

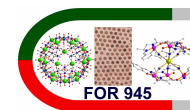
Advanced numerical methods for spin systems

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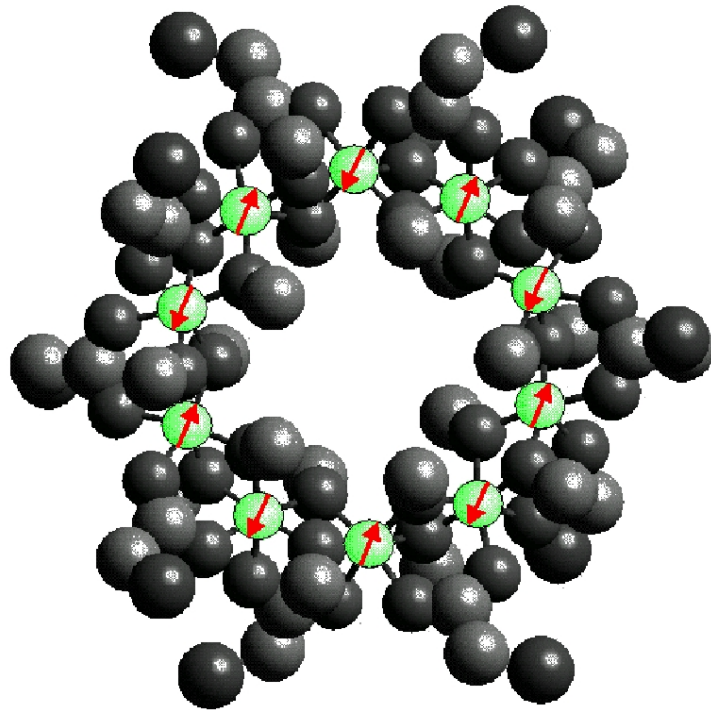
<http://obelix.physik.uni-bielefeld.de/~schnack/>

Seminar, Johann-Wolfgang-von-Goethe-Universität
Frankfurt am Main, 24. 04. 2015



The problem

You have got a molecule!



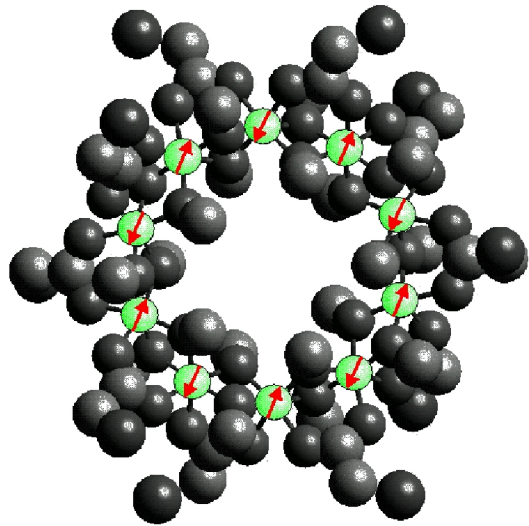
Congratulations!

You have got an idea about the modeling!

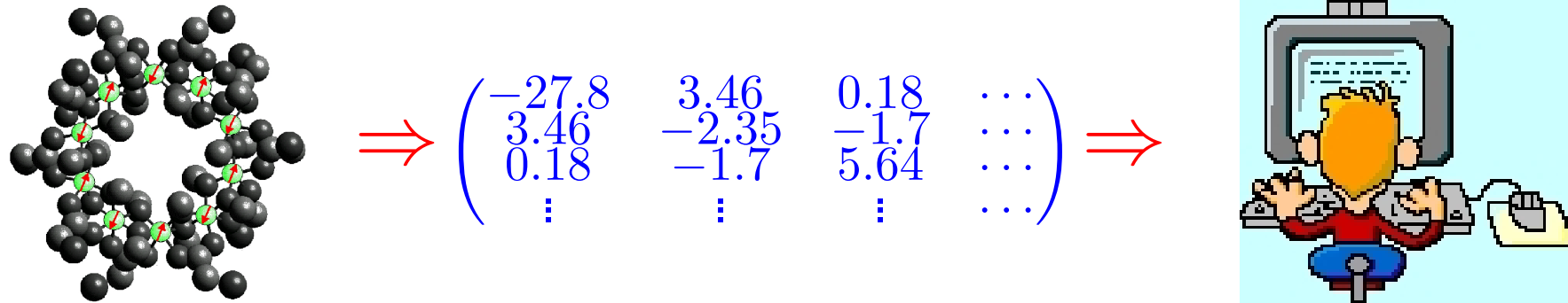
$$\tilde{H} = -2 \sum_{i < j} J_{ij} \vec{\tilde{s}}(i) \cdot \vec{\tilde{s}}(j) + g \mu_B B \sum_i^N \tilde{s}_z(i)$$

Heisenberg

Zeeman



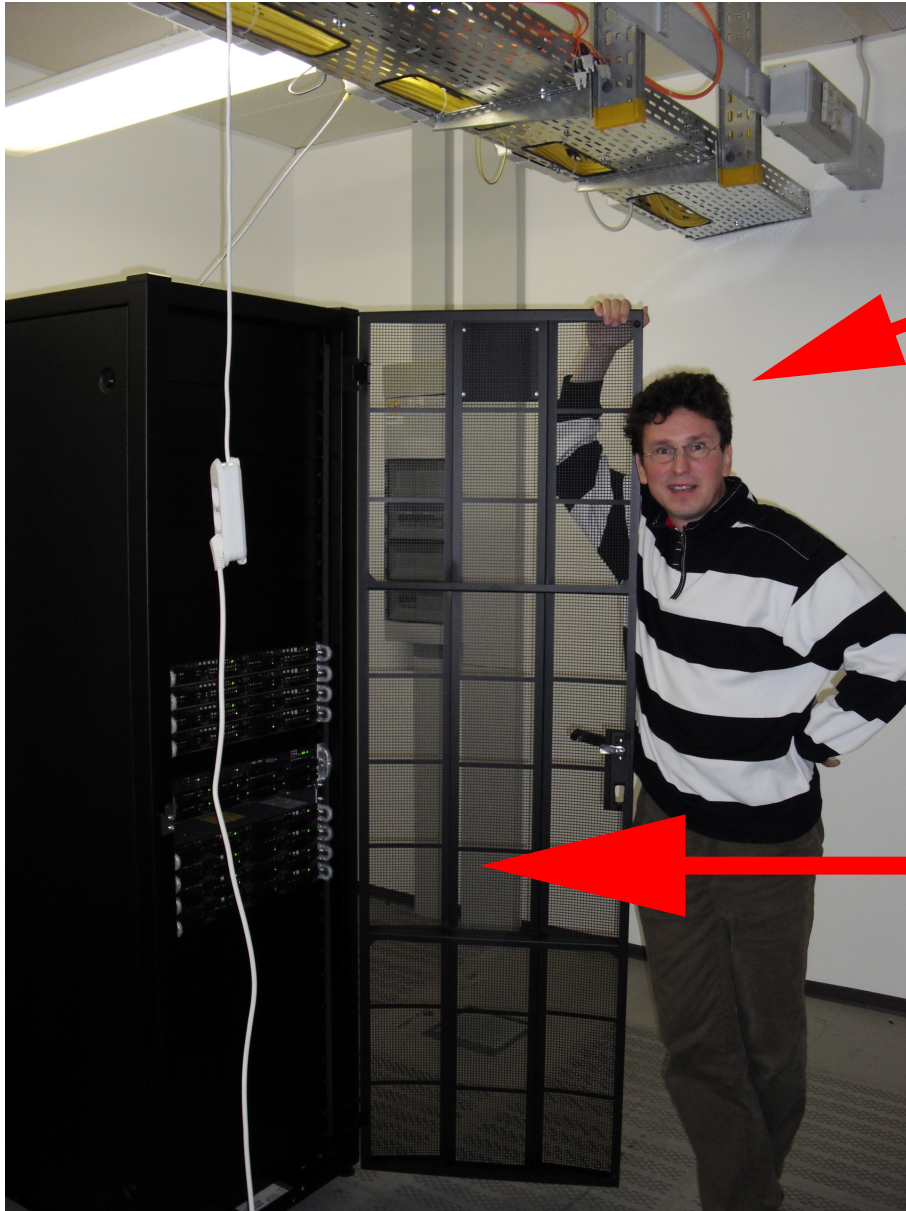
In the end it's always a big matrix!



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

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



$$\begin{pmatrix} 3 & 42 & 4711 \\ 42 & 0 & 3.14 \\ 4711 & 3.14 & 8 \\ -17 & 007 & 13 \\ 1.8 & 15 & 081 \end{pmatrix}$$

1. Complete diagonalization (easy)
2. Complete diagonalization (SU(2) & point group)
3. Finite-Temperature Lanczos
4. DMRG
5. QMC

We are the sledgehammer team of matrix diagonalization.
Please send inquiries to jschnack@uni-bielefeld.de!

How can one calculate such things?

(Partition function, observables in the canonical ensemble)

Complete diagonalization: The easy version

Most physicists do this!

Model Hamiltonian – Heisenberg and more

$$\underline{H} = -2 \sum_{i < j} J_{ij} \underline{\tilde{S}}_i \cdot \underline{\tilde{S}}_j + \sum_{i,j} \underline{\tilde{S}}_i \cdot \mathbf{D}_{ij} \cdot \underline{\tilde{S}}_j + \mu_B B \sum_i^N g_i \tilde{S}_i^z$$

Heisenberg
Anisotropy, ...
Zeeman

The Heisenberg model including anisotropy, and dipol-dipol interaction if necessary, as well as a Zeeman term describes the magnetic spectrum of many molecules with high accuracy.

Reason: Ions of the iron group have quenched angular momentum $\langle \underline{l} \rangle \approx 0$ due to chemical binding, remaining spin-orbit coupling treated perturbatively with the help of anisotropy terms. This is different for rare earth ions!

Since the dimension of Hilbert space equals $(2s + 1)^N$ the Hamiltonian can be diagonalized completely for small molecules. For larger ones approximate methods are used.

Product basis and symmetries

Product basis, total dimension: $\dim(\mathcal{H}) = (2s + 1)^N$

$$\tilde{S}_u^z |m_1, \dots, m_u, \dots, m_N\rangle = m_u |m_1, \dots, m_u, \dots, m_N\rangle$$

These states span the Hilbert space and are used to construct symmetry-related basis states. Use $a_u = s_u - m_u$ for computation (integer).

Symmetries of the Heisenberg model without anisotropy

$$\left[\tilde{H}, \tilde{S}^2 \right] = 0 \quad , \quad \left[\tilde{H}, \tilde{S}_z \right] = 0$$

Additional (point group) symmetries are possible, e.g. shifts on a ring molecule.

Decomposition into mutually orthogonal subspaces

If $[\tilde{H}, \tilde{S}_z] = 0$, the Hilbert space \mathcal{H} can be decomposed into mutually orthogonal subspaces $\mathcal{H}(M)$ (M is the quantum number belonging to \tilde{S}_z)

$$[\tilde{H}, \tilde{S}_z] = 0 \quad : \quad \mathcal{H} = \bigoplus_{M=-S_{\max}}^{+S_{\max}} \mathcal{H}(M), \quad S_{\max} = Ns$$

$\mathcal{H}(M)$ contains all states $|m_1, \dots, m_u, \dots, m_N\rangle$ with $\sum_i m_i = M$.

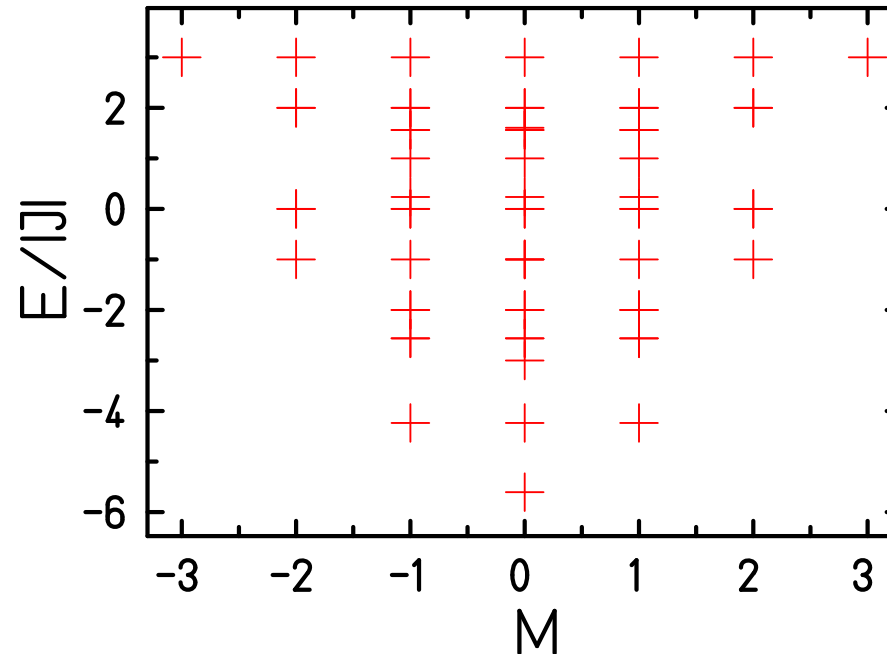
The Hamiltonian is diagonalized in all subspaces separately. The dimension of the largest subspace determines whether a Hamiltonian can be diagonalized completely. If further symmetries apply this dimension will be further reduced.

For practical purposes $\vec{s}_i \cdot \vec{s}_j = s_i^z s_j^z + \frac{1}{2} [s_i^+ s_j^- + s_i^- s_j^+]$.

Example: spin ring with $N = 6, s = 1/2$

- Total dimension of \mathcal{H} : $Dim(\mathcal{H}) = (2 \times 1/2 + 1)^6 = 64$;
- $M = 3$: $|\Omega\rangle = |+++++\rangle$; $Dim(\mathcal{H}(M)) = 1$;
- $M = 2$: $| - + + + + \rangle$ and cyclic shifts; $Dim(\mathcal{H}(M)) = 6$;
- $M = 1$: $| - - + + + \rangle, | - + - + + \rangle, | - + + - + \rangle$ and cyclic shifts;
 $Dim(\mathcal{H}(M)) = 15$;
- $M = 0$: $| - - - + + \rangle, | - - + - + \rangle, | - + - - + \rangle, | - + - + - \rangle$
and cyclic shifts; $Dim(\mathcal{H}(M)) = 20$;
- Dimensional check: $64 = 1 + 6 + 15 + 20 + 15 + 6 + 1 \checkmark$
- Inclusion of translational symmetry leads to orthogonal subspaces $\mathcal{H}(M, k)$ with $k = 0, \dots, 5$. Then the largest dimension is 4.

Exact diagonalization



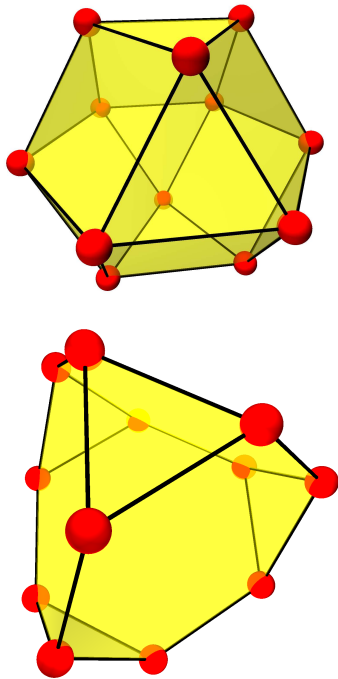
- Numerically exact diagonalization feasible up to RAM size;
- Example: 10,000x10,000 complex*16, 1.6 GB RAM needed;
- Not much we can do at this point, wait for more RAM 😊

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).

Idea of ITO

$$\begin{aligned}
 \underline{H}_{\text{Heisenberg}} &= -2 \sum_{i < j} J_{ij} \vec{s}_i \cdot \vec{s}_j \\
 &= 2\sqrt{3} \sum_{i < j} J_{ij} \underline{T}^{(0)}(\{k_i\}, \{\bar{k}_i\} | k_i = k_j = 1)
 \end{aligned}$$

Irreducible Tensor Operator approach

- Express spin operators and functions thereof as ITOs;
- Use vector coupling basis $|\alpha S M\rangle$ and recursive recoupling.

(1) Gatteschi, Tsukerblat, Coronado, Waldmann, ...
 (2) R. Schnalle, Ph.D. thesis, Osnabrück University (2009)

Idea of ITO: dimer

$$\begin{aligned}
 \left\{ \mathbf{s}_{\sim}^{(1)}(1) \otimes \mathbf{s}_{\sim}^{(1)}(2) \right\}^{(0)} &= \sum_{q_1, q_2} C_{q_1 q_2 0}^{1 1 0} \cdot \mathfrak{s}_{\sim q_1}^{(1)}(1) \mathfrak{s}_{\sim q_2}^{(1)}(2) \\
 &= \frac{1}{\sqrt{3}} \left(\mathfrak{s}_{\sim -1}^{(1)}(1) \cdot \mathfrak{s}_{\sim 1}^{(1)}(2) + \mathfrak{s}_{\sim 1}^{(1)}(1) \cdot \mathfrak{s}_{\sim -1}^{(1)}(2) - \mathfrak{s}_{\sim 0}^{(1)}(1) \cdot \mathfrak{s}_{\sim 0}^{(1)}(2) \right) \\
 &= -\frac{1}{\sqrt{3}} \mathbf{s}_{\sim}(1) \cdot \mathbf{s}_{\sim}(2)
 \end{aligned}$$

$$\underline{H}_{\text{dimer}} = -2J \mathbf{s}_{\sim}(1) \cdot \mathbf{s}_{\sim}(2) = 2J \sqrt{3} \left\{ \mathbf{s}_{\sim}^{(1)}(1) \otimes \mathbf{s}_{\sim}^{(1)}(2) \right\}^{(0)}$$

Idea of ITO: trimer

$$\underline{T}_{\dots}^{(k)}(k_1, k_2, k_3, \bar{k}_1) = \left\{ \left\{ \underline{\mathbf{s}}^{(k_1)}(1) \otimes \underline{\mathbf{s}}^{(k_2)}(2) \right\}^{(\bar{k}_1)} \otimes \underline{\mathbf{s}}^{(k_3)}(3) \right\}^{(k)}$$

$$\begin{aligned} \underline{H}_{\Delta} &= -2J \left(\underline{\mathbf{s}}(1) \cdot \underline{\mathbf{s}}(2) + \underline{\mathbf{s}}(2) \cdot \underline{\mathbf{s}}(3) + \underline{\mathbf{s}}(3) \cdot \underline{\mathbf{s}}(1) \right) \\ &= 2J \sqrt{3} \left(\underline{T}_{\dots}^{(0)}(1, 1, 0, 0) + \underline{T}_{\dots}^{(0)}(1, 0, 1, 1) + \underline{T}_{\dots}^{(0)}(0, 1, 1, 1) \right) \end{aligned}$$

Vector coupling basis $|\alpha S M\rangle$ needs to be constructed similarly:

$$|\alpha S M\rangle = |s_1, s_2, S_{12}, s_3, S, M\rangle$$

Idea of ITO: recoupling

$$\langle \alpha_1 s_1 \alpha_2 s_2 S || \left\{ \tilde{\mathbf{T}}^{(k_1)} \otimes \tilde{\mathbf{T}}^{(k_2)} \right\}_q^{(k)} || \alpha'_1 s'_1 \alpha'_2 s'_2 S' \rangle$$

$$=$$

$$[(2S + 1) (2S' + 1) (2k + 1)]^{\frac{1}{2}} \begin{pmatrix} s_1 & s'_1 & k_1 \\ s_2 & s'_2 & k_2 \\ S & S' & k \end{pmatrix} \langle \alpha_1 s_1 || \tilde{\mathbf{T}}^{(k_1)} || \alpha'_1 s'_1 \rangle \langle \alpha_2 s_2 || \tilde{\mathbf{T}}^{(k_2)} || \alpha'_2 s'_2 \rangle$$

- Recursive evaluation of matrix elements – recoupling of compound tensors – using reduced matrix elements (WE theorem) and Wigner-9J symbols.
- Block diagonal structure; evaluation of $\mathcal{H}(S, M = S)$ only.

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 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).

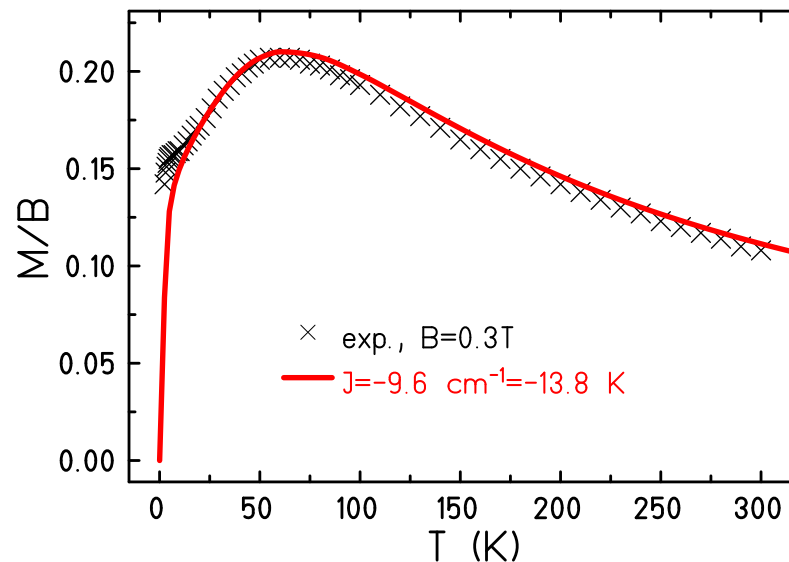
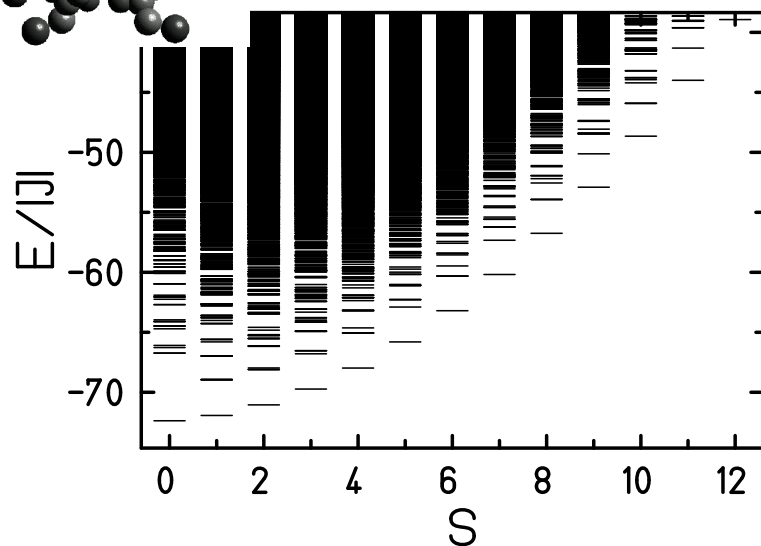
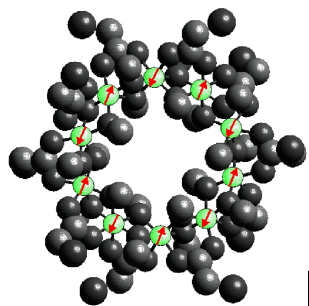
(4) R. Schnalle and J. Schnack, *Int. Rev. Phys. Chem.* **29**, 403-452 (2010) \Leftarrow contains EVERYTHING.

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: Fe₁₀



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

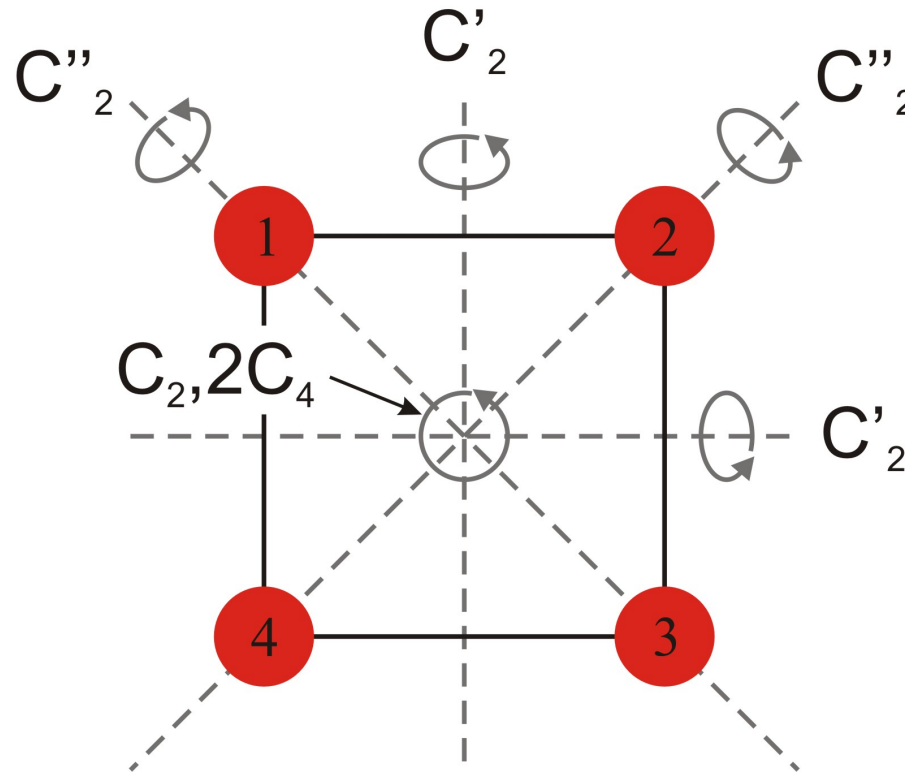
- (1) R. Schnalle and J. Schnack, *Int. Rev. Phys. Chem.* **29**, 403-452 (2010).
- (2) C. Delfs *et al.*, *Inorg. Chem.* **32**, 3099 (1993).

Point Group Symmetry II

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

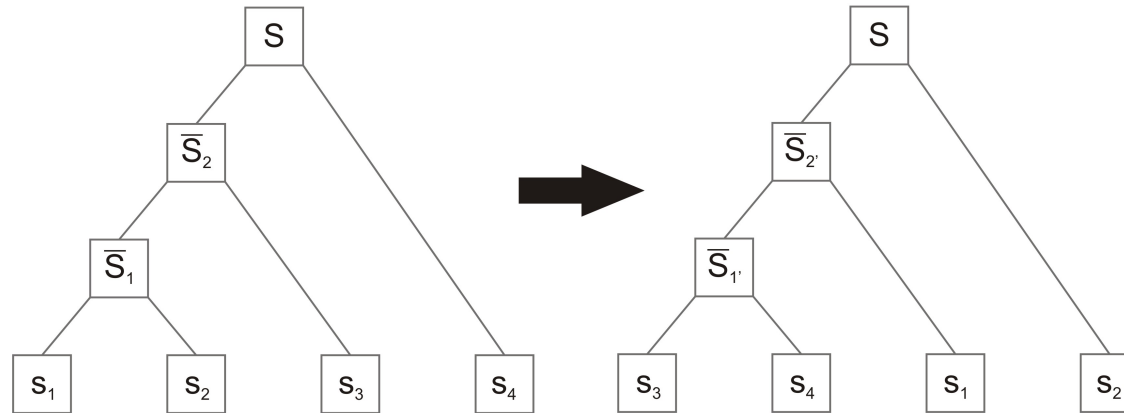
- Serious problem: application of $\tilde{G}(R)$, i.e. permutation of spins, leads to different coupling schemes: $a \Rightarrow b$;
- Solution: implementation of graph-theoretical results to evaluate recoupling coefficients ${}_a\langle \alpha' S M | \alpha S M \rangle_b$.

Point Group Symmetry III – example square



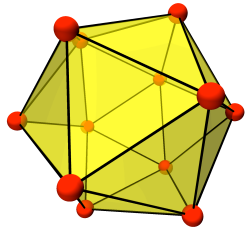
$$|s_1 s_2 \bar{s}_1 s_3 \bar{s}_2 s_4 SM\rangle \xrightarrow{\tilde{G}(3412)} |s_3 s_4 \bar{s}_1 s_1 \bar{s}_2 s_2 SM\rangle$$

Point Group Symmetry IV – binary trees

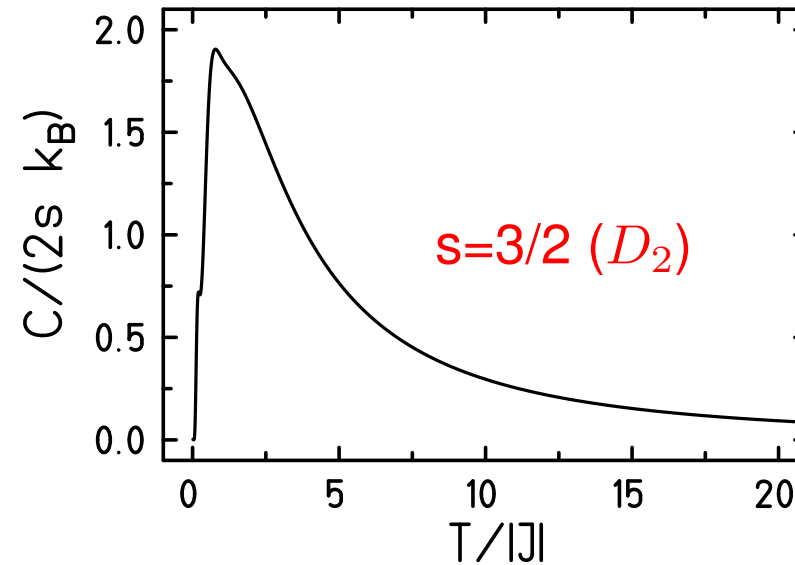
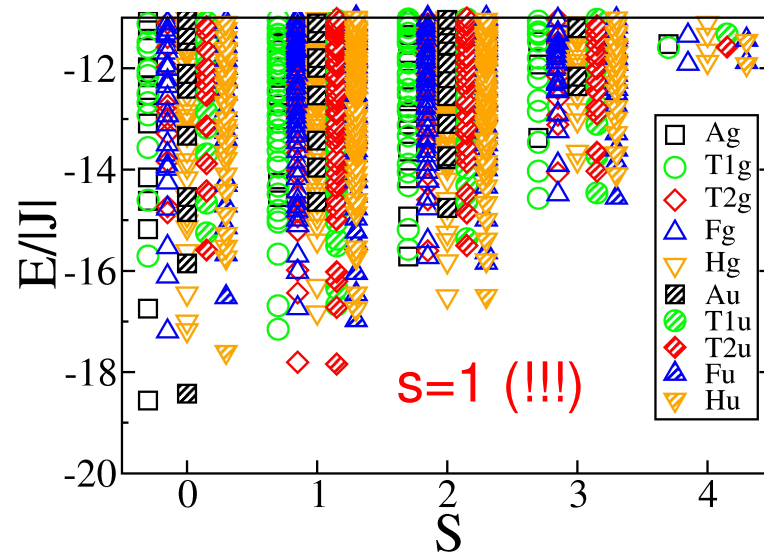


- **Recoupling coefficient $\langle s_1 s_2 \bar{S}_1 s_3 \bar{S}_2 s_4 S M | s_3 s_4 \bar{S}_{1'} s_1 \bar{S}_{2'} s_2 S M \rangle$ can be evaluated by a graphical transformation of one binary tree into the other (1,2).**
- Exchange and flop operations generate a recoupling formula consisting of square 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).

World-leading, but ...

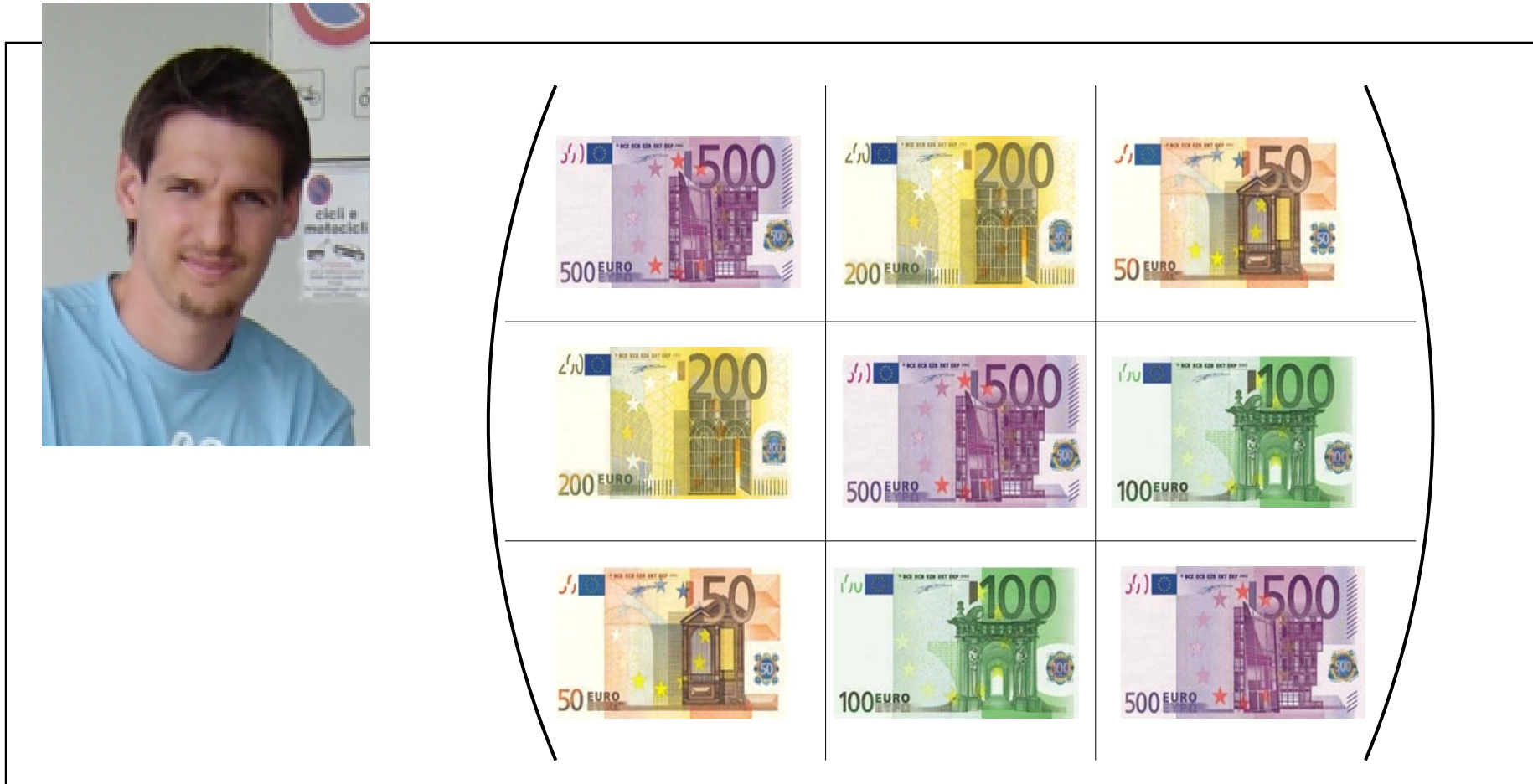
This world-leading method
was developed in Osnabrück,
unfortunately ...

World-leading, but ...

... too late!

**There are more powerful and
easy to program methods.**

Nevertheless, matrix theory goes on ...

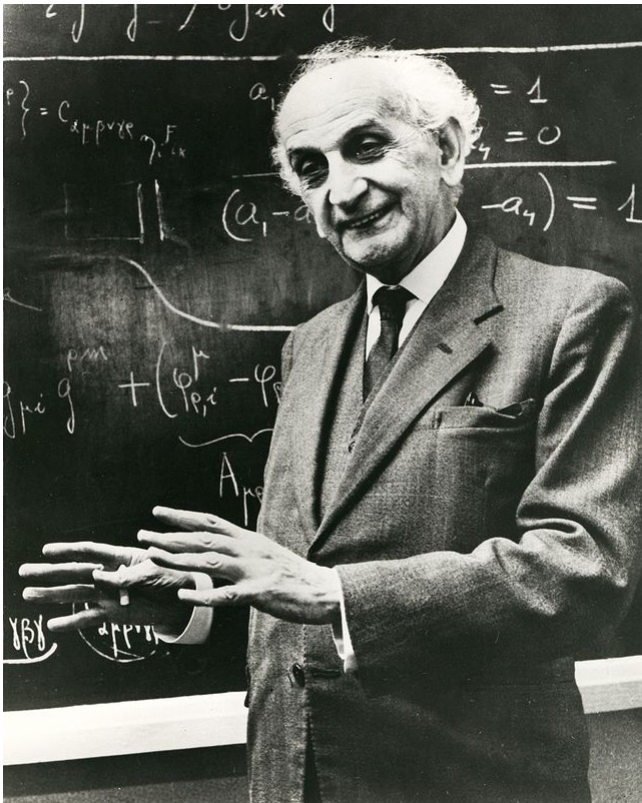


... at the Hessische Landesbank!

Finite-temperature Lanczos Method

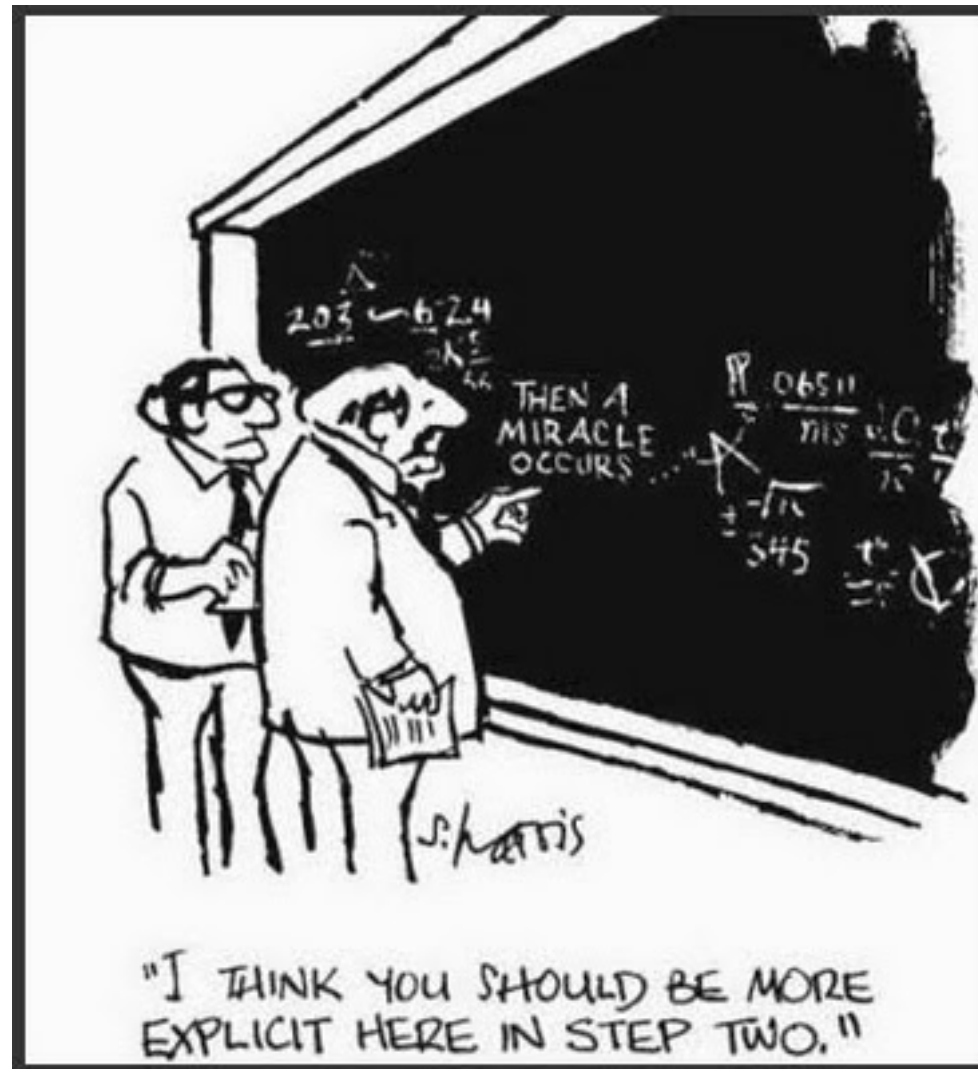
(Good for dimensions up to 10^{10} .)

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:**
 $\{ |\phi\rangle, \tilde{H} |\phi\rangle, \tilde{H}^2 |\phi\rangle, \tilde{H}^3 |\phi\rangle, \dots \}$
- 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).



Finite-temperature Lanczos Method I

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

$$\langle \nu | \exp \{ -\beta \tilde{H} \} | \nu \rangle \approx \sum_n \langle \nu | n(\nu) \rangle \exp \{ -\beta \epsilon_n \} \langle n(\nu) | \nu \rangle \quad (\text{Step 2})$$

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

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

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

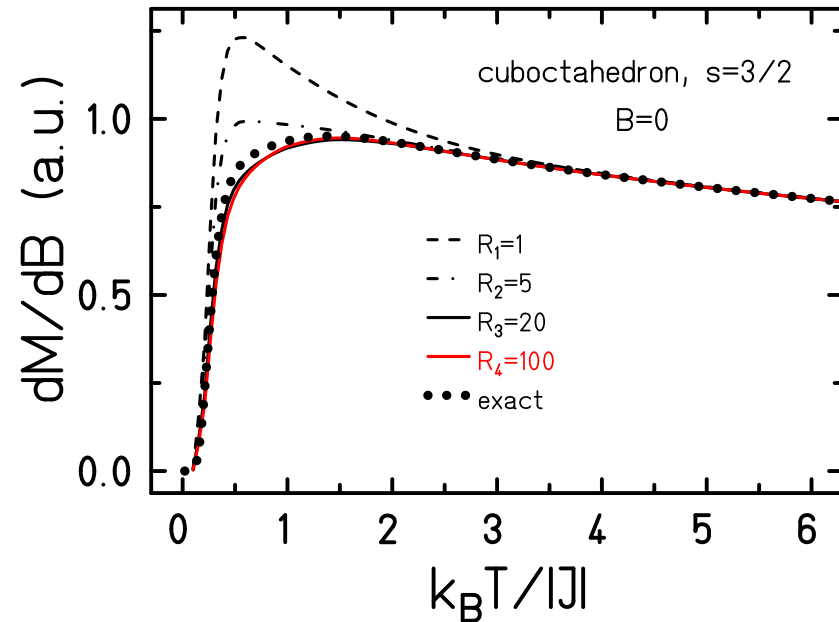
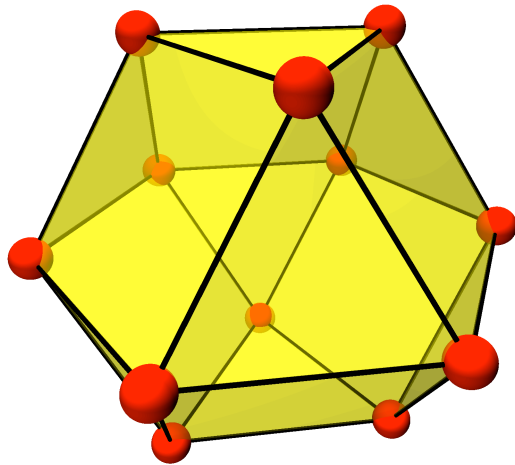
Finite-temperature Lanczos Method II

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

- Approximation better if symmetries taken into account.
- Γ denotes the used irreducible representations.

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

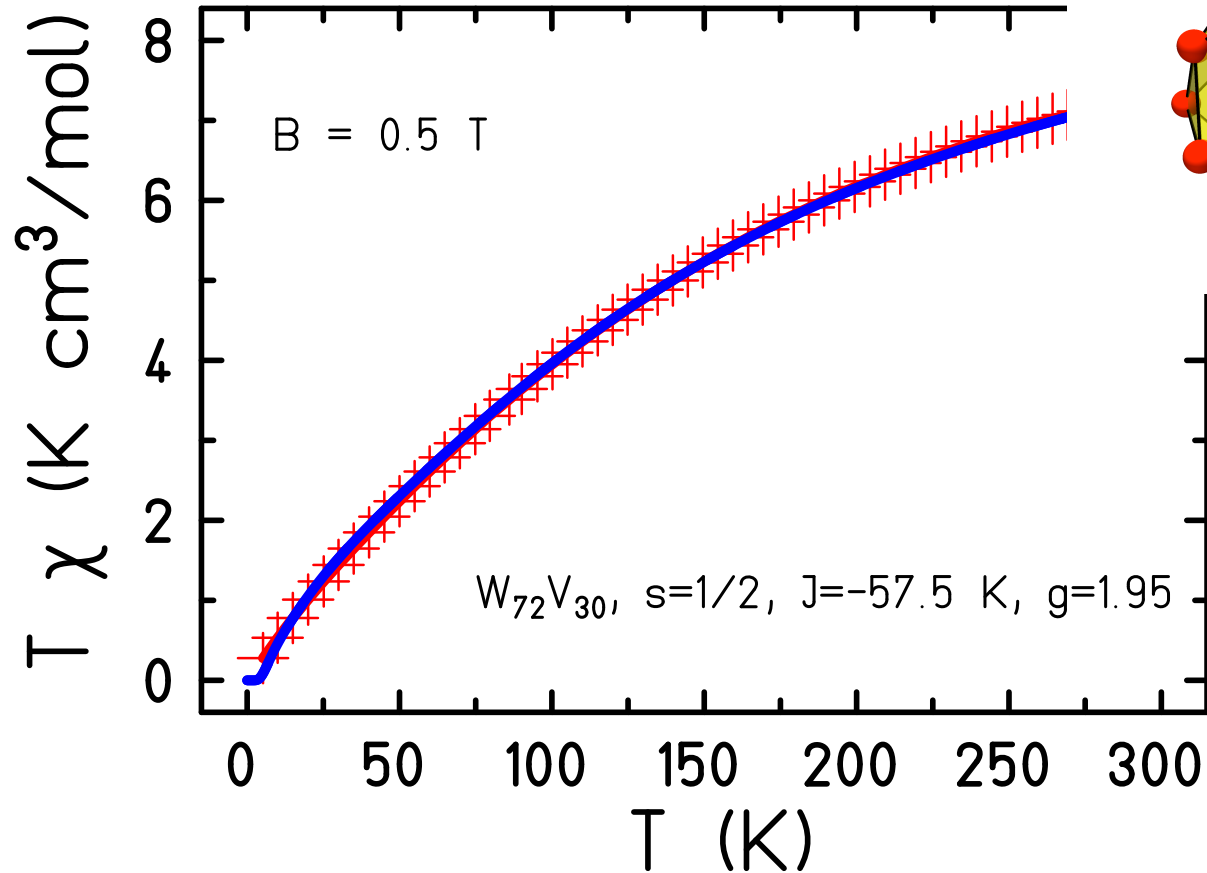
How good is finite-temperature Lanczos?



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

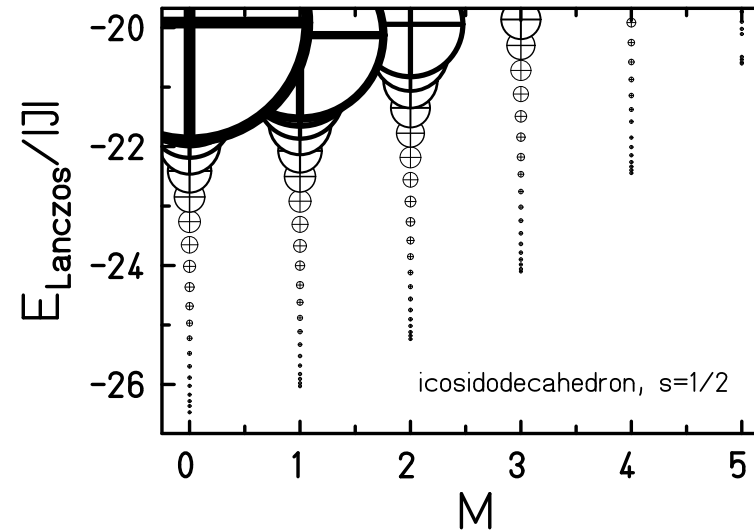
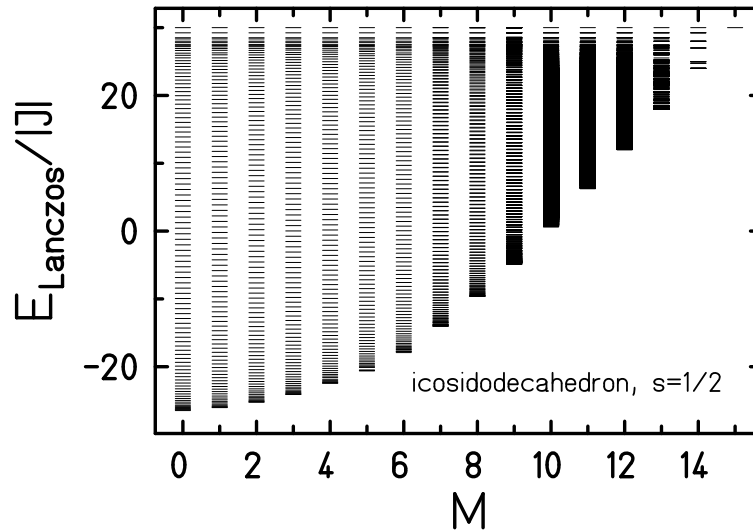
Exact results: R. Schnalle and J. Schnack, *Int. Rev. Phys. Chem.* **29**, 403-452 (2010).
 FTLM: J. Schnack and O. Wendland, *Eur. Phys. J. B* **78**, 535-541 (2010).

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.

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

Anisotropic magnetic molecules I – Theory

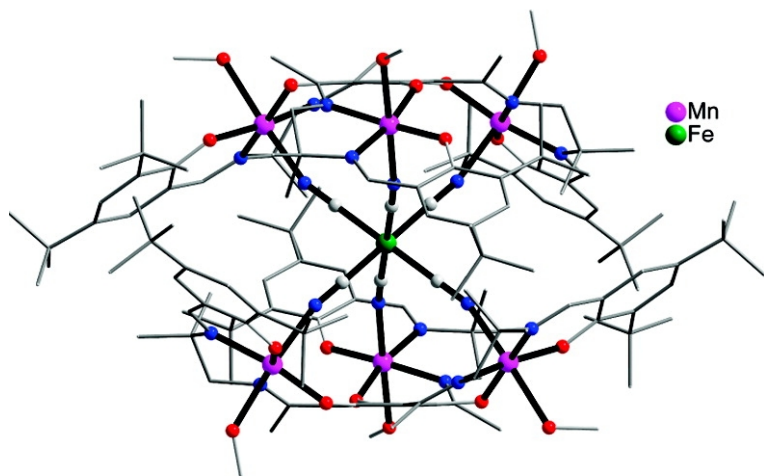
$$\tilde{H}(\vec{B}) = - \sum_{i,j} J_{ij} \vec{\tilde{S}}(i) \cdot \vec{\tilde{S}}(j) + \sum_i d_i (\vec{e}_i \cdot \vec{\tilde{S}}(i))^2 + \mu_B \vec{B} \cdot \sum_i^N \mathbf{g}_i \cdot \vec{\tilde{S}}(i)$$

- $[\tilde{H}, \tilde{S}^2] \neq 0, [\tilde{H}, \tilde{S}_z] \neq 0;$
- You have to diagonalize $\tilde{H}(\vec{B})$ for every field (direction and strength)!
 \Rightarrow Orientational average.
- If you are lucky, point group symmetries still exist. Use them!
- Easy: $\dim(\mathcal{H}) < 30,000$; possible: $30,000 < \dim(\mathcal{H}) < 140,000$

T. Glaser *et al.* *et* J. Schnack, *Inorg. Chem.* **48**, 607 (2009).

Single Molecule Magnets V

Rational design of strict C_3 symmetry:

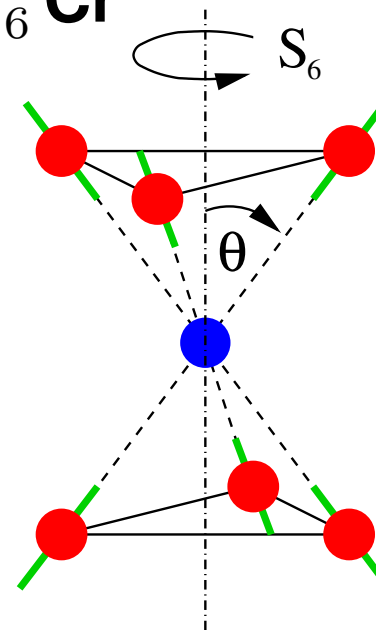
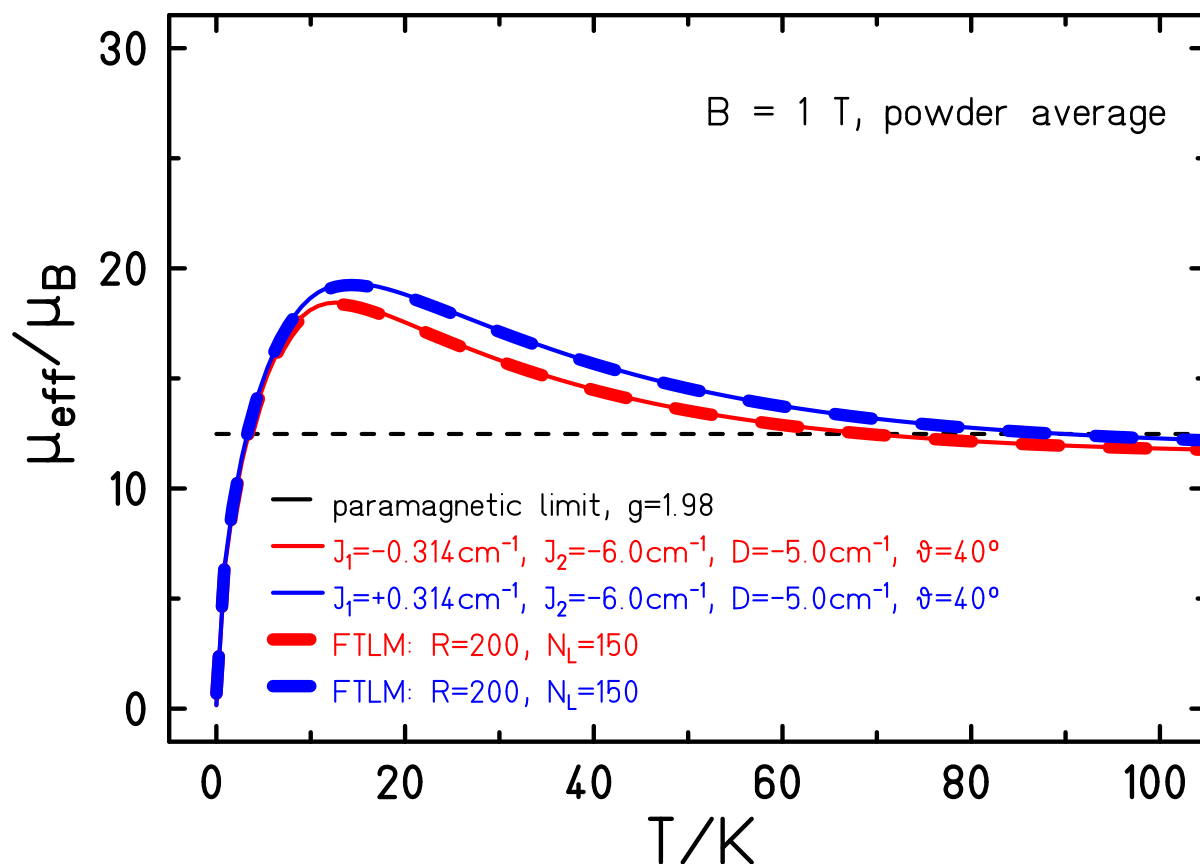


- Idea of Thorsten Glaser (Bielefeld): C_3 symmetric alignment of local easy axes (easy axis \equiv Jahn-Teller axis);
- Various ions could be used so far, e.g. Mn_6Cr (1), Mn_6Fe (2), ...
- Advantage: no E -terms, i.e. no (less) tunneling;
- Problem: exchange interaction sometimes antiferromagnetic.

T. Glaser *et al.*, *Angew. Chem.-Int. Edit.* **45**, 6033 (2006).

T. Glaser *et al.*, *Inorg. Chem.* **48**, 607 (2009).

Glaser-type molecules: $\text{Mn}_6\text{Cr}^{\text{III}}$

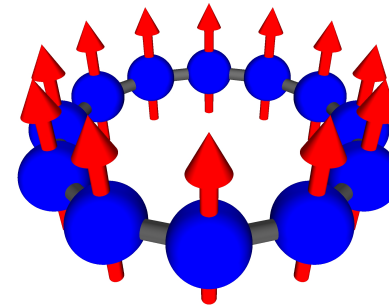
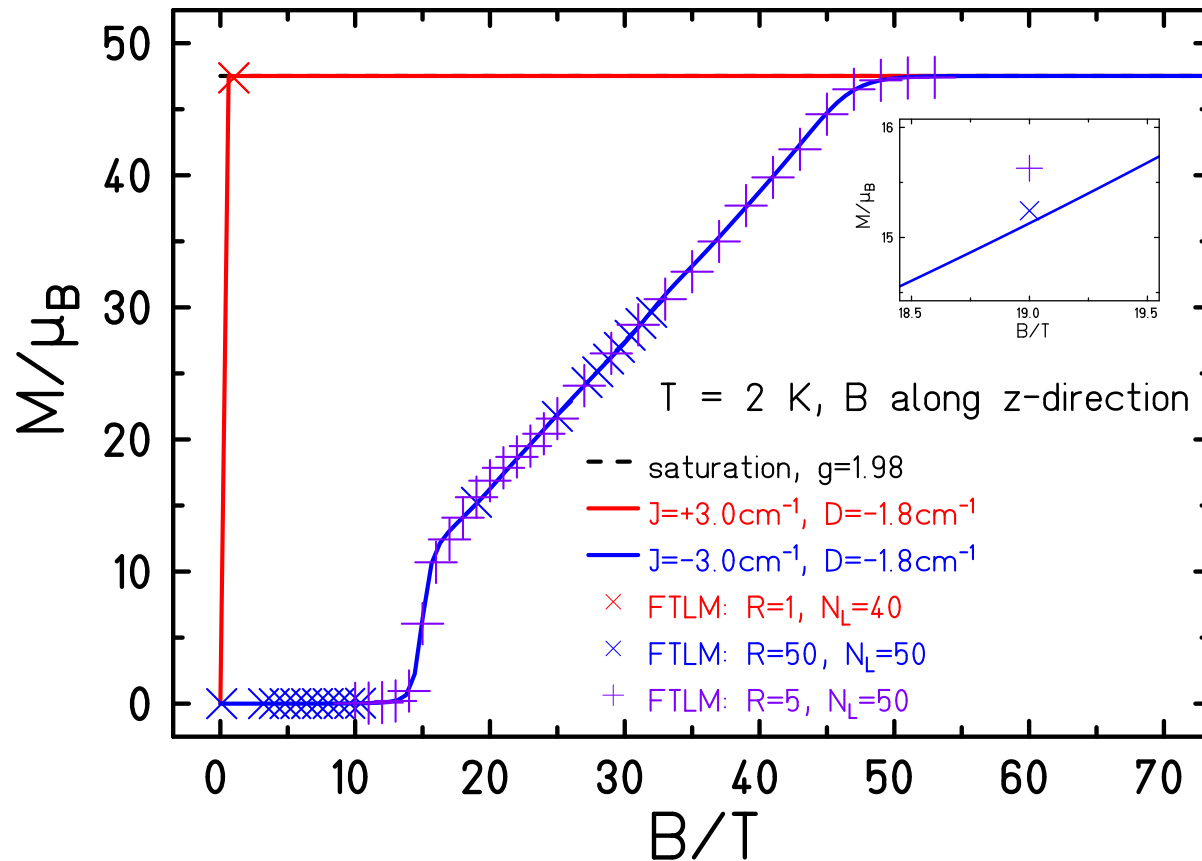


$s = 2, s = 3/2$
 $\dim(\mathcal{H}) = 62,500$
 non-collinear easy axes

Hours compared to days, notebook compared to supercomputer!

O. Hanebaum, J. Schnack, Eur. Phys. J. B **87**, 194 (2014)

A fictitious $Mn_{12}^{III} - M_z$ vs B_z



$s = 2$

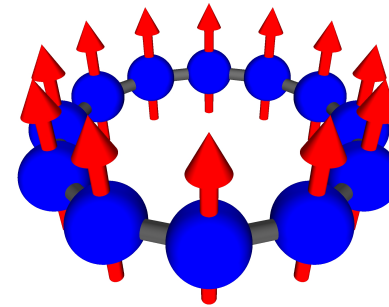
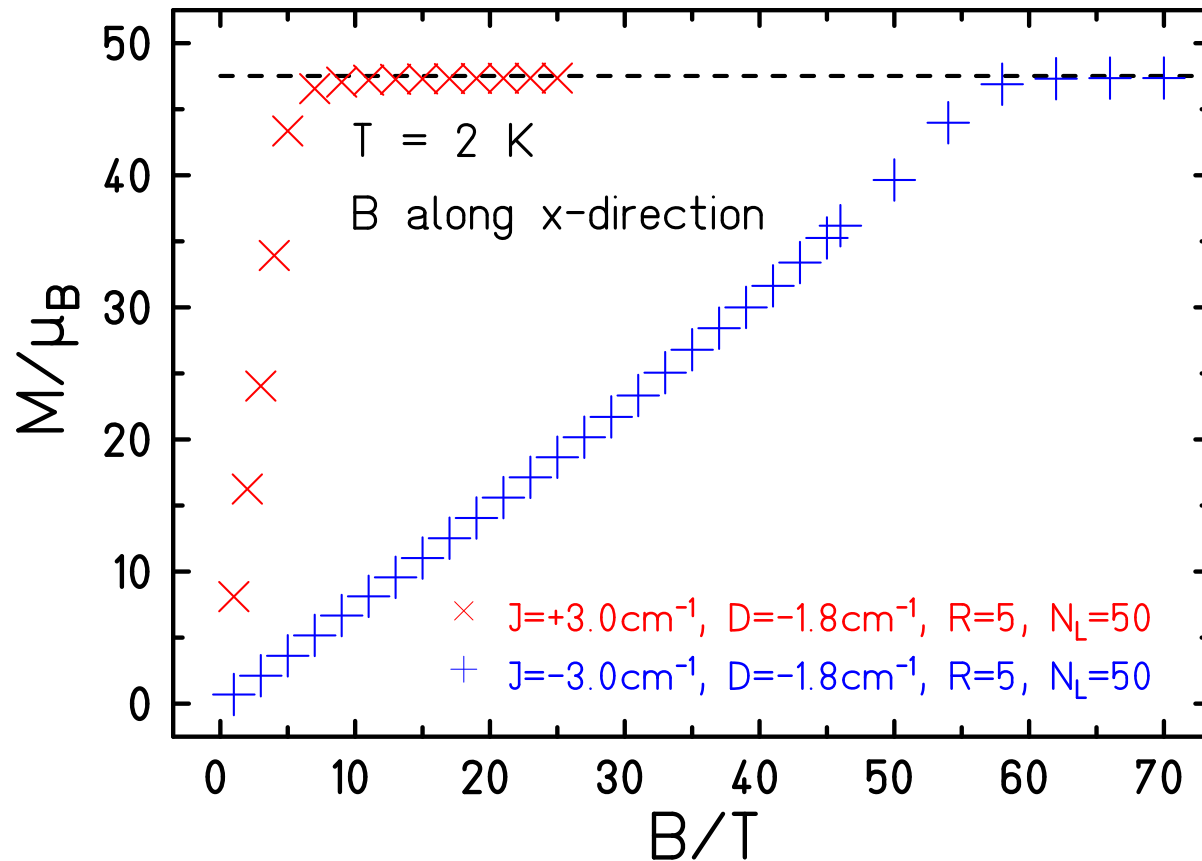
$\dim(\mathcal{H}) = 244, 140, 625$

collinear easy axes

A few days compared to *impossible!*

O. Hanebaum, J. Schnack, Eur. Phys. J. B **87**, 194 (2014)

A fictitious $\text{Mn}_{12}^{\text{III}}$ – M_x vs B_x



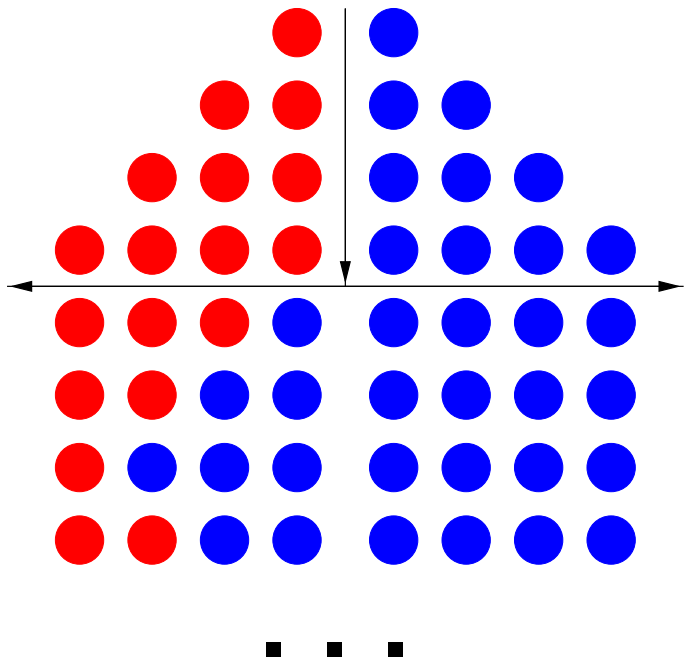
No other method can deliver these curves!

O. Hanebaum, J. Schnack, Eur. Phys. J. B **87**, 194 (2014)

Density Matrix Renormalization Group

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

Density Matrix Renormalization Group

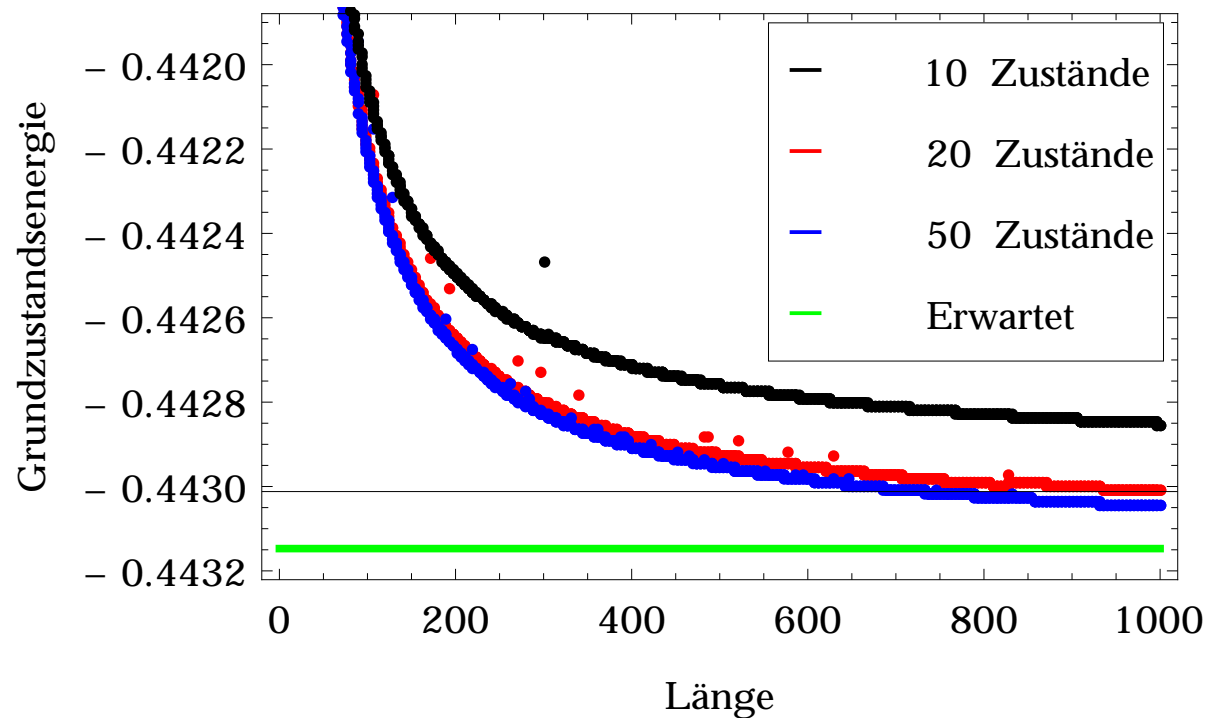


Again: build your appropriate reduced basis set

- Naive idea: start with small system, diagonalize \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.

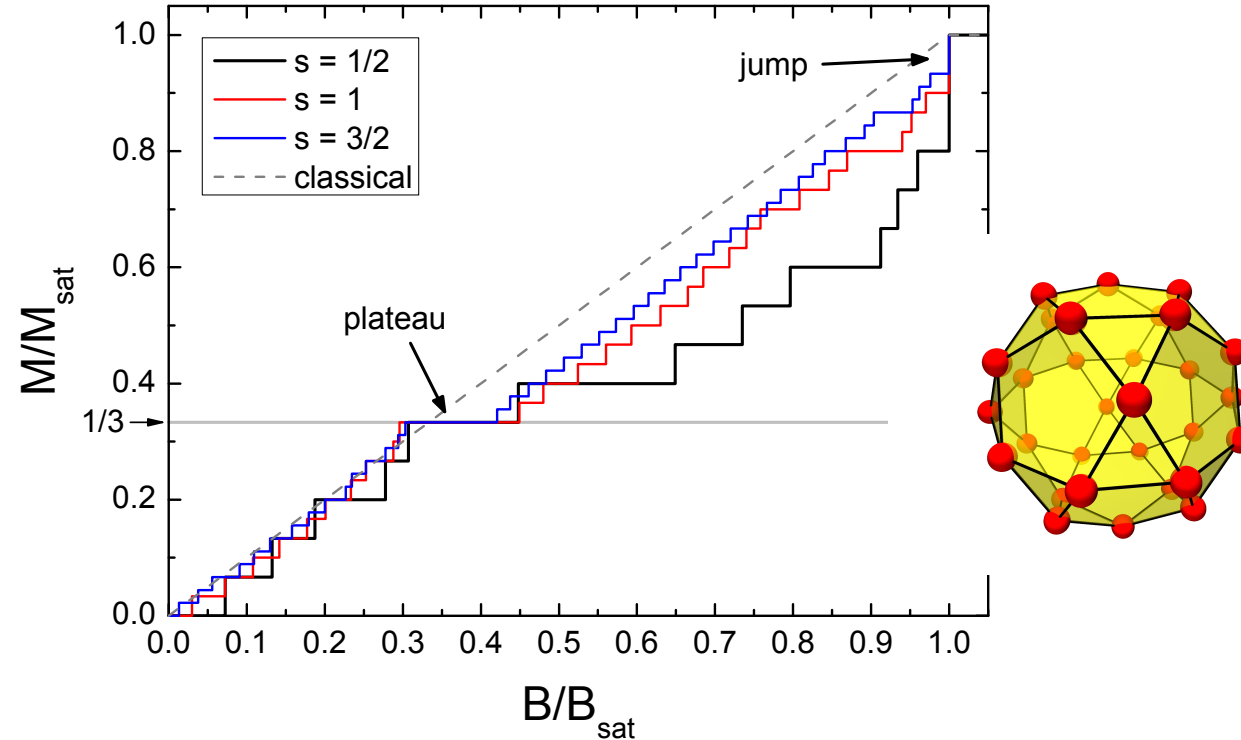
(1) S. R. White, Phys. Rev. Lett. **69**, 2863 (1992).
 (2) S. R. White, Phys. Rev. B **48**, 10345 (1993).
 (3) U. Schollwöck, Rev. Mod. Phys. **77**, 259 (2005).

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 !

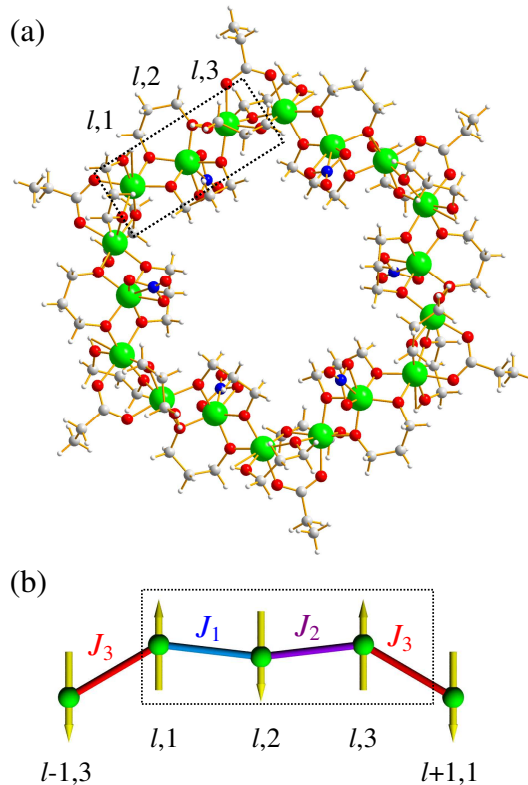
Density Matrix Renormalization Group



- 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

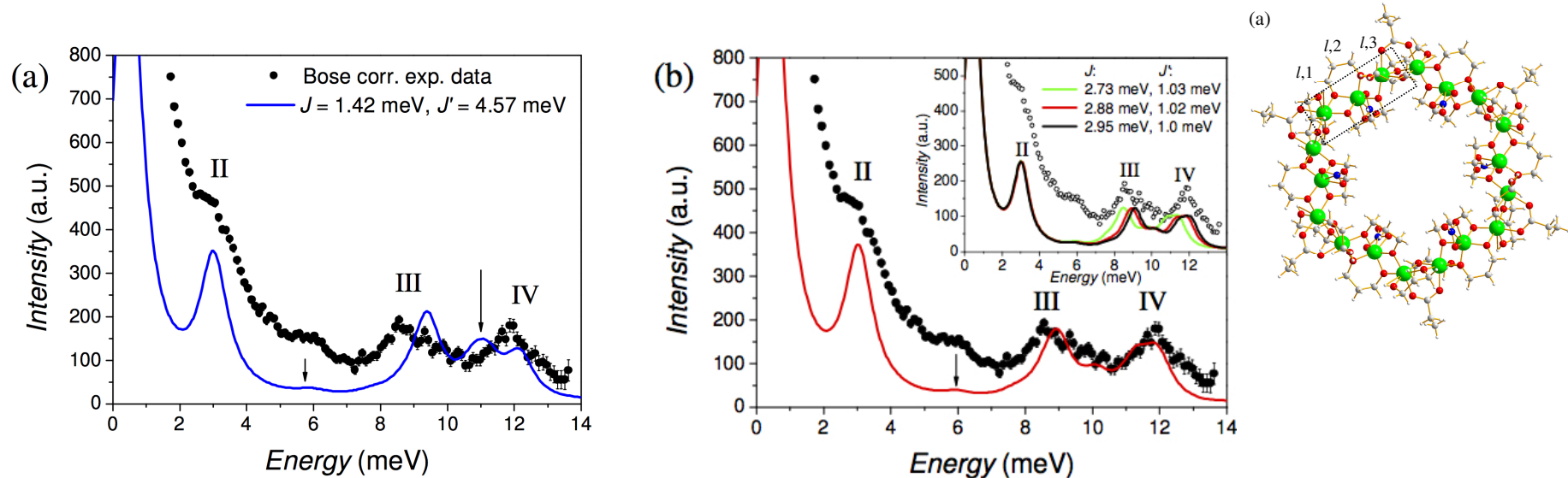


Evaluation of correlation functions, e.g. for INS:

- $S_{jj'}^{zz}(\omega) \equiv \sum_n \langle 0 | \mathcal{S}_j^z | n \rangle \langle n | \mathcal{S}_{j'}^z | 0 \rangle \delta(\hbar\omega - E_n + E_0)$; 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); 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).

Dynamical Density Matrix Renormalization 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. 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

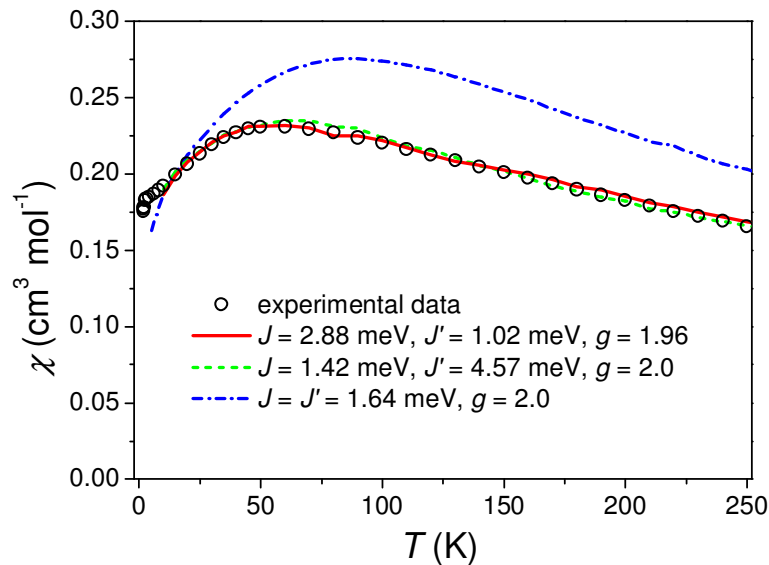
Chopped (sliced) partition function:

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

$$= \sum_{\nu} \langle \nu | \left[\exp \left\{ -\beta \tilde{H} / m \right\} \right]^m | \nu \rangle$$

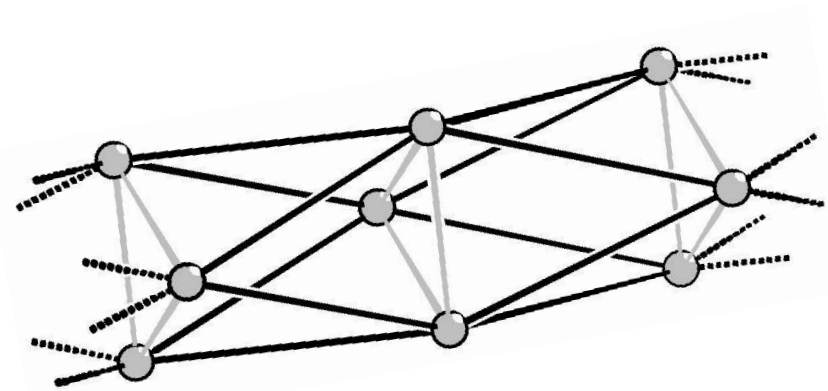
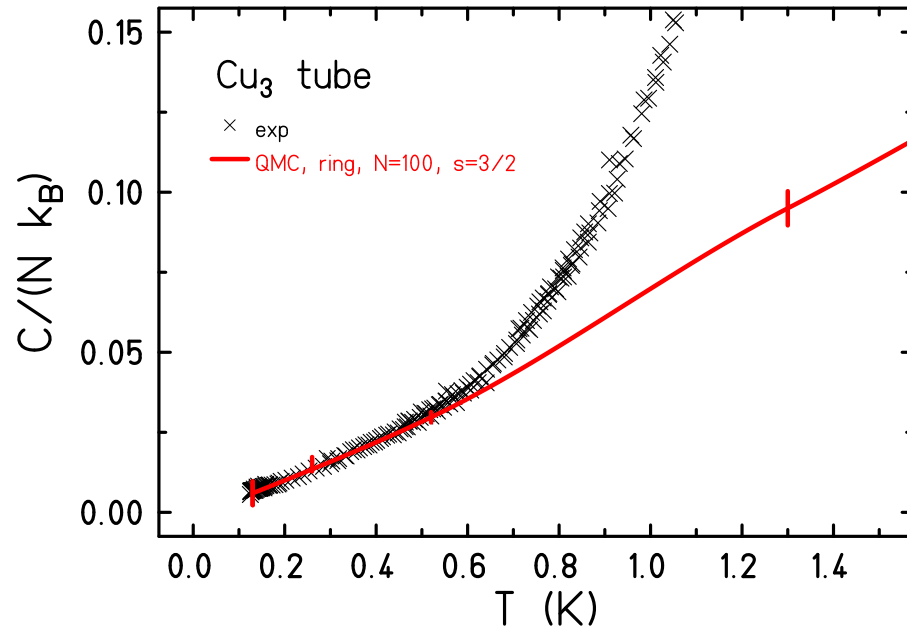
$$= \sum_{\nu, \alpha, \beta, \dots} \langle \nu | \exp \left\{ -\beta \tilde{H} / m \right\} | \alpha \rangle \langle \alpha | \dots$$

$$\approx \sum_{\nu, \alpha, \beta, \dots} \langle \nu | \left\{ 1 - \beta \tilde{H} / m \right\} | \alpha \rangle \langle \alpha | \dots$$
- 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).

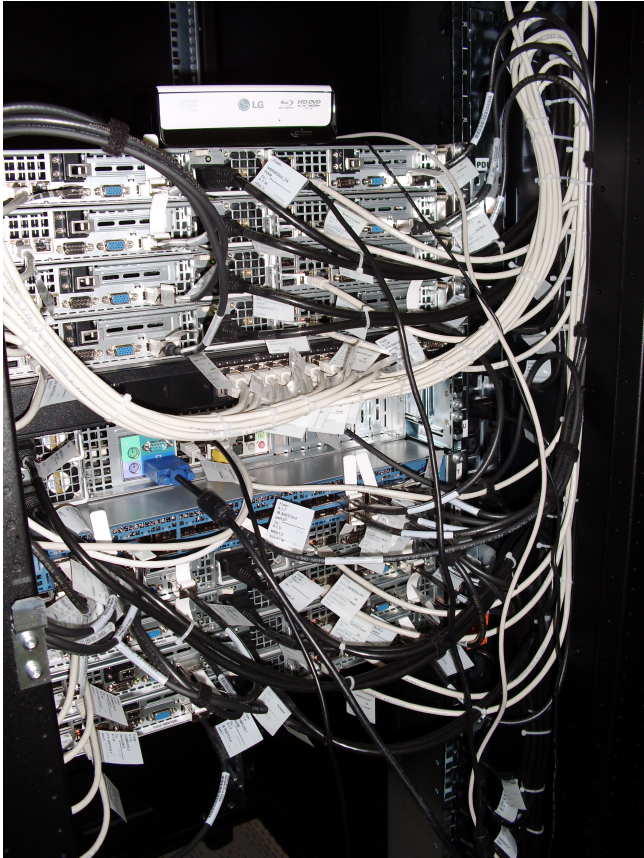
Quantum Monte Carlo



- [(CuCl₂tachH)₃Cl]Cl₂: 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} . DMRG for big 1-d systems. QMC for non-frustrated systems. ALPS!
- Magnetic molecules for storage, q-bits, MCE, and since they are nice.
- Often, the juice is in the anisotropic terms.

(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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- M. Czopnik, T. Glaser, O. Hanebaum, Chr. Heesing, M. Höck, N.B. Ivanov, F. Kaiser, H.-T. Langwald, S. Leiding, A. Müller, R. Schnalle, Chr. Schröder, J. Ummethum (Bielefeld)
- K. Bärwinkel, H.-J. Schmidt, M. Neumann (Osnabrück)
- M. Luban (Ames Lab, USA); P. Kögerler (Aachen, Jülich, Ames); D. Collison, R.E.P. Winpenny, E.J.L. McInnes, F. Tuna (Man U); L. Cronin, M. Murrie (Glasgow); E. Brechin (Edinburgh); H. Nojiri (Sendai, Japan); A. Postnikov (Metz); W. Wernsdorfer (Grenoble); M. Evangelisti (Zaragosa); E. Garlatti, S. Carretta, G. Amoretti, P. Santini (Parma); Gopalan Rajaraman (Mumbai)
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Thank you very much for your
attention.

The end.

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