Calculating the energy spectra of magnetic molecules: application of real- and spin-space symmetries

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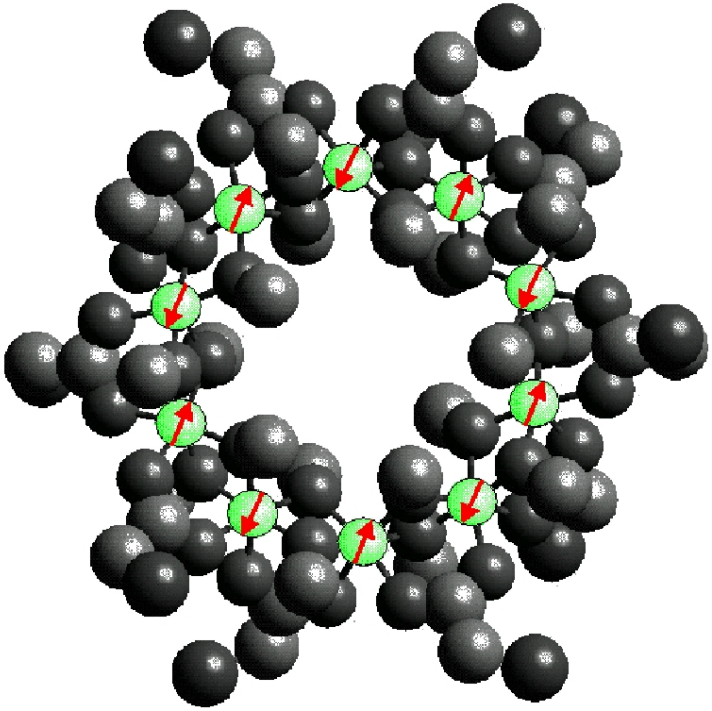
Contents for you today

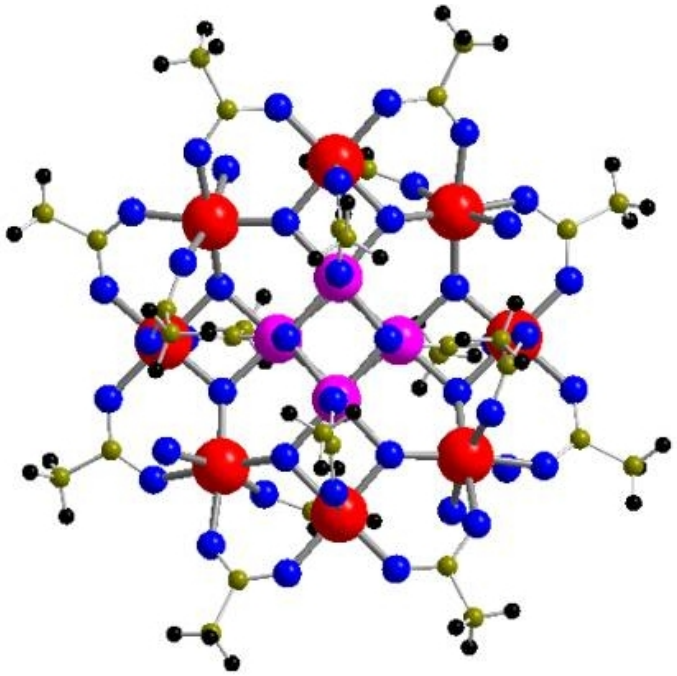


Fe_{10}

1. Magnetic molecules
2. Up to date theory modeling
3. SU(2) symmetry
4. Point group symmetry
5. Results

Magnetic Molecules

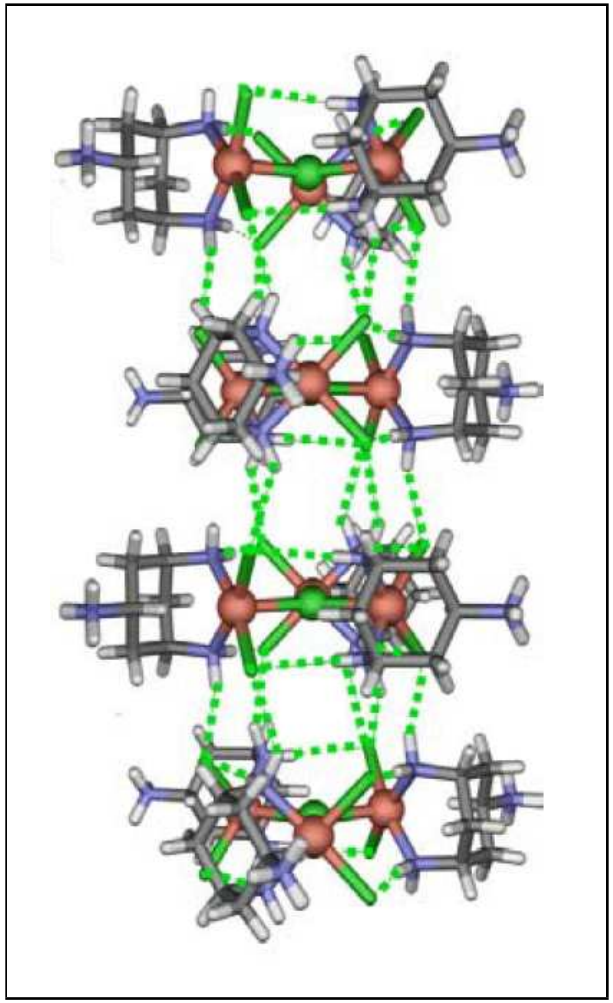
The beauty of magnetic molecules I



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)

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

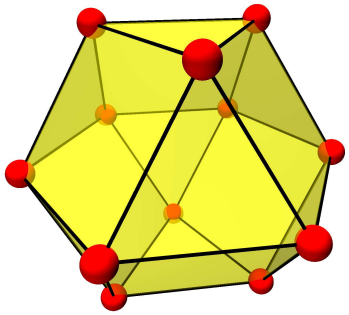
Exchange/Anisotropy Dzyaloshinskii-Moriya Zeeman

Isotropic Hamiltonian

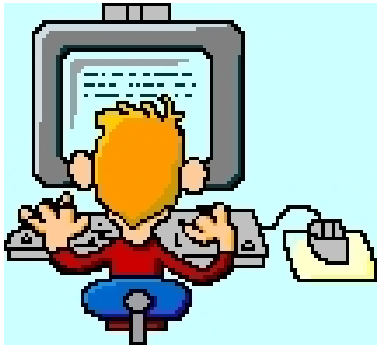
$$\underset{\sim}{H} = -2 \sum_{i<j} J_{ij} \vec{\underset{\sim}{s}}(i) \cdot \vec{\underset{\sim}{s}}(j) + g \mu_B B \sum_{i}^{N} \underset{\sim}{s}_z(i)$$

Heisenberg Zeeman

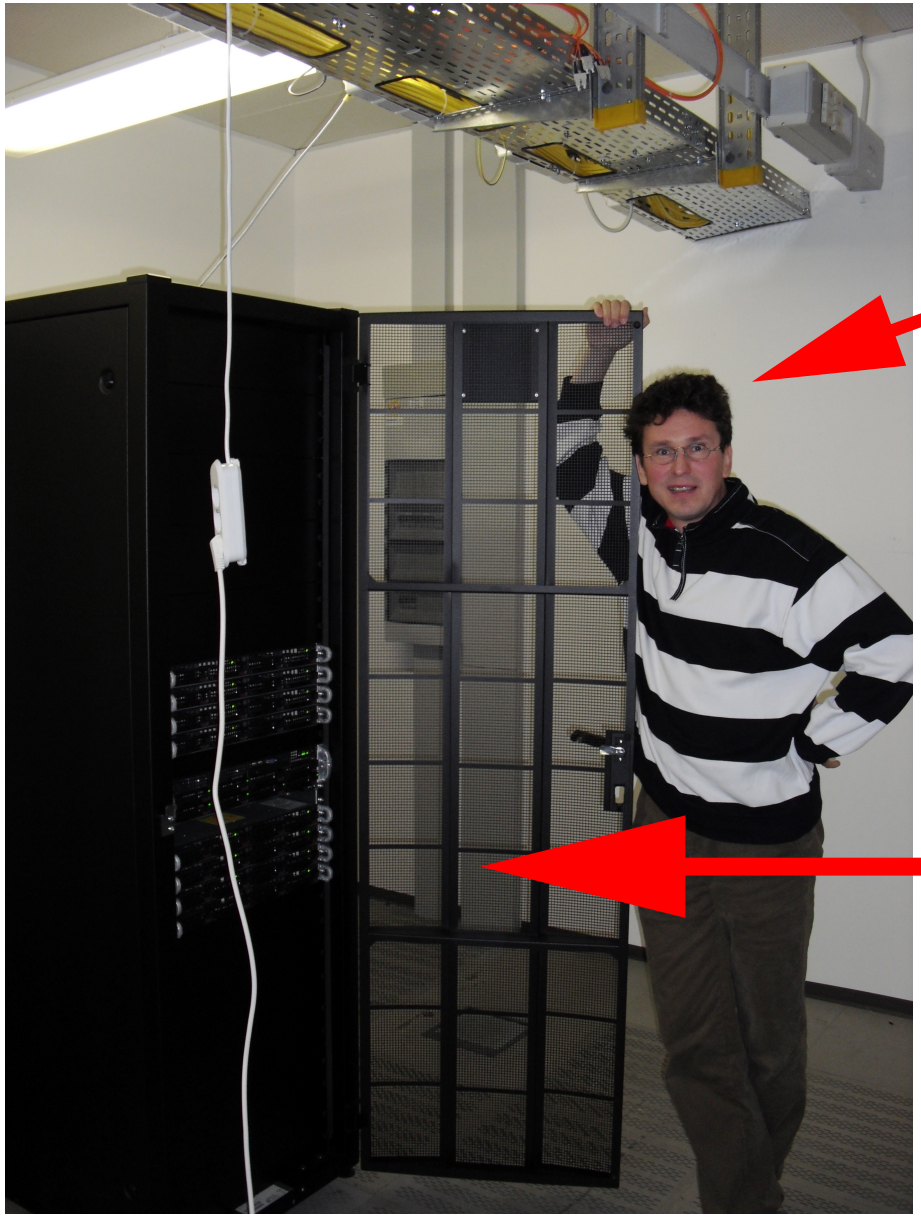
In the end it's always a big matrix!



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



Thank God, we have computers

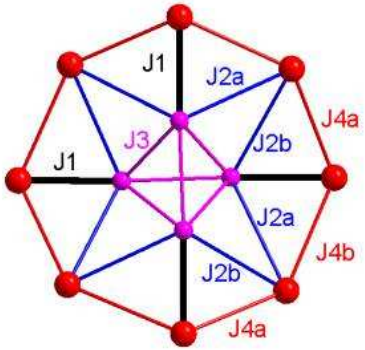


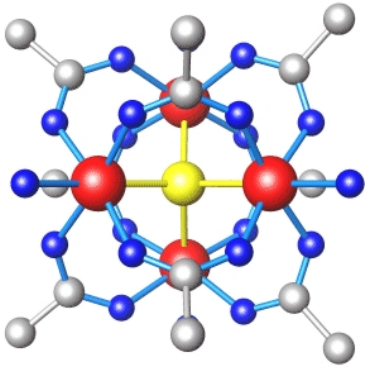
“cell professor”

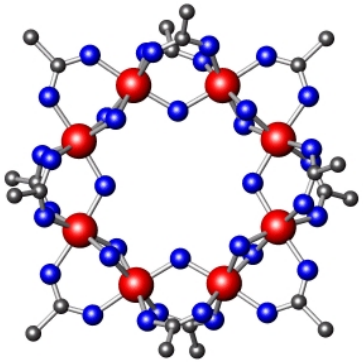
128 cores, 384 GB RAM

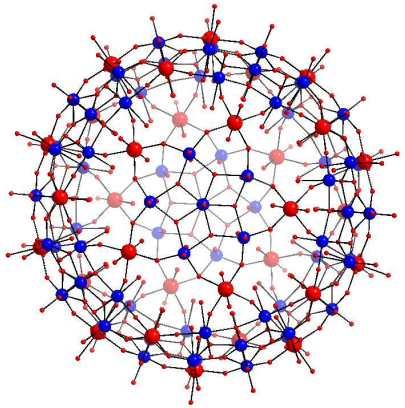
. . . but that’s not enough!

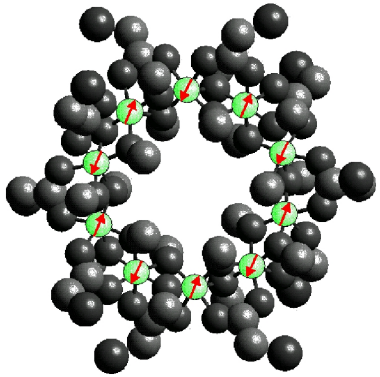
Magnetic Molecules











possess symmetries! Use them!

SU(2) and point group symmetry!


Die spinnen,
die Bielefelder!

Bielefeld ???

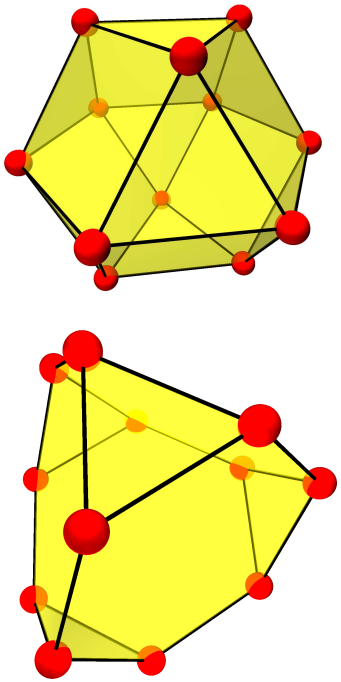
Wir wollen in Ruhe Matrizen diagonalisieren.

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

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

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

$$\left\{ \underset{\sim}{\mathbf{s}}^{(1)}(1) \otimes \underset{\sim}{\mathbf{s}}^{(1)}(2) \right\}^{(0)} = \sum_{q_1,q_2} C^{1\,1\,0}_{q_1\,q_2\,0} \cdot \underset{\sim}{s}^{(1)}_{q_1}(1) \underset{\sim}{s}^{(1)}_{q_2}(2)$$

$$= \frac{1}{\sqrt{3}} \left(\underset{\sim}{s}^{(1)}_{-1}(1) \cdot \underset{\sim}{s}^{(1)}_{1}(2) + \underset{\sim}{s}^{(1)}_{1}(1) \cdot \underset{\sim}{s}^{(1)}_{-1}(2) - \underset{\sim}{s}^{(1)}_{0}(1) \cdot \underset{\sim}{s}^{(1)}_{0}(2) \right)$$

$$= -\frac{1}{\sqrt{3}} \underset{\sim}{\mathbf{s}}(1) \cdot \underset{\sim}{\mathbf{s}}(2)$$

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

Idea of ITO: trimer

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

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

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

$$\langle \alpha_1\, s_1\, \alpha_2\, s_2\, S || \left\{ \underset{\sim}{\mathbf{T}}^{(k_1)} \otimes \underset{\sim}{\mathbf{T}}^{(k_2)} \right\}^{(k)}_{q} || \alpha_1'\, s_1'\, \alpha_2'\, s_2'\, S' \rangle$$

$$=$$

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

- 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.

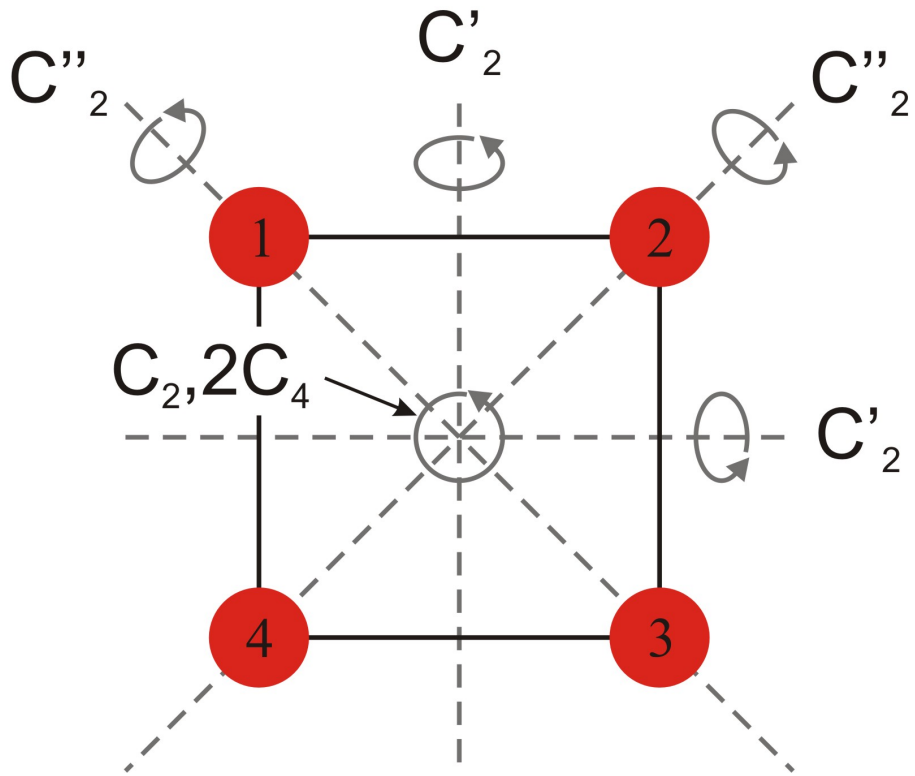
(1) M. Tinkham, *Group Theory and Quantum Mechanics*, Dover.
(2) O. Waldmann, Phys. Rev. B **61**, 6138 (2000).
(3) R. Schnalle, Ph.D. thesis, Osnabrück University (2009).
(4) R. Schnalle and J. Schnack, Int. Rev. Phys. Chem. **29** (2010) 403-452.

Point Group Symmetry II

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

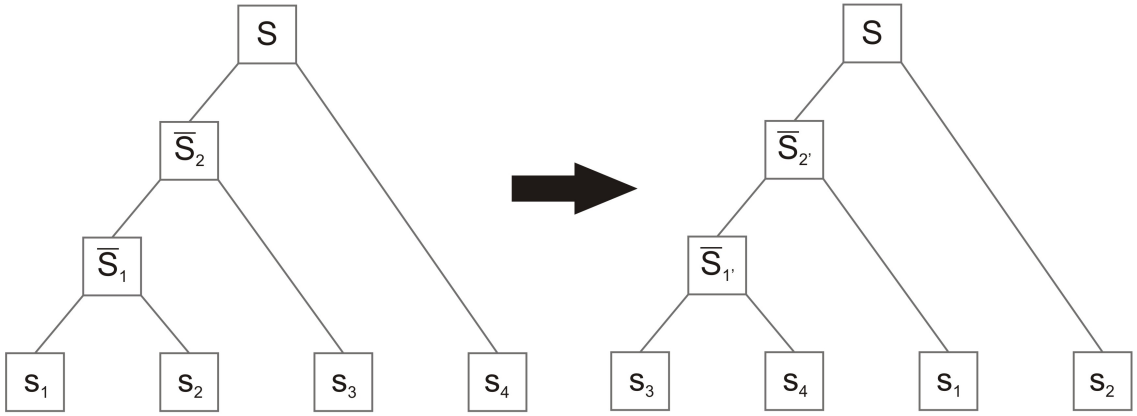
- Serious problem: application of $\underset{\sim}{G}(R)$, i.e. permutation of spins, leads to different coupling schemes;
- Solution: implementation of graph-theoretical results to evaluate recoupling coefficients ${}_a\langle\,\alpha'\,S\,M\,|\,\alpha\,S\,M\,\rangle_b$.

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

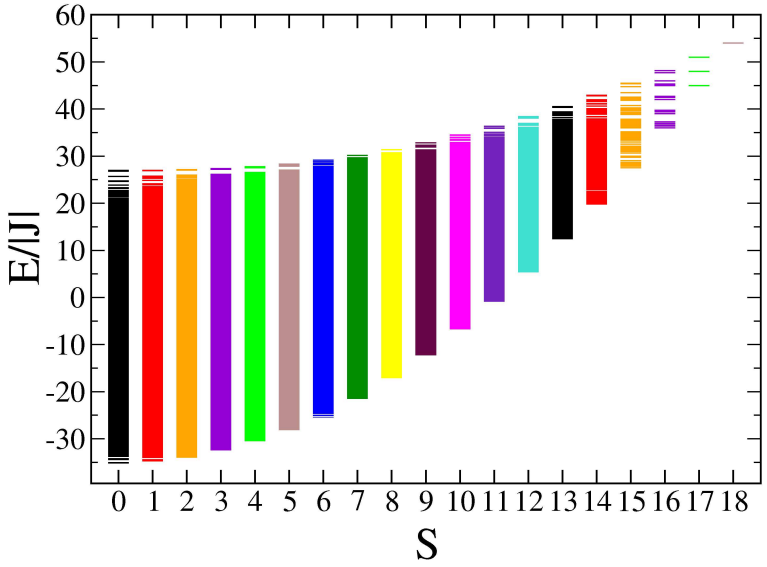


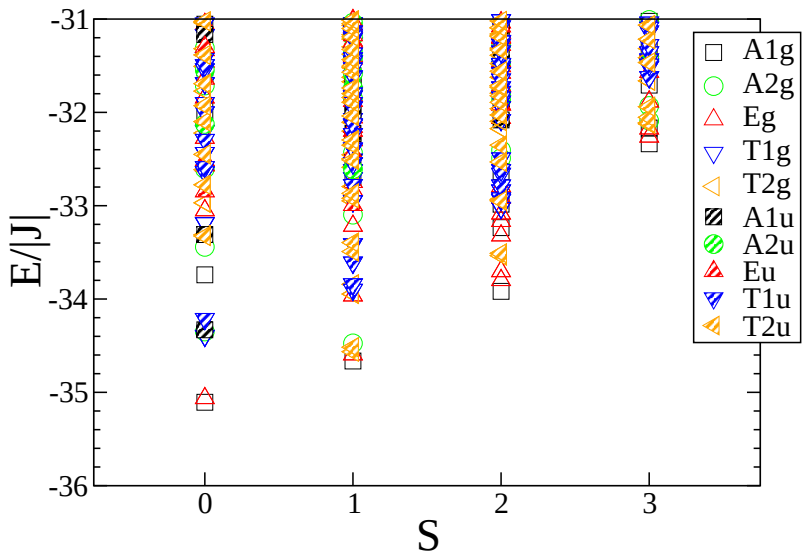
- Recoupling coefficient $\langle s_1 s_2 \overline{S}_1 s_3 \overline{S}_2 s_4 SM \,|\, s_3 s_4 \overline{S}_{1'} s_1 \overline{S}_{2'} s_2 SM \rangle$ can be evaluated by a graphical transformation of one binary tree into the orther (1,2).
- Exchange and flop operations generate a recoupling formula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

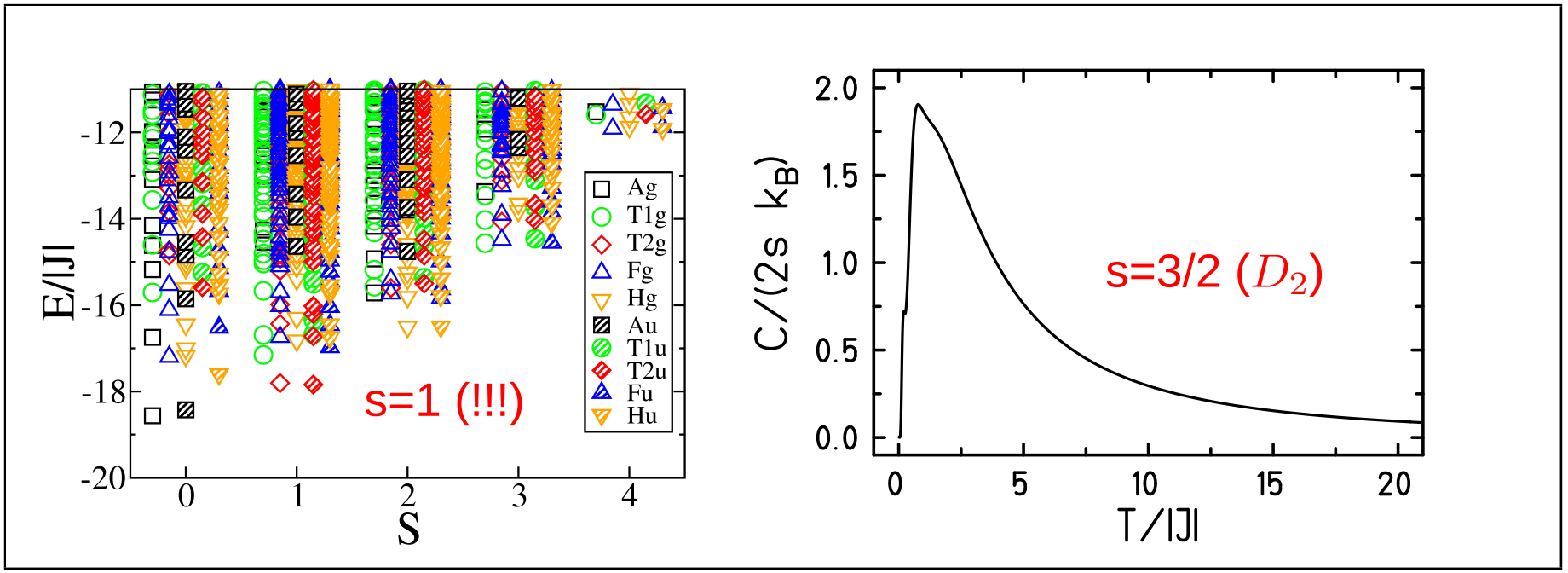




Cuboctahedron, $s = 3/2$, Hilbert space dimension 16,777,216; symmetry O_h (1).
Evaluation of recoupling coefficients very time consuming (1,2).

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

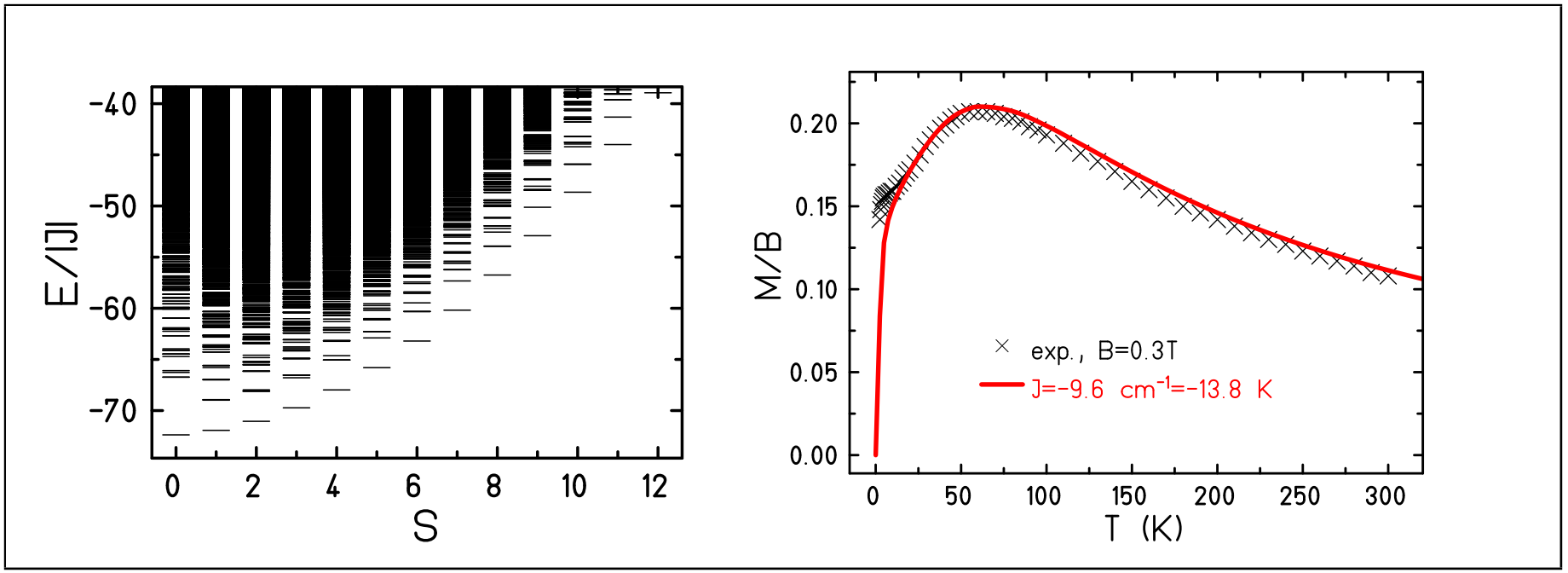
Results II: Icosahedron



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.

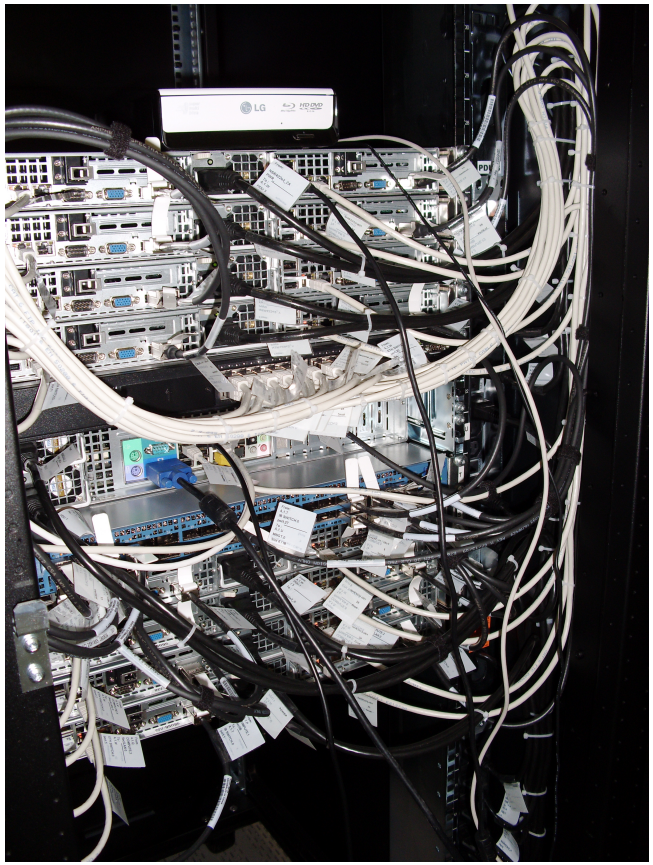
Results III: Fe_{10}



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.

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.
- Open: Search for compatible symmetries and coupling schemes.

Matrix theory goes on . . .

. . . at the Hessische Landesbank!

Thank you very much for your attention.

Molecular Magnetism Web

www.molmag.de

Highlights. Tutorials. Who is who. Conferences.