New Exact and Approximate Methods to Treat Spin Hamiltonians of Magnetic Molecules

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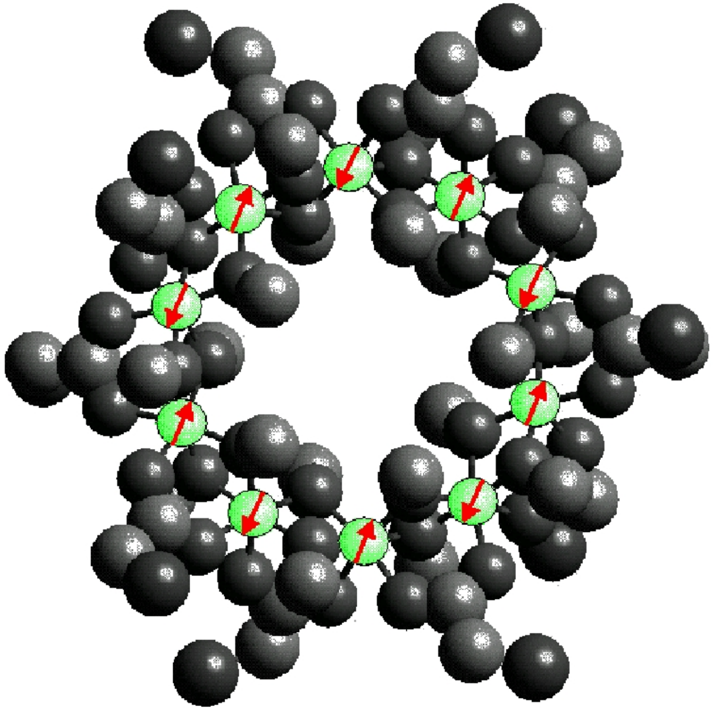
Contents for you today

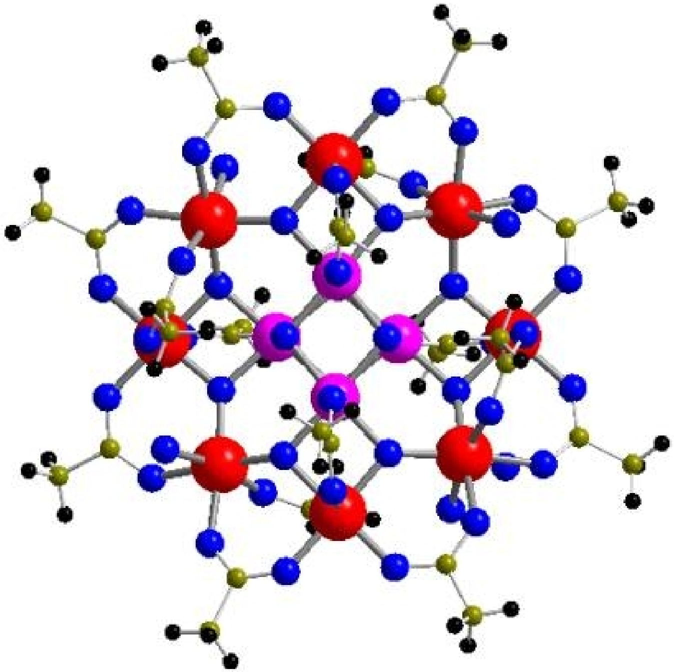


Fe$_{10}$

1. Magnetic molecules
2. Up to date theory modeling
3. SU(2) symmetry
4. Point group symmetry
5. Finite-temperature Lanczos
6. Anisotropic Magnetic Molecules

Magnetic Molecules

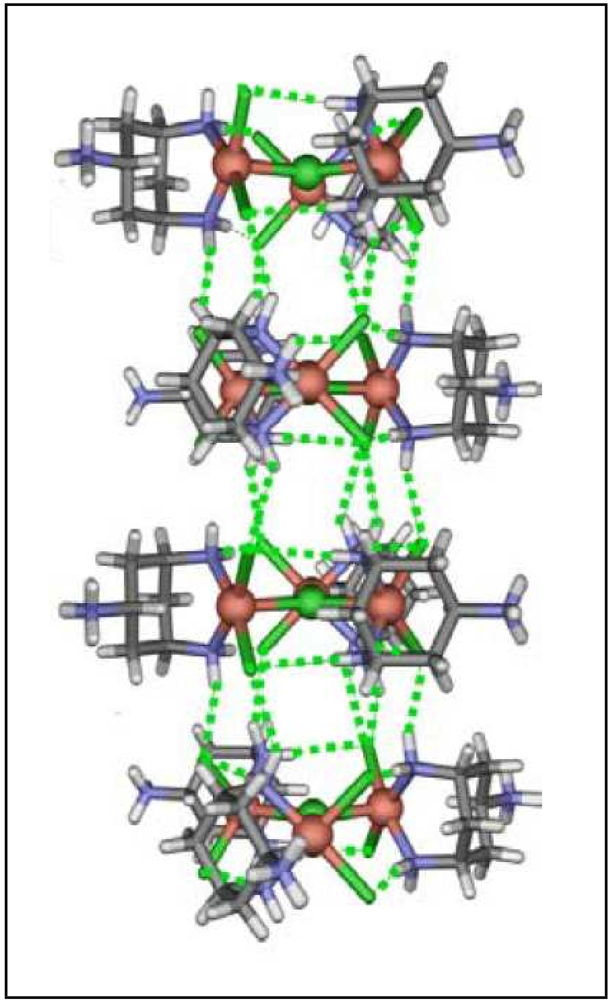
The beauty of magnetic molecules I



Mn_{12}

- Inorganic or organic macro molecules, 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);
- Speculative applications: magnetic storage devices, magnets in biological systems, light-induced nano switches, displays, catalysts, transparent magnets, qubits for quantum computers.

The beauty of magnetic molecules II



- Dimers (Fe_2), tetrahedra (Cr_4), cubes (Cr_8);
- Rings, especially iron and chromium rings
- 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.

Up to date theory modeling

Model Hamiltonian (spin only)

$$\underset{\sim}{H} \;=\; \sum_{i,j} \underset{\sim}{\vec{s}}(i) \cdot \mathbf{J}_{ij} \cdot \underset{\sim}{\vec{s}}(j) \;+\; \sum_{i,j} \vec{D}_{ij} \cdot \left[\underset{\sim}{\vec{s}}(i) \times \underset{\sim}{\vec{s}}(j)\right] \;+\; \mu_B\, \vec{B} \sum_{i}^{N} \mathbf{g}_i\, \underset{\sim}{\vec{s}}(i)$$

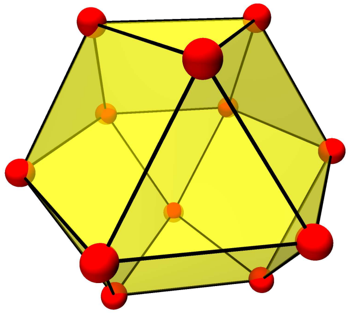
Exchange/Anisotropy Dzyaloshinskii-Moriya Zeeman

Isotropic Hamiltonian

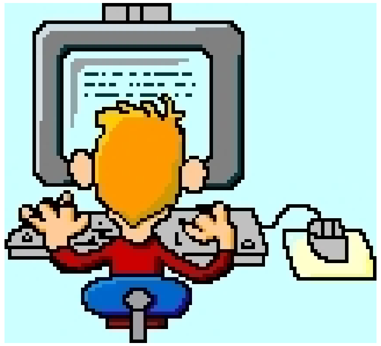
$$\underset{\sim}{H} \;=\; -2 \sum_{i<j} J_{ij}\, \underset{\sim}{\vec{s}}(i) \cdot \underset{\sim}{\vec{s}}(j) \;+\; g\, \mu_B\, B \sum_{i}^{N} \underset{\sim}{s}_z(i)$$

Heisenberg Zeeman

In the end it's always a big matrix!



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



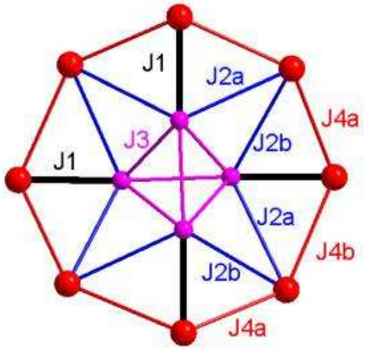
Thank God, we have computers

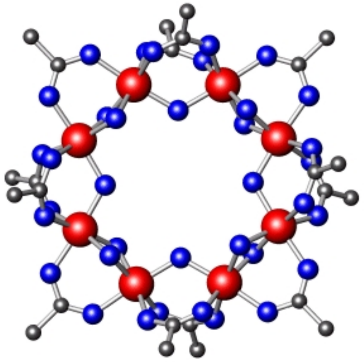
“cell professor”

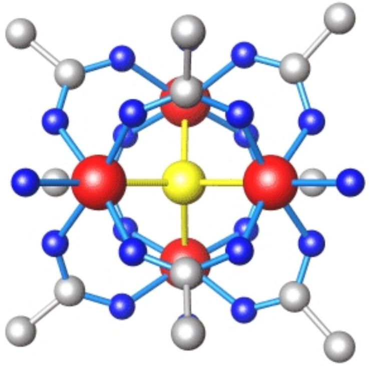
128 cores, 384 GB RAM

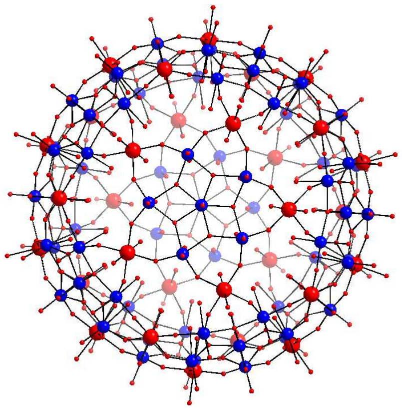
. . . but that’s not enough!

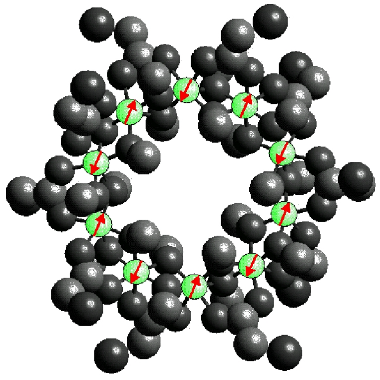
Magnetic Molecules











possess symmetries! Use them!

SU(2) and point group symmetry!


Die spinnen, die Bielefelder!

Bielefeld ???

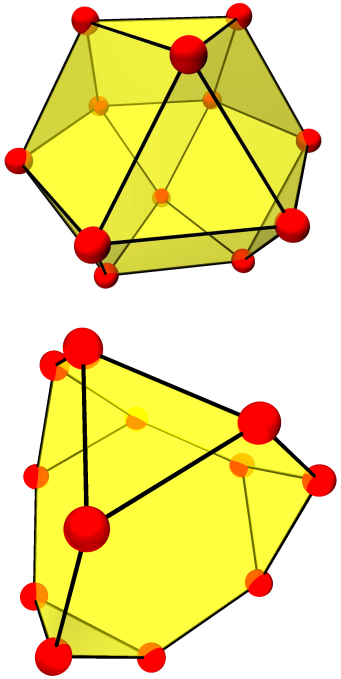

www.ruthe.de
Ruthe
HÖR GUT ZU, TOBIAS! Wir wollen in Ruhe Matrizen diagonalisieren. DESHALB MÜSSEN WIR JETZT AN EINEN ORT ZIEHEN, VON DEM KEINER WEISS, DASS ER EXISTIERT!
NACH BIELEFELD??

SU(2) 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:

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

Idea of ITO

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

Irreducible Tensor Operator approach

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

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

Idea of ITO: dimer

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

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

Idea of ITO: trimer

$$\underset{\sim\therefore}{\mathbf{T}}^{(k)}(k_1,k_2,k_3,\overline{k}_1) \quad = \quad \left\{ \left\{ \underset{\sim}{\mathbf{s}}^{(k_1)}(1) \otimes \underset{\sim}{\mathbf{s}}^{(k_2)}(2) \right\}^{(\overline{k}_1)} \otimes \underset{\sim}{\mathbf{s}}^{(k_3)}(3) \right\}^{(k)}$$

$$\begin{aligned} \underset{\sim}{H}_{\triangle} \quad &= \quad -2J \left(\underset{\sim}{\mathbf{s}}(1) \cdot \underset{\sim}{\mathbf{s}}(2) + \underset{\sim}{\mathbf{s}}(2) \cdot \underset{\sim}{\mathbf{s}}(3) + \underset{\sim}{\mathbf{s}}(3) \cdot \underset{\sim}{\mathbf{s}}(1) \right) \\ &= \quad 2J\sqrt{3} \left(\underset{\sim\therefore}{T}^{(0)}(1,1,0,0) + \underset{\sim\therefore}{T}^{(0)}(1,0,1,1) + \underset{\sim\therefore}{T}^{(0)}(0,1,1,1) \right) \end{aligned}$$

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

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

Idea of ITO: recoupling

$$
\begin{aligned}
&\langle \alpha_1\, s_1\, \alpha_2\, s_2\, S || \left\{ \underset{\sim}{\mathbf{T}}^{(k_1)} \otimes \underset{\sim}{\mathbf{T}}^{(k_2)} \right\}^{(k)}_{q} || \alpha_1'\, s_1'\, \alpha_2'\, s_2'\, S' \rangle \\
&= \\
&[(2S+1)\,(2S'+1)\,(2k+1)]^{\frac{1}{2}} \begin{pmatrix} s_1 & s_1' & k_1 \\ s_2 & s_2' & k_2 \\ S & S' & k \end{pmatrix} \langle \alpha_1\, s_1 || \underset{\sim}{\mathbf{T}}^{(k_1)} || \alpha_1'\, s_1' \rangle \langle \alpha_2\, s_2 || \underset{\sim}{\mathbf{T}}^{(k_2)} || \alpha_2'\, s_2' \rangle
\end{aligned}
$$

- 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

Point Group Symmetry I

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

Point Group Symmetry

- Projection on irreducible representations Γ (Wigner);
- *Basis function generating machine (1)*;
- Orthonormalization necessary.

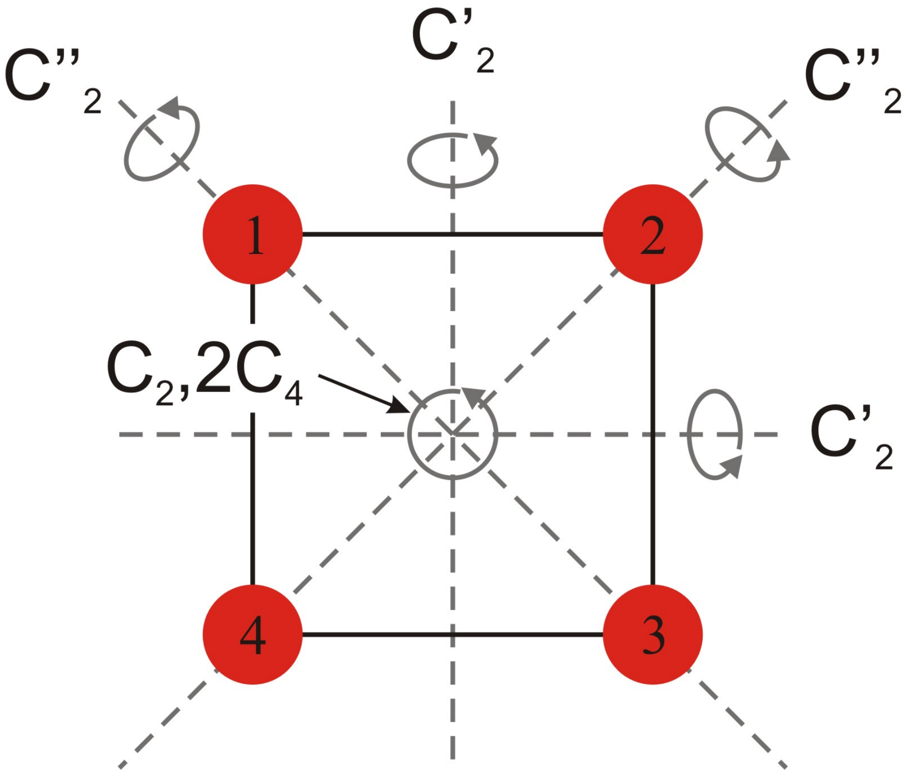
(1) M. Tinkham, *Group Theory and Quantum Mechanics*, Dover.
(2) O. Waldmann, Phys. Rev. B **61**, 6138 (2000).
(3) R. Schnalle, Ph.D. thesis, Osnabrück University (2009).
(4) R. Schnalle and J. Schnack, Int. Rev. Phys. Chem. **29** (2010) 403-452.

Point Group Symmetry II

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

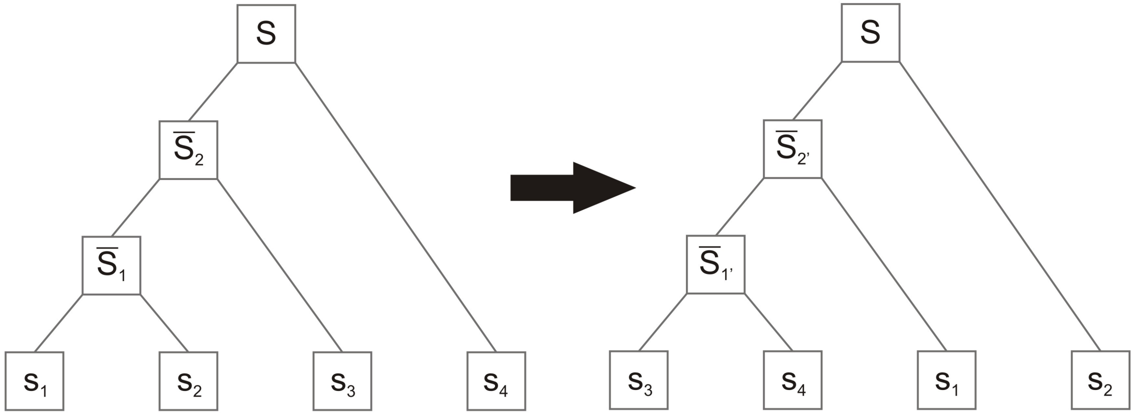
- Serious problem: application of $\underset{\sim}{G}(R)$, i.e. permutation of spins, leads to different coupling schemes;
- Solution: implementation of graph-theoretical results to evaluate recoupling coefficients ${}_a\langle\,\alpha'\,S\,M\,|\,\alpha\,S\,M\,\rangle_b$.

Point Group Symmetry III – example square



$$| \, s_1 s_2 \overline{S}_1 s_3 \overline{S}_2 s_4 S M \, \rangle \xrightarrow{\underset{\sim}{G}(3\,4\,1\,2)} | \, s_3 s_4 \overline{S}_{1'} s_1 \overline{S}_{2'} s_2 S M \, \rangle$$

Point Group Symmetry IV – binary trees



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

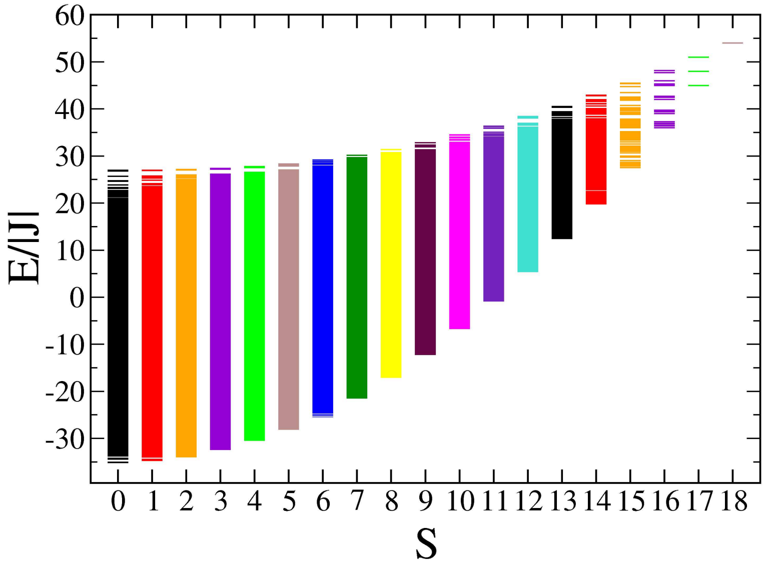
- Exchange and flop operations generate a recoupling formula consisting of square roots, Wigner-6J symbols and sums over intermediate spins.

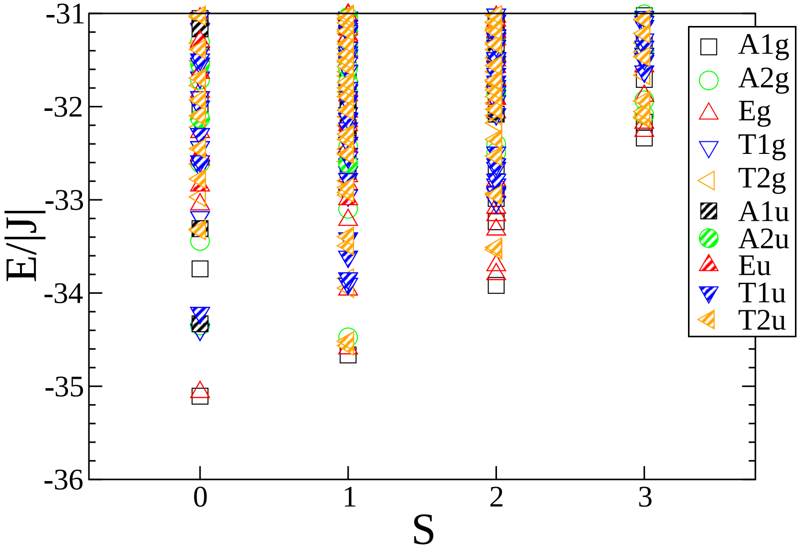
- Open: optimal coupling for a given symmetry? (3)

(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 (2010) Bielefeld University.

Results

Results I: Cuboctahedron

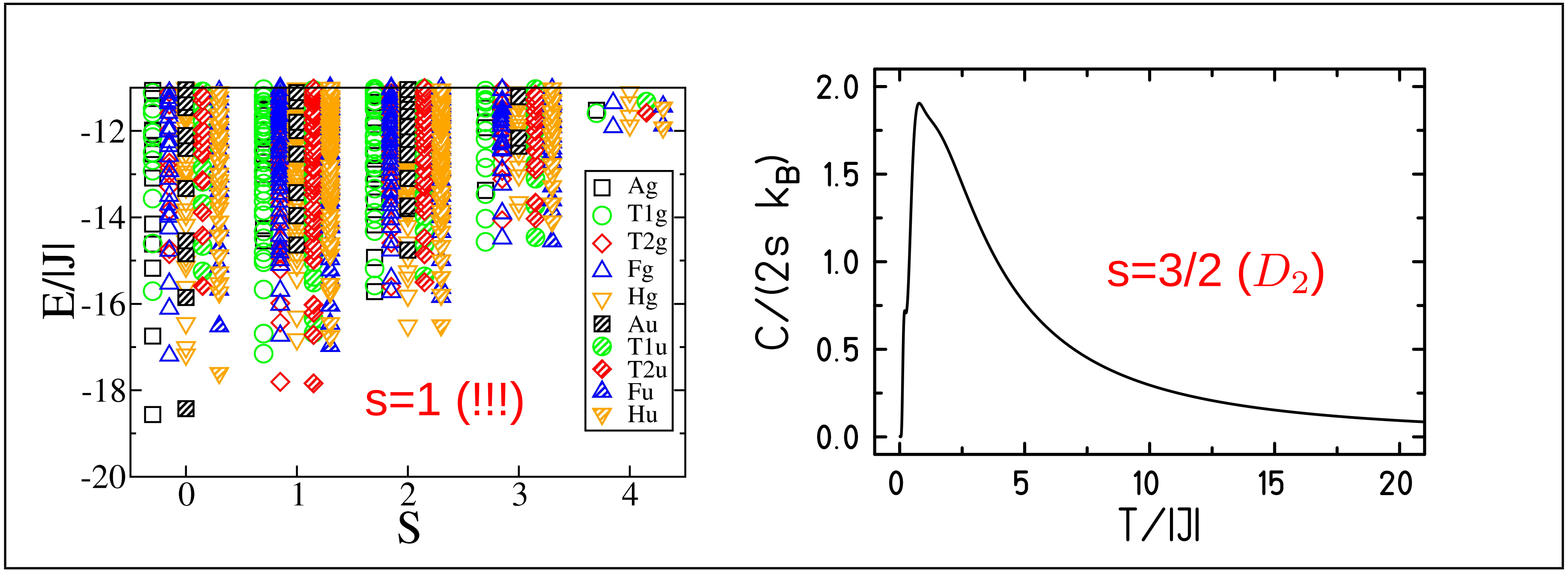




Cuboctahedron, $s = 3/2$, Hilbert space dimension 16,777,216; symmetry O_h (1).
Evaluation of recoupling coefficients very time consuming (1,2).

(1) J. Schnack and R. Schnalle, Polyhedron **28**, 1620 (2009);
(2) R. Schnalle and J. Schnack, Phys. Rev. B **79**, 104419 (2009).

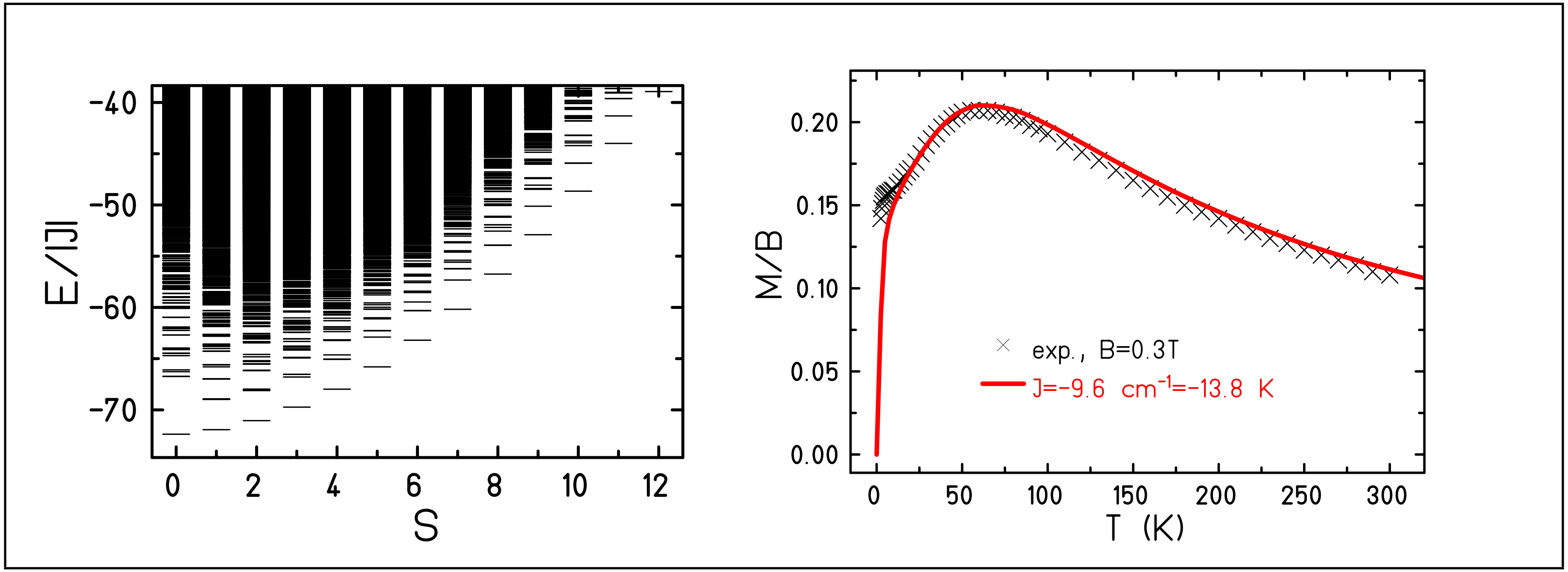
Results II: Icosahedron



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

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

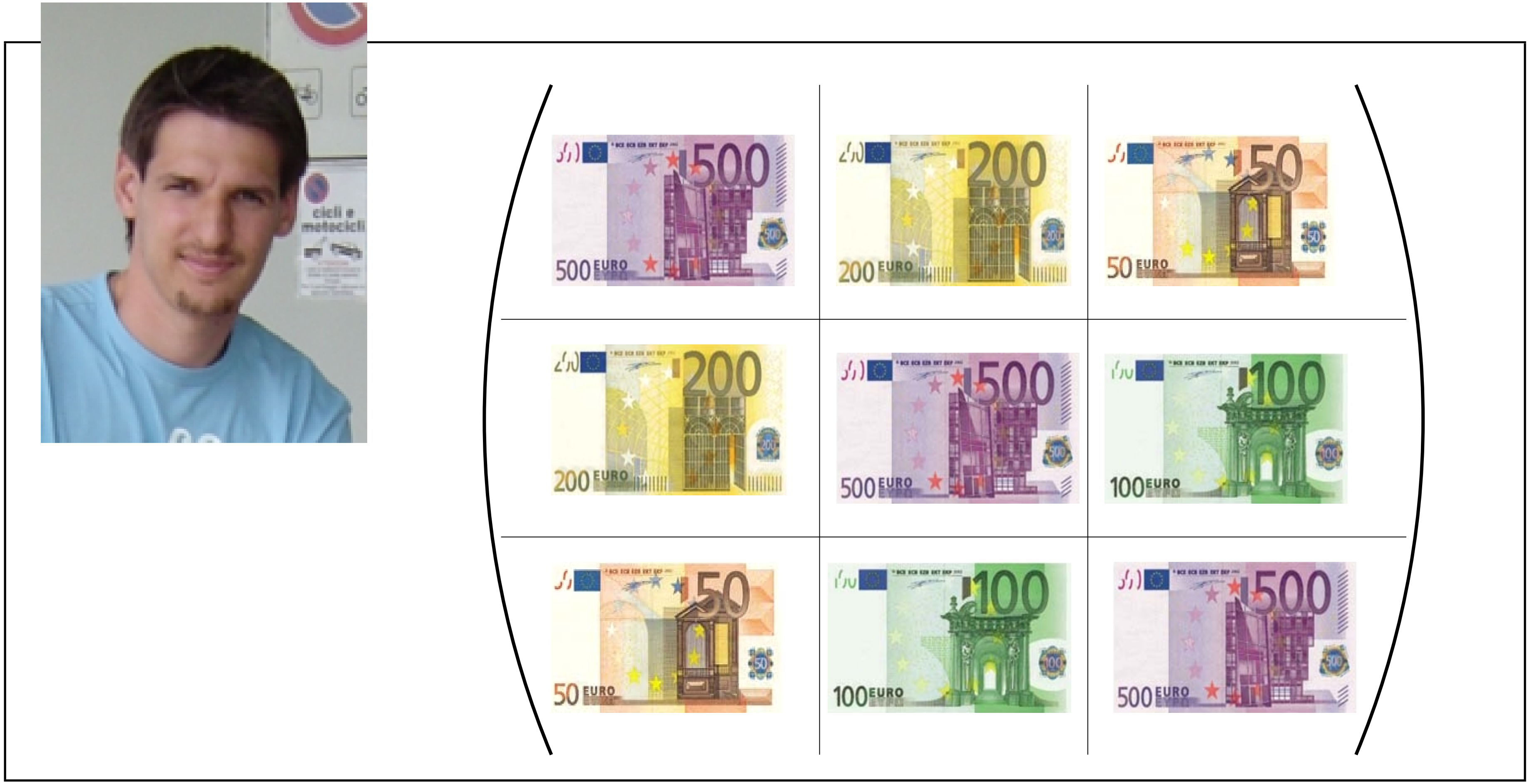
Results III: Fe$_{10}$



Spin ring, $N = 10$, $s = 5/2$, Hilbert space dimension 60,466,176; symmetry D_2
Symmetry C_{10} would lead to more complicated recoupling coefficients & complex representation (1).

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

Matrix theory goes on . . .

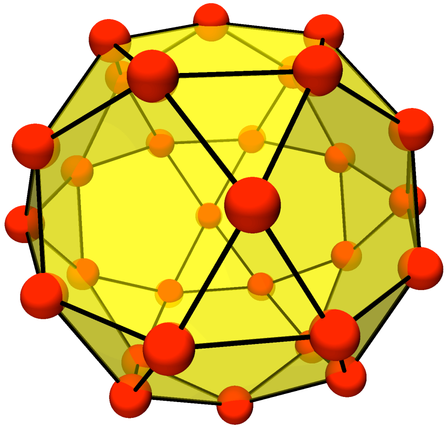


. . . at the Hessische Landesbank!

Finite-temperature Lanczos for

The icosidodecahedron $s = 1/2$

DIMENSION = 1,073,741,824



The idea of thermal Lanczos

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

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

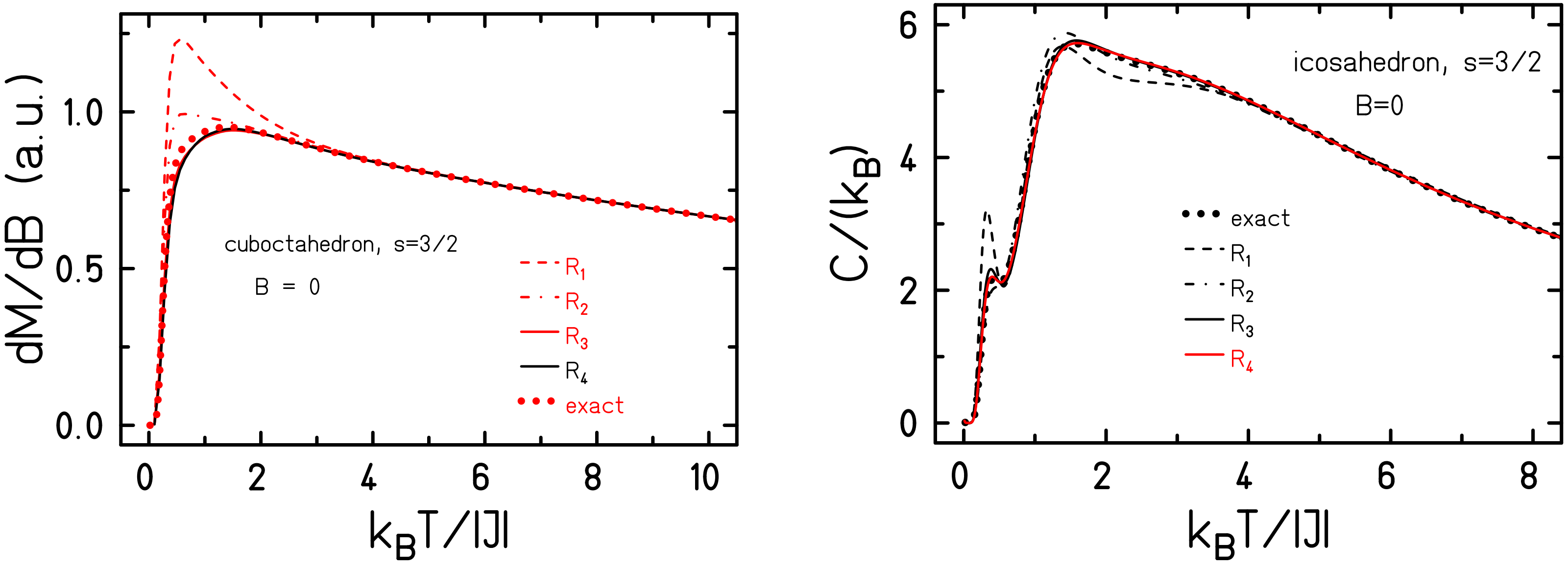
J. Jaklic and P. Prelovsek, Phys. Rev. B **49**, 5065 (1994).

Final form of thermal Lanczos

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

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

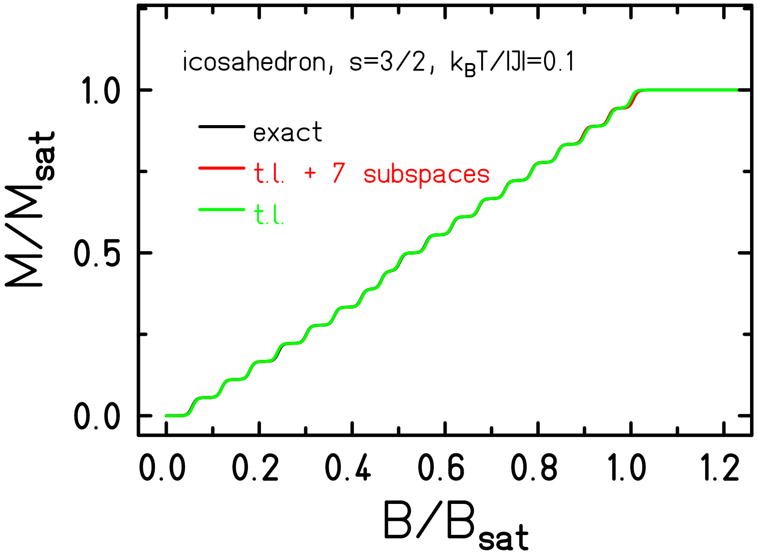
How good is thermal Lanczos?

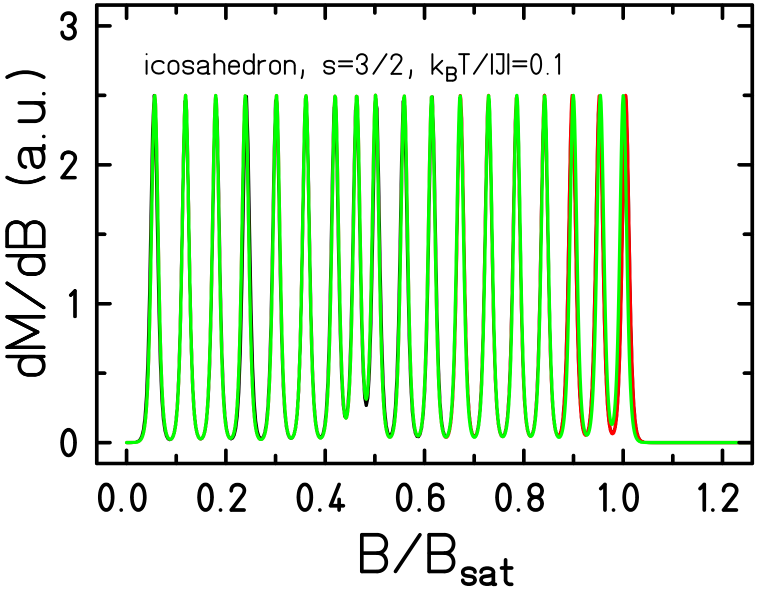


- Works very well, see e.g. cuboctahedron and icosahedron.
- $N = 12, s = 3/2$: Considered $< 100,000$ states instead of 16,777,216.

R. Schnalle and J. Schnack, Int. Rev. Phys. Chem. 29 (2010) 403-452
J. Schnack and O. Wendland, Eur. Phys. J. B, submitted, arXiv:1009.2889

How good is thermal Lanczos?

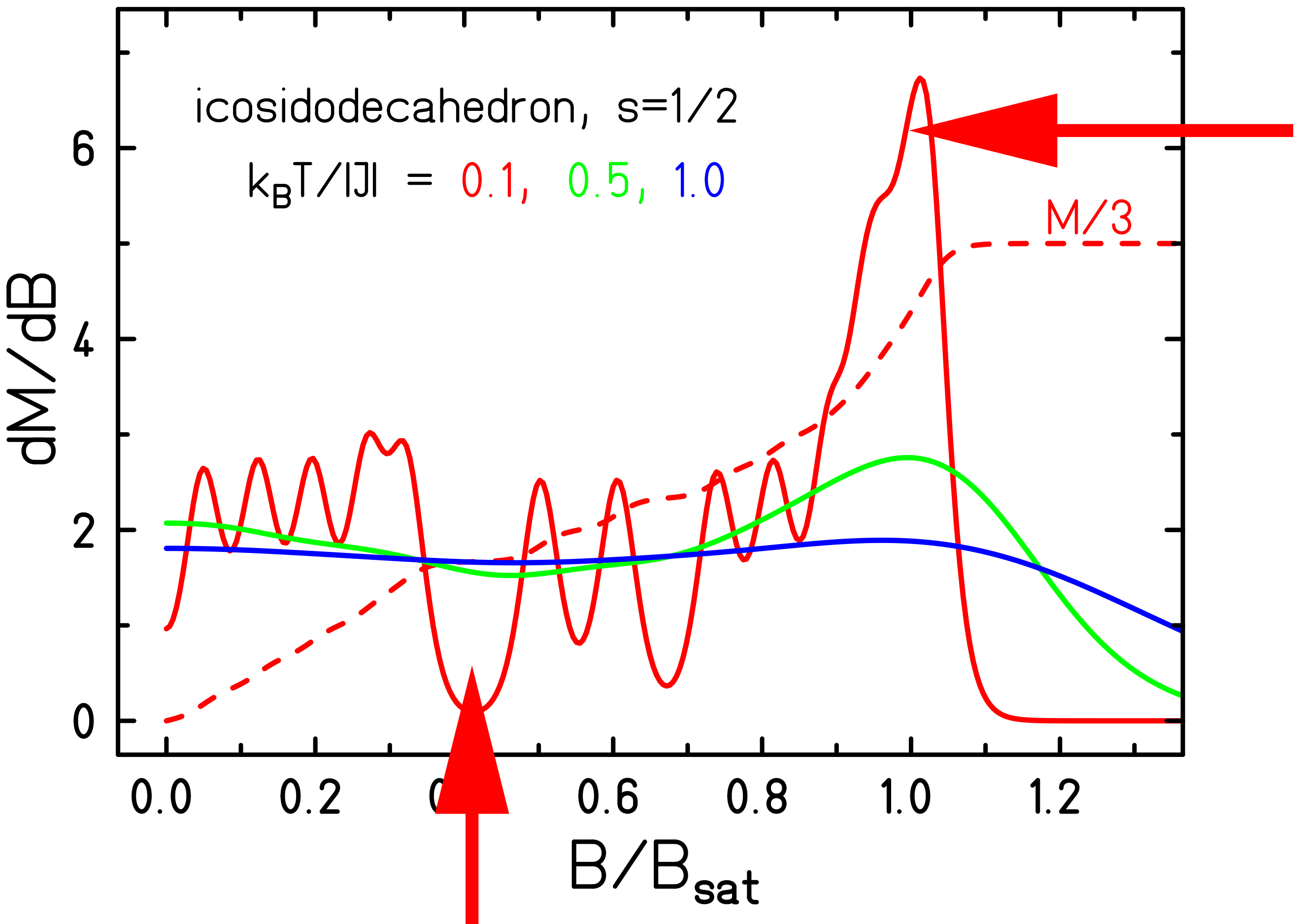




- Large degeneracies and small subspaces problematic.
- Small subspaces can be included exactly.

J. Schnack and O. Wendland, Eur. Phys. J. B, submitted, arXiv:1009.2889

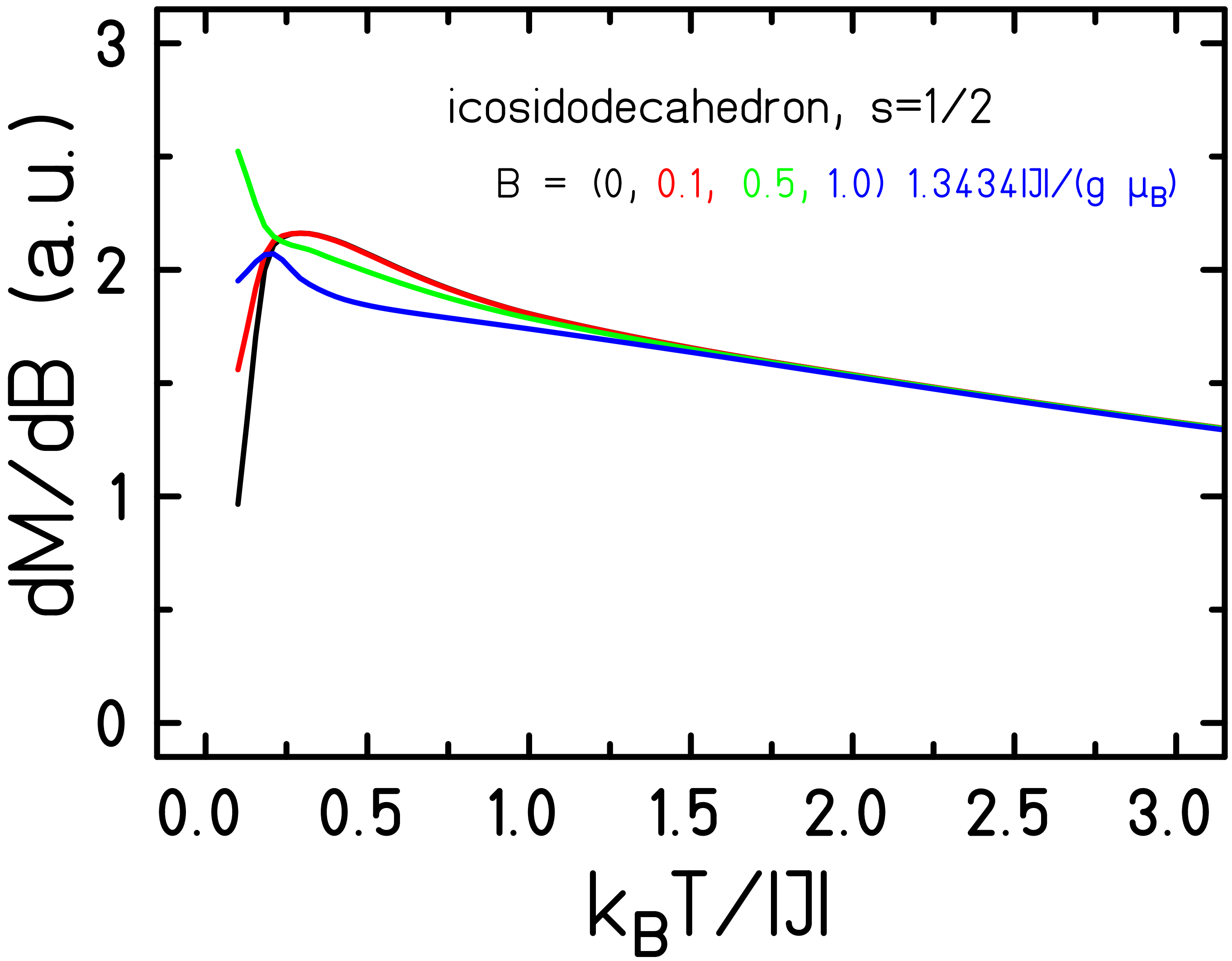
Icosidodecahedron $s = 1/2$



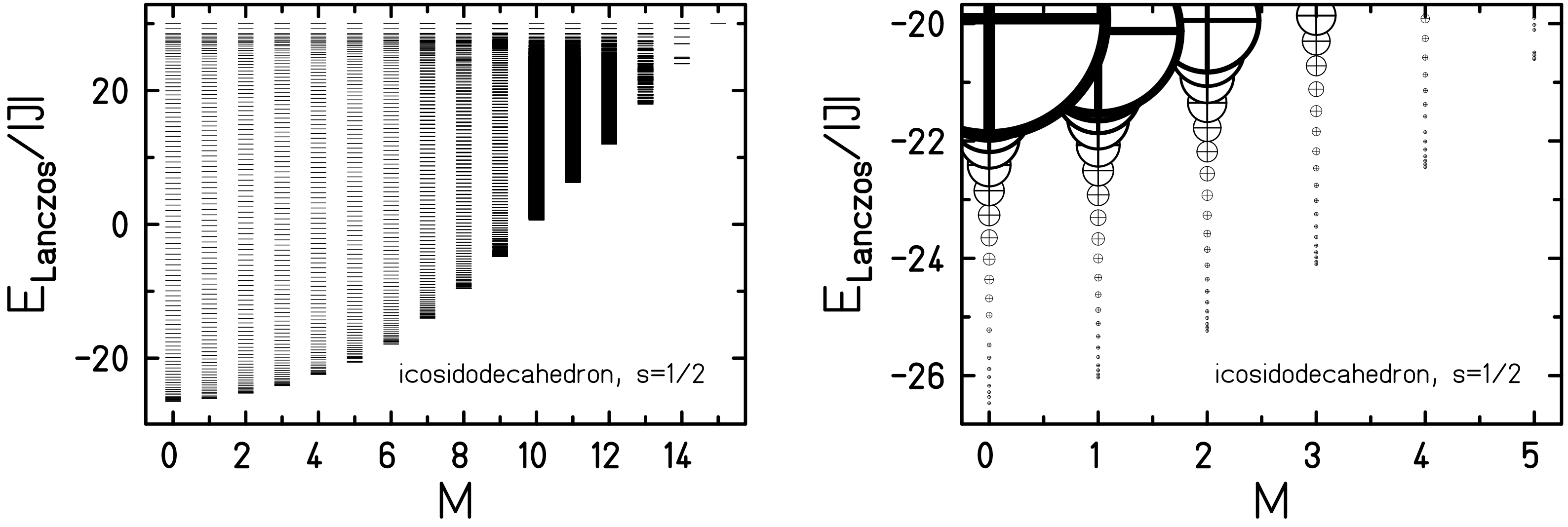
jump

plateau and dip (rapidly vanish with T)

Icosidodecahedron $s = 1/2$



Icosidodecahedron $s = 1/2$



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

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

Anisotropic Magnetic Molecules

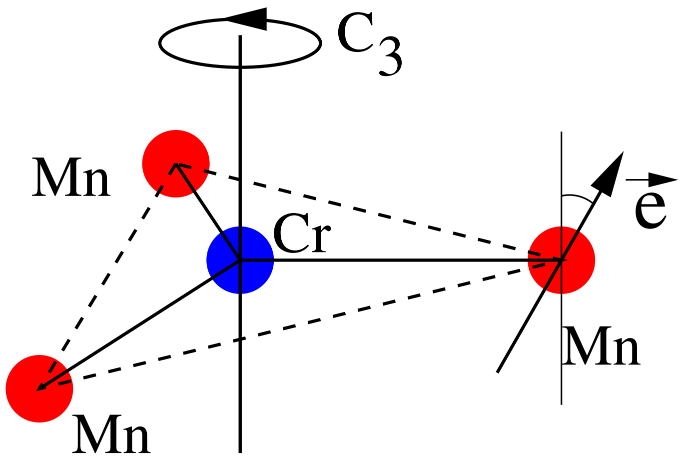
Anisotropic magnetic molecules I – Theory

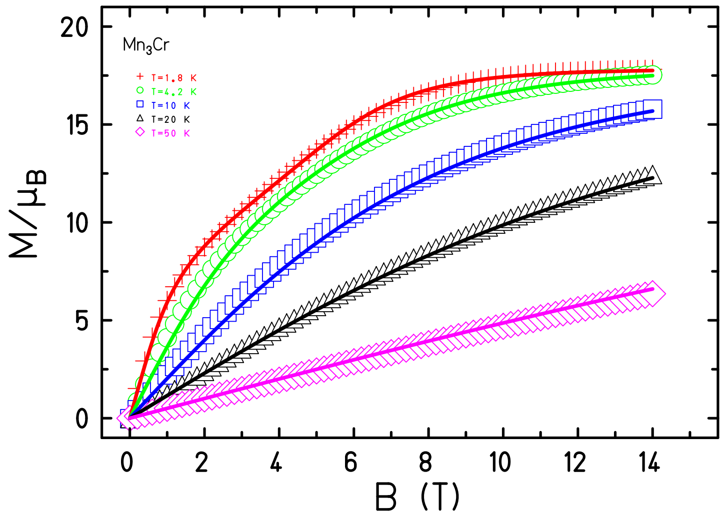
$$\underset{\sim}{H}(\vec{B}) \;=\; -\sum_{i,j} J_{ij}\,\underset{\sim}{\vec{s}}(i)\cdot\underset{\sim}{\vec{s}}(j) \;+\sum_{i} d_i\left(\vec{e}_i\cdot\underset{\sim}{\vec{s}}(i)\right)^2 + \;\mu_B\,\vec{B}\cdot\sum_{i}^{N}\mathbf{g}_i\cdot\underset{\sim}{\vec{s}}(i)$$

- $\left[\underset{\sim}{H}, \underset{\sim}{\vec{S}}^2\right] \neq 0$, $\left[\underset{\sim}{H}, \underset{\sim}{S}_z\right] \neq 0$;
- You have to diagonalize $\underset{\sim}{H}(\vec{B})$ 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$(\mathcal{H}) < 140,000$

(1) J. Schnack, Condens. Matter Phys. **12**, 323 (2009);

Anisotropic magnetic molecules II – Example



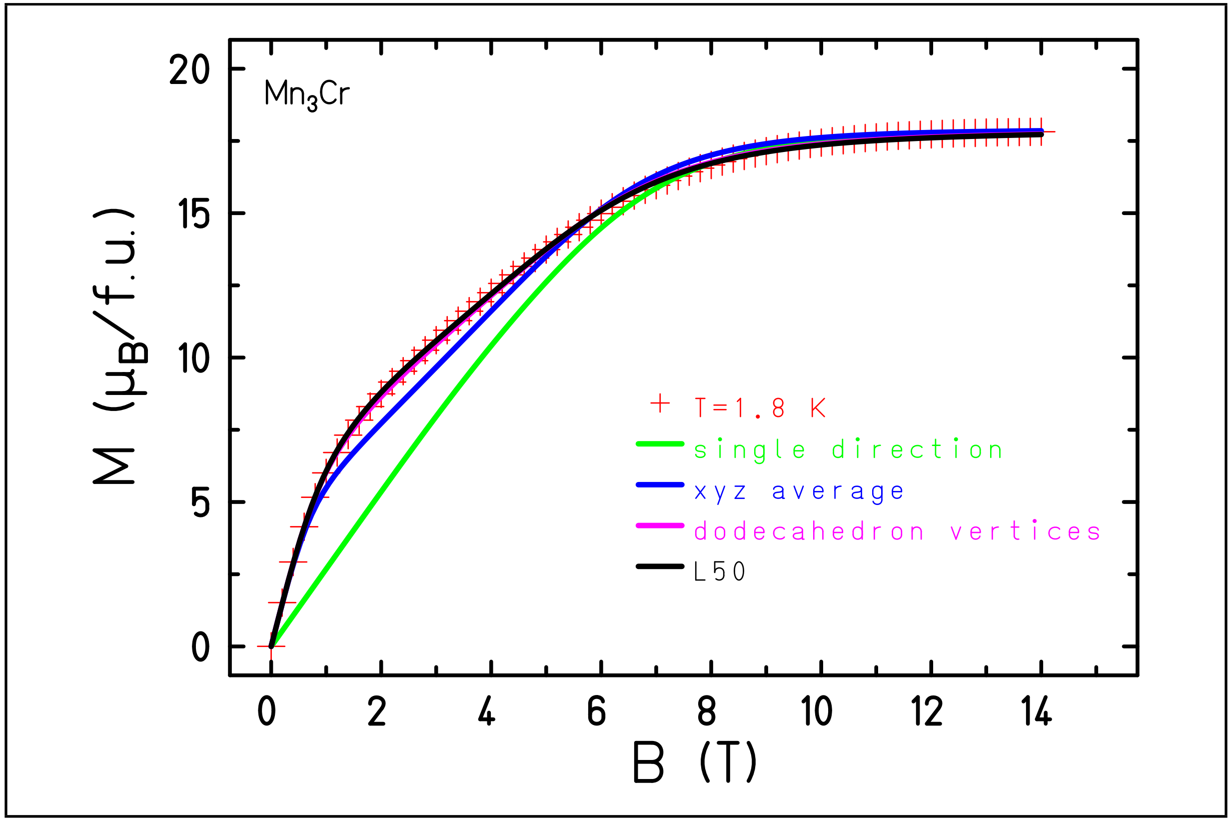


What can be achieved? $\mathrm{Mn_3Cr}$:

- Two couplings: J_1 to central Cr, J_2 between Mn; Mn: s=5/2, g=2.0; Cr: s=3/2, g=1.95
- Model Mn anisotropy by local axis $\vec{e}(\vartheta, \phi)$. Due to C_3 symmetry $\vartheta_{\text{Mn1}} = \vartheta_{\text{Mn2}} = \vartheta_{\text{Mn3}}$. Only relative $\phi = 120^\circ$ determined.
- Model Cr anisotropy by local axis $\vec{e}(\vartheta, \phi)$. Due to C_3 symmetry $\vartheta_{\text{Cr}} = 0, \phi_{\text{Cr}} = 0$.
- Result: $J_1 = -0.29$ cm^{-1}, $J_2 = -0.08$ cm^{-1}, $d_{\text{Mn}} = -1.21$ cm^{-1}, $\vartheta_{\text{Mn}} = 22^\circ$, $d_{\text{Cr}} = +0.17$ cm^{-1}.

M. Prinz *et al.*, Inorg. Chem. **49**, 607 (2010) 2093-2102.

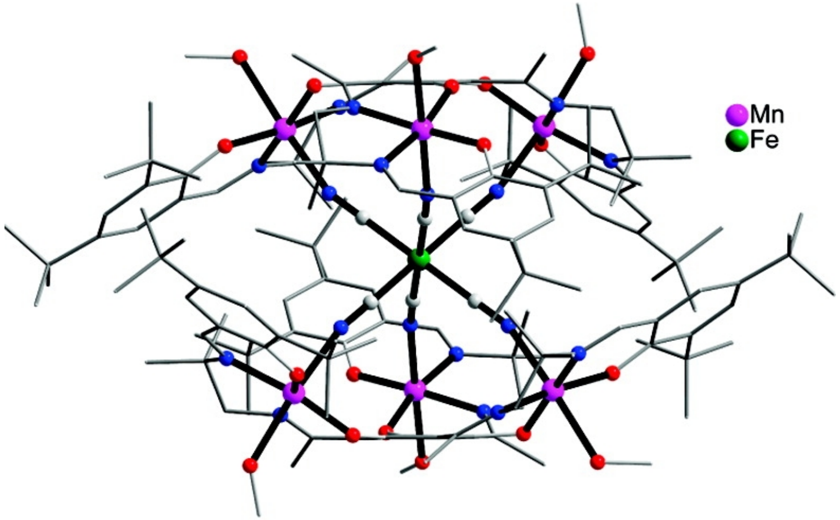
$\mathrm{Mn_3Cr}$ III – Angular averaging



For a good fit you need several directions, at least 10.

V. I. Lebedev and D. N. Laikov, Dokl. Akad. Nauk **366**, 741 (1999); and link to program on `www.molmag.de`

Mn$_6$Fe I



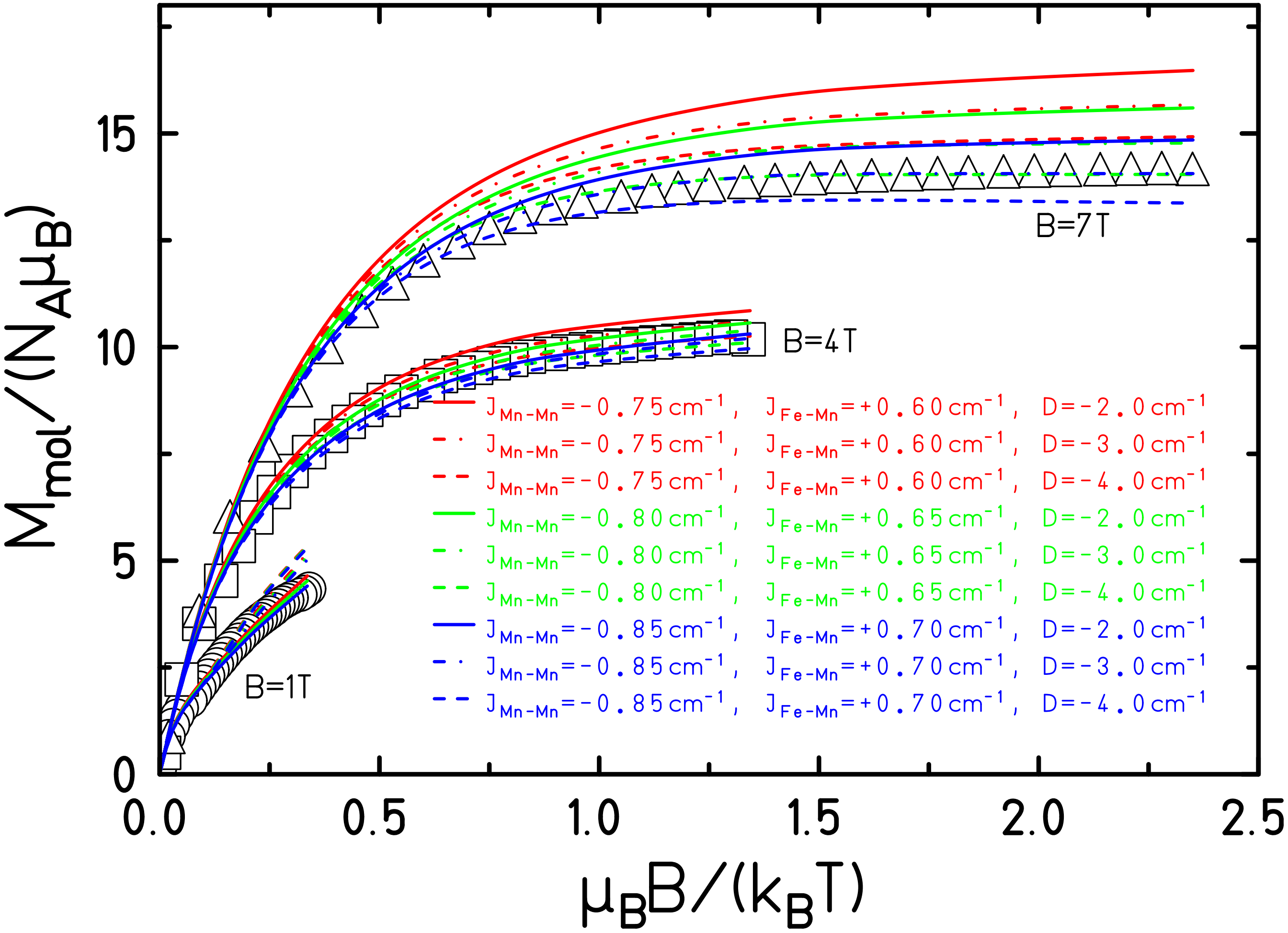
- Rational design of strict C_3 symmetry of local easy axes (Thorsten Glaser): e.g. Mn$_6$Cr (1), Mn$_6$Fe (2)

- Mn$_6$Fe: J_1 between Mn in caps, J_2 to central Fe; Mn anisotropy modeled by local axis $\vec{e}(\vartheta, \phi)$ with $\vartheta_{\text{Mn1}} = \vartheta_{\text{Mn2}} = \vartheta_{\text{Mn3}} = 36.5°$. Only relative $\phi = 120°$ determined.

- Mn: s=2, g=1.98; Fe: s=1/2, g-tensor.

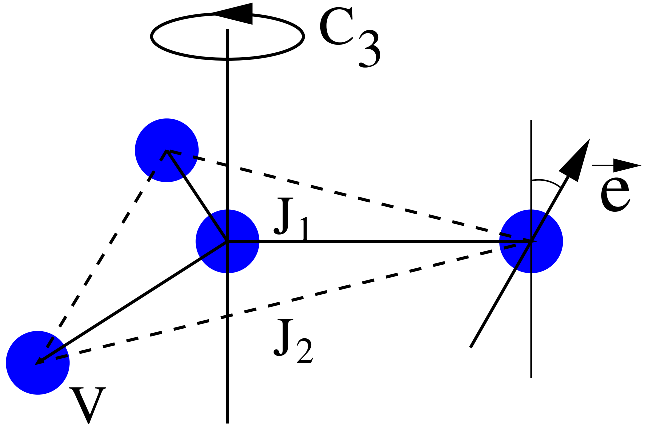
(1) T. Glaser, M. Heidemeier, T. Weyhermüller, R. D. Hoffmann, H. Rupp, P. Müller, Angew. Chem.-Int. Edit. **45**, 6033 (2006).
(2) T. Glaser, M. Heidemeier, E. Krickemeyer, H. Bögge, A. Stammler, R. Fröhlich, E. Bill, J. Schnack, Inorg. Chem. **48**, 607 (2009).

Mn_6Fe II – Results



T. Glaser, M. Heidemeier, E. Krickemeyer, H. Bögge, A. Stammler, R. Fröhlich, E. Bill, J. Schnack, Inorg. Chem. **48**, 607 (2009).

V_4 I

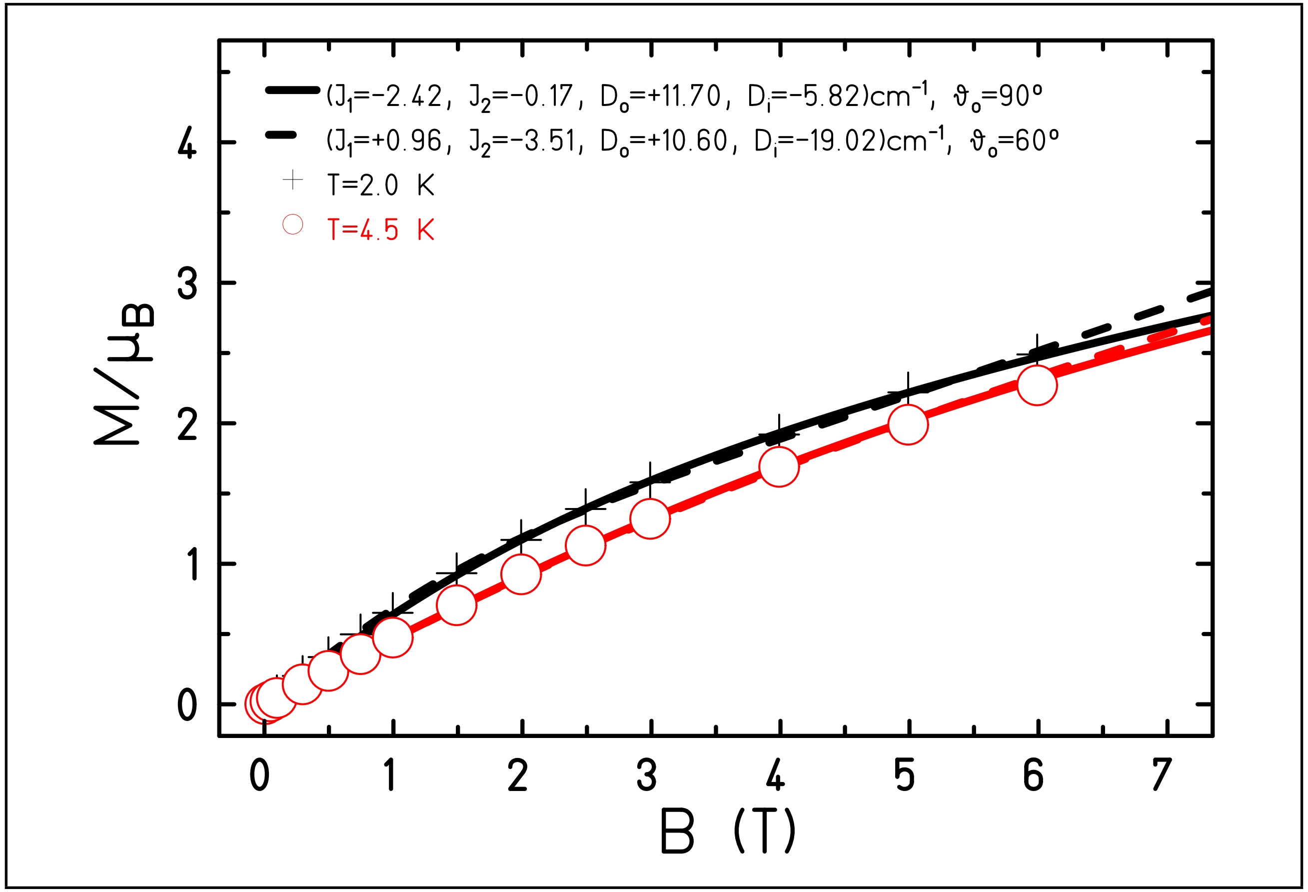


$[V^{III}_4Cl_6(thme)_2(bipy)_3]$

- 4 V^{III}_4 ions with $s = 1$; approximate C_3 symmetry;
- 2 exchange interactions;
- Central V: axial anisotropy;
- Outer Vs: local anisotropy axis with azimuthal angle ϑ.
- Powder average.

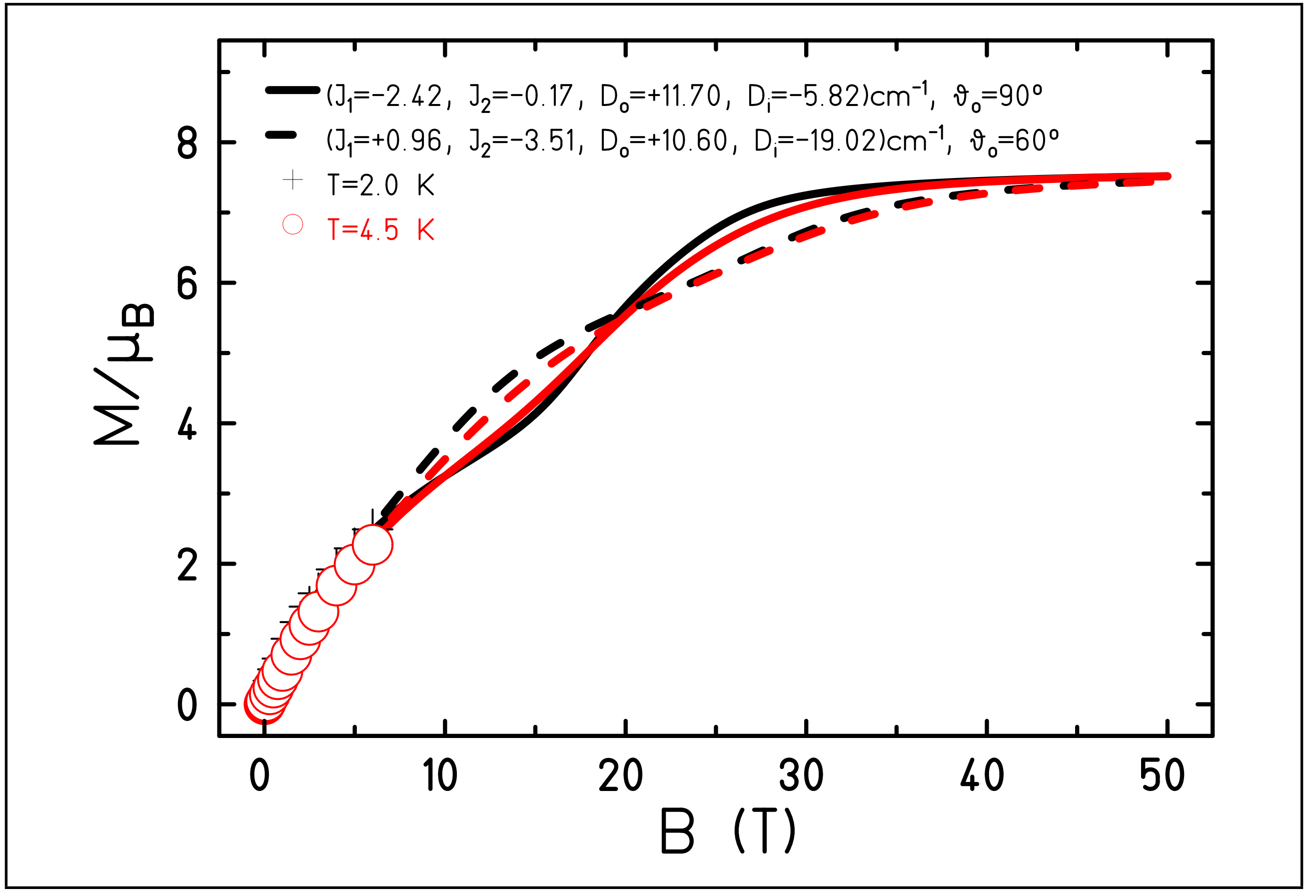
Ian S. Tidmarsh, Luke J. Batchelor, Emma Scales, Rebecca H. Laye, Lorenzo Sorace, Andrea Caneschi, Jürgen Schnack and Eric J.L. McInnes, Dalton Trans. (2009) 9402

V_4 II



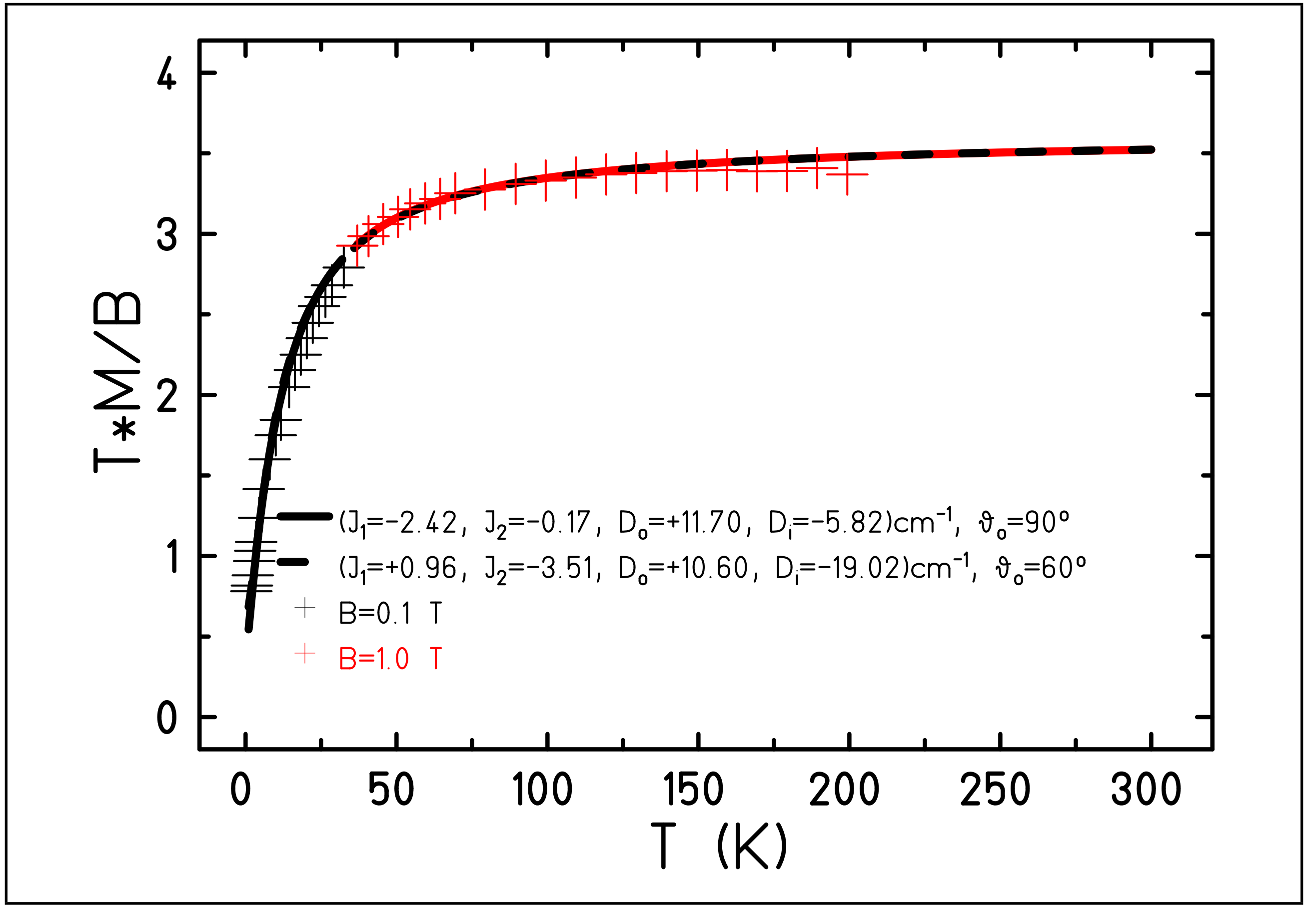
Two equally good parameter sets.

V_4 III



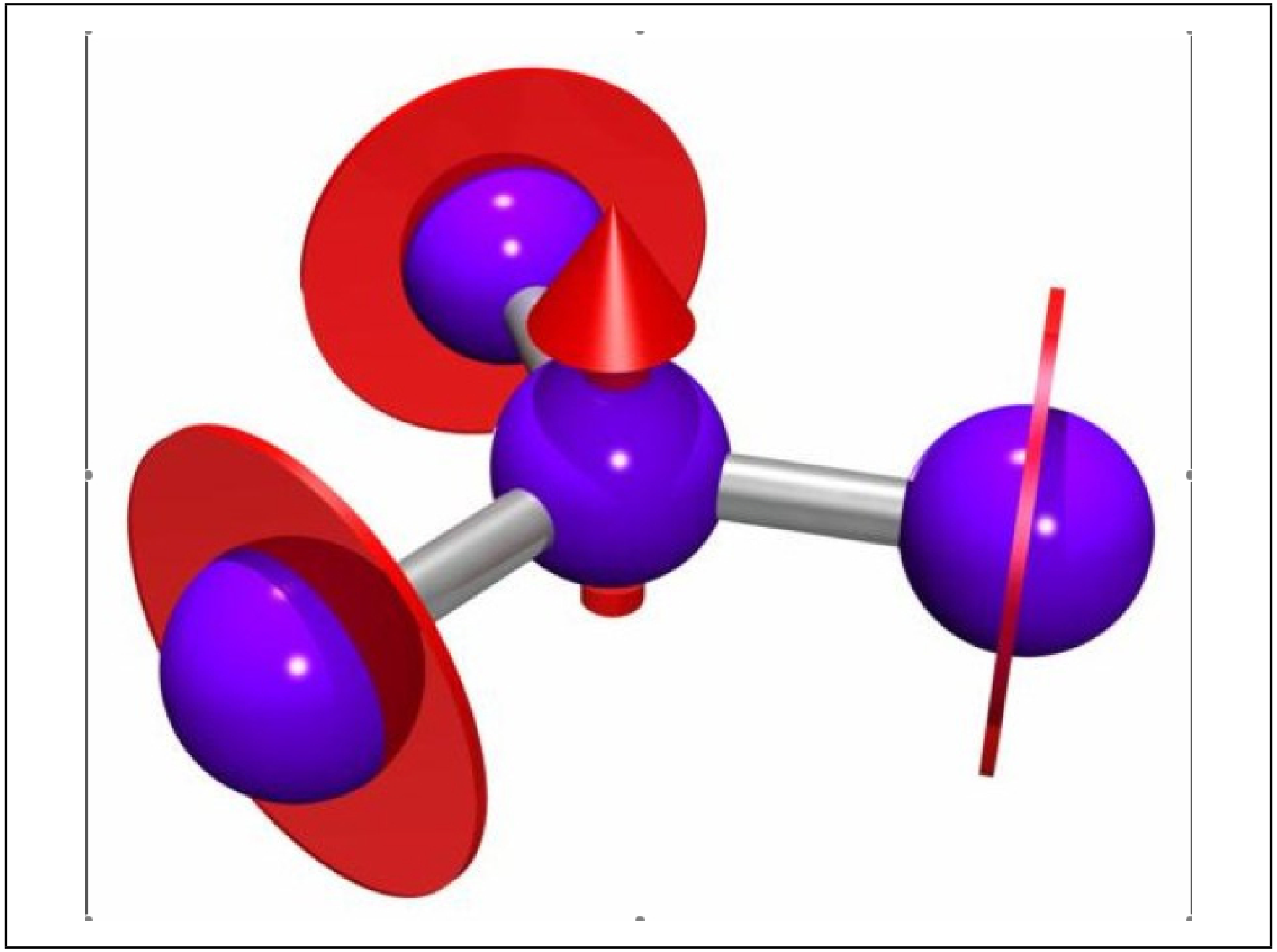
High fields could distinguish.

V_4 IV



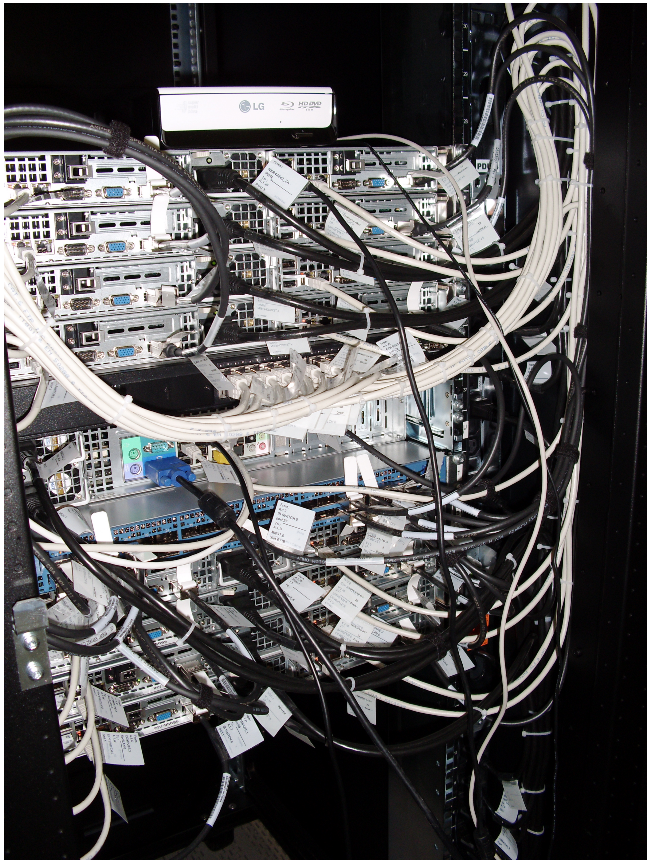
Accuracy of measurement limits modeling.

V$_4$ – Anisotropy tensors



Cartoon of anisotropy tensors.

Summary



- Bielefeld does exist! It's a nice place for matrix diagonalization.
- One can indeed exploit $SU(2)$ and point group symmetries together. Good for molecules, since they are of finite size.
- Problem: Recoupling coefficients.
- Finite-temperature Lanczos is a good approximate method for Hilbert space dimensions below 10^{10}.
- Anisotropic Hamiltonians with several parameters can be accurately treated today.

Thank you very much for your attention.

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