

# Advanced quantum methods for the largest magnetic molecules

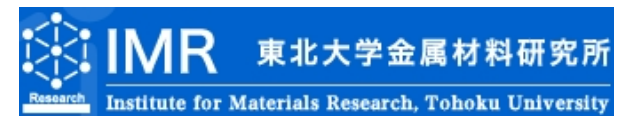
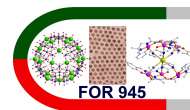
Jürgen Schnack

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<http://obelix.physik.uni-bielefeld.de/~schnack/>

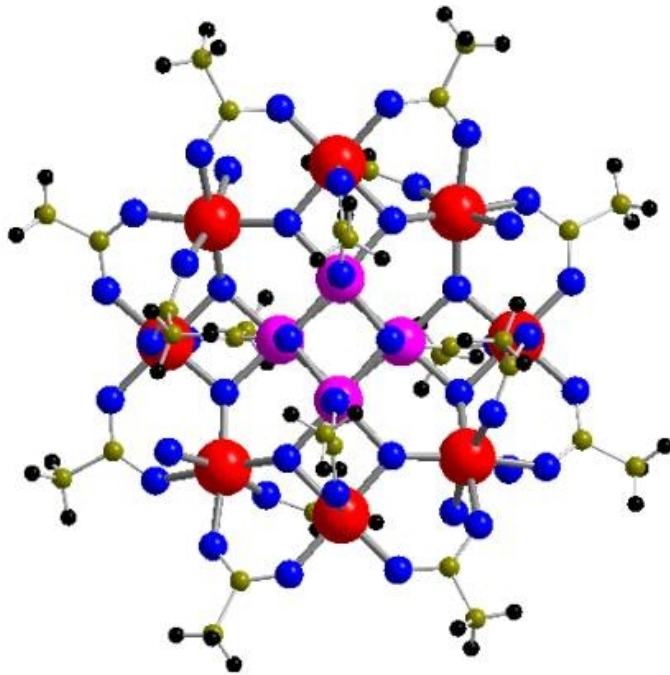
Seminar Physik der kondensierten Materie

Universität Mainz, Minkowski-Raum, 8. 11. 2012



# Beauty of Magnetic Molecules

# The beauty of magnetic molecules I

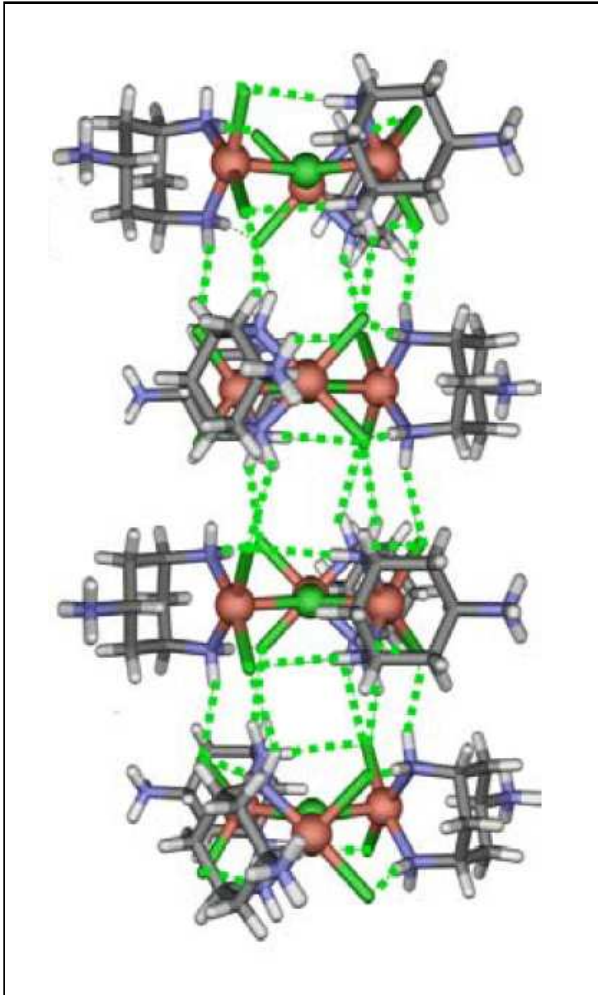


Mn<sub>12</sub>

- Inorganic or organic macro molecules, e.g. polyoxometalates, where paramagnetic ions such as Iron (Fe), Chromium (Cr), Copper (Cu), Nickel (Ni), Vanadium (V), Manganese (Mn), or rare earth ions are embedded in a host matrix;
- Pure organic magnetic molecules: magnetic coupling between high spin units (e.g. free radicals);
- Single spin quantum number  $1/2 \leq s \leq 7/2$ ;
- Intermolecular interaction relatively small, therefore measurements reflect the thermal behaviour of a single molecule.

*Magnetism goes Nano*, Ed. Stefan Blügel, Thomas Brückel, and Claus M. Schneider, FZ Jülich, Institute of Solid State Research, Lecture Notes **36** Jülich 2005

## The beauty of magnetic molecules II

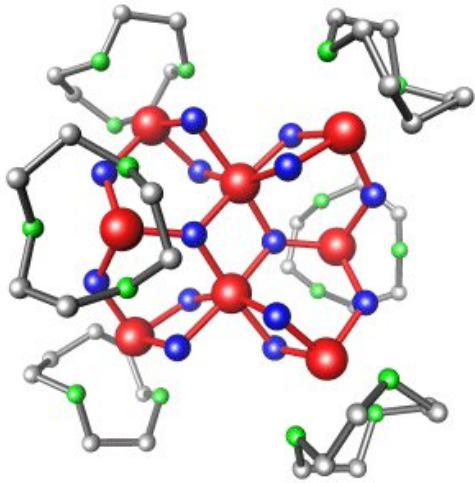


- Dimers ( $\text{Fe}_2$ ), tetrahedra ( $\text{Cr}_4$ ), cubes ( $\text{Cr}_8$ );
- Rings, especially iron rings ( $\text{Fe}_6$ ,  $\text{Fe}_8$ ,  $\text{Fe}_{10}$ , ...);
- Complex structures ( $\text{Mn}_{12}$ ) – drosophila of molecular magnetism;
- “Soccer balls”, more precisely icosidodecahedra ( $\text{Fe}_{30}$ ) and other macro molecules;
- Chain like and planar structures of interlinked magnetic molecules, e.g. triangular Cu chain:

J. Schnack, H. Nojiri, P. Kögerler, G. J. T. Cooper, L. Cronin, Phys. Rev. B 70, 174420 (2004)

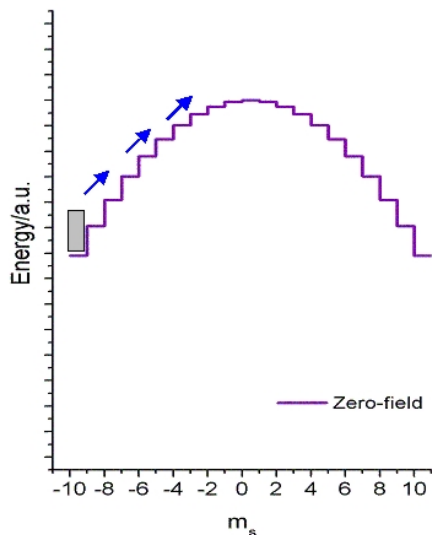


# The beauty of magnetic molecules III



- Single Molecule Magnets (SMM): magnetic molecules with large ground state moment;
- Example:  $S = 10$  for  $Mn_{12}$  or  $Fe_8$ ;
- Anisotropy dominates approximate single-spin Hamiltonian:

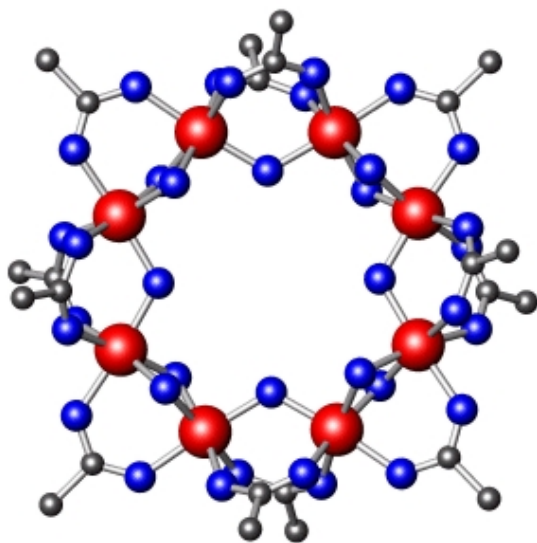
$$\underline{H} = -D\underline{S}_z^2 + \underline{H}', \quad [\underline{S}_z, \underline{H}'] \neq 0$$



- Single molecule shows: metastable magnetization, hysteresis, ground state magnetization tunneling, thermally and phonon assisted tunneling.
- Today's major efforts: improve stability of magnetization; investigate on surfaces.

# The beauty of magnetic molecules IV

## Why magnetic molecules?

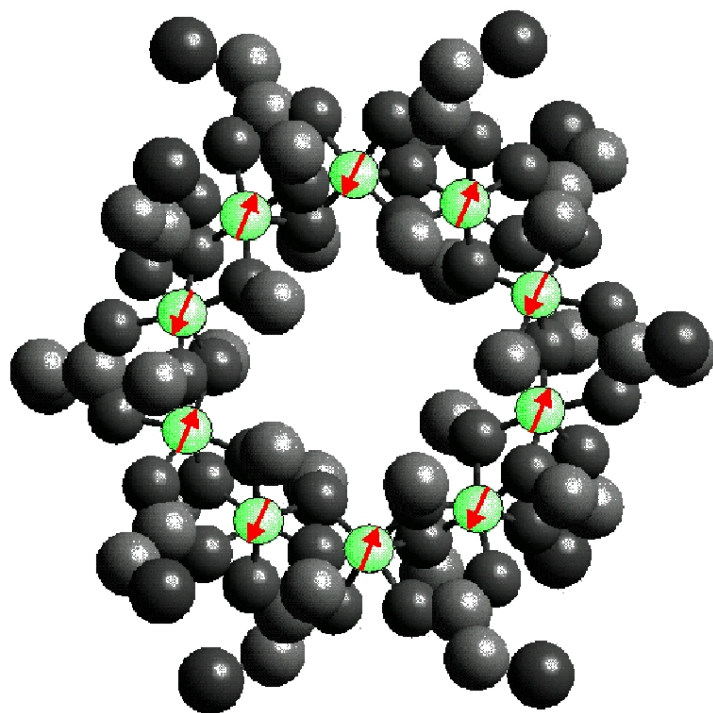


Cr<sub>8</sub>

- Interacting spin system largely decoupled from remaining degrees of freedom;
- Transition few-spin system  $\Rightarrow$  many-spin system, contribution to understanding of bulk magnetism;
- Transition quantum spin system ( $s = 1/2$ )  $\Rightarrow$  classical spin system ( $s_{\text{Fe}} = 5/2, s_{\text{Gd}} = 7/2$ );
- Easy to produce, single crystals with  $> 10^{17}$  identical molecules can be synthesized and practically completely characterized;
- **Speculative applications: magnetic storage devices, magnets in biological systems, light-induced nano switches, displays, catalysts, qubits for quantum computers.**

# The problem

# You have got a molecule!

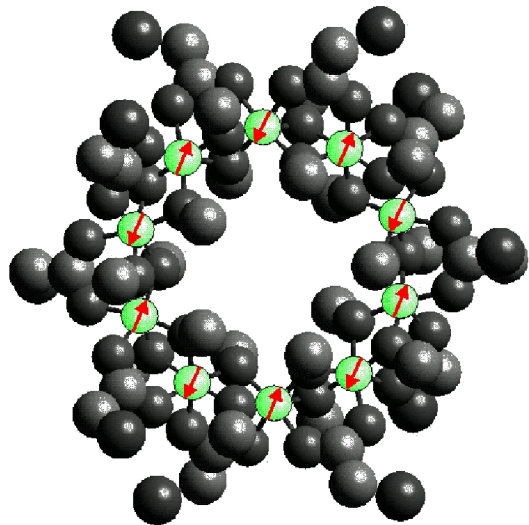


Congratulations!

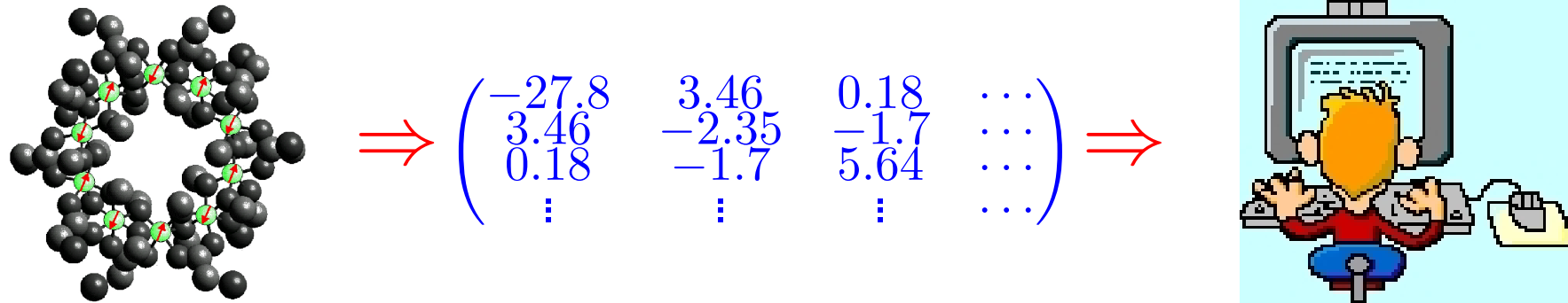
You have got an idea about the modeling!

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

Heisenberg
Zeeman



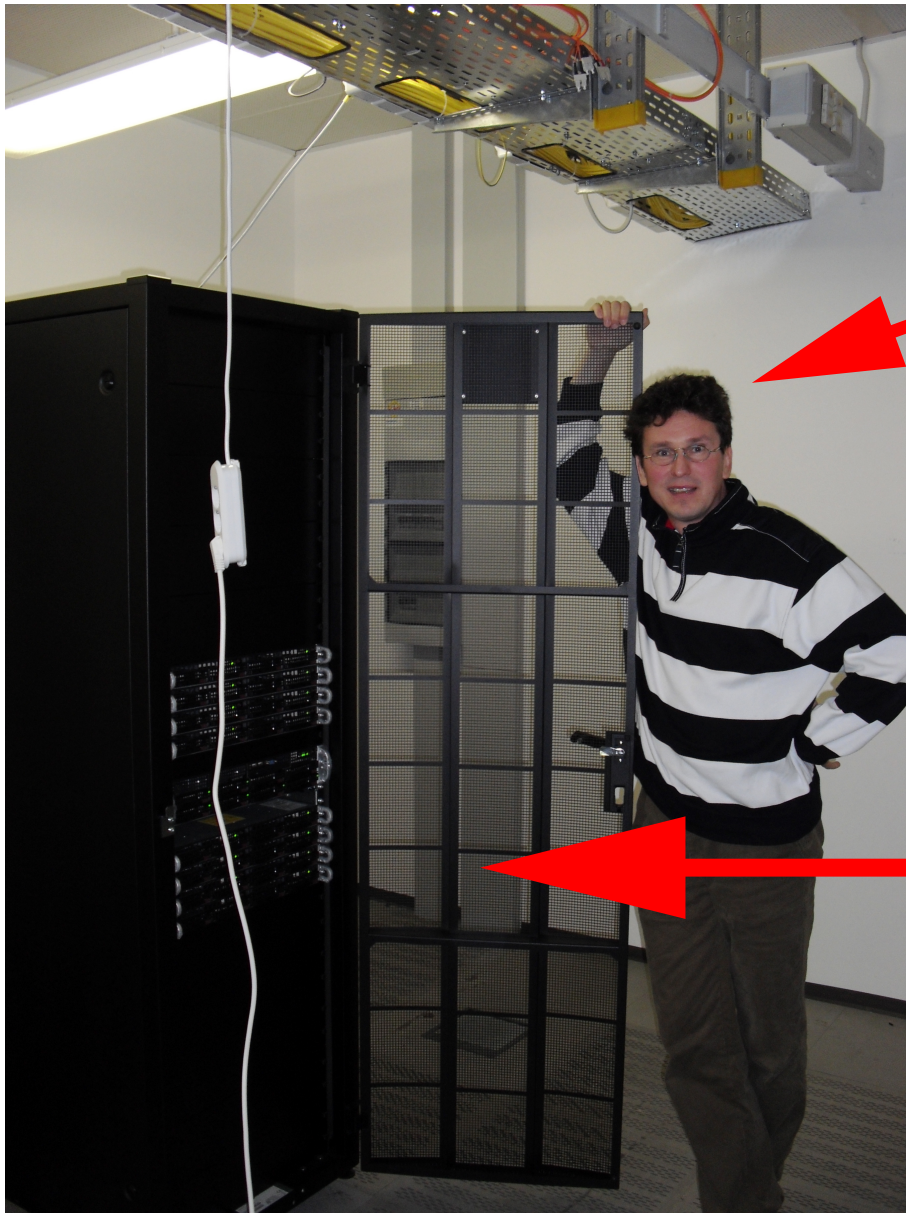
In the end it's always a big matrix!



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

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

+ examples of problems that can be solved with these methods.

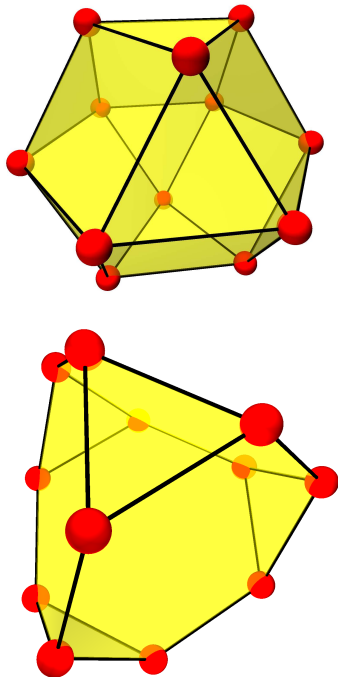


# Complete diagonalization: SU(2) & point group symmetry

Quantum chemists need to be much smarter since they have smaller computers!

- (1) D. Gatteschi and L. Pardi, *Gazz. Chim. Ital.* **123**, 231 (1993).
- (2) J. J. Borrás-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).

# Irreducible Tensor Operator approach



## Spin rotational symmetry SU(2):

- $\underline{H} = -2 \sum_{i < j} J_{ij} \underline{\tilde{S}}_i \cdot \underline{\tilde{S}}_j + g\mu_B \underline{\tilde{S}} \cdot \underline{\tilde{B}} ;$

- Physicists employ:  $[\underline{H}, \underline{S}_z] = 0;$

- Chemists employ:  $[\underline{H}, \underline{\tilde{S}}^2] = 0, [\underline{H}, \underline{S}_z] = 0;$

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. Borrás-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

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

## Method:

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

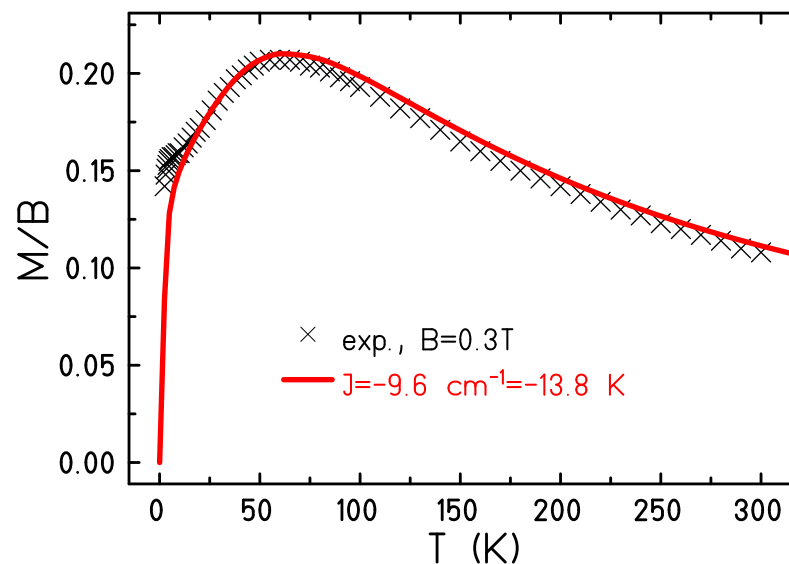
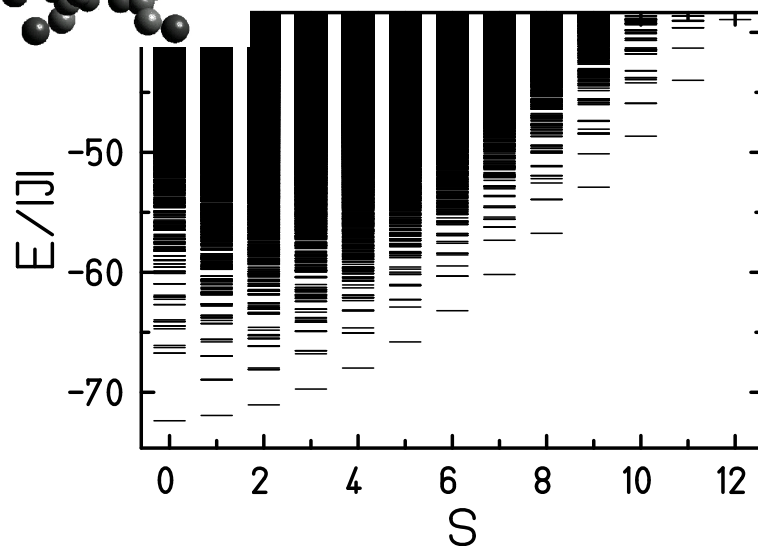
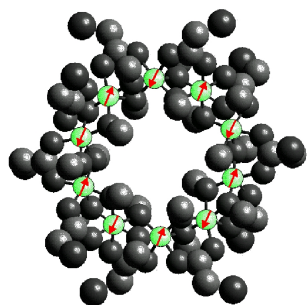
(1) M. Tinkham, *Group Theory and Quantum Mechanics*, Dover.

(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)  $\Leftarrow$  contains EVERYTHING.

# Example: Fe<sub>10</sub>



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

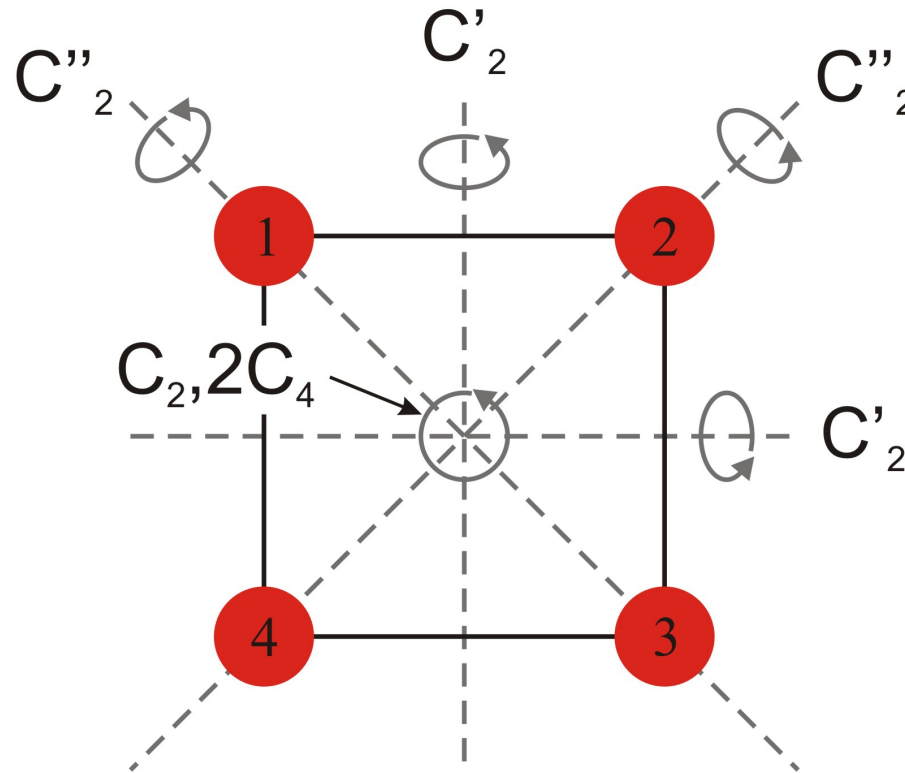
- (1) R. Schnalle and J. Schnack, *Int. Rev. Phys. Chem.* **29**, 403-452 (2010).
- (2) C. Delfs *et al.*, *Inorg. Chem.* **32**, 3099 (1993).

# Point Group Symmetry II

$$\tilde{G}(R) |\alpha S M\rangle_a = |\alpha S M\rangle_b = \sum_{\alpha'} |\alpha' S M\rangle_a {}_a\langle \alpha' S M | \alpha S M \rangle_b$$

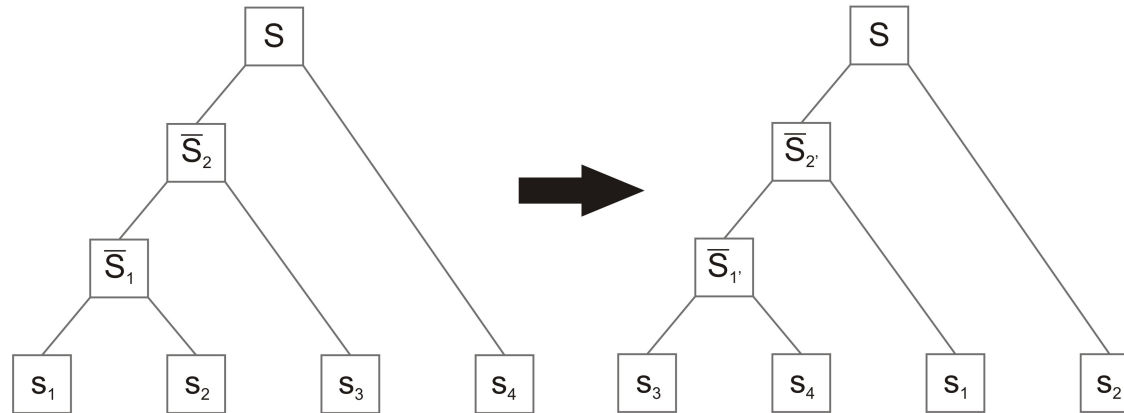
- Serious problem: application of  $\tilde{G}(R)$ , i.e. permutation of spins, leads to different coupling schemes:  $a \Rightarrow b$ ;
- Solution: implementation of graph-theoretical results to evaluate recoupling coefficients  ${}_a\langle \alpha' S M | \alpha S M \rangle_b$ .

# Point Group Symmetry III – example square



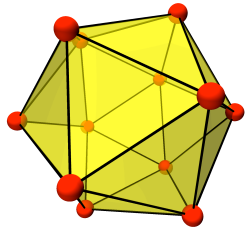
$$|s_1 s_2 \bar{s}_1 s_3 \bar{s}_2 s_4 SM\rangle \xrightarrow{\tilde{G}(3412)} |s_3 s_4 \bar{s}_1 s_1 \bar{s}_2 s_2 SM\rangle$$

# Point Group Symmetry IV – binary trees

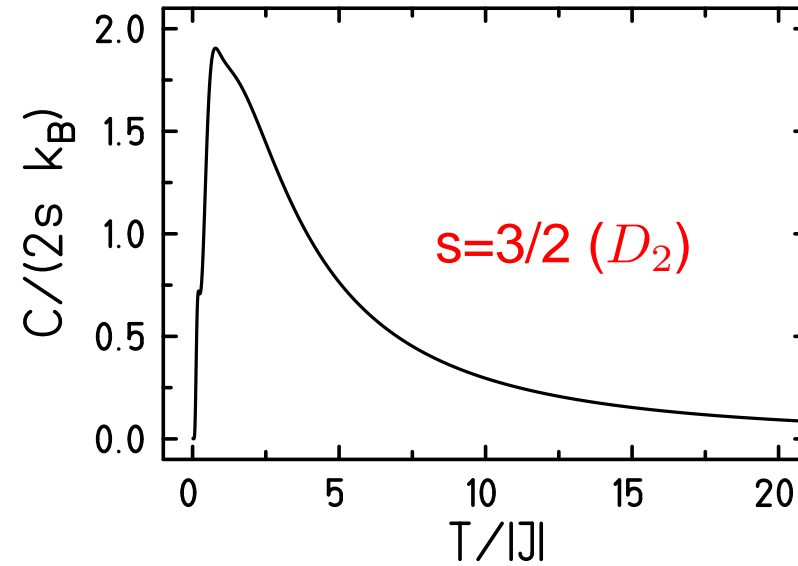
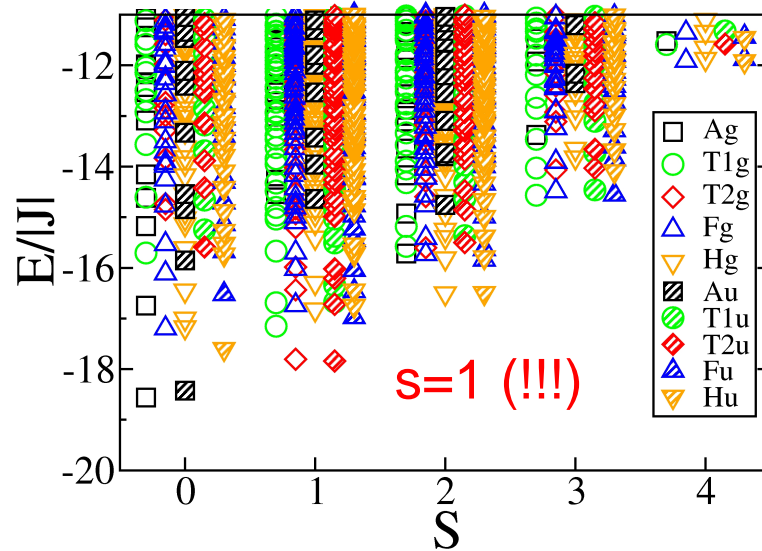


- Recoupling coefficient  $\langle s_1 s_2 \bar{S}_1 s_3 \bar{S}_2 s_4 S M | s_3 s_4 \bar{S}_{1'} s_1 \bar{S}_{2'} s_2 S M \rangle$  can be evaluated by a graphical transformation of one binary tree into the other (1,2).
- Exchange and flop operations generate a recoupling formula consisting of square roots, Wigner-6J symbols, and sums over intermediate spins.
- Open question: optimal coupling for a given symmetry? (3)

(1) V. Fack, S. N. Pitre, and J. van der Jeugt, *Comp. Phys. Comm.* **86**, 105 (1995).  
 (2) V. Fack, S. N. Pitre, and J. van der Jeugt, *Comp. Phys. Comm.* **101**, 155 (1997).  
 (3) M. Geisler, Bachelor Thesis, Bielefeld University (2010).



# Example: Icosahedron



Icosahedron,  $s = 3/2$ , Hilbert space dimension 16,777,216; symmetry  $I_h$ ; Evaluation of recoupling coefficients for  $s = 3/2$  in  $I_h$  **practically impossible** (1).

(1) R. Schnalle and J. Schnack, Int. Rev. Phys. Chem. **29**, 403-452 (2010).



# Finite-temperature Lanczos Method

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

# Finite-temperature Lanczos Method I

$$Z(T, B) = \sum_{\nu} \langle \nu | \exp \left\{ -\beta \tilde{H} \right\} | \nu \rangle$$

$$\langle \nu | \exp \left\{ -\beta \tilde{H} \right\} | \nu \rangle \approx \sum_n \langle \nu | n(\nu) \rangle \exp \left\{ -\beta \epsilon_n \right\} \langle n(\nu) | \nu \rangle$$

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

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

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

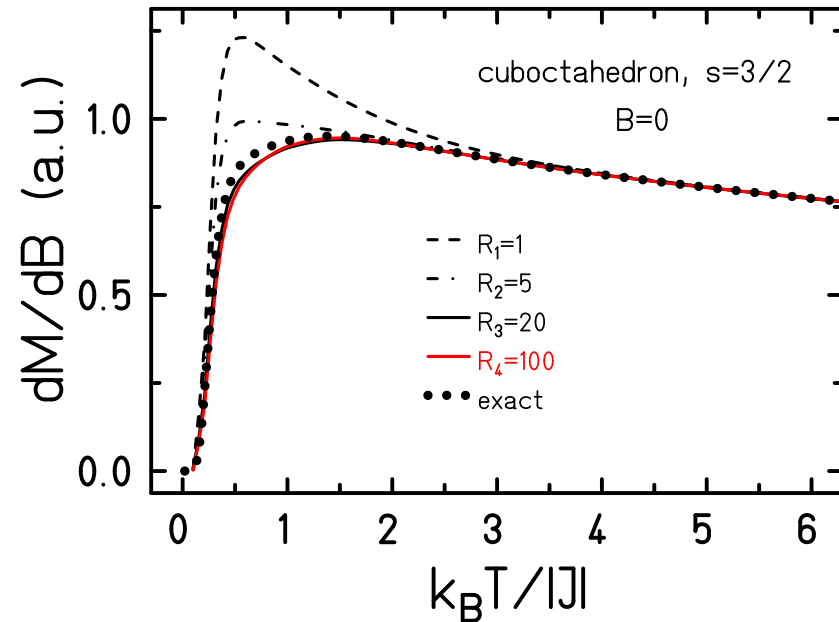
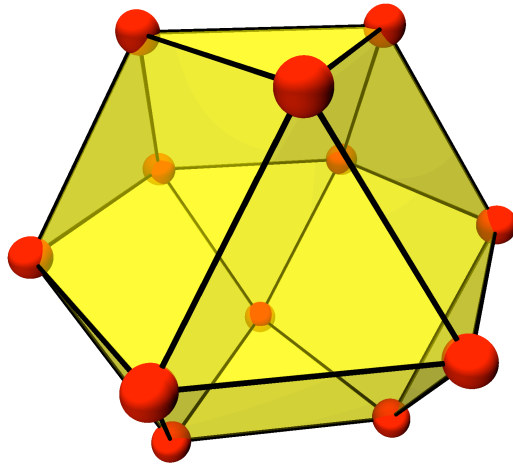
## Finite-temperature Lanczos Method II

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

- Approximation better if symmetries taken into account.
- $\Gamma$  denotes the used irreducible representations.

J. Schnack and O. Wendland, Eur. Phys. J. B **78** (2010) 535-541

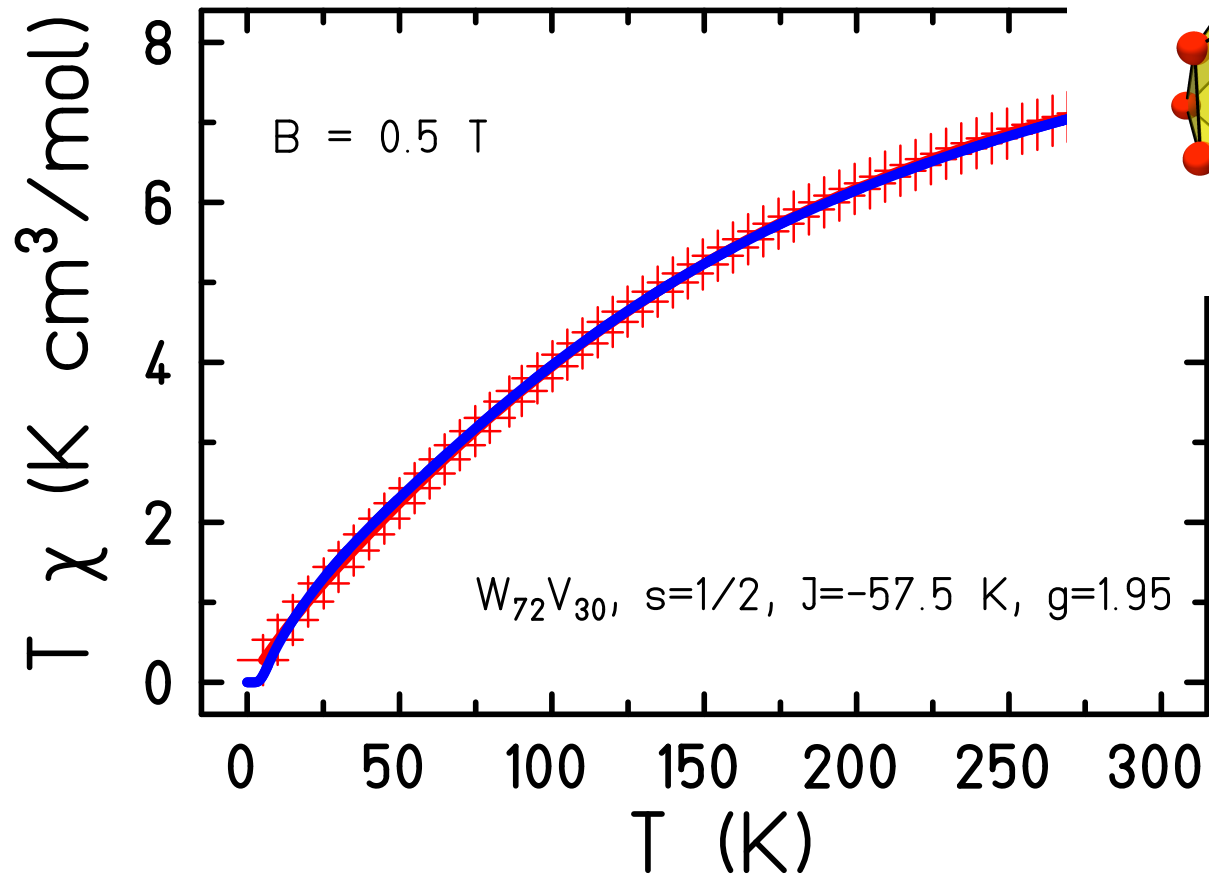
# How good is finite-temperature Lanczos?



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

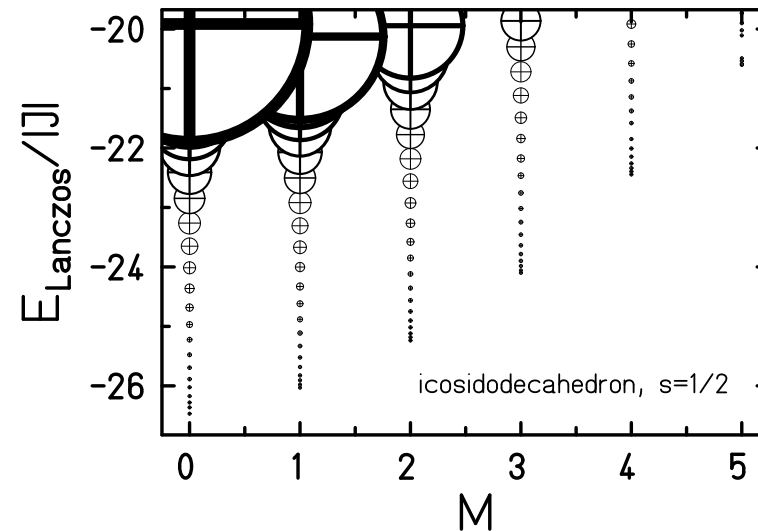
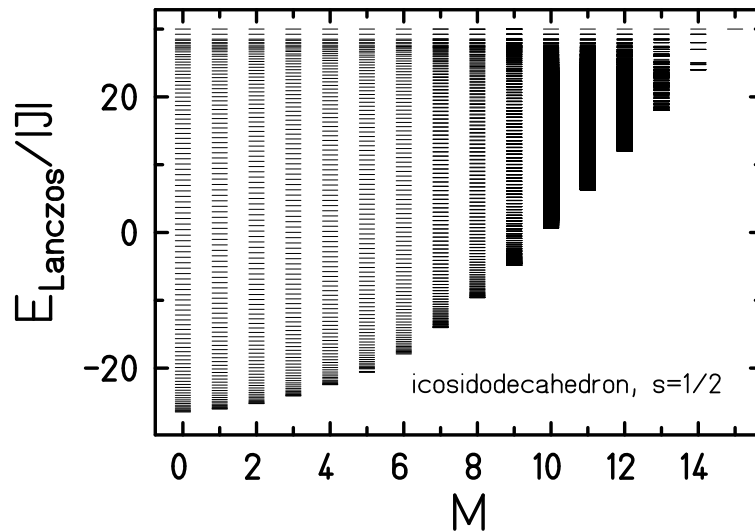
Exact results: R. Schnalle and J. Schnack, *Int. Rev. Phys. Chem.* **29**, 403-452 (2010).  
 FTLM: J. Schnack and O. Wendland, *Eur. Phys. J. B* **78**, 535-541 (2010).

# Icosidodecahedron $s = 1/2$



Exp. data: A. M. Todea, A. Merca, H. Bögge, T. Glaser, L. Engelhardt, R. Prozorov, M. Luban, A. Müller, Chem. Commun., 3351 (2009).

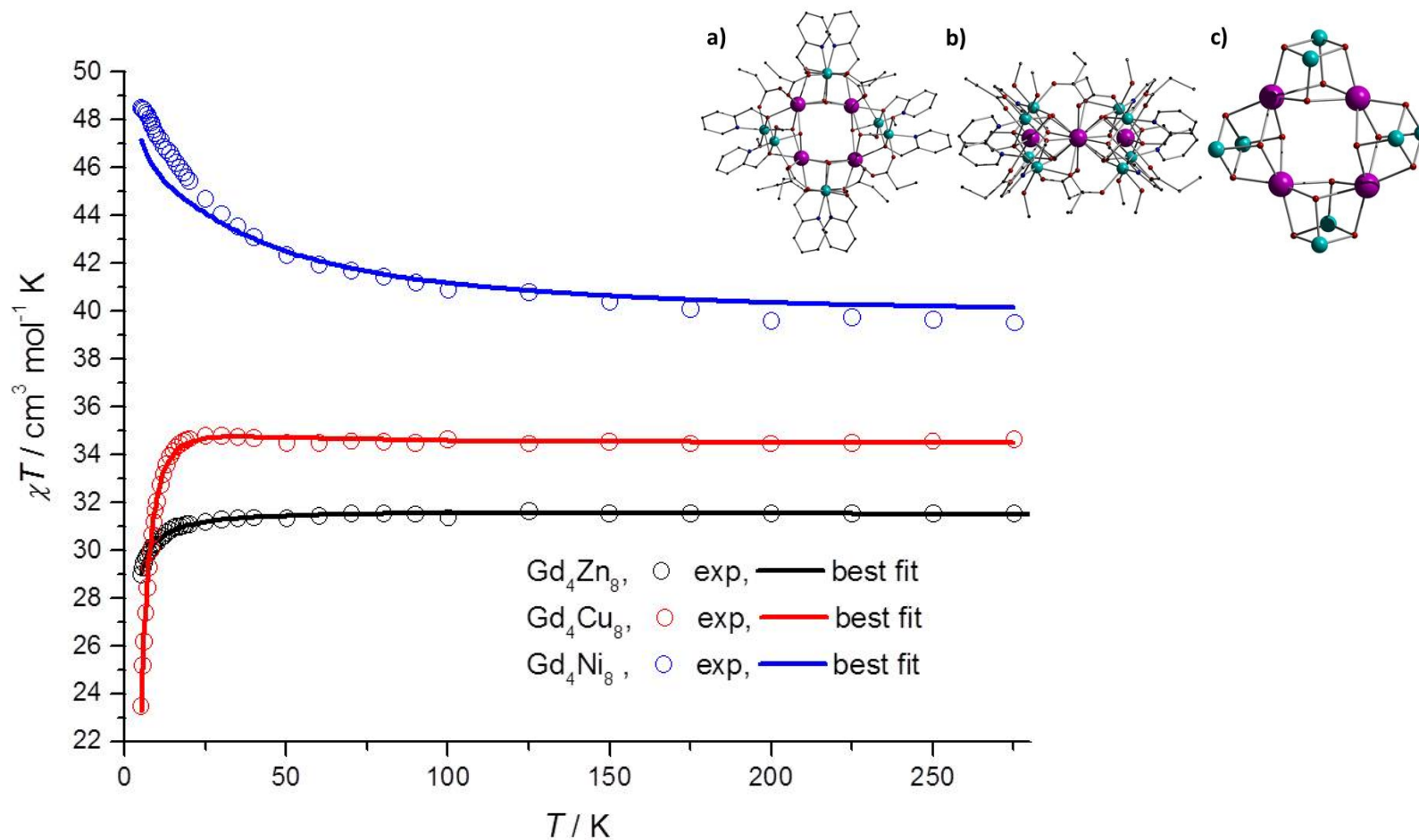
# Icosidodecahedron $s = 1/2$



- The true spectrum will be much denser. This is miraculously compensated for by the weights.

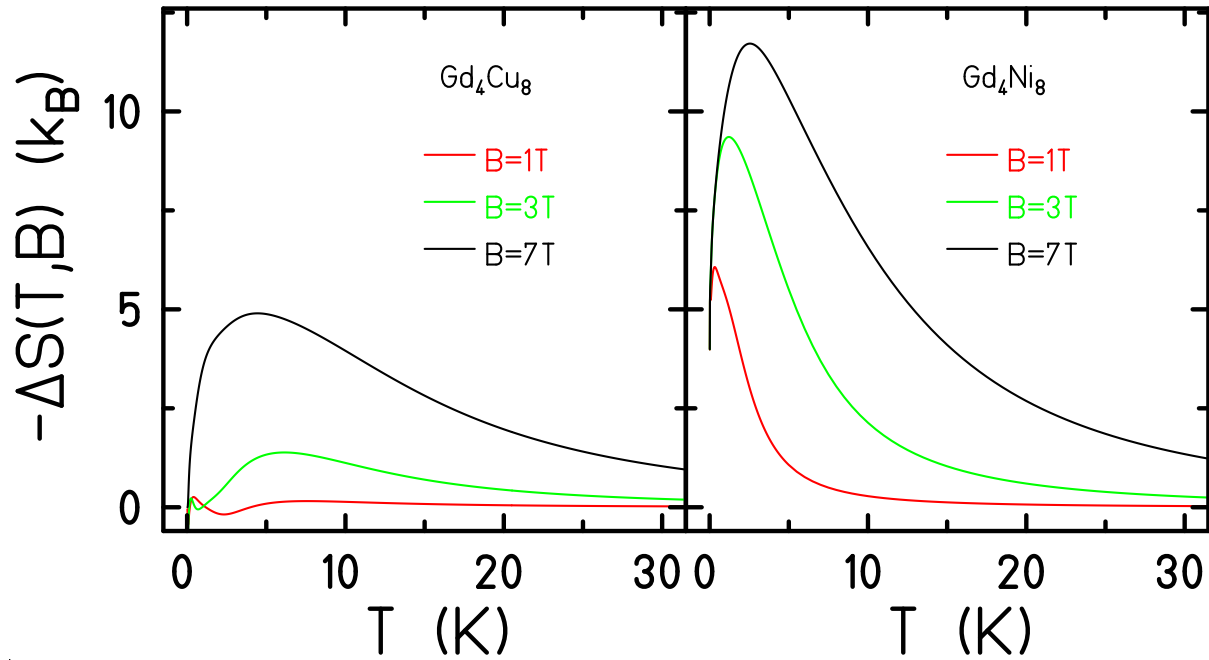
$$Z(T, B) \approx \sum_{\Gamma} \frac{\dim(\mathcal{H}(\Gamma))}{R_{\Gamma}} \sum_{\nu=1}^{R_{\Gamma}} \sum_{n=1}^{N_L} \exp\{-\beta\epsilon_n\} |\langle n(\nu, \Gamma) | \nu, \Gamma \rangle|^2$$

# Gd<sub>4</sub>M<sub>8</sub> – Susceptibility



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

# Gd<sub>4</sub>M<sub>8</sub> – magnetocaloric properties



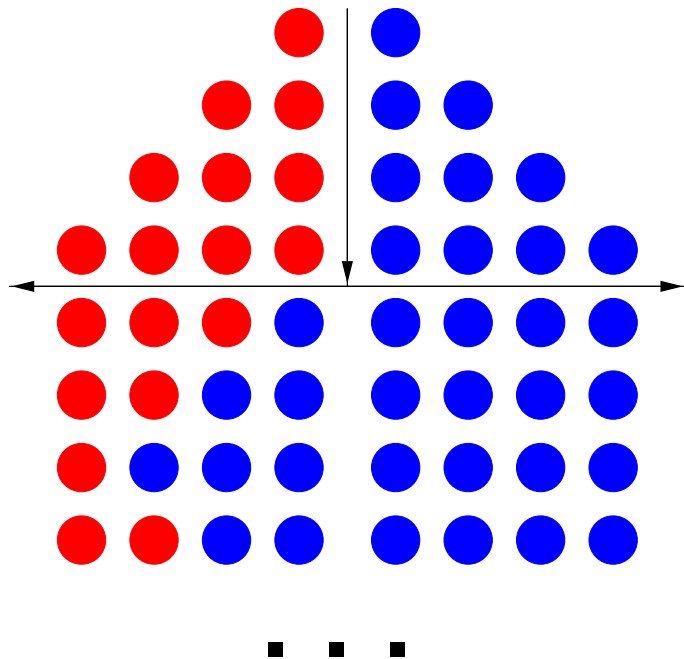
$$\left(\frac{\partial T}{\partial B}\right)_S = -\frac{T}{C} \left(\frac{\partial S}{\partial B}\right)_T$$



# Density Matrix Renormalization Group

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

# Density Matrix Renormalization Group

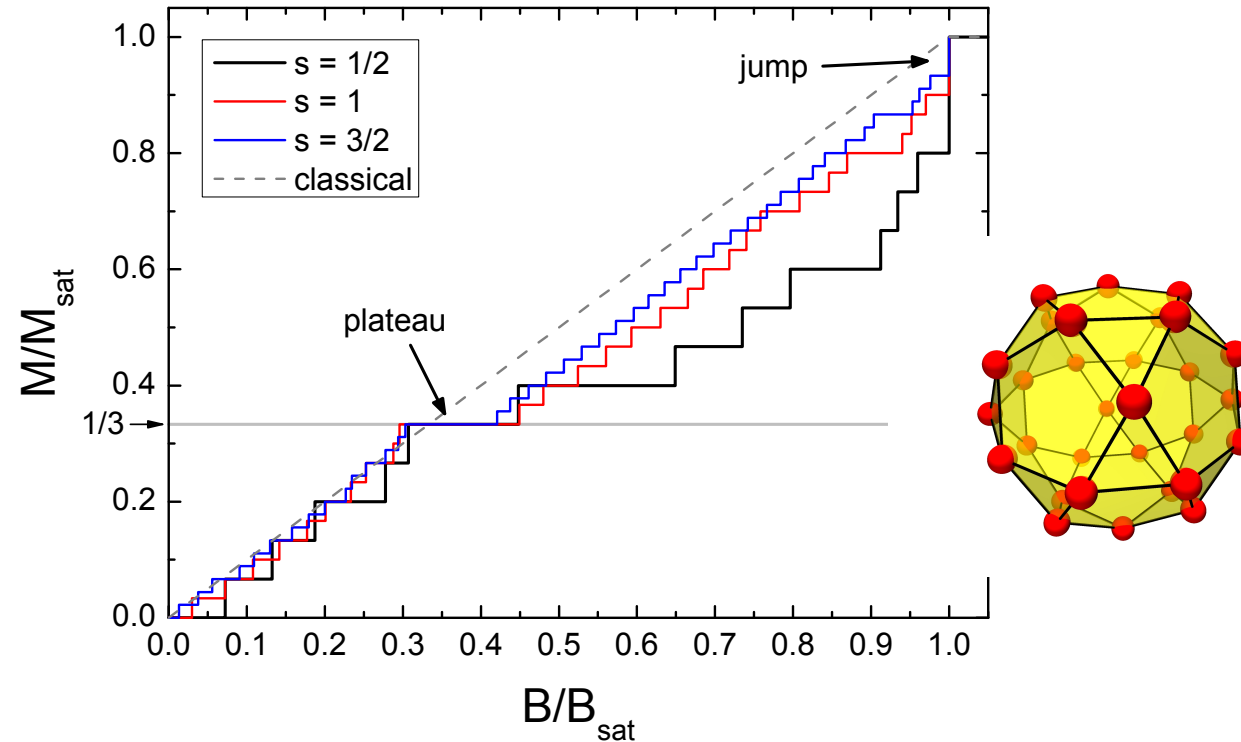


## Variational method:

- Naive idea: start with small system, diagonalize  $\tilde{H}$ , keep only  $m$  lowest states, enlarge system, diagonalize  $\tilde{H}$ , 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).

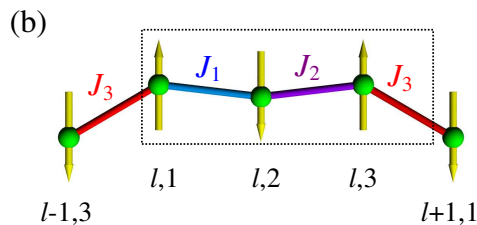
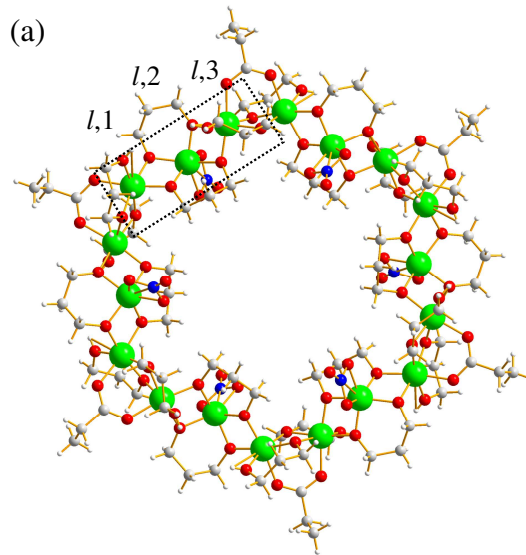
# Density Matrix Renormalization Group



- 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. **327** (2013) 103

# Dynamical Density Matrix Renormalization Group

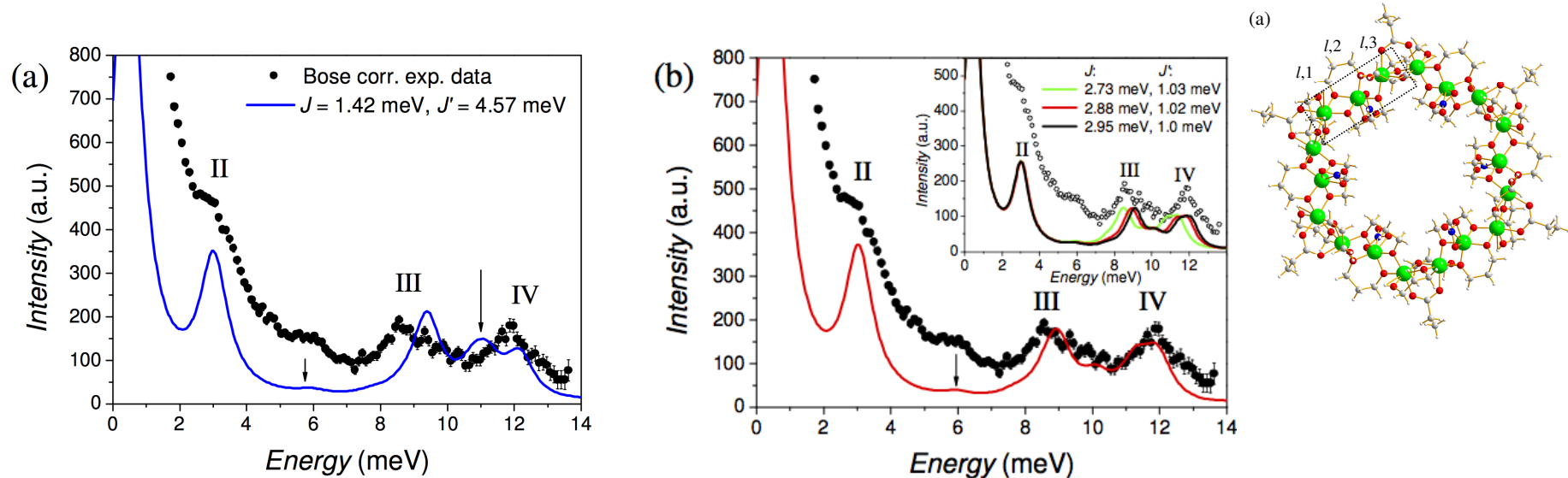


## Evaluation of correlation functions, e.g. for INS:

- $S_{jj'}^{zz}(\omega) \equiv \sum_n \langle 0 | \mathcal{S}_j^z | n \rangle \langle n | \mathcal{S}_{j'}^z | 0 \rangle \delta(\hbar\omega - E_n + E_0)$ ; transitions from the ground state;
- $S_{jj'}^{zz}(\omega) \approx \frac{1}{\pi} \langle 0 | \mathcal{S}_j^z \frac{\eta}{(E_0 + \hbar\omega - \tilde{H})^2 + \eta^2} \mathcal{S}_{j'}^z | 0 \rangle$ ;
- Use DMRG ground state and DMRG representation of  $\tilde{H}$  (1,2);  $\eta$  – 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).

# Dynamical Density Matrix Renormalization Group



- Accurate description of low-lying excitations for the giant ferric wheel  $\text{Fe}_{18}$ . Hilbert space dimension  $10^{14}$ .
- Determination of model parameters.

(1) J. Ummethum, J. Nehr Korn, 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).

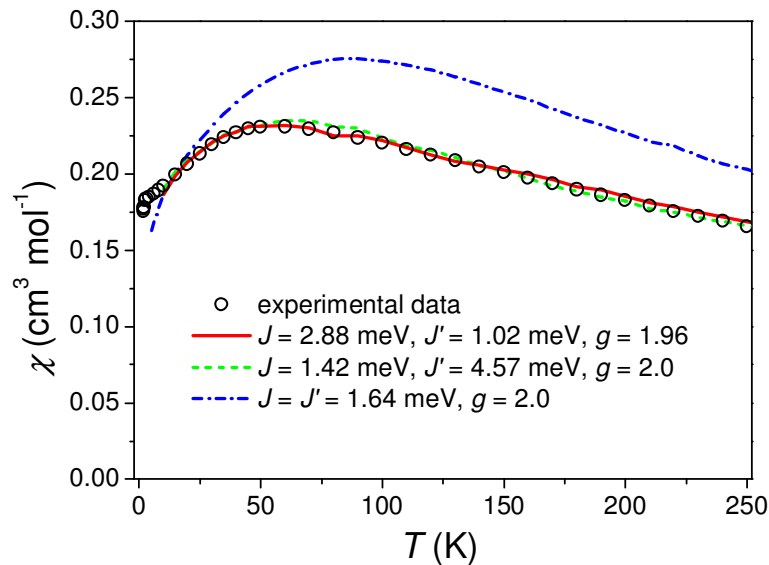
# Quantum Monte Carlo

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

# Quantum Monte Carlo

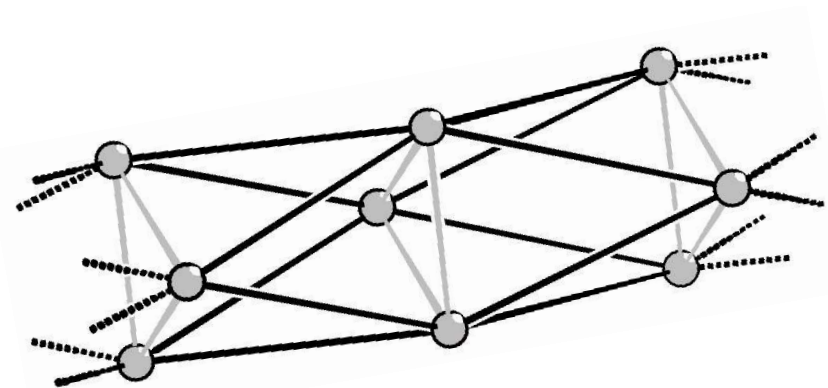
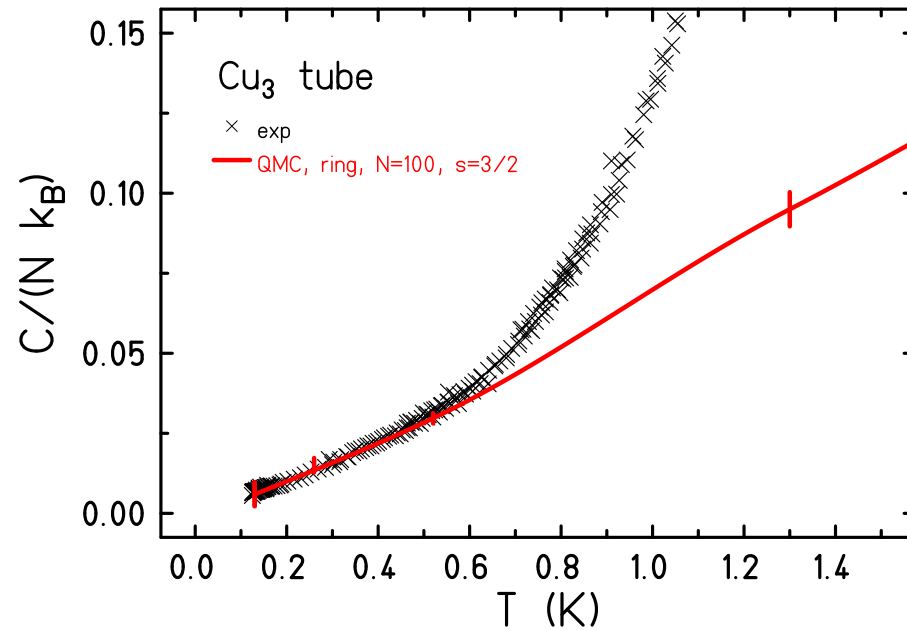
## Chopped (sliced) partition function:

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

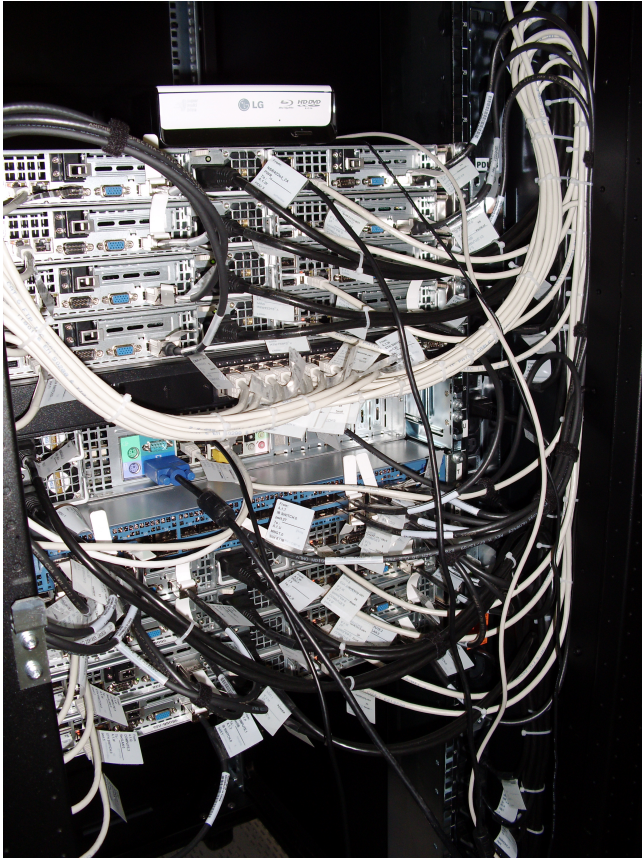


- [(CuCl<sub>2</sub>tachH)<sub>3</sub>Cl]Cl<sub>2</sub>: spins on triangles effectively coupled to  $s = 3/2$ , treatment as chain  $\Rightarrow$  Luttinger liquid behavior, i.e.  $C \propto T$ .
- 100 spins  $s = 3/2$  are no problem for QMC.

(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 (Zaragoza, Spain)
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The end.

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