Advanced quantum methods for the largest magnetic molecules

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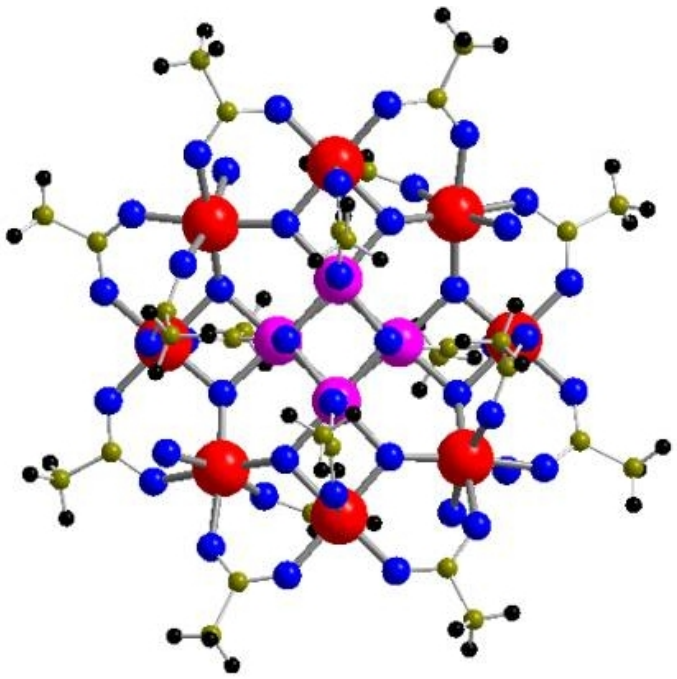
German subtitle:

Früher hatten wir Ideen,
heute haben wir Computer!

Beauty of Magnetic Molecules

The beauty of magnetic molecules I

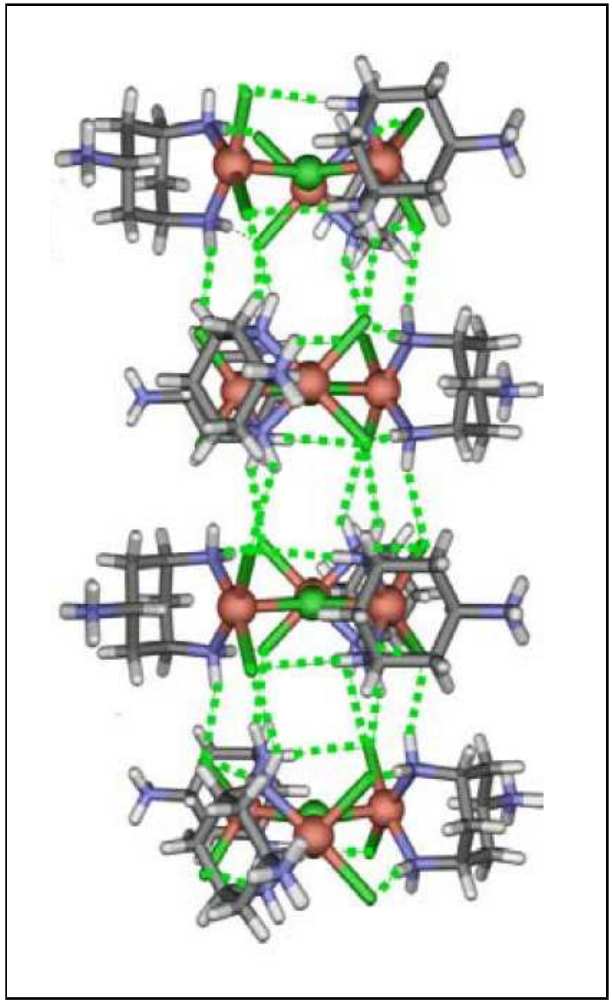


Mn_{12}

- Inorganic or organic macro molecules, e.g. poly-oxometalates, 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

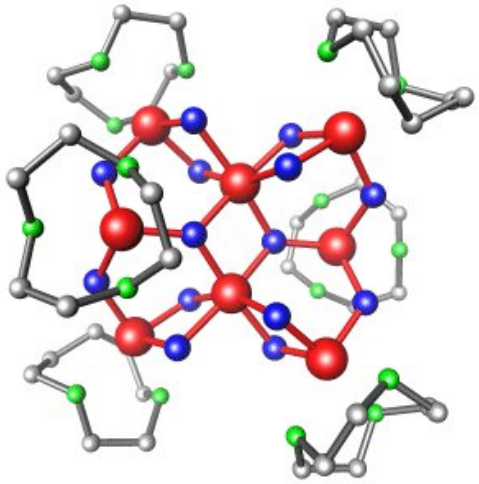
The beauty of magnetic molecules II

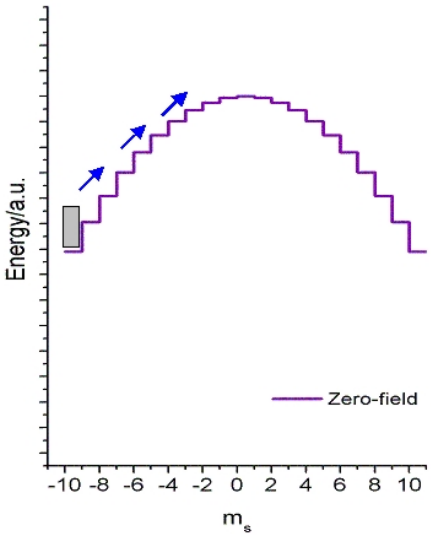


- Dimers (Fe_2), tetrahedra (Cr_4), cubes (Cr_8);
- Rings, especially iron rings (Fe_6, Fe_8, Fe_{10}, . . .);
- Complex structures (Mn_{12}) – drosophila of molecular magnetism;
- “Soccer balls”, more precisely icosidodecahedra (Fe_{30}) and other macro molecules;
- Chain like and planar structures 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



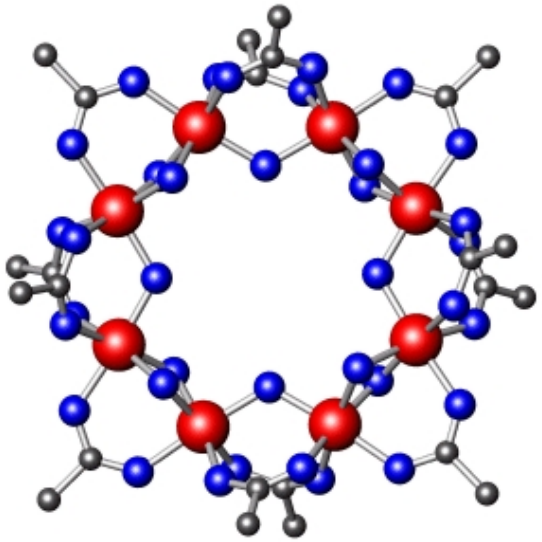


- Single Molecule Magnets (SMM): magnetic molecules with large ground state moment;
- Example: $S = 10$ for Mn_{12} or Fe_8;
- Anisotropy dominates approximate single-spin Hamiltonian:

$$\underset{\sim}{H} = -D\underset{\sim}{S}_z^2 + \underset{\sim}{H}', \qquad \left[\underset{\sim}{S}_z, \underset{\sim}{H}'\right] \neq 0$$

- 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?

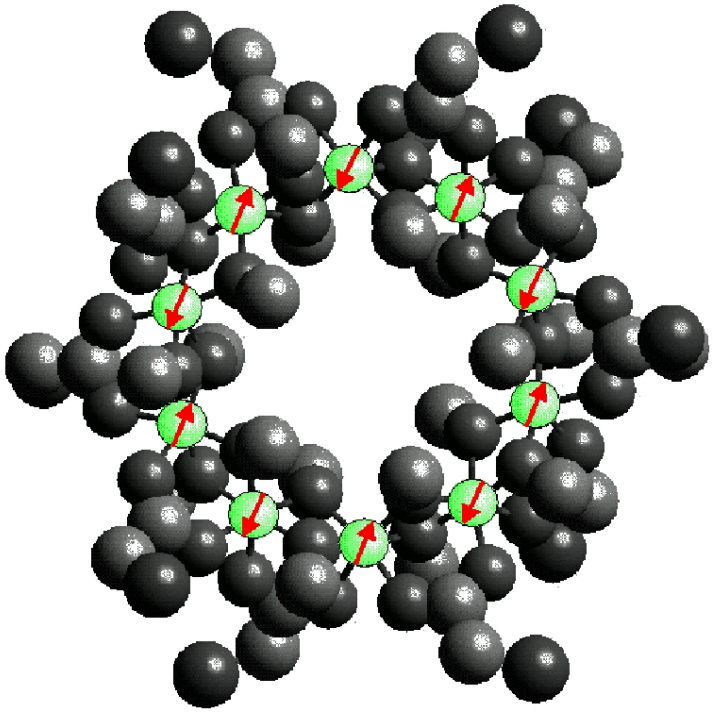


Cr_8

- 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!

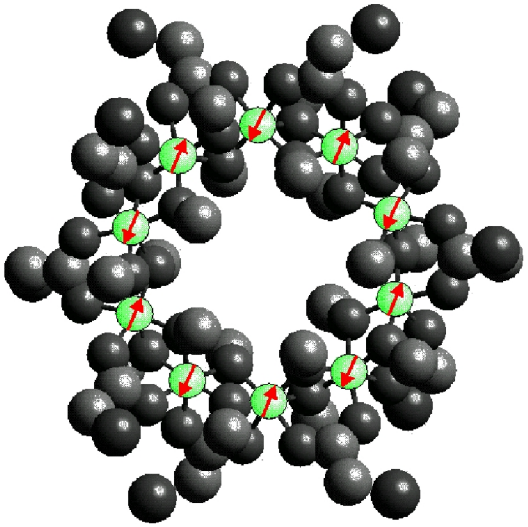


Congratulations!

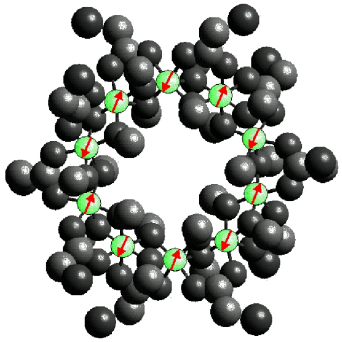
You have got an idea about the modeling!

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

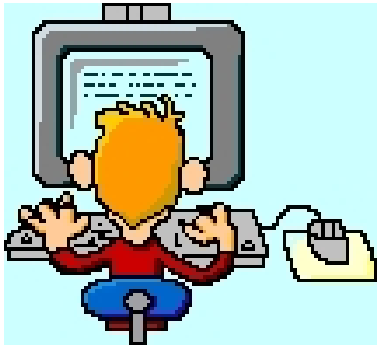
Heisenberg Zeeman



In the end it's always a big matrix!



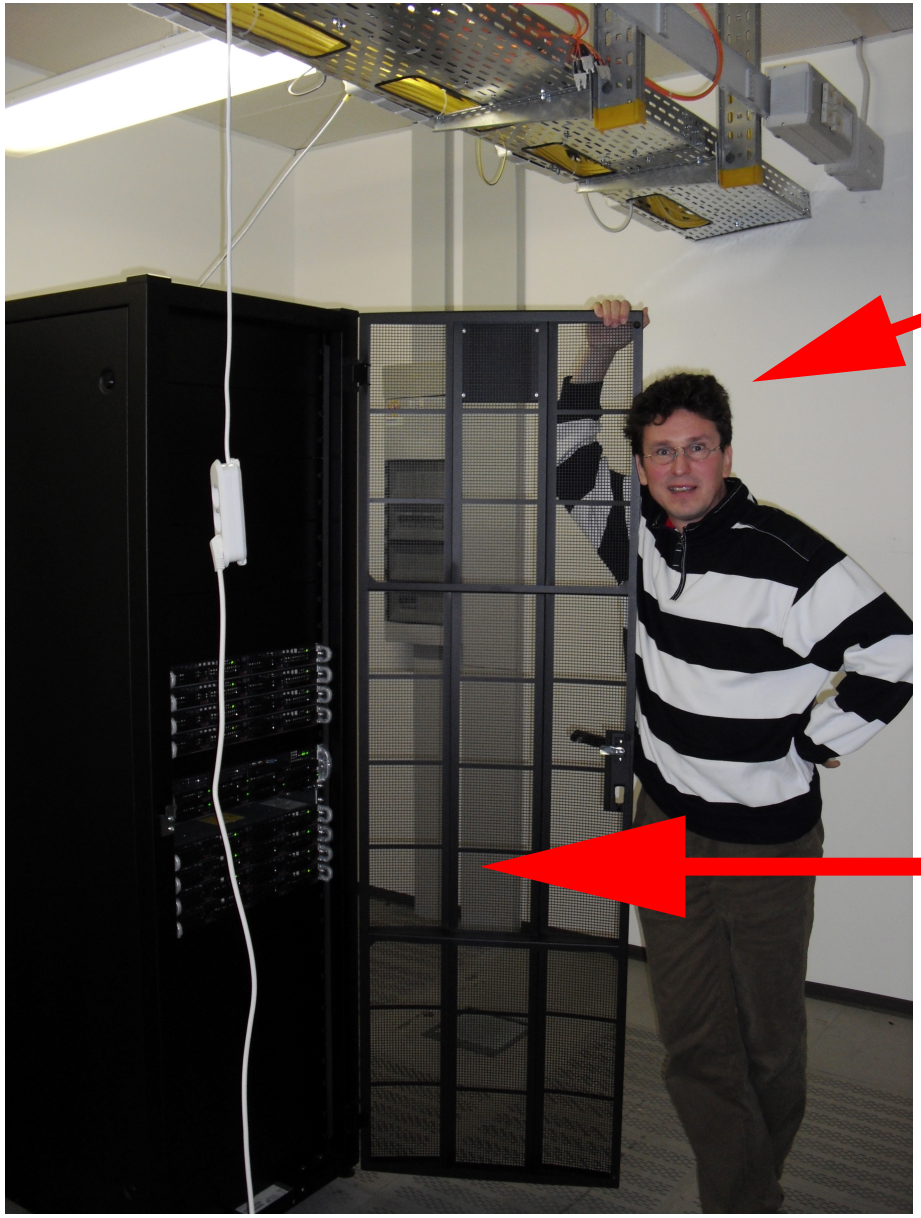
$$\Rightarrow \begin{pmatrix} -27.8 & 3.46 & 0.18 & \cdots \\ 3.46 & -2.35 & -1.7 & \cdots \\ 0.18 & -1.7 & 5.64 & \cdots \\ \vdots & \vdots & \vdots & \cdots \end{pmatrix} \Rightarrow$$



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

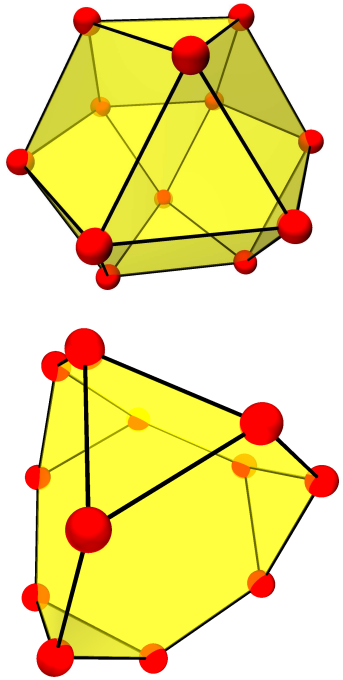
+ examples of problems that can be solved with these methods.

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. 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).

Irreducible Tensor Operator approach



Spin rotational symmetry SU(2):

- $\underset{\sim}{H} = -2\sum_{i<j} J_{ij}\ \vec{\underset{\sim}{s}}_i \cdot \vec{\underset{\sim}{s}}_j + g\mu_B \vec{\underset{\sim}{S}} \cdot \vec{B}$;
- Physicists employ: $\left[\underset{\sim}{H}, \underset{\sim}{S}_z\right] = 0$;
- Chemists employ: $\left[\underset{\sim}{H}, \vec{\underset{\sim}{S}}^2\right] = 0$, $\left[\underset{\sim}{H}, \underset{\sim}{S}_z\right] = 0$;

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

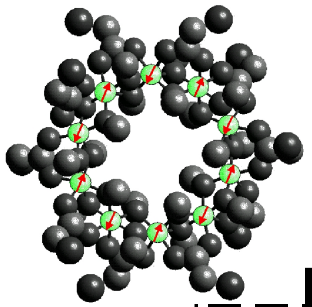
(1) M. Tinkham, *Group Theory and Quantum Mechanics*, Dover.
(2) D. Gatteschi and L. Pardi, Gazz. Chim. Ital. **123**, 231 (1993).
(3) O. Waldmann, Phys. Rev. B **61**, 6138 (2000).
(4) R. Schnalle and J. Schnack, Int. Rev. Phys. Chem. **29**, 403-452 (2010) ⇐ contains EVERYTHING.

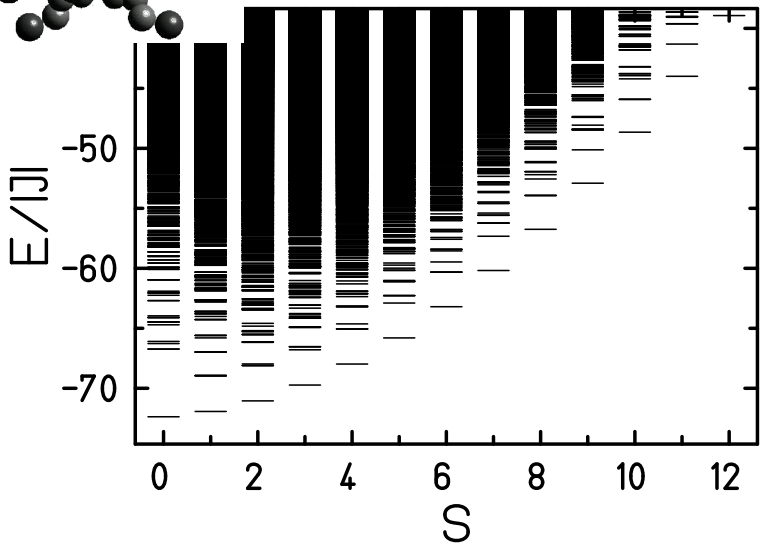
Decomposition of Hamilton Matrix

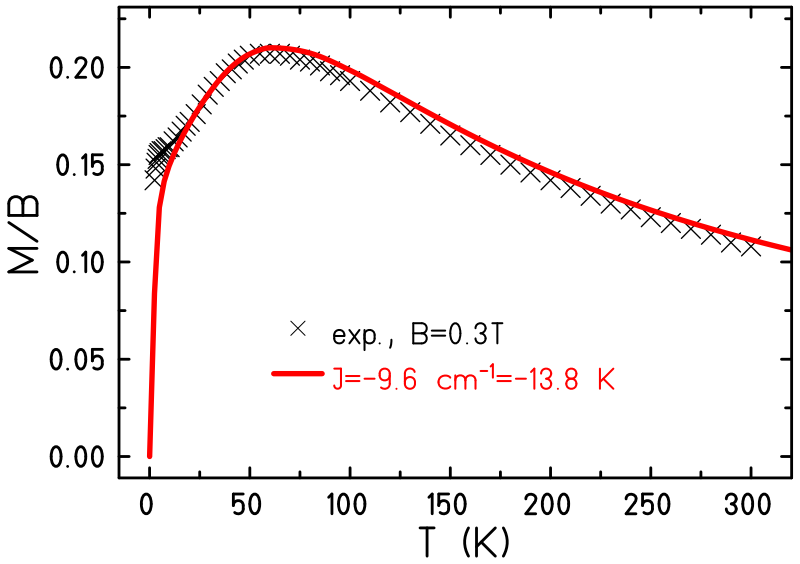
M_1 Γ_1	0	0	0
0	M_1 Γ_2	0	0
0	0	M_2 Γ_1	0
0	0	0	M_2 Γ_2

Block diagonal due to symmetry-adapted basis.
Only separate blocks need to be diagonalized.

Example: Fe_{10}







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

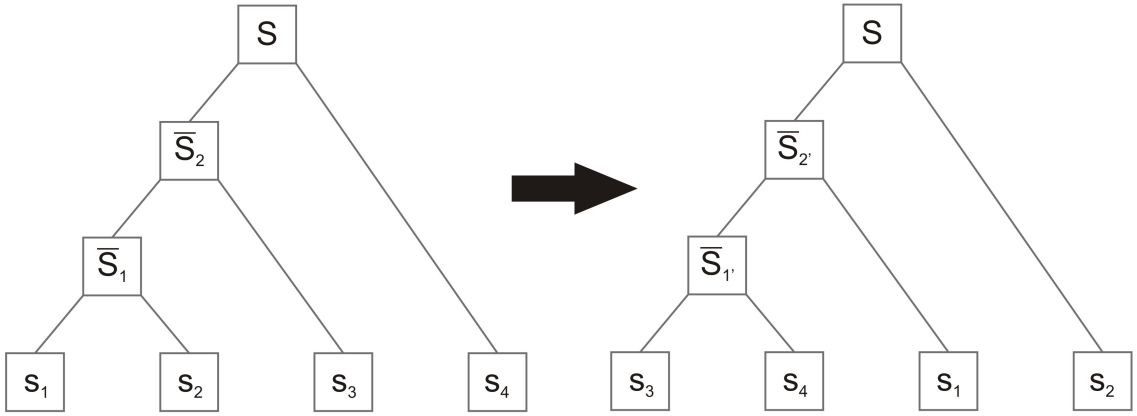
(1) R. Schnalle and J. Schnack, Int. Rev. Phys. Chem. **29**, 403-452 (2010).
(2) C. Delfs *et al.*, Inorg. Chem. **32**, 3099 (1993).

Point Group Symmetry II

$$\underset{\sim}{G}(R)\,|\,\alpha\,S\,M\,\rangle_a = \,|\,\alpha\,S\,M\,\rangle_b = \sum_{\alpha'} |\,\alpha'\,S\,M\,\rangle_a\;{}_a\langle\,\alpha'\,S\,M\,|\,\alpha\,S\,M\,\rangle_b$$

- Serious problem: application of $\underset{\sim}{G}(R)$, 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 IV – binary trees



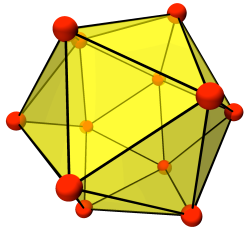
- Recoupling coefficient $\langle s_1 s_2 \overline{S}_1 s_3 \overline{S}_2 s_4 SM \,|\, s_3 s_4 \overline{S}_{1'} s_1 \overline{S}_{2'} s_2 SM \rangle$ can be evaluated by a graphical transformation of one binary tree into the other (1,2).

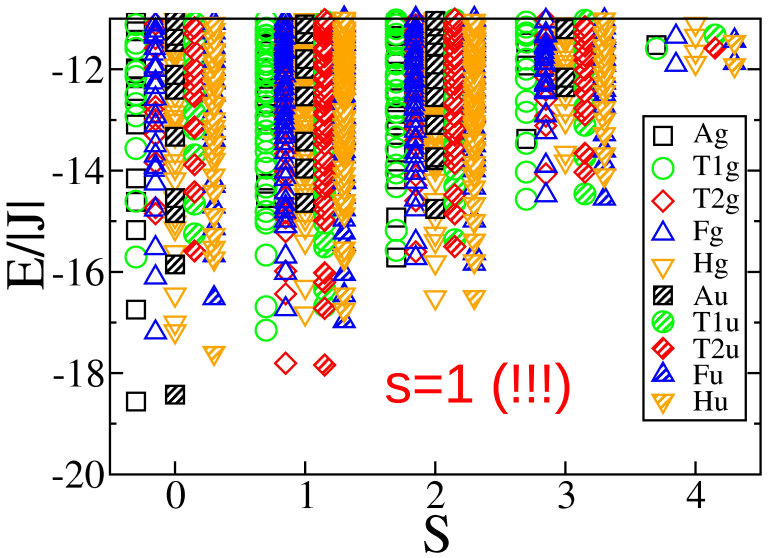
- Exchange and flop operations generate a recoupling formula consisting of square roots, Wigner-6J symbols, and sums over intermediate spins.

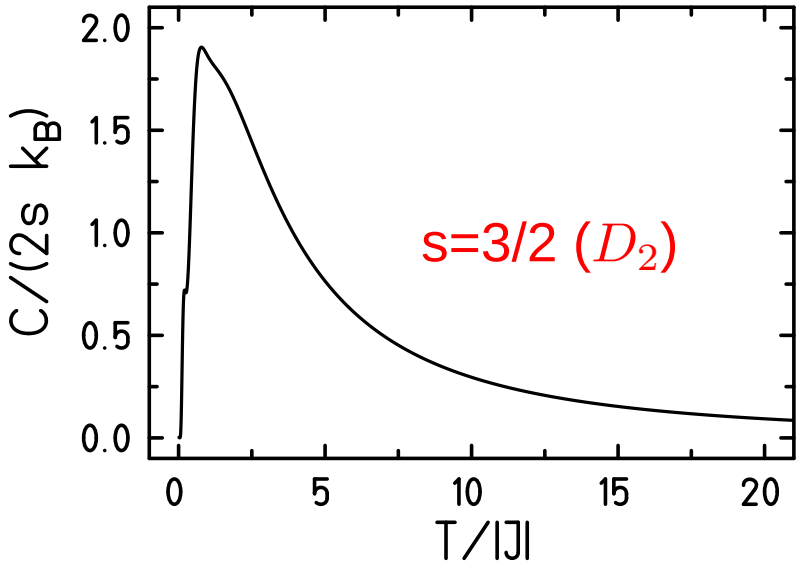
- Open question: optimal coupling for a given symmetry? (3)

(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).

World-leading, but . . .

This world-leading method was developed in Osnabrück, unfortunately . . .

World-leading, but . . .

it is too late!
There are more powerful and easy to program methods.

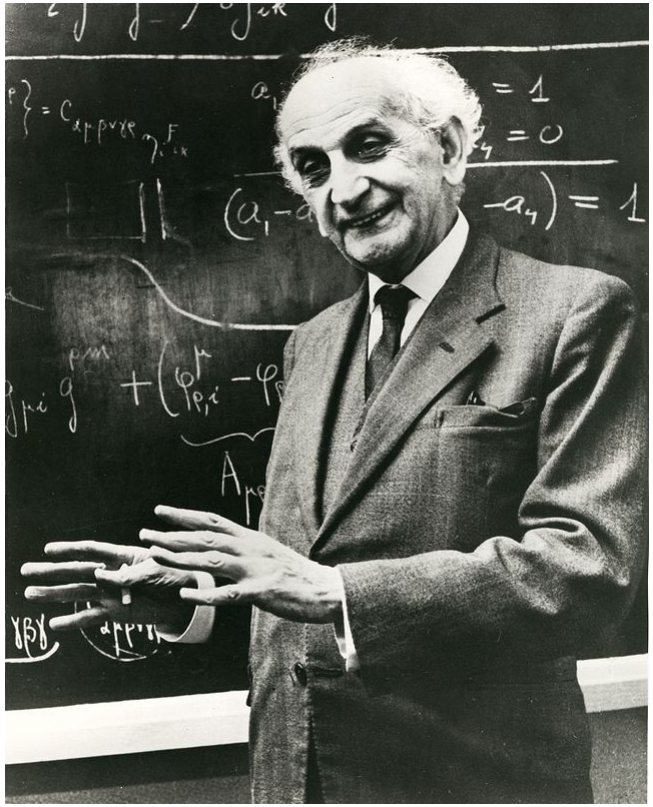
Matrix theory goes on . . .

. . . at the Hessische Landesbank!

Finite-temperature Lanczos Method

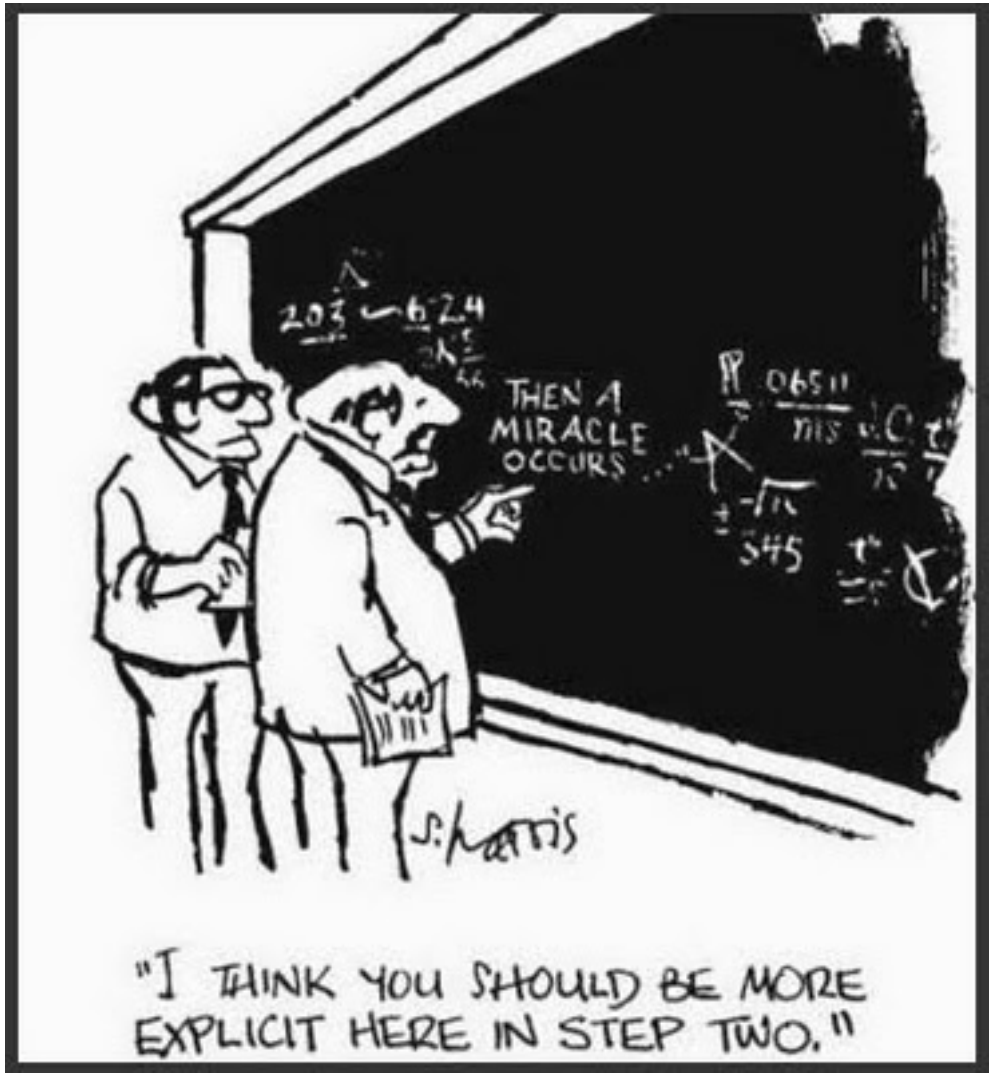
(Good for dimensions up to 10^{10}.)

Lanczos – a Krylov space method



- Idea: exact diagonalization in reduced basis sets.
- But which set to choose???
- Idea: generate the basis set with the operator you want to diagonalize:
  $\left\{ |\phi\rangle, \underset{\sim}{H}|\phi\rangle, \underset{\sim}{H}^2|\phi\rangle, \underset{\sim}{H}^3|\phi\rangle, \ldots \right\}$
- But which starting vector to choose???
- Idea: almost any will do!
- Cornelius Lanczos (Lánczos Kornél, 1893-1974)

(1) C. Lanczos, J. Res. Nat. Bur. Stand. **45**, 255 (1950).


THEN A MIRACLE OCCURS
"I THINK YOU SHOULD BE MORE EXPLICIT HERE IN STEP TWO."

Finite-temperature Lanczos Method I

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

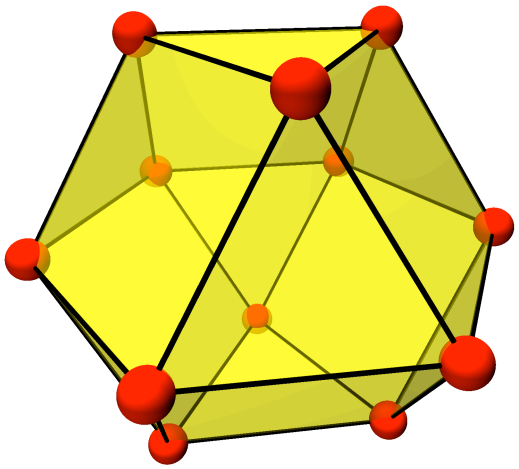
$$\langle \nu | \exp\left\{-\beta \underset{\sim}{H}\right\} | \nu \rangle \approx \sum_{n} \langle \nu | n(\nu) \rangle \exp\{-\beta\epsilon_n\} \langle n(\nu) | \nu \rangle \qquad \text{(Step 2)}$$

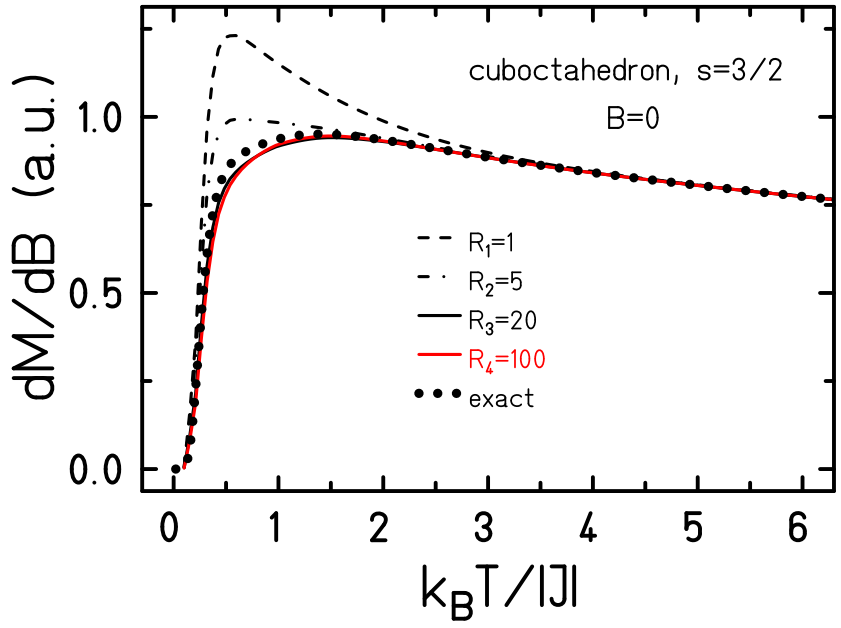
$$Z(T,B) \approx \frac{\dim(\mathcal{H})}{R} \sum_{\nu=1}^{R} \sum_{n=1}^{N_L} \exp\{-\beta\epsilon_n\} |\langle n(\nu) | \nu \rangle|^2$$

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

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

How good is finite-temperature Lanczos?

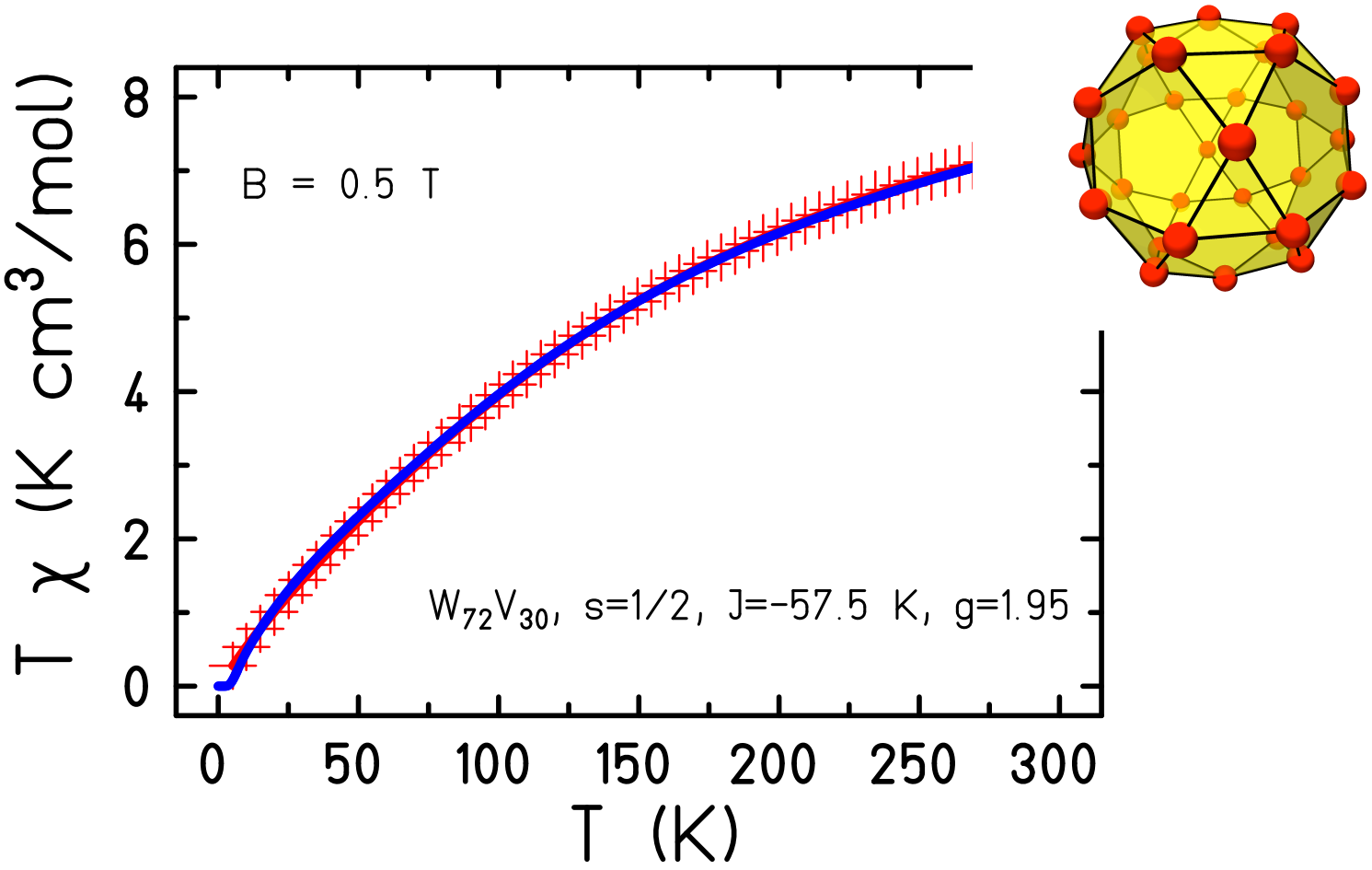




- Works very well: compare frustrated cuboctahedron.
- $N = 12, s = 3/2$: Considered $< 100,000$ states instead of 16,777,216.

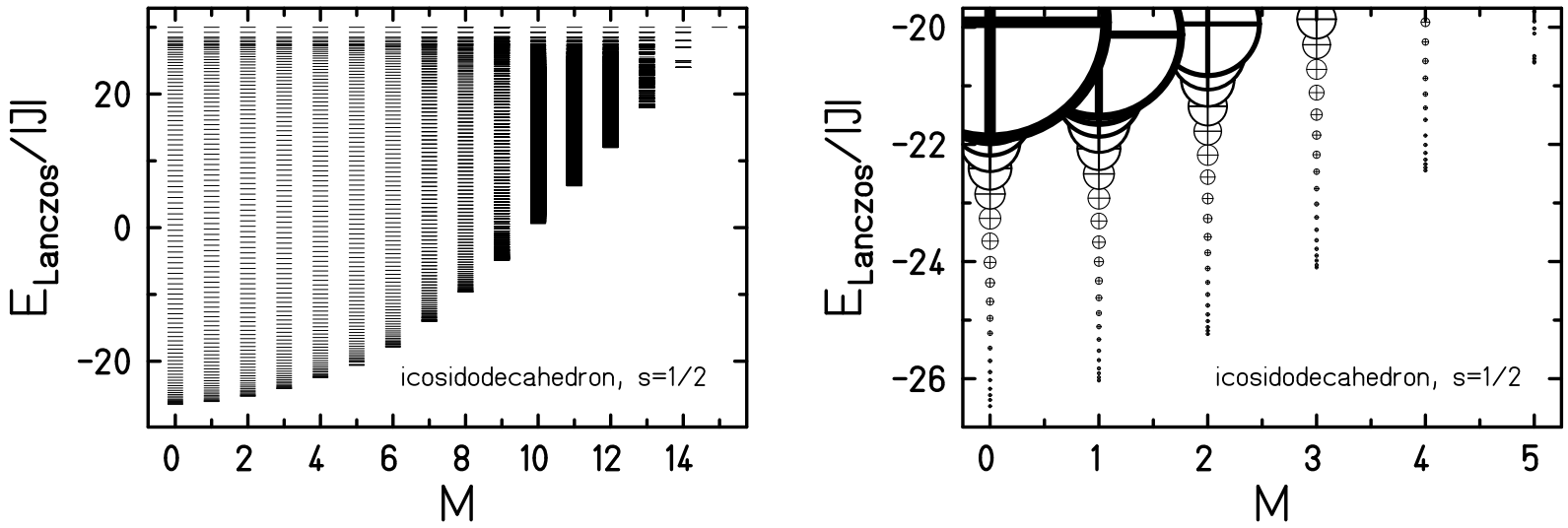
Exact results: R. Schnalle and J. Schnack, Int. Rev. Phys. Chem. **29**, 403-452 (2010).
FTLM: J. Schnack and O. Wendland, Eur. Phys. J. B **78**, 535-541 (2010).

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).

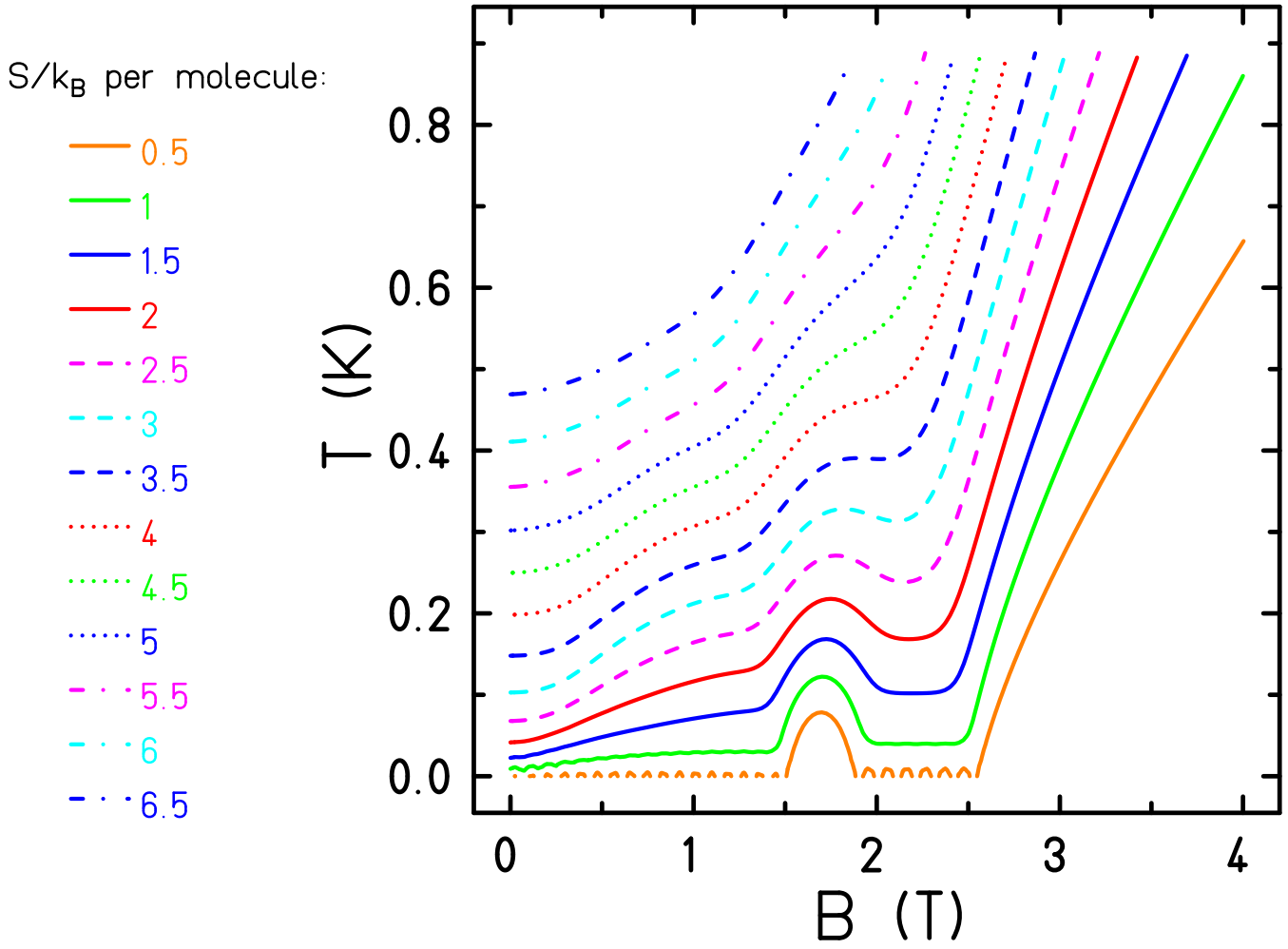
Icosidodecahedron $s = 1/2$



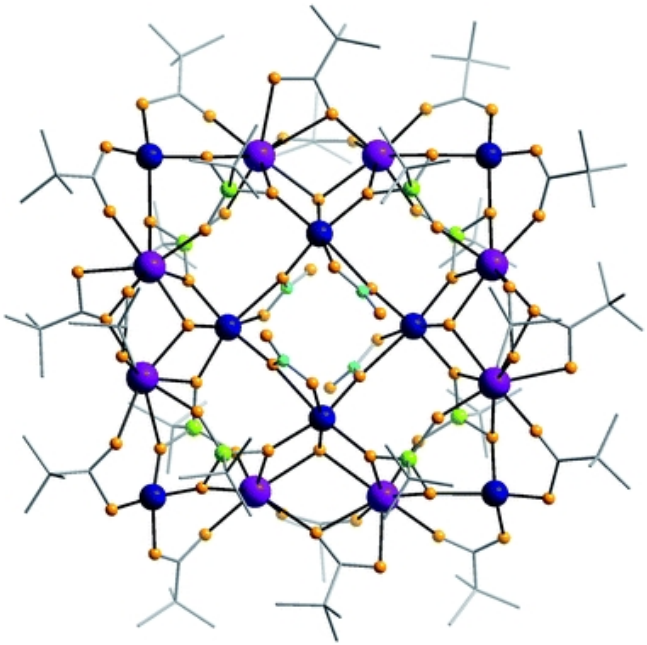
- The true spectrum will be much denser. This is miraculously compensated for by the weights.

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

What is it good for? Magnetocaloric effect!



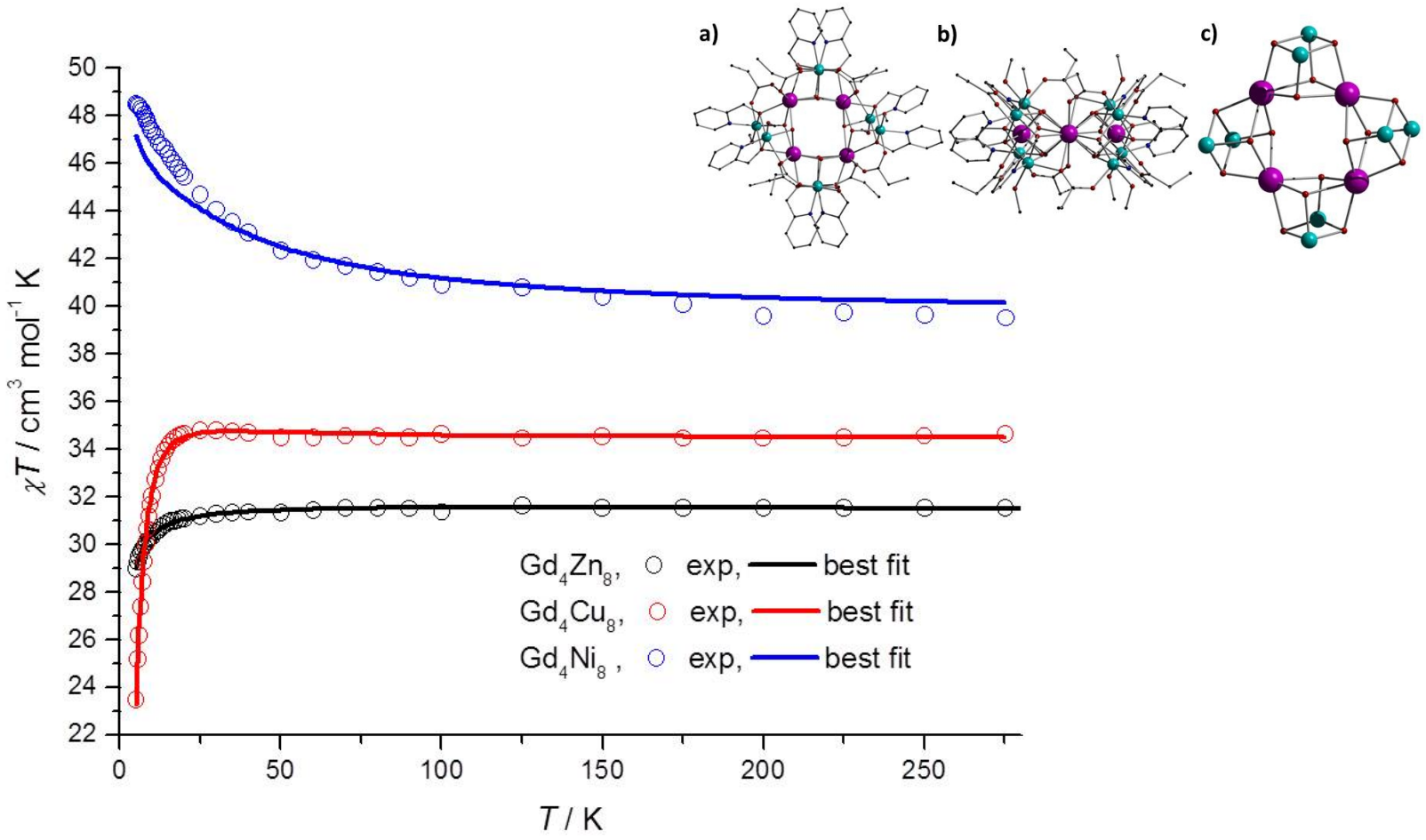
Magnetocaloric effect – Why Gd compounds?



- High spin of $s = 7/2$;
- Weak exchange $\Rightarrow$ high density of states;
- Can vary the entropy with moderate fields.
- But large Hilbert spaces!
  Exact modeling impossible.

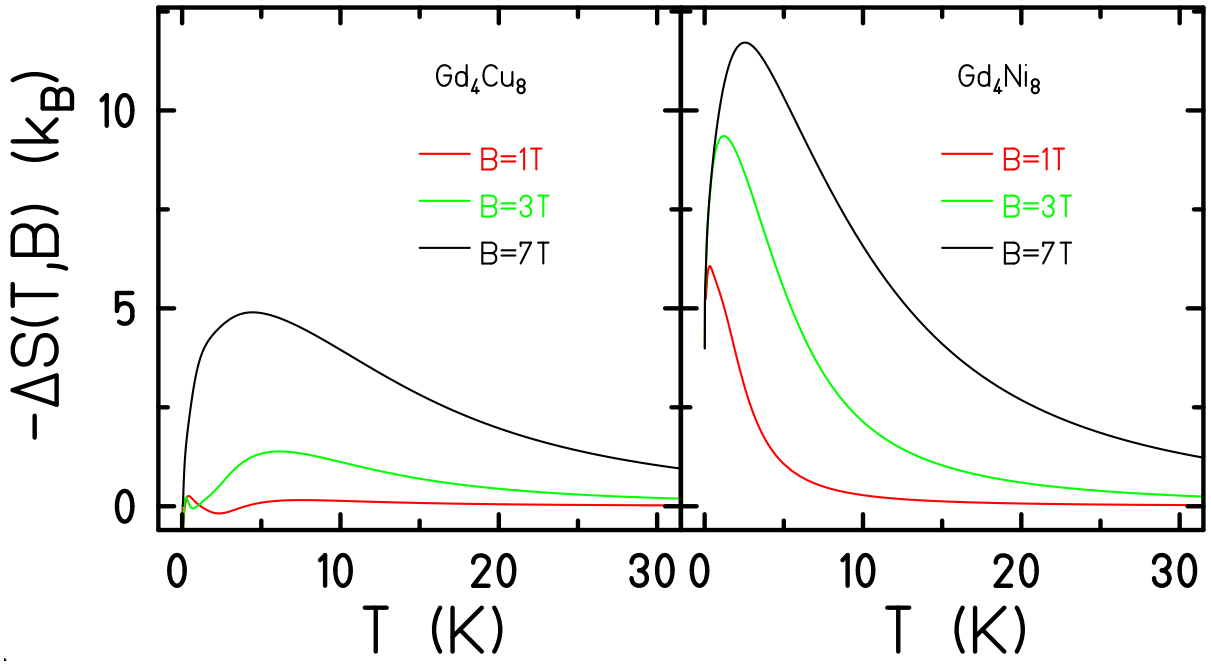
Yan-Zhen Zheng, Marco Evangelisti, Richard E. P. Winpenny, Chem. Sci. **2**, 99-102 (2011)

Gd_4M_8 – Susceptibility



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

Gd$_4$M$_8$ – magnetocaloric properties

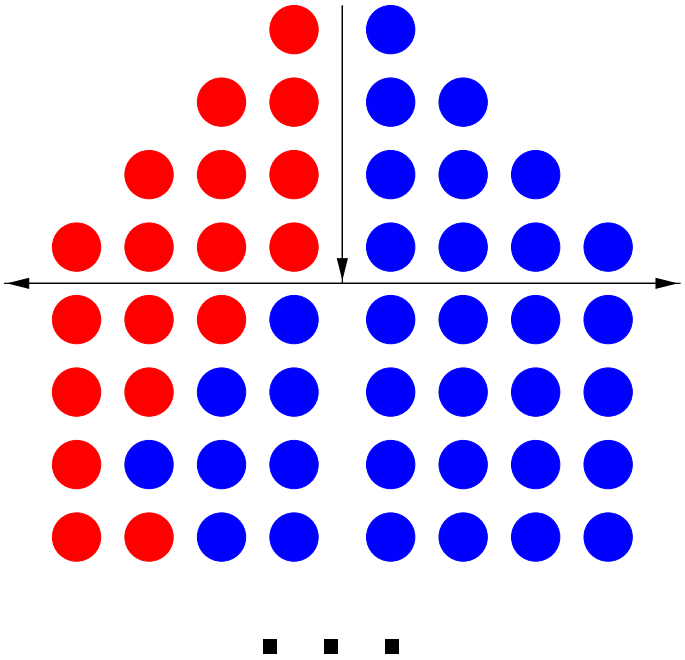


$$\left(\frac{\partial T}{\partial B}\right)_S = -\frac{T}{C}\left(\frac{\partial S}{\partial B}\right)_T$$

Density Matrix Renormalization Group

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

Density Matrix Renormalization Group

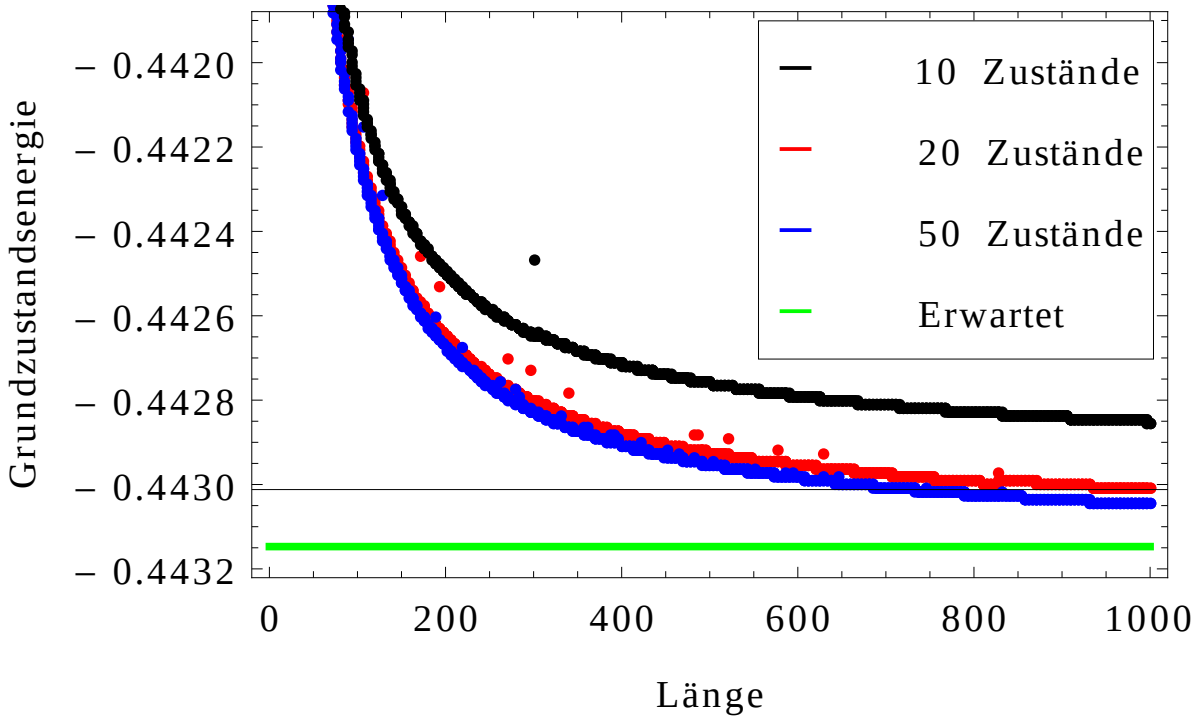


Again: build your appropriate reduced basis set

- 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.

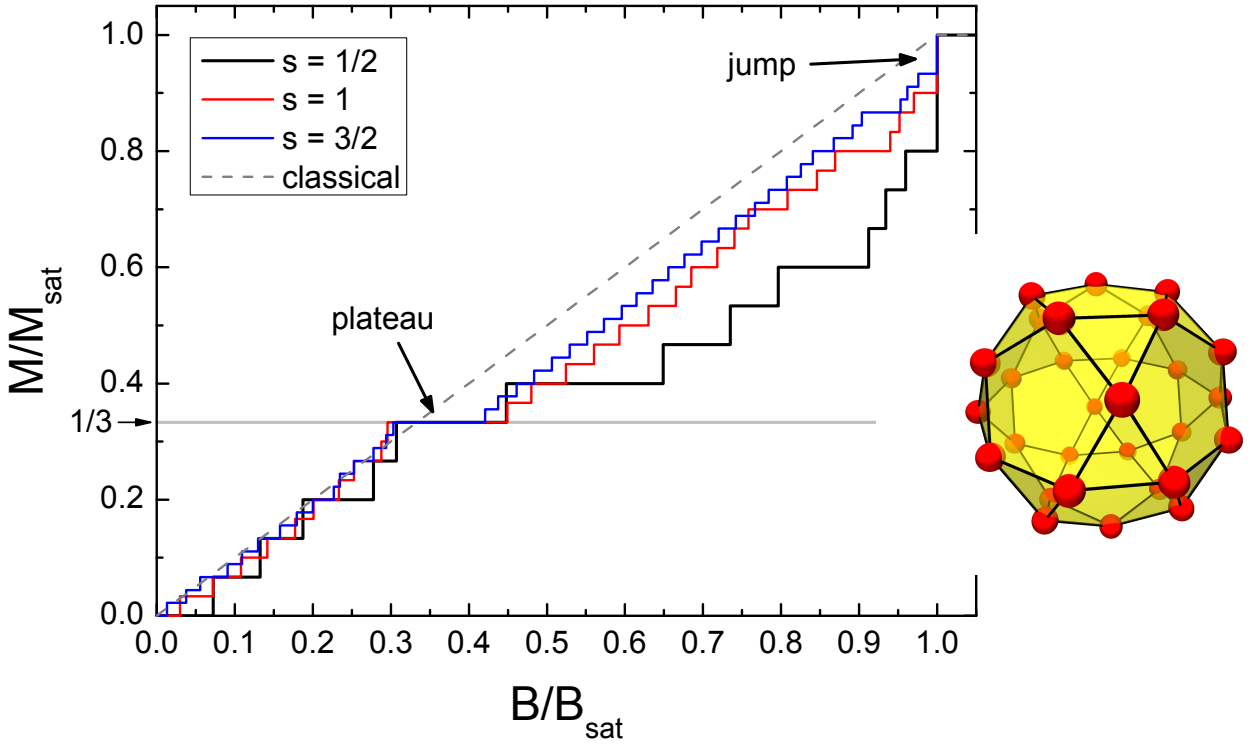
(1) S. R. White, Phys. Rev. Lett. **69**, 2863 (1992).
(2) S. R. White, Phys. Rev. B **48**, 10345 (1993).
(3) U. Schollwöck, Rev. Mod. Phys. **77**, 259 (2005).

DMRG spin chain $s = 1/2$



- Simple example: 1000 spins with $s = 1/2$; Hilbert space dimension $2^{1000} \approx 10^{301}$.
- Approaches result known from Bethe ansatz with matrices as small as 50×50!

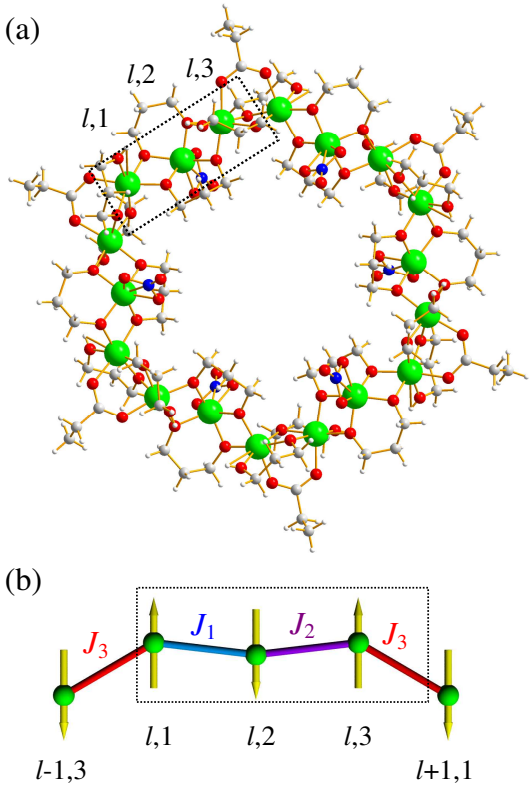
Density Matrix Renormatization Group



- 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. **327** (2013) 103

Dynamical Density Matrix Renormatization Group

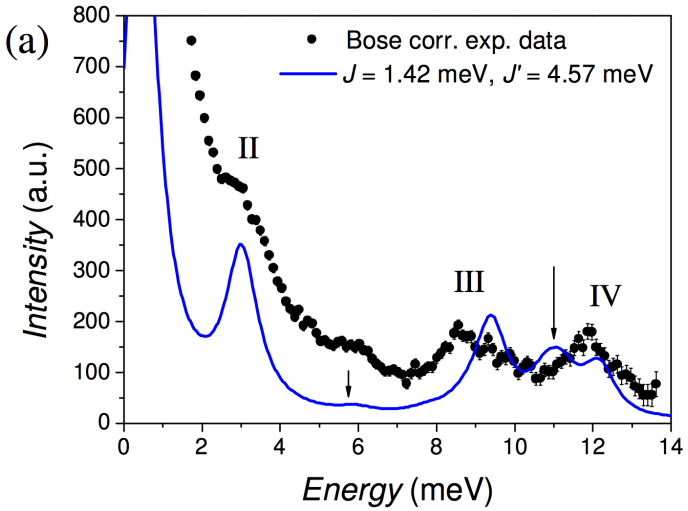


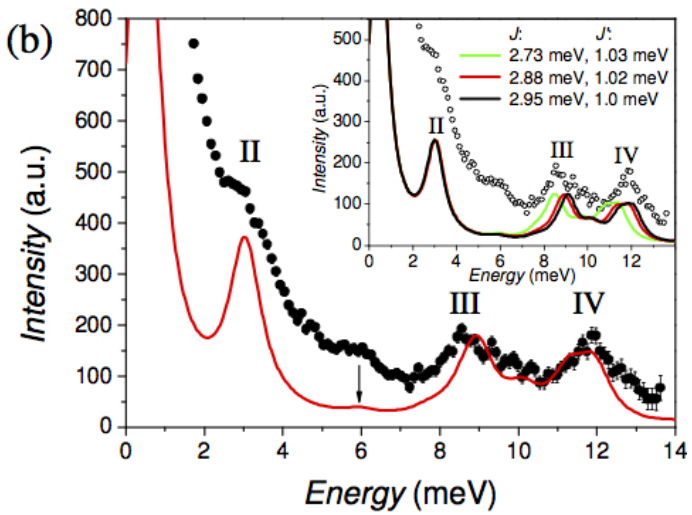
Evaluation of correlation functions, e.g. for INS:

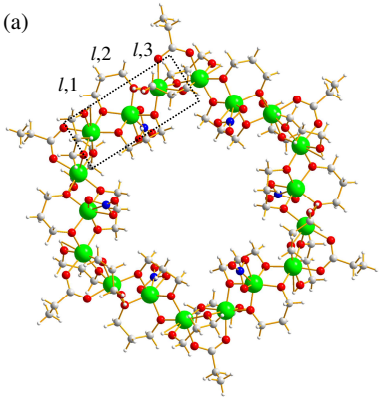
- $S^{zz}_{jj'}(\omega) \equiv \sum_n \langle 0|\underset{\sim}{s}^z_j|n\rangle\langle n|\underset{\sim}{s}^z_{j'}|0\rangle\,\delta(\hbar\omega - E_n + E_0)$; transitions from the ground state;
- $S^{zz}_{jj'}(\omega) \approx \frac{1}{\pi}\langle 0|\underset{\sim}{s}^z_j \frac{\eta}{(E_0+\hbar\omega-\underset{\sim}{H})^2+\eta^2}\underset{\sim}{s}^z_{j'}|0\rangle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

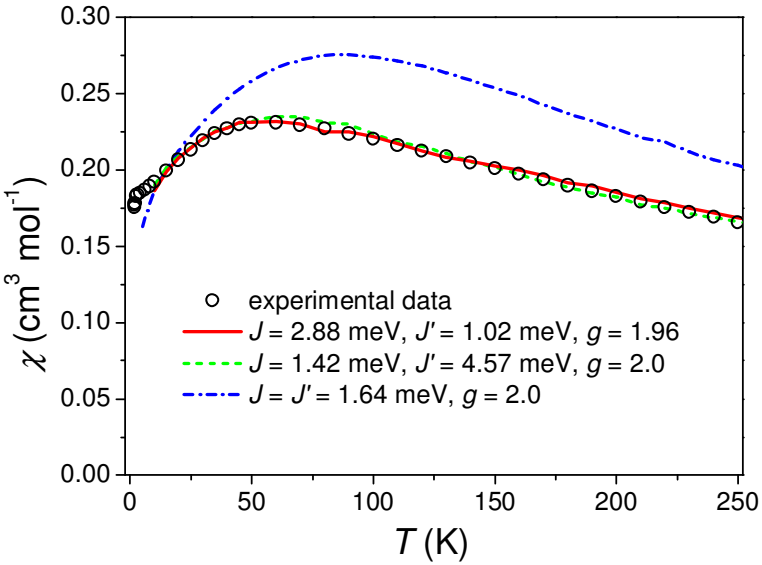
- Determination of model parameters.

(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



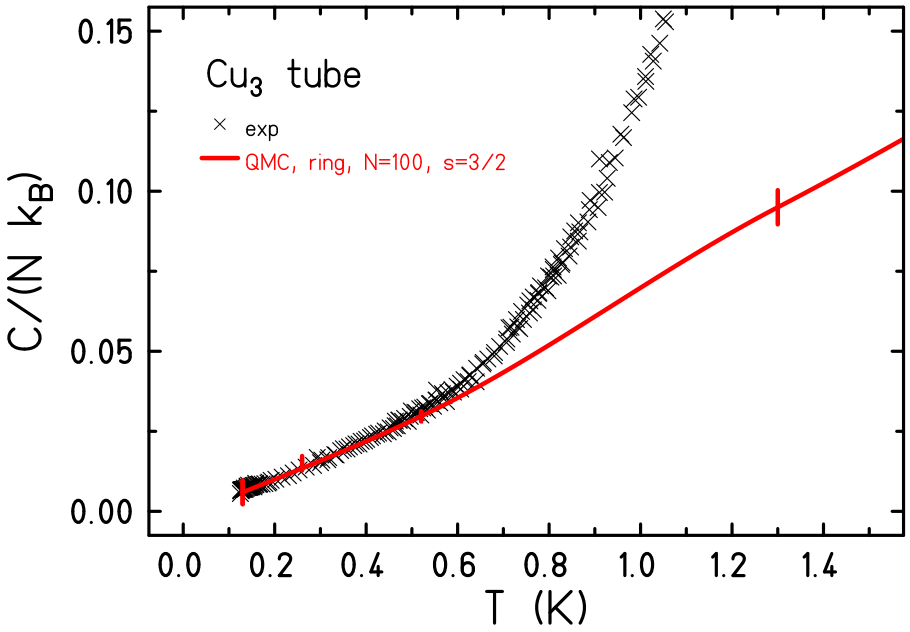
Chopped (sliced) partition function:

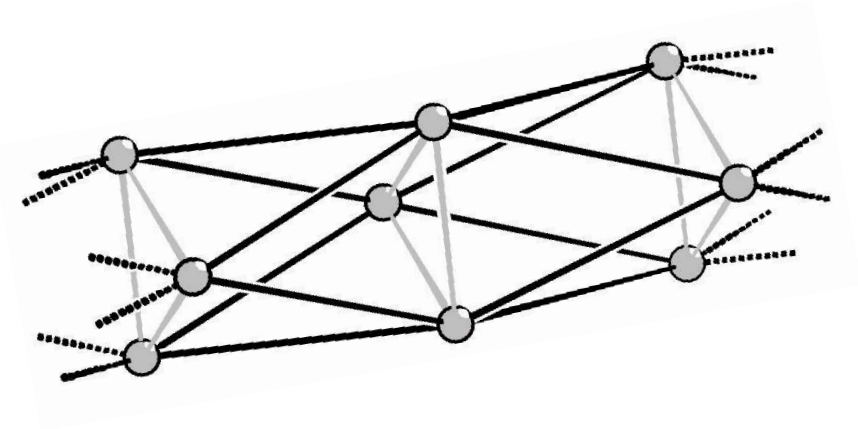
- $$Z(T,B) = \sum_\nu \langle \nu | \exp\left\{-\beta \underset{\sim}{H}\right\} | \nu \rangle$$
$$= \sum_\nu \langle \nu | \left[\exp\left\{-\beta \underset{\sim}{H}/m\right\}\right]^m | \nu \rangle$$
$$= \sum_{\nu,\alpha,\beta,\ldots} \langle \nu | \exp\left\{-\beta \underset{\sim}{H}/m\right\} | \alpha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

- 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

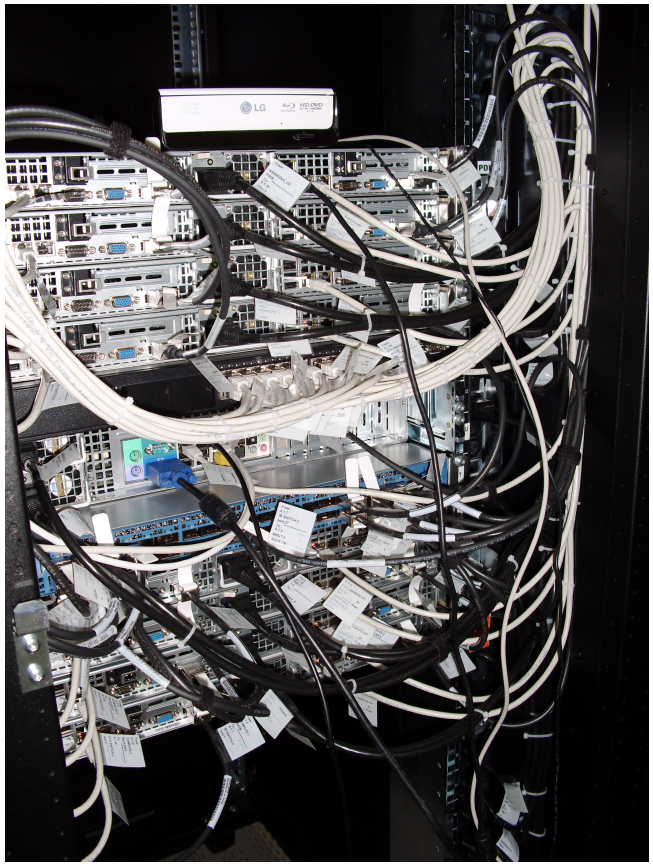




- $[(CuCl_2tachH)_3Cl]Cl_2$: spins on triangles effectively coupled to $s = 3/2$, treatment as chain $\Rightarrow$ Luttinger liquid behavior, i.e. $C \propto T$.
- 100 spins $s = 3/2$ are no problem for QMC.

(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)

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- 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)
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Thank you very much for your attention.

The end.

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