Advanced quantum methods for the largest magnetic molecules

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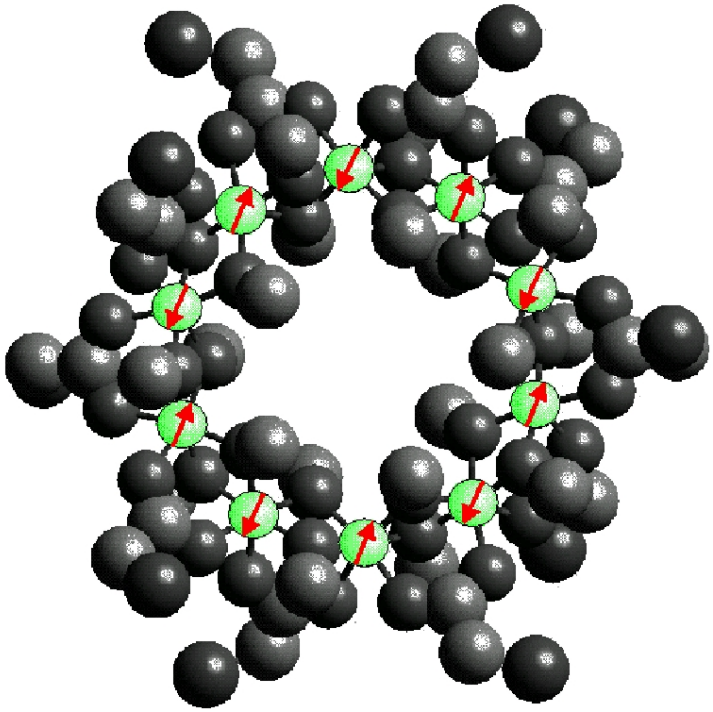
Institute for Materials Research, Tohoku University

The problem

You have got a molecule!

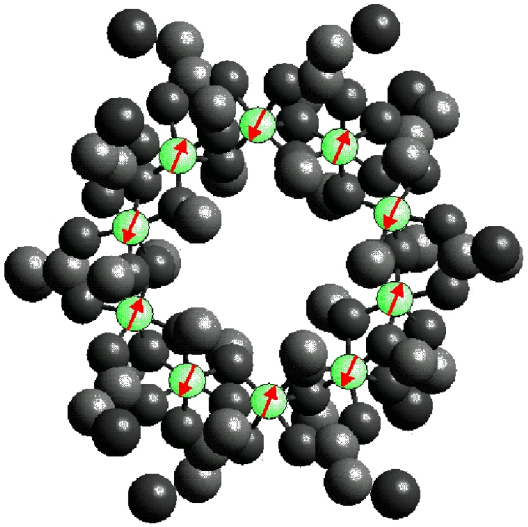


Congratulations!

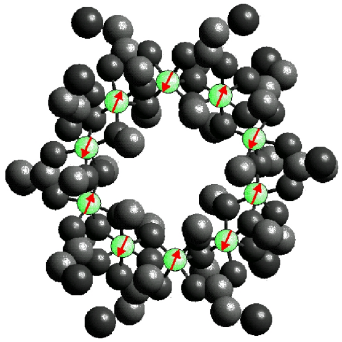
You have got an idea about the modeling!

$$\underset{\sim}{H} = -2\sum_{i<j} J_{ij}\,\underset{\sim}{\vec{s}}(i)\cdot\underset{\sim}{\vec{s}}(j) + g\,\mu_B\,B\sum_{i}^{N}\underset{\sim}{s}_z(i)$$

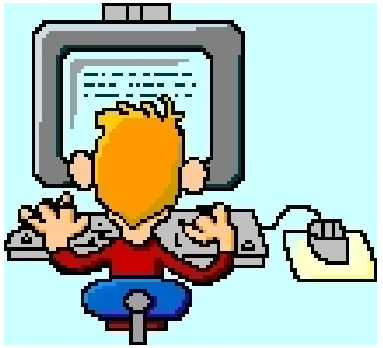
Heisenberg Zeeman



In the end it's always a big matrix!



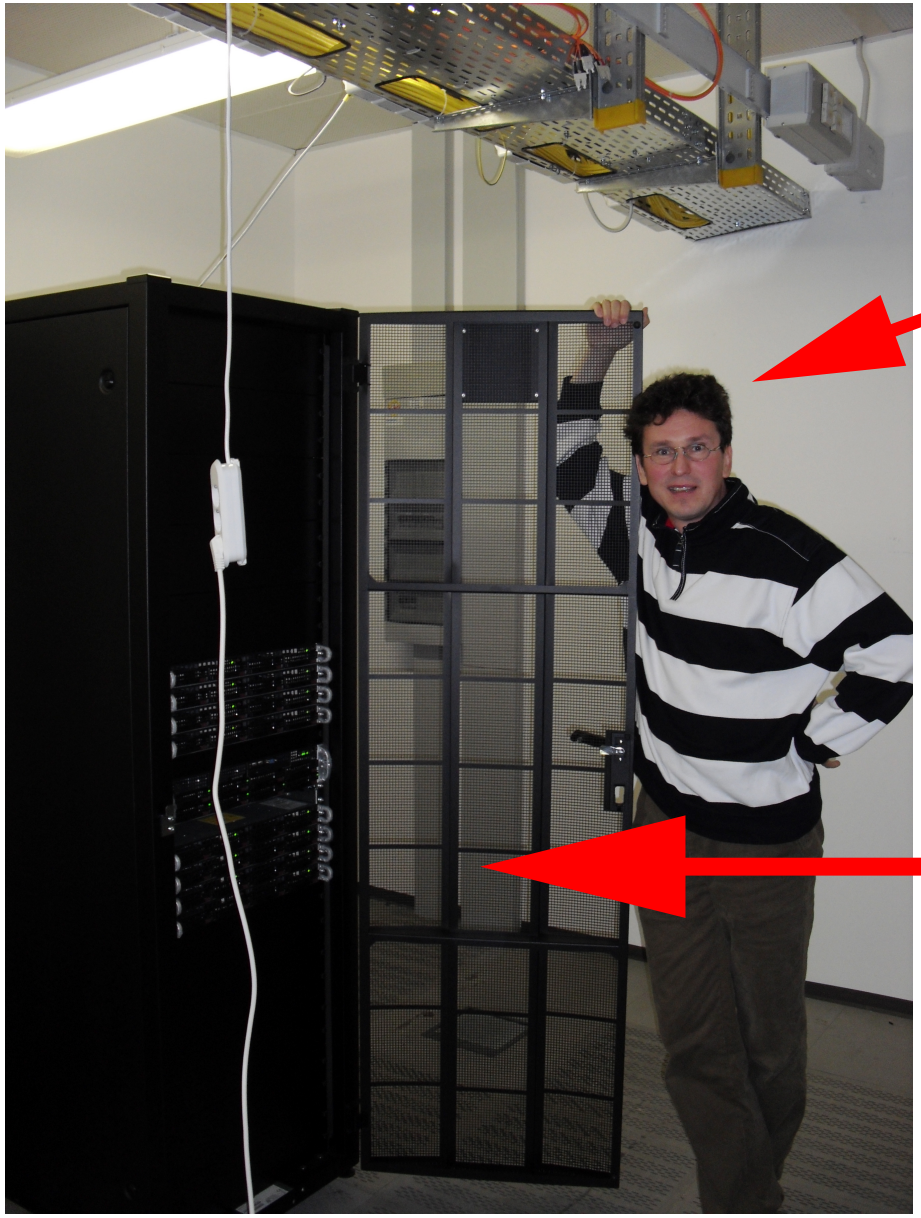
$$\Rightarrow \begin{pmatrix} -27.8 & 3.46 & 0.18 & \cdots \\ 3.46 & -2.35 & -1.7 & \cdots \\ 0.18 & -1.7 & 5.64 & \cdots \\ \vdots & \vdots & \vdots & \cdots \end{pmatrix} \Rightarrow$$



Fe^{III}_{10}: $N = 10, s = 5/2$

Dimension=60,466,176. Maybe too big?

Thank God, we have computers



“Espresso-doped multi-core”

128 cores, 384 GB RAM

. . . but that’s not enough!

Contents for you today

Traditional approach

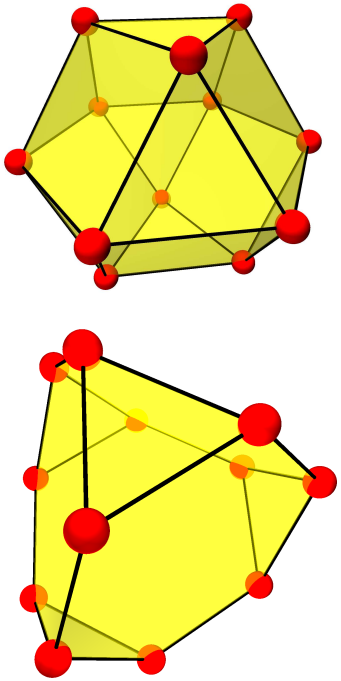
1. Complete diagonalization

Approximate methods

1. Finite-temperature Lanczos
2. DMRG & DDMRG
3. QMC

Complete diagonalization: SU(2) & point group symmetry

Irreducible Tensor Operator approach



Spin rotational symmetry SU(2):

- $\underset{\sim}{H} = -2\sum_{i<j} J_{ij}\ \underset{\sim}{\vec{s}}_i \cdot \underset{\sim}{\vec{s}}_j + g\mu_B \underset{\sim}{\vec{S}} \cdot \vec{B}$;
- $\left[\underset{\sim}{H}, \underset{\sim}{\vec{S}}^2\right] = 0,\ \left[\underset{\sim}{H}, \underset{\sim}{S}_z\right] = 0;$
- Irreducible Tensor Operator (ITO) approach;
- Free program MAGPACK (2) available.

(1) D. Gatteschi and L. Pardi, Gazz. Chim. Ital. **123**, 231 (1993).
(2) J. J. Borras-Almenar, J. M. Clemente-Juan, E. Coronado, and B. S. Tsukerblat, Inorg. Chem. **38**, 6081 (1999).
(3) B. S. Tsukerblat, *Group theory in chemistry and spectroscopy: a simple guide to advanced usage*, 2nd ed. (Dover Publications, Mineola, New York, 2006).

Point Group Symmetry

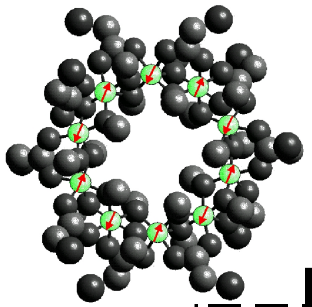
$$|\,\alpha'\,S\,M\,\Gamma\,\rangle = \mathcal{P}^{(\Gamma)}\,|\,\alpha\,S\,M\,\rangle = \left(\frac{l_\Gamma}{h}\sum_R \left(\chi^{(\Gamma)}(R)\right)^*\,\underset{\sim}{G}(R)\right)\,|\,\alpha\,S\,M\,\rangle$$

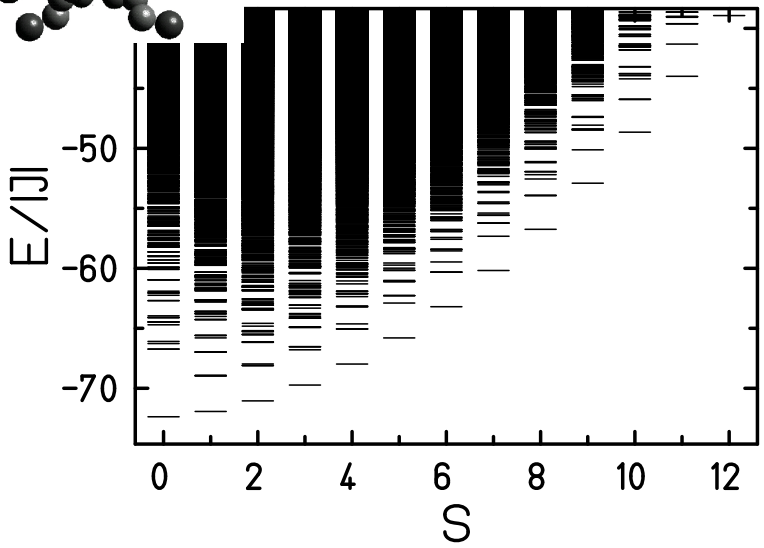
Method:

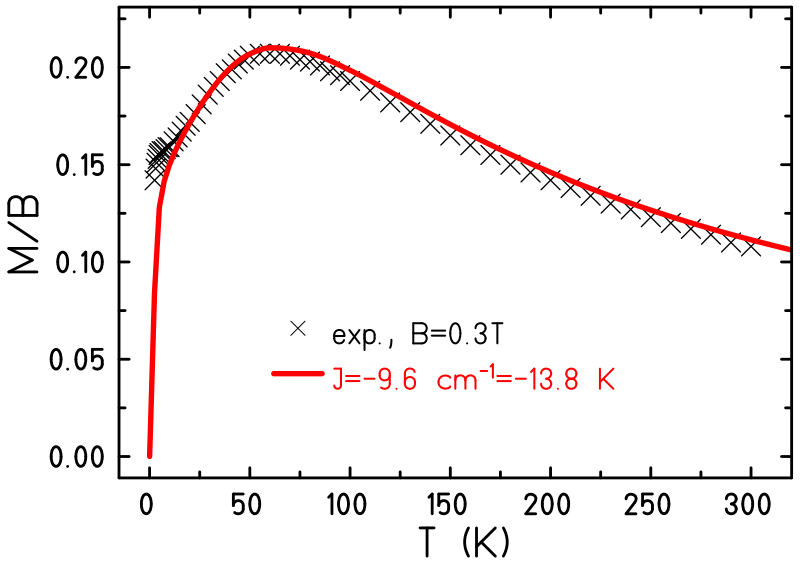
- Projection on irreducible representations Γ of the point group (1,2);
- No free program, things are a bit complicated (3,4).

(1) M. Tinkham, *Group Theory and Quantum Mechanics*, Dover.
(2) D. Gatteschi and L. Pardi, Gazz. Chim. Ital. **123**, 231 (1993).
(3) O. Waldmann, Phys. Rev. B **61**, 6138 (2000).
(4) R. Schnalle and J. Schnack, Int. Rev. Phys. Chem. **29**, 403-452 (2010) ⇐ contains EVERYTHING.

Example: Fe_{10}







Spin ring, $N = 10$, $s = 5/2$, Hilbert space dimension 60,466,176; symmetry D_2 (1).

(1) R. Schnalle and J. Schnack, Int. Rev. Phys. Chem. **29**, 403-452 (2010).
(2) C. Delfs *et al.*, Inorg. Chem. **32**, 3099 (1993).

Finite-temperature Lanczos Method

(Good for dimensions up to 10^{10}.)

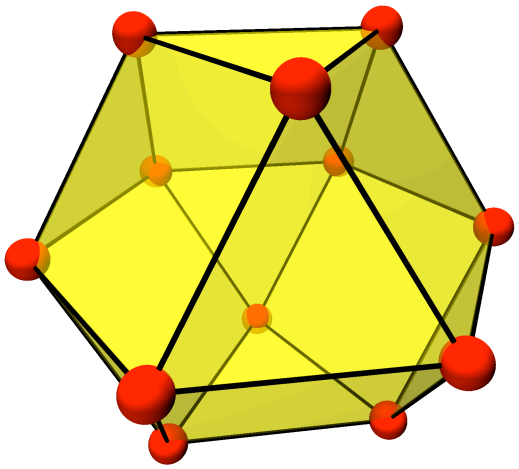
Finite-temperature Lanczos Method I

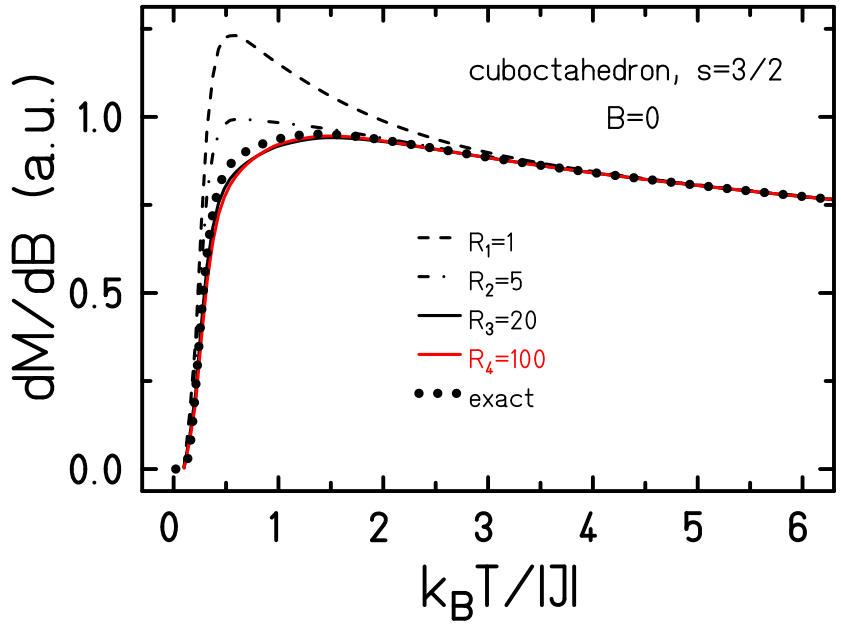
$$
\begin{aligned}
Z(T,B) &= \sum_{\nu} \langle\, \nu \,|\, \exp\left\{-\beta \underset{\sim}{H}\right\} \,|\, \nu \,\rangle \\
\langle\, \nu \,|\, \exp\left\{-\beta \underset{\sim}{H}\right\} \,|\, \nu \,\rangle &\approx \sum_{n} \langle\, \nu \,|\, n(\nu) \,\rangle \exp\left\{-\beta \epsilon_n\right\} \langle\, n(\nu) \,|\, \nu \,\rangle \\
Z(T,B) &\approx \frac{\dim(\mathcal{H})}{R} \sum_{\nu=1}^{R} \sum_{n=1}^{N_L} \exp\left\{-\beta \epsilon_n\right\} |\langle\, n(\nu) \,|\, \nu \,\rangle|^2
\end{aligned}
$$

- $|\, n(\nu) \,\rangle$ n-th Lanczos eigenvector starting from $|\, \nu \,\rangle$
- Partition function replaced by a small sum: $R = 1 \ldots 10, N_L \approx 100$.

J. Jaklic and P. Prelovsek, Phys. Rev. B **49**, 5065 (1994).

How good is finite-temperature Lanczos?

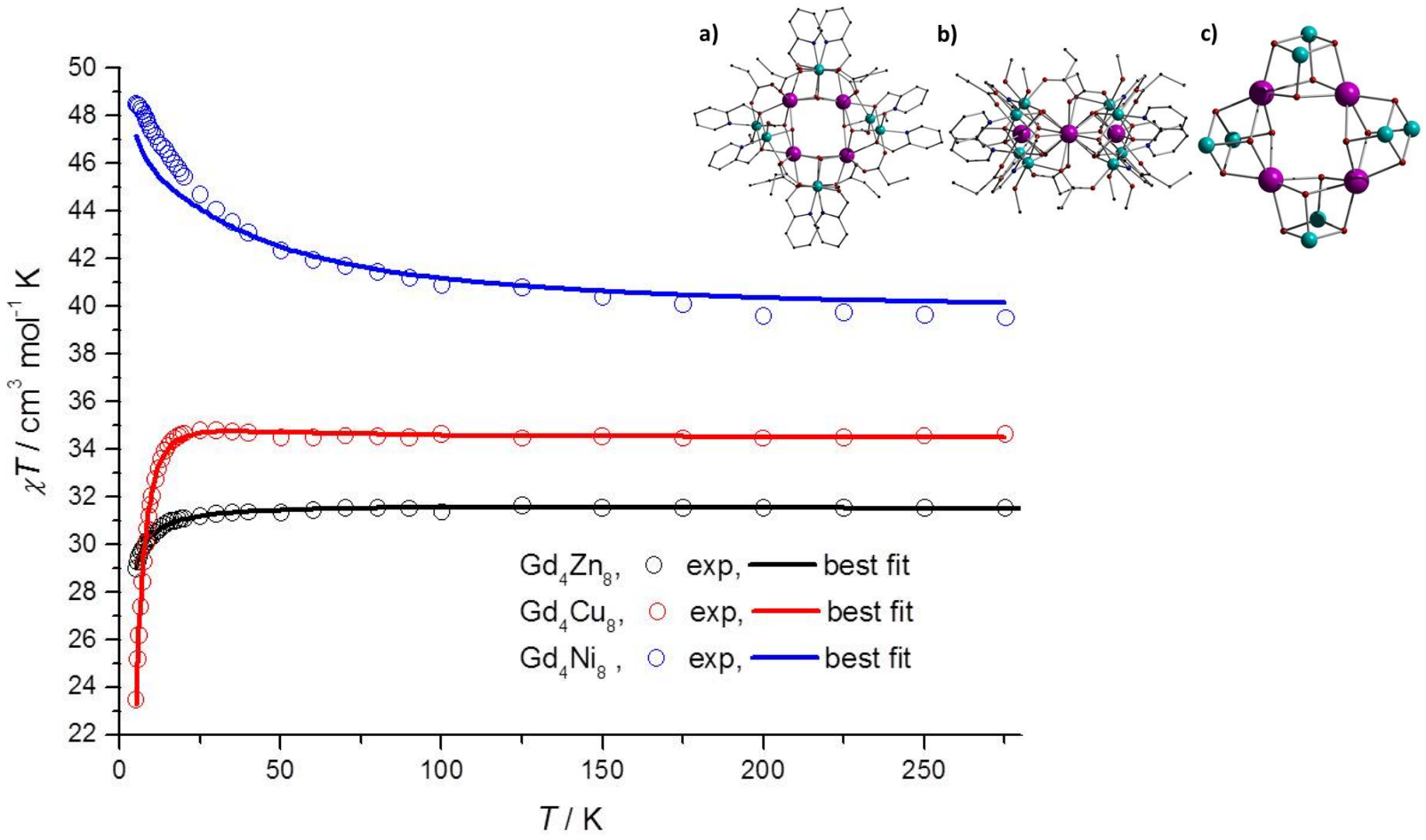




- Works very well: compare frustrated cuboctahedron.
- $N = 12, s = 3/2$: Considered $< 100,000$ states instead of 16,777,216.

Exact results: R. Schnalle and J. Schnack, Int. Rev. Phys. Chem. **29**, 403-452 (2010).
FTLM: J. Schnack and O. Wendland, Eur. Phys. J. B **78**, 535-541 (2010).

Gd_4M_8 – Susceptibility

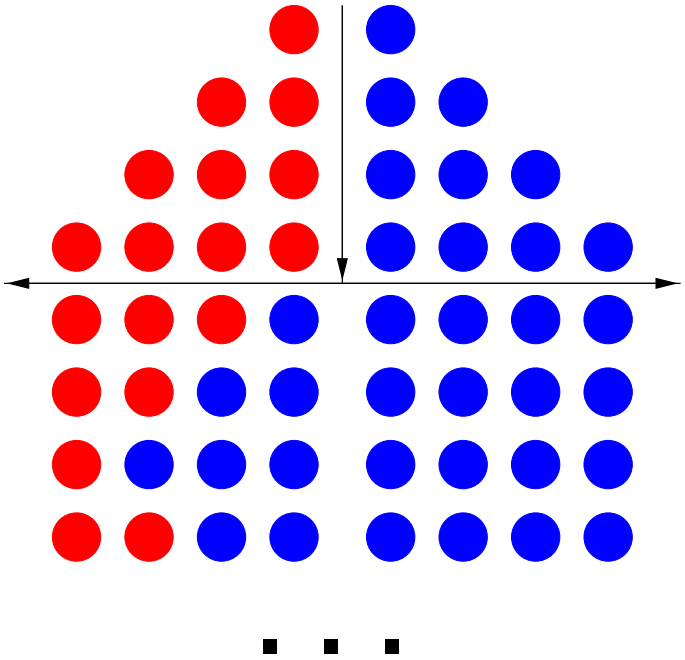


T. N. Hooper, J. Schnack, St. Piligkos, M. Evangelisti, E. K. Brechin, Angew. Chem. Int. Ed. **51** (2012) 4633-4636.

Density Matrix Renormalization Group

(Best for one-dimensional systems, even for huge sizes.)

Density Matrix Renormalization Group

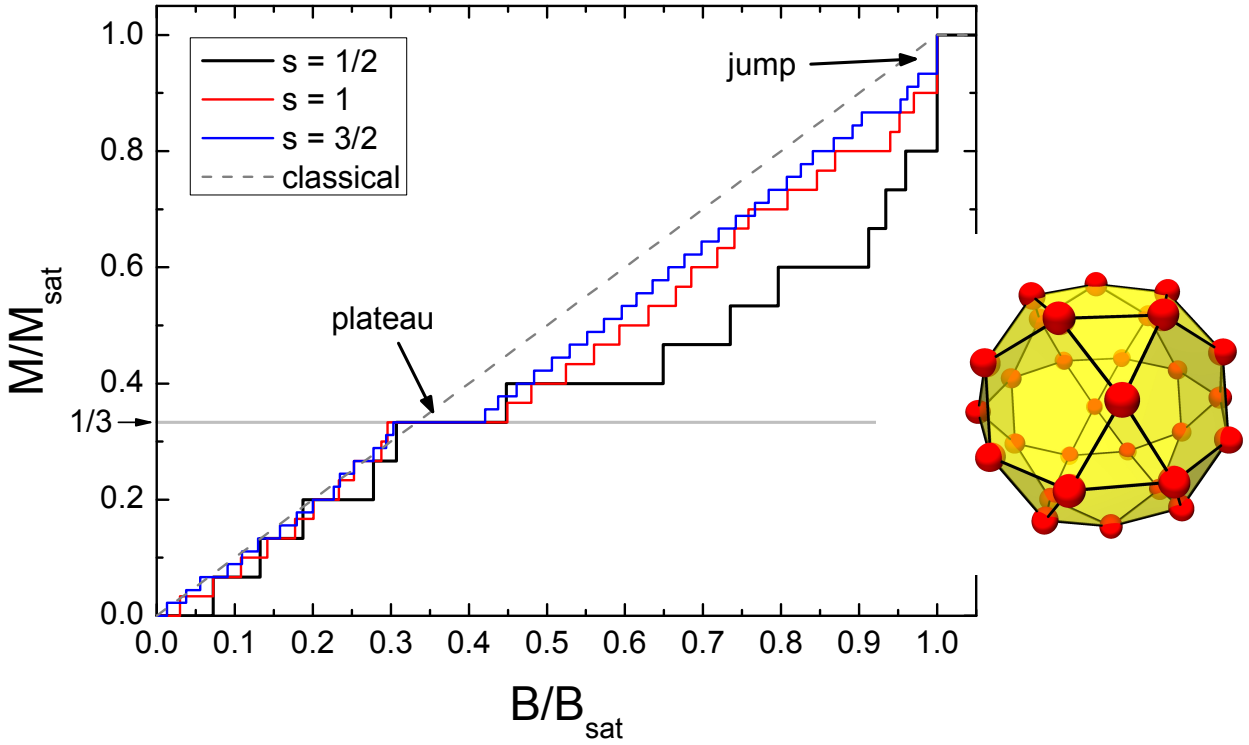


Variational method:

- Naive idea: start with small system, diagonalize $\underset{\sim}{H}$, keep only m lowest states, enlarge system, diagonalize $\underset{\sim}{H}$, keep only m lowest states, ...
- Better: similar idea, use low-lying eigenstates of density matrix of part of system (1,2,3).
- Technical procedure: growth of system & sweeps.

(1) S. R. White, Phys. Rev. Lett. **69**, 2863 (1992).
(2) S. R. White, Phys. Rev. B **48**, 10345 (1993).
(3) U. Schollwöck, Rev. Mod. Phys. **77**, 259 (2005).

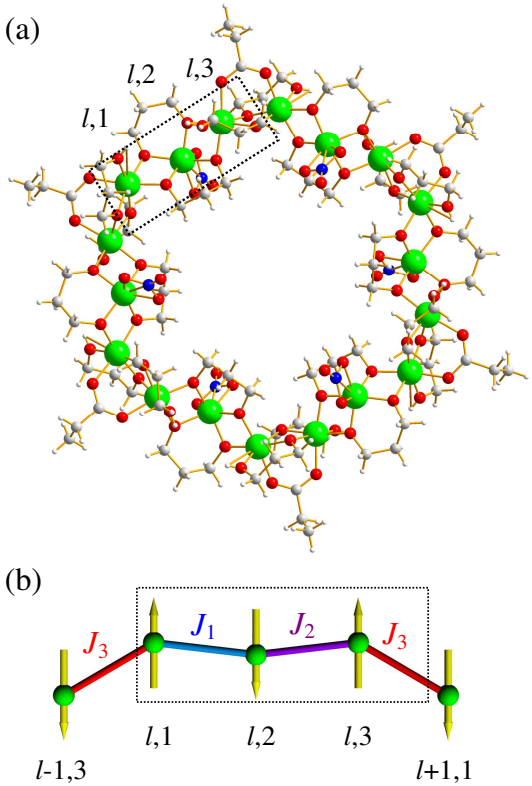
Density Matrix Renormatization Group



- DMRG yields ground states + very few low-lying states in orthogonal subspaces.
- Magnetization curve for $T = 0$, resonance energies for spectroscopy.

(1) J. Ummethum, J. Schnack, and A. Laeuchli, J. Magn. Magn. Mater. (2012), doi: 10.1016/j.jmmm.2012.09.037

Dynamical Density Matrix Renormatization Group

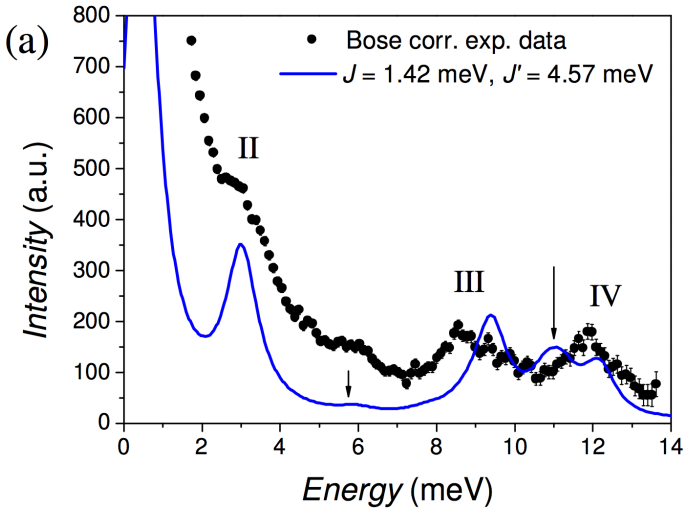


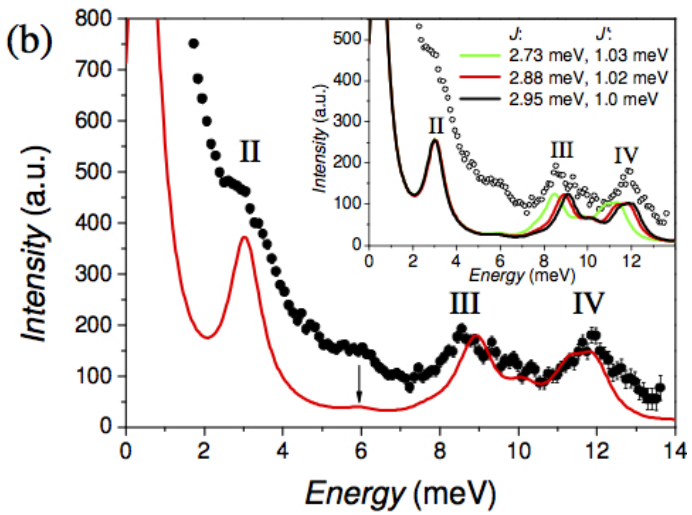
Evaluation of correlation functions, e.g. for INS:

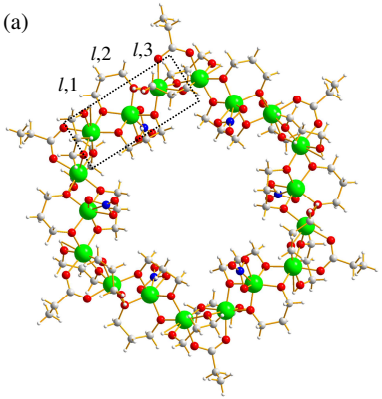
- $S^{zz}_{jj'}(\omega) \equiv \sum_n \langle 0|\underset{\sim}{s}^z_j|n\rangle\langle n|\underset{\sim}{s}^z_{j'}|0\rangle\,\delta(\hbar\omega - E_n + E_0)$; transitions from the ground state;
- $S^{zz}_{jj'}(\omega) \approx \frac{1}{\pi}\langle 0|\underset{\sim}{s}^z_j \frac{\eta}{(E_0+\hbar\omega-\underset{\sim}{H})^2+\eta^2}\underset{\sim}{s}^z_{j'}|0\rangle$;
- Use DMRG ground state and DMRG representation of $\underset{\sim}{H}$ (1,2); η – finite broadening.

(1) T. D. Kühner and S. R. White, Phys. Rev. B **60**, 335 (1999).
(2) E. Jeckelmann, Phys. Rev. B **66**, 045114 (2002).
(3) P. King, T. C. Stamatatos, K. A. Abboud, and G. Christou, Angew. Chem. Int. Ed. **45**, 7379 (2006).
(4) O. Waldmann *et al.*, Phys. Rev. Lett. **102**, 157202 (2009).

Dynmical Density Matrix Renormatization Group







- Accurate description of low-lying excitations for the giant ferric wheel Fe_{18}. Hilbert space dimension 10^{14}.

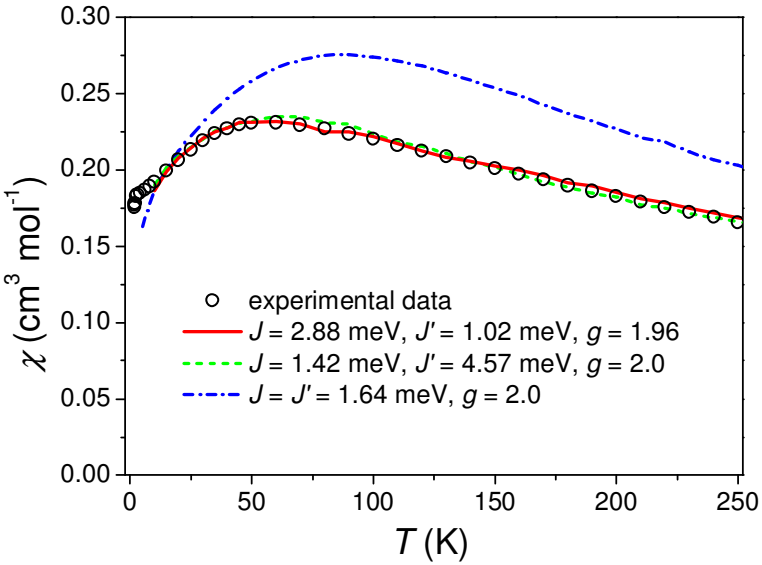
- Determination of model parameters.

(1) J. Ummethum, J. Nehrkorn, S. Mukherjee, N. B. Ivanov, S. Stuiber, Th. Strässle, P. L. W. Tregenna-Piggott, H. Mutka, G. Christou, O. Waldmann, J. Schnack, Phys. Rev. B **86**, 104403 (2012).

Quantum Monte Carlo

(Very good for non-frustrated systems, even for huge sizes.)

Quantum Monte Carlo



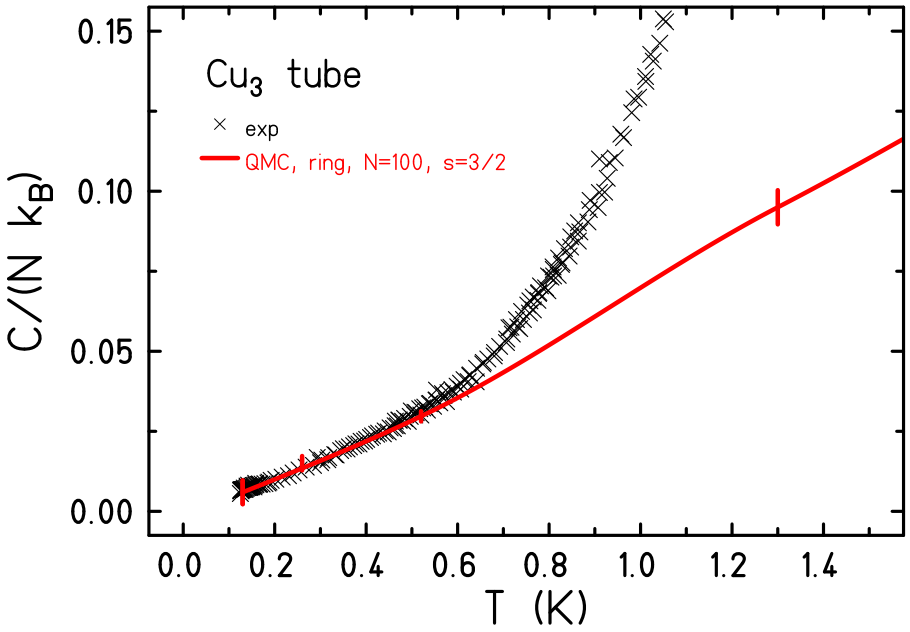
Chopped (sliced) partition function:

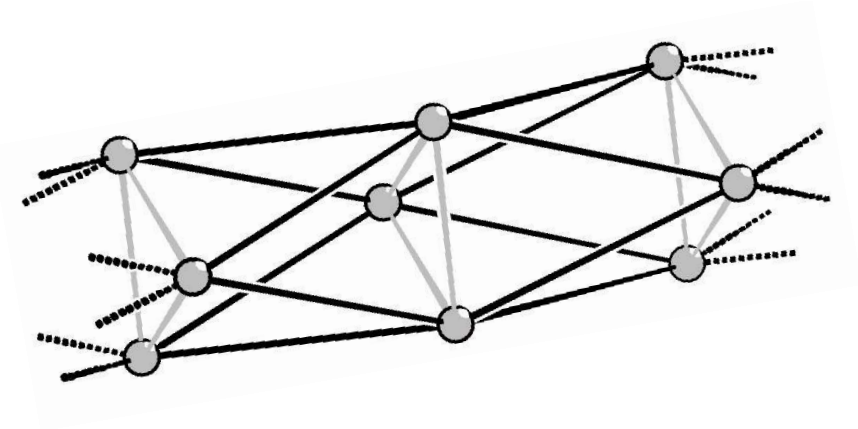
- $$Z(T,B) = \sum_\nu \langle \nu | \exp\left\{-\beta \underset{\sim}{H}\right\} | \nu \rangle$$
$$= \sum_\nu \langle \nu | \left[\exp\left\{-\beta \underset{\sim}{H}/m\right\}\right]^m | \nu \rangle$$
$$= \sum_{\nu,\alpha,\beta,\ldots} \langle \nu | \exp\left\{-\beta \underset{\sim}{H}/m\right\} | \alpha \rangle\langle \alpha | \cdots$$
$$\approx \sum_{\nu,\alpha,\beta,\ldots} \langle \nu | \left\{1 - \beta \underset{\sim}{H}/m\right\} | \alpha \rangle\langle \alpha | \cdots$$

- Bad/no convergence for frustrated systems (negative sign problem).

(1) A. W. Sandvik and J. Kurkijärvi, Phys. Rev. B **43**, 5950 (1991).
(2) A. W. Sandvik, Phys. Rev. B **59**, R14157 (1999).
(3) L. Engelhardt and M. Luban, Phys. Rev. B **73**, 054430 (2006); L. Engelhardt *et al.*, Phys. Rev. B **79**, 014404 (2009).
(4) J. Ummethum *et al.*, Phys. Rev. B **86**, 104403 (2012).

Quantum Monte Carlo

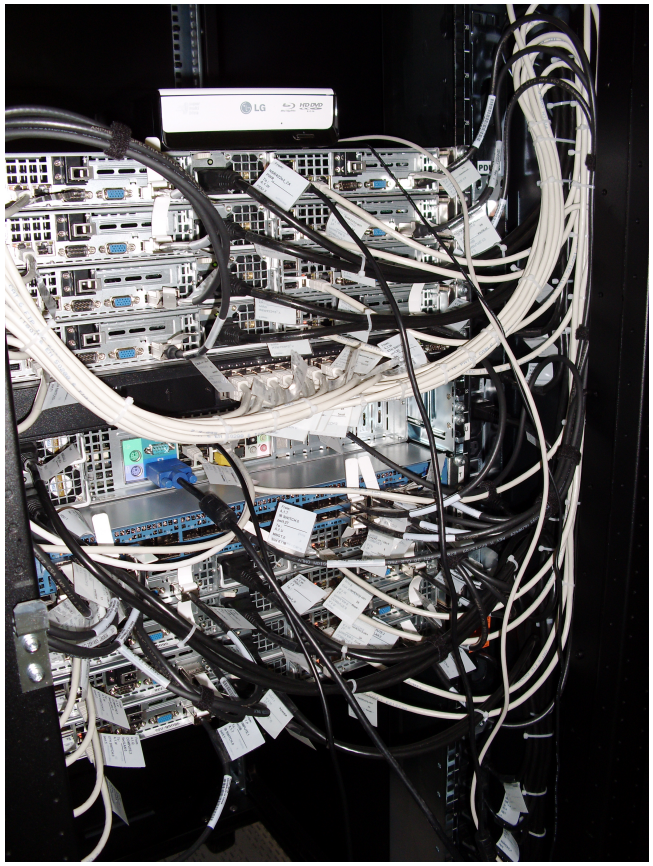




- $[(CuCl_2tachH)_3Cl]Cl_2$: spins on triangles effectively coupled to $s = 3/2$, treatment as chain $\Rightarrow$ Luttinger liquid behavior, i.e. $C \propto T$.
- 100 spins $s = 3/2$ are no problem for QMC.

(1) N. B. Ivanov, J. Schnack, R. Schnalle, J. Richter, P. Kögerler, G.N. Newton, L. Cronin, Y. Oshima, Hiroyuki Nojiri, Phys. Rev. Lett. **105**, 037206 (2010).

Summary



- Exact diagonalization is great but limited.
- Finite-temperature Lanczos is a good approximate method for Hilbert space dimensions smaller than 10^{10}.
- Density Matrix Renormalization Group for big 1-d systems.
- Quantum Monte Carlo very powerful for non-frustrated systems.
- Most of it is freely available in ALPS (1).

(1) A. Albuquerque *et al.*, J. Magn. Magn. Mater. **310**, 1187 (2007).
(2) http://alps.comp-phys.org (English, Japanese, Chinese)

Many thanks to my collaborators worldwide

- T. Glaser, Chr. Heesing, M. Höck, N.B. Ivanov, S. Leiding, A. Müller, R. Schnalle, Chr. Schröder, J. Ummethum, O. Wendland (Bielefeld)
- K. Bärwinkel, H.-J. Schmidt, M. Neumann (Osnabrück)
- M. Luban (Ames Lab, USA); P. Kögerler (Aachen, Jülich, Ames); R.E.P. Winpenny, E.J.L. McInnes (Man U, UK); L. Cronin, M. Murrie (Glasgow, UK); E. Brechin (Edinburgh, UK); H. Nojiri (Sendai, Japan); A. Postnikov (Metz, France); M. Evangelisti (Zaragosa, Spain)
- J. Richter, J. Schulenburg (Magdeburg); A. Honecker (Göttingen); U. Kortz (Bremen); A. Tennant, B. Lake (HMI Berlin); B. Büchner, V. Kataev, H.-H. Klauß (Dresden); P. Chaudhuri (Mühlheim); J. Wosnitza (Dresden-Rossendorf); J. van Slageren (Stuttgart); R. Klingeler (Heidelberg); O. Waldmann (Freiburg)

Thank you very much for your attention.

The end.

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