the antiferromagnetic $s = 1$ Heisenberg chain, Phys. Rev. B 48 (1993) 3844.

[26] U. Schollwöck, The density-matrix renormalization group, Rev. Mod. Phys. 77 (2005) 259–315.

[27] M. Exler, J. Schnack, Evaluation of the low-lying energy spectrum of magnetic Keplerate molecules using the density-matrix renormalization group technique, Phys. Rev. B 67 (2003) 094440, doi: 10.1103/PhysRevB.67.094440.

[28] J. Ummethum, J. Schnack, A. Laeuchli, Large-scale numerical investigations of the antiferromagnetic Heisenberg icosidodecahedron, J. Magn. Magn. Mater. 327 (2013) 103 – 109, doi:10.1016/j.jmmm.2012.09.037.

[29] A. Müller, S. Sarkar, S. Q. N. Shah, H. Bögge, M. Schmidtmann, S. Sarkar, P. Kögerler, B. Hauptfleisch, A. Trautwein, V. Schünemann, Archimedean synthesis and magic numbers: "Sizing"

giant molybdenum-oxide-based molecular spheres of the Keplerate type, Angew. Chem. Int. Ed. 38 (1999) 3238.

[30] A. Müller, M. Luban, C. Schröder, R. Modler, P. Kögerler, M. Axenovich, J. Schnack, P. C. Canfield, S. Bud'ko, N. Harrison, Classical and quantum magnetism in giant Keplerate magnetic molecules, Chem. Phys. Chem. 2 (2001) 517, doi:10.1002/1439-7641(20010917)2:8/9¡517::AID-CPHC517¿3.0.CO;2-1.

[31] T. D. Kühner, S. R. White, Dynamical correlation functions using the density matrix renormalization group, Phys. Rev. B 60 (1999) 335–343, doi:10.1103/PhysRevB.60.335.

[32] E. Jeckelmann, Dynamical density-matrix renormalization-group method, Phys. Rev. B 66 (2002) 045114, doi:10.1103/PhysRevB.66.045114.

[33] J. Ummethum, J. Nehrkorn, S. Mukherjee, N. B. Ivanov, S. Stuiber, T. Strässle, P. L. W. Tregenna-Piggott, H. Mutka, G. Christou, O. Waldmann, J. Schnack, Discrete antiferromagnetic spin-wave excitations in the giant ferric wheel Fe_{18}, Phys. Rev. B 86 (2012) 104403, doi:10.1103/PhysRevB.86.104403.

[34] A. W. Sandvik, J. Kurkijärvi, Quantum Monte Carlo simulation method for spin systems, Phys. Rev. B 43 (1991) 5950–5961, doi:10.1103/PhysRevB.43.5950.

[35] A. W. Sandvik, Stochastic series expansion method with operator-loop update, Phys. Rev. B 59 (1999) R14157–R14160, doi:10.1103/PhysRevB.59.R14157.

[36] A. W. Sandvik, Computational Studies of Quantum Spin Systems, AIP Conf. Proc. 1297 (2010) 135–338, doi:10.1063/1.3518900.

[37] P. Henelius, A. W. Sandvik, Sign problem in Monte Carlo simulations of frustrated quantum spin systems, Phys. Rev. B 62 (2000) 1102–1113.

[38] L. Engelhardt, M. Luban, Low temperature magnetization and the excitation spectrum of antiferromagnetic Heisenberg spin rings, Phys. Rev. B 73 (2006) 054430.

[39] L. P. Engelhardt, C. A. Muryn, R. G. Pritchard, G. A. Timco, F. Tuna, R. E. P. Winpenny, Octa-, deca-, trideca-, and tetradecanuclear heterometallic cyclic chromium-copper cages, Angew. Chem. Int. Edit. 47 (2008) 924–927.

[40] L. Engelhardt, C. Martin, R. Prozorov, M. Luban, G. A. Timco, R. E. P. Winpenny, High-field magnetic properties of the magnetic molecule Cr[sub 10]Cu[sub 2], Phys. Rev. B 79 014404, doi: 10.1103/PhysRevB.79.014404.

[41] A. M. Todea, A. Merca, H. Bögge, T. Glaser, L. Engelhardt, R. Prozorov, M. Luban, A. Müller, Polyoxotungstates now also with pentagonal units: supramolecular chemistry and tuning of magnetic exchange in (M)M512V30 Keplerates (M = Mo, W), Chem. Commun. (2009) 3351–3353doi:10.1039/B907188A.

[42] L. Engelhardt, C. Rainey, Tool for Magnetic Analysis Package, 2010.

[43] J. J. Borras-Almenar, J. M. Clemente-Juan, E. Coronado, B. S. Tsukerblat, MAGPACK$_1$ A package to calculate the energy levels, bulk magnetic properties, and inelastic neutron scattering spectra of high nuclearity spin clusters, J. Comp. Chem. 22 (2001) 985–991, doi: 10.1002/jcc.1059.

[44] A. Albuquerque, F. Alet, P. Corboz, P. Dayal, A. Feiguin, S. Fuchs, L. Gamper, E. Gull, S. Gürtler, A. Honecker, R. Igarashi, M. Körner, A. Kozhevnikov, A. Läuchli, S. Manmana, M. Matsumoto, I. McCulloch, F. Michel, R. Noack, G. Pawlowski, L. Pollet, T. Pruschke, U. Schollwöck, S. Todo, S. Trebst, M. Troyer, P. Werner, S. Wessel, The ALPS project release 1.3: Open-source software for strongly correlated systems, J. Magn. Magn. Mater. 310 (2007) 1187 – 1193, doi:DOI: 10.1016/j.jmmm.2006.10.304.

[45] L. Pollet, S. M. A. Rombouts, K. Van Houcke, K. Heyde, Optimal Monte Carlo updating, Phys. Rev. E 70 (2004) 056705, doi: 10.1103/PhysRevE.70.056705.

[46] F. Alet, S. Wessel, M. Troyer, Generalized directed loop method for quantum Monte Carlo simulations, Phys. Rev. E 71 (2005) 036706, doi: 10.1103/PhysRevE.71.036706.

[47] Y. Zheng, Q.-C. Zhang, L.-S. Long, R.-B. Huang, A. Müller, J. Schnack, L.-S. Zheng, Z. Zheng, Molybdate templated assembly of $Ln_{12}Mo_4$-type clusters (Ln = Sm, Eu, Gd) containing a truncated tetrahedron core, Chem. Commun. 49 (2013) 36–38, doi:10.1039/C2CC36530H.

[48] J. Schnack, Effects of frustration on magnetic molecules: a survey from Olivier Kahn until today, Dalton Trans. 39 (2010) 4677 – 4686, doi:10.1039/B925358K.

[49] N. B. Ivanov, J. Schnack, R. Schnalle, J. Richter, P. Kögerler, G. N. Newton, L. Cronin, Y. Oshima, H. Nojiri, Heat Capacity Reveals the Physics of a Frustrated Spin Tube, Phys. Rev. Lett. 105 (2010) 037206, doi:10.1103/PhysRevLett.105.037206.

[50] H. F. Trotter, On the product of semi-groups of operators, Proc. Amer. Math. Soc. 10 (1959) 545–551, doi:10.1090/S0002-9939-1959-0108732-6.

[51] M. Suzuki, Generalized Trotter's formula and systematic approximants of exponential operators and inner derivations with applications to many-body problems, Commun. Math. Phys. 51 (1976) 183–190, doi:10.1007/BF01609348.

[52] M. Suzuki, On the convergence of exponential operators – the Zassenhaus formula, BCH formula and systematic approximants, Commun. Math. Phys. 57 (1977) 193–200, doi:10.1007/BF01614161.

[53] K. L. Taft, C. D. Delfs, G. C. Papaefthymiou, S. Foner, D. Gatteschi, S. J. Lippard, $[Fe(OMe)_2(O_2CCH_2Cl)]_{10}$, a molecular ferric wheel, J. Am. Chem. Soc. 116 (1994) 823.

[54] P. King, T. C. Stamatatos, K. A. Abboud, G. Christou, Reversible Size Modification of Iron and Gallium Molecular Wheels: A Ga_{10} Gallic Wheel and Large Ga_{18} and Fe_{18} Wheels, Angew. Chem. Int. Ed. 45 (44) (2006) 7379–7383.

[55] J. Schnack, M. Luban, Rotational modes in molecular magnets with antiferromagnetic Heisenberg exchange, Phys. Rev. B 63 (2000) 014418, doi:10.1103/PhysRevB.63.014418.

[56] A. Honecker, J. Schulenburg, J. Richter, Magnetization plateaus in frustrated antiferromagnetic quantum spin models, J. Phys.: Condens. Matter 16 (2004) S749.

[57] E. Micotti, Y. Furukawa, K. Kumagai, S. Carretta, A. Lascialfari, F. Borsa, G. A. Timco, R. E. P. Winpenny, Local spin moment distribution in antiferromagnetic molecular rings probed by NMR, Phys. Rev. Lett. 97 (2006) 267204, URL http://dx.doi.org/10.1103/PhysRevLett.97.267204.

[58] Y. Furukawa, Y. Nishisaka, K.-i. Kumagai, P. Kögerler, F. Borsa, Local spin moment configuration in the frustrated $s = 1/2$ Heisenberg triangular antiferromagnet V15 determined by NMR, Phys. Rev. B 75 (2007) 220402, doi:10.1103/PhysRevB.75.220402.

[59] M. Prinz, K. Kuepper, C. Taubitz, M. Raekers, B. Biswas, T. Weyhermüller, M. Uhlarz, J. Wosnitza, J. Schnack, A. V. Postnikov, C. Schröder, S. J. George, M. Neumann, , P. Chaudhuri, A Star-Shaped Heteronuclear $Cr^{III}Mn^{II}_3$ Species and Its Precise Electronic and Magnetic Structure: Spin Frustration Studied by X-Ray Spectroscopic, Magnetic, and Theoretical Methods, Inorg. Chem. 49 (2010) 2093–2102, doi:10.1021/ic9012119.