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

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Universität Bielefeld

Deutsche Forschungsgemeinschaft DFG

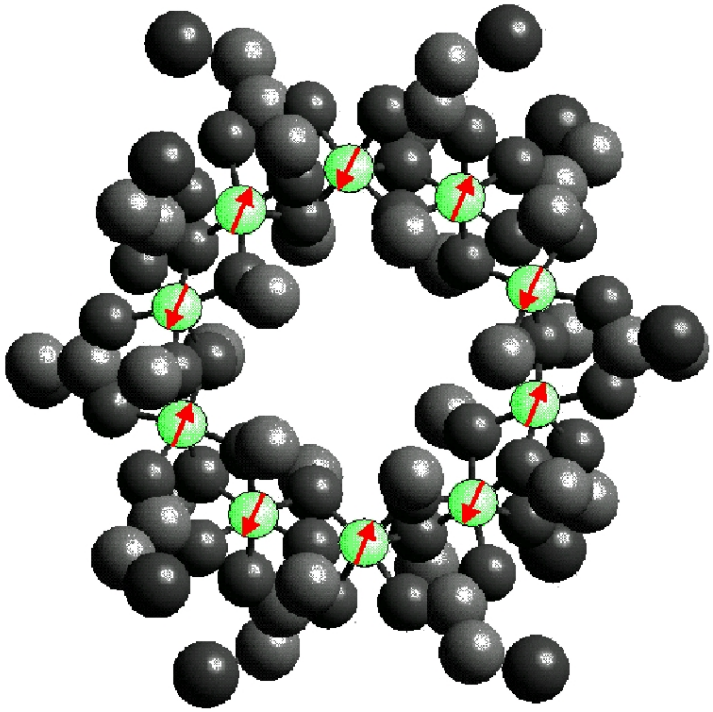
FOR 945

IMR Research 東北大学金属材料研究所 Institute for Materials Research, Tohoku University

I'll deliver the food to you!

The problem

You have got a molecule!

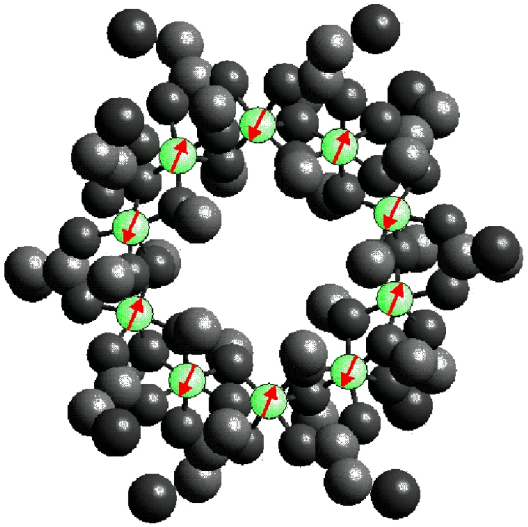


Congratulations!

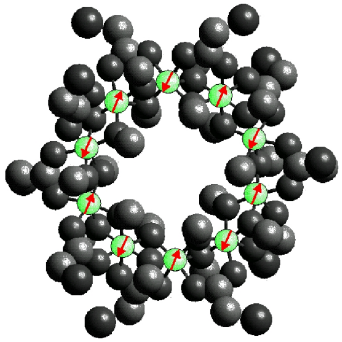
You have got an idea about the modeling!

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

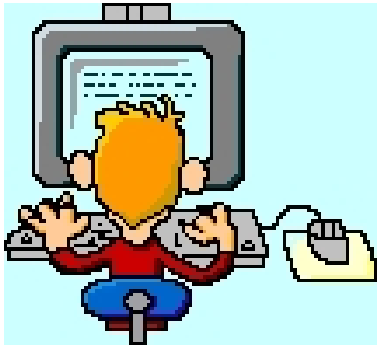
Heisenberg Zeeman



In the end it's always a big matrix!



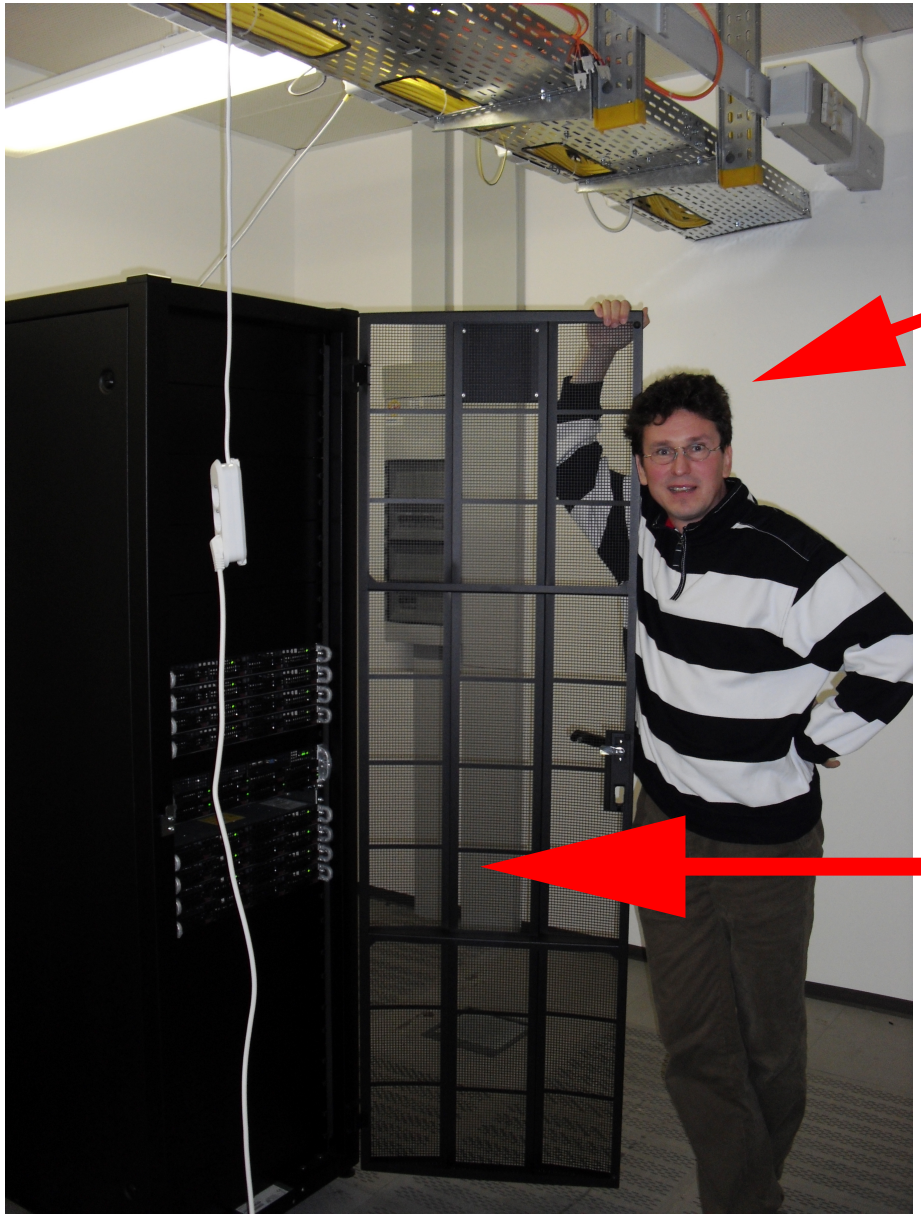
$$\Rightarrow \begin{pmatrix} -27.8 & 3.46 & 0.18 & \cdots \\ 3.46 & -2.35 & -1.7 & \cdots \\ 0.18 & -1.7 & 5.64 & \cdots \\ \vdots & \vdots & \vdots & \cdots \end{pmatrix} \Rightarrow$$



Fe_{10}^{III}: $N = 10, s = 5/2$

Dimension=60,466,176. Maybe too big?

Thank God, we have computers

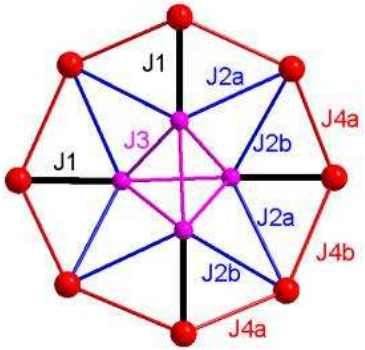


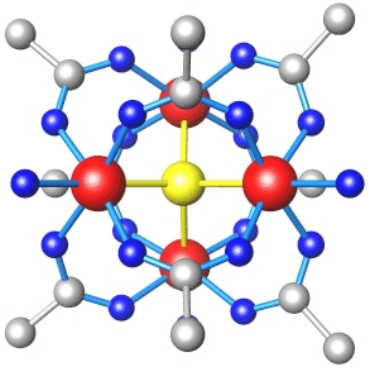
“cell professor”

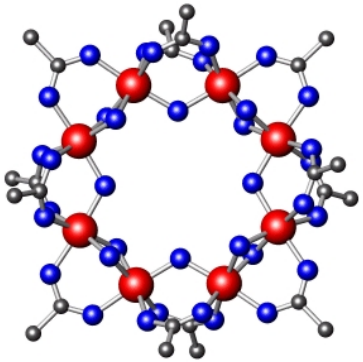
128 cores, 384 GB RAM

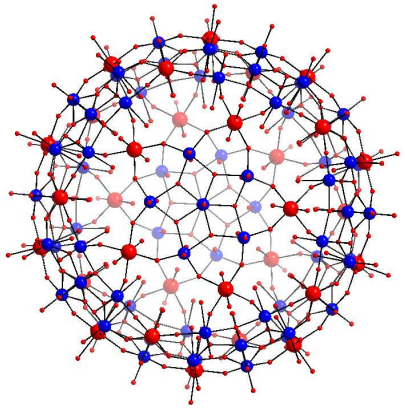
. . . but that’s not enough!

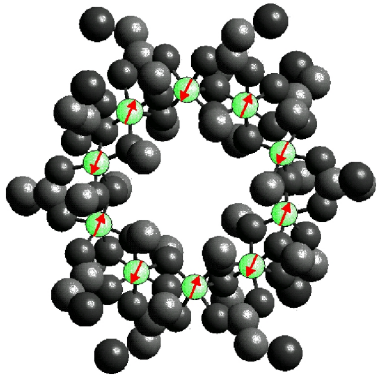
Magnetic Molecules











possess symmetries! Use them!

Key question:

Can we employ SU(2) symmetry together with arbitrary point group symmetries?

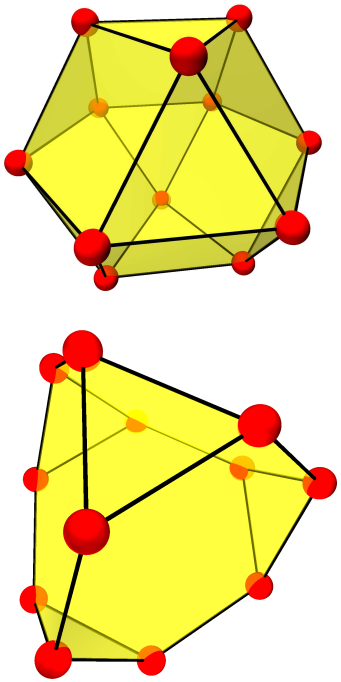
Here comes the meat!

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)

Point group symmetry

(Ph.D. of Roman Schnalle)

Point Group Symmetry I

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

Method:

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

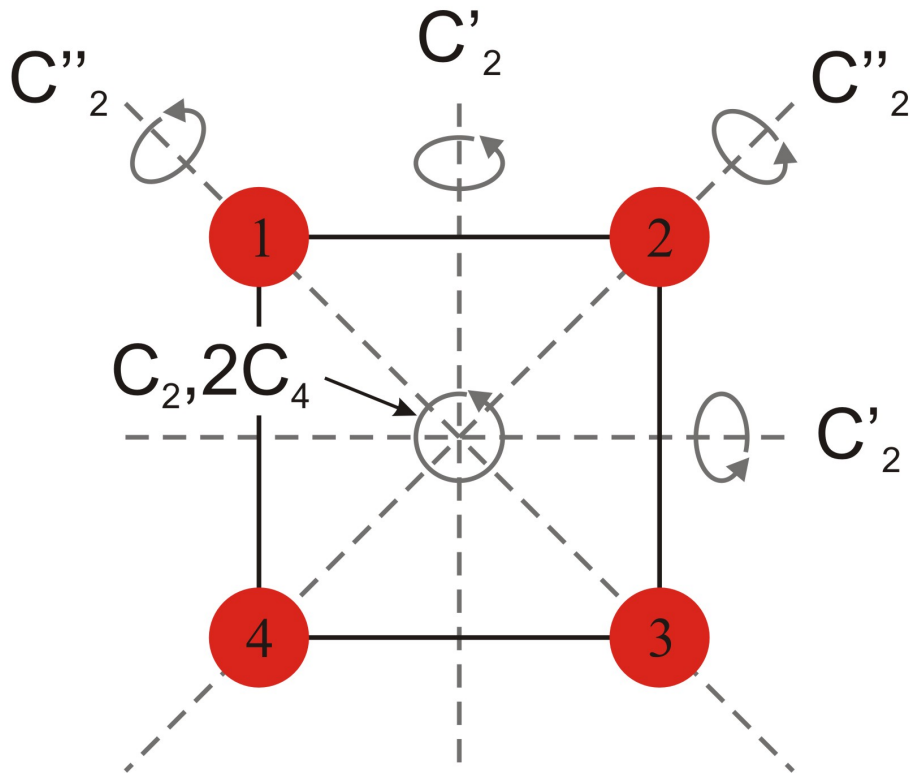
(1) M. Tinkham, *Group Theory and Quantum Mechanics*, Dover.
(2) D. Gatteschi and L. Pardi, Gazz. Chim. Ital. **123**, 231 (1993).
(3) O. Waldmann, Phys. Rev. B **61**, 6138 (2000).
(4) R. Schnalle and J. Schnack, Int. Rev. Phys. Chem. **29**, 403-452 (2010).

Point Group Symmetry II

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

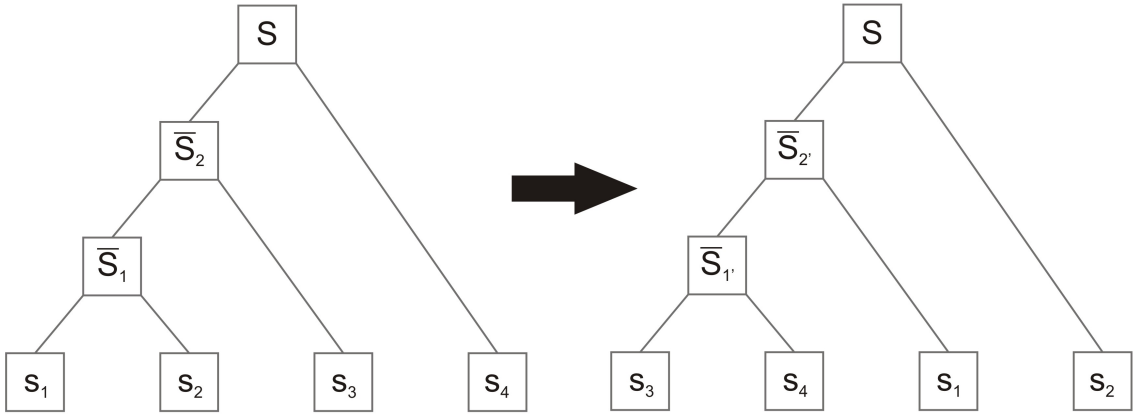
- Serious problem: application of $\underset{\sim}{G}(R)$, i.e. permutation of spins, leads to different coupling schemes: $a \Rightarrow b$;
- Solution: implementation of graph-theoretical results to evaluate recoupling coefficients ${}_a\langle\,\alpha'\,S\,M\,|\,\alpha\,S\,M\,\rangle_b$.

Point Group Symmetry III – example square



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

Point Group Symmetry IV – binary trees

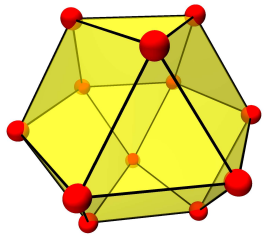


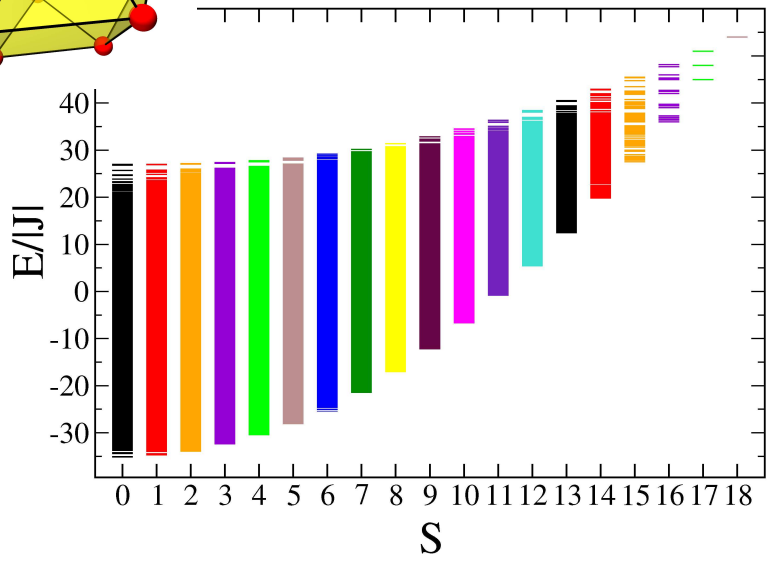
- Recoupling coefficient $\langle s_1 s_2 \overline{S}_1 s_3 \overline{S}_2 s_4 SM \,|\, s_3 s_4 \overline{S}_{1'} s_1 \overline{S}_{2'} s_2 SM \rangle$ can be evaluated by a graphical transformation of one binary tree into the other (1,2).
- Exchange and flop operations generate a recoupling formula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

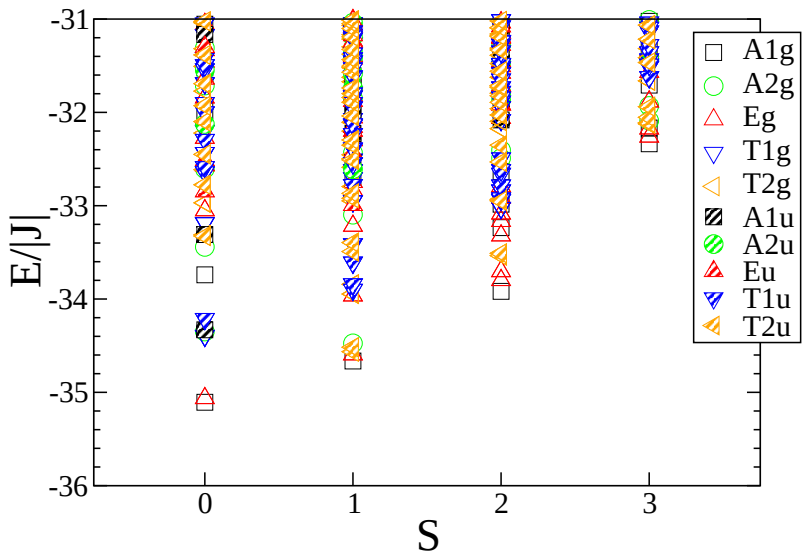
(1) V. Fack, S. N. Pitre, and J. van der Jeugt, Comp. Phys. Comm. **86**, 105 (1995).
(2) V. Fack, S. N. Pitre, and J. van der Jeugt, Comp. Phys. Comm. **101**, 155 (1997).
(3) M. Geisler, Bachelor Thesis, Bielefeld University (2010).

Results

Results I: Cuboctahedron



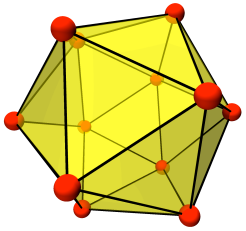


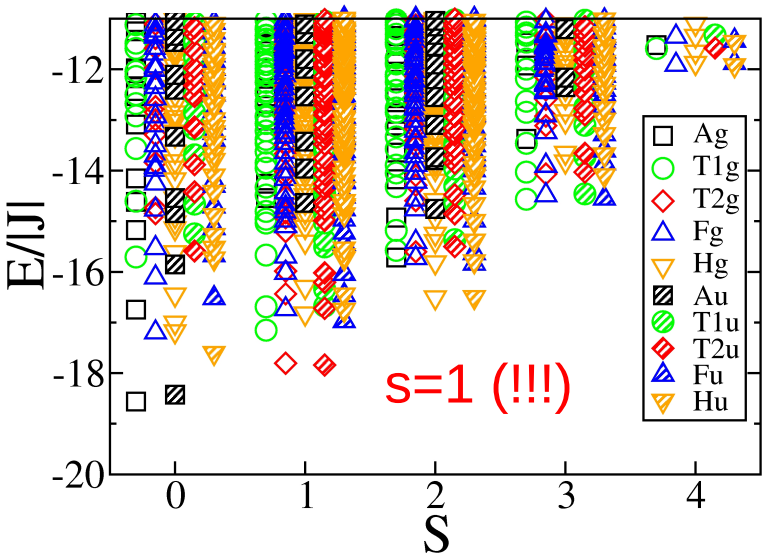


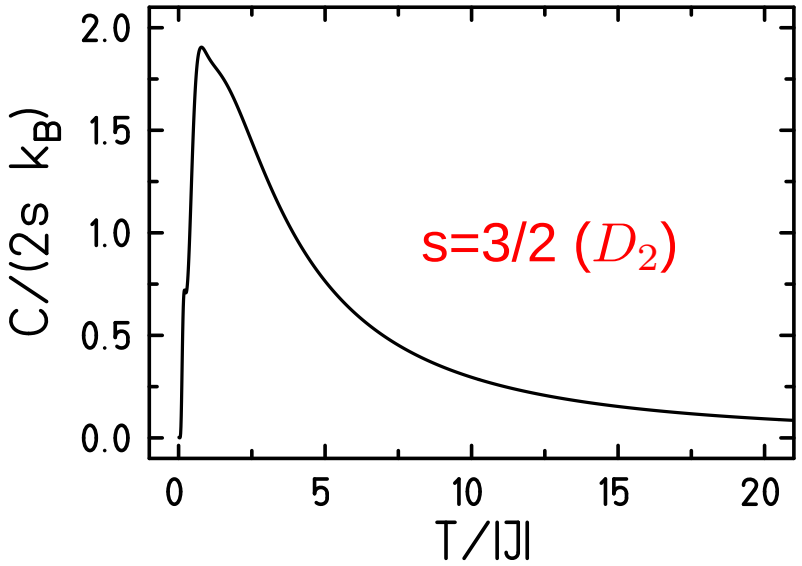
Cuboctahedron, $s = 3/2$, Hilbert space dimension 16,777,216; symmetry O_h (1).
Evaluation of recoupling coefficients very time consuming (1,2).

(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



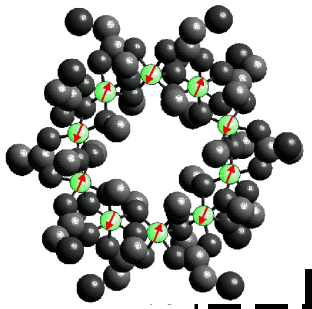


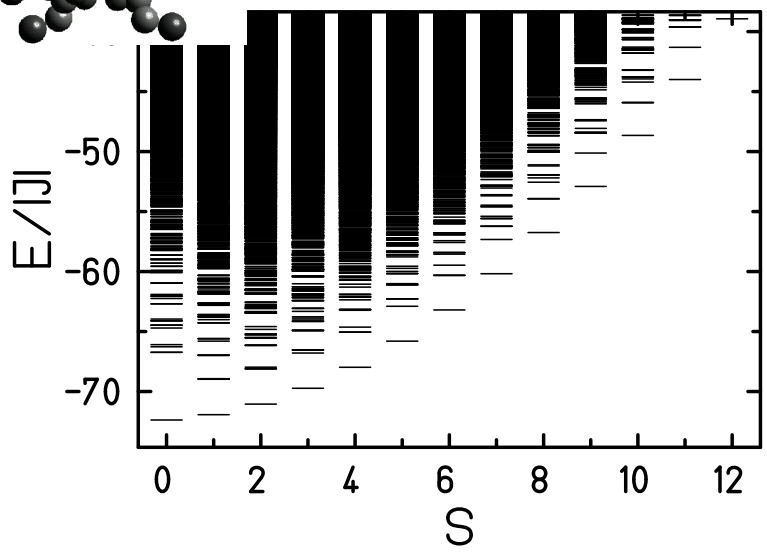


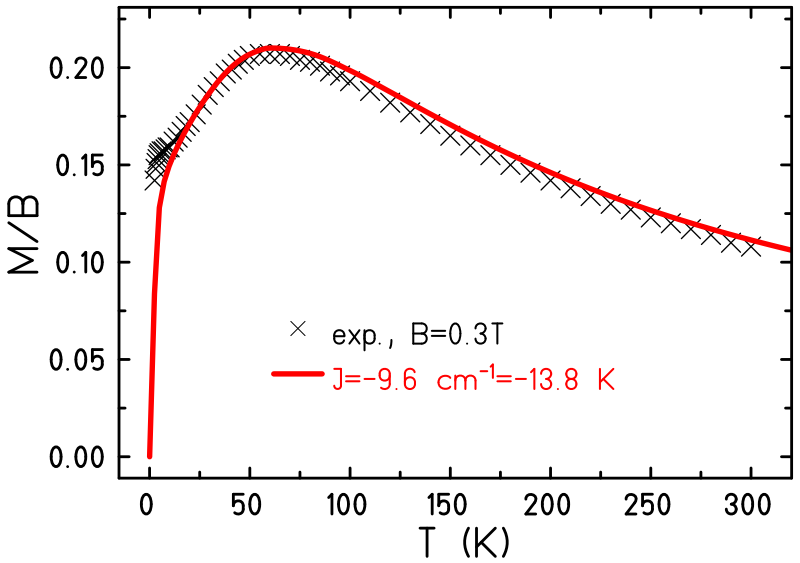
Icosahedron, $s = 3/2$, Hilbert space dimension 16,777,216; symmetry I_h;
Evaluation of recoupling coefficients for $s = 3/2$ in I_h **practically impossible** (1).

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

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**, 403-452 (2010).
(2) C. Delfs *et al.*, Inorg. Chem. **32**, 3099 (1993).

Matrix theory goes on . . .

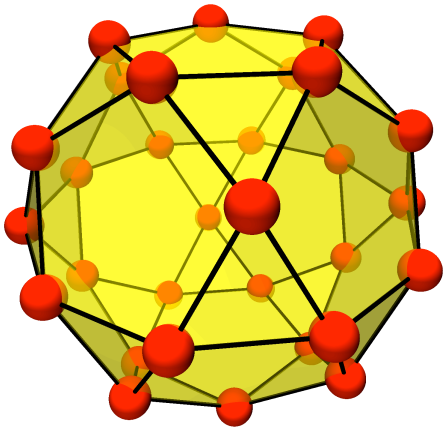
. . . at the Hessische Landesbank!

This could be the end . . .

. . . but you have got another molecule!

N=30, s=1/2

DIMENSION = 1,073,741,824



Congratulations!

The idea of finite-temperature Lanczos

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

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

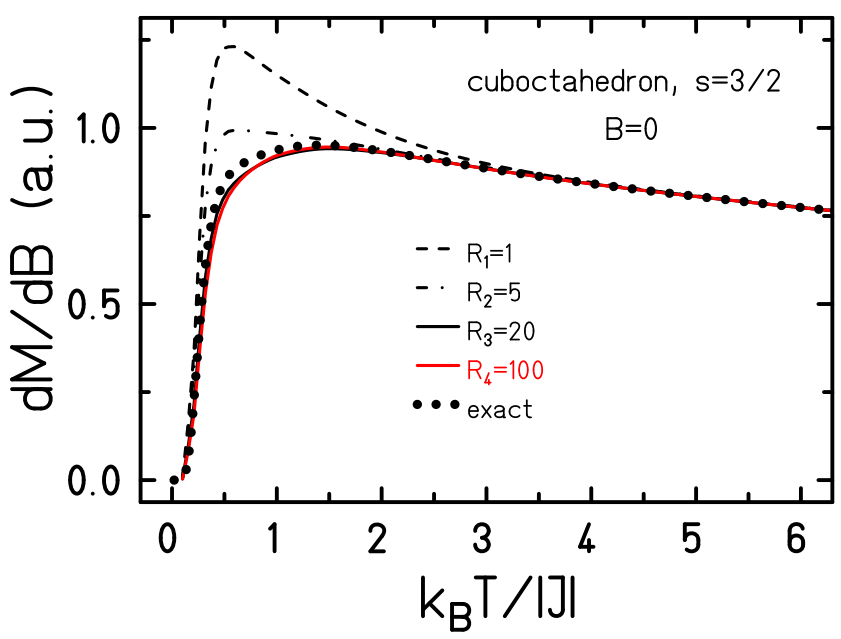
J. Jaklic and P. Prelovsek, Phys. Rev. B **49**, 5065 (1994).

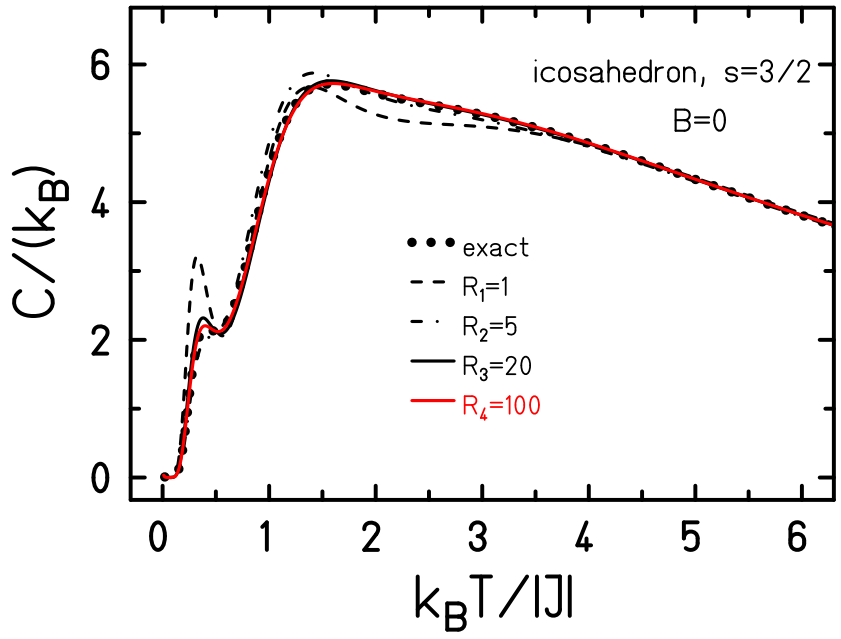
Final form of finite-temperature Lanczos

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

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

How good is finite-temperature Lanczos?

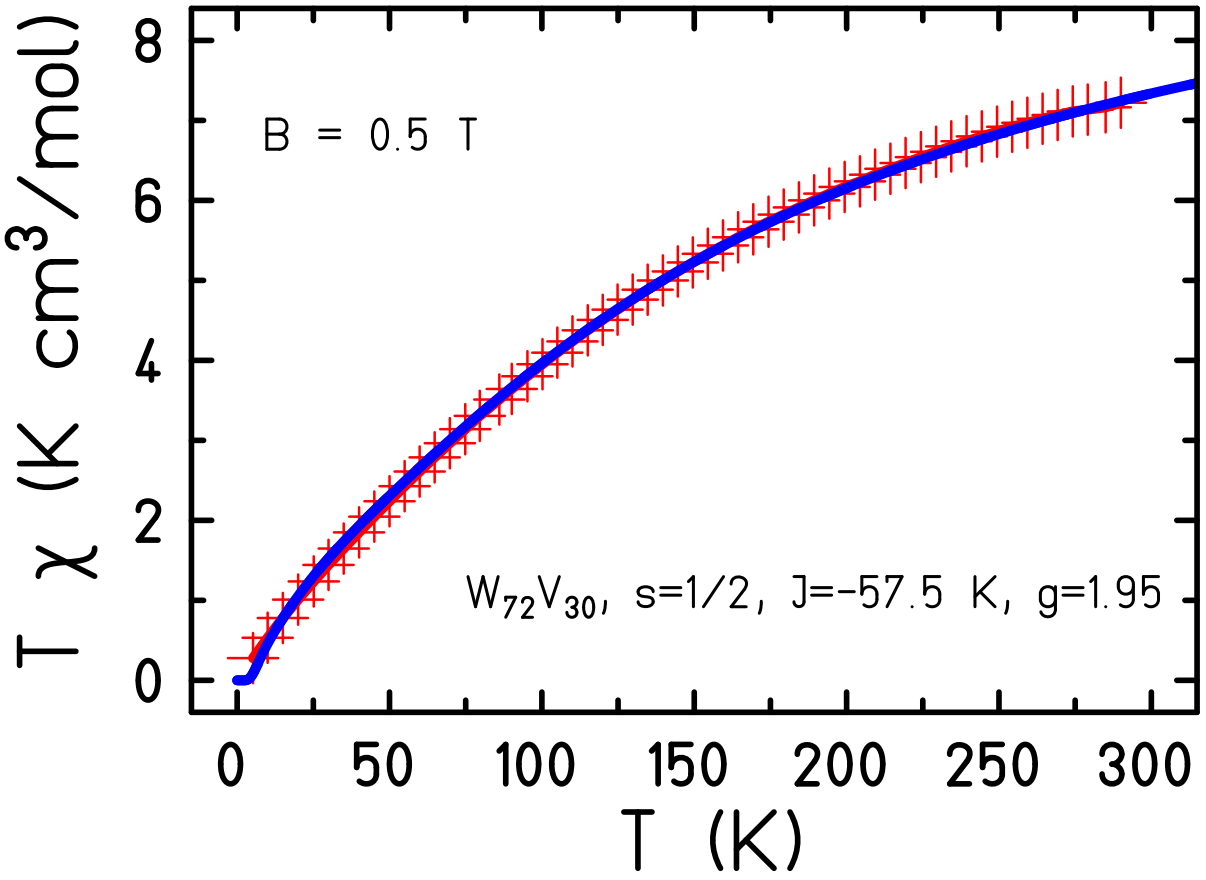




- Works very well, see e.g. cuboctahedron and icosahedron.
- $N = 12, s = 3/2$: Considered $< 100,000$ states instead of 16,777,216.

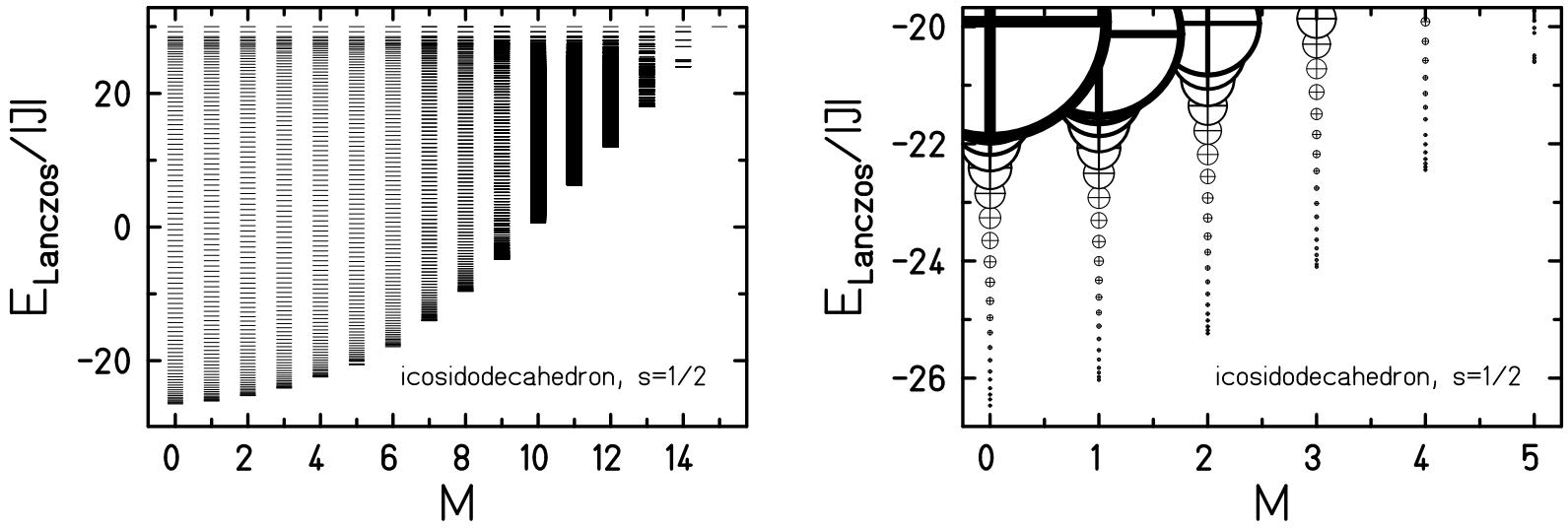
Exact results: R. Schnalle and J. Schnack, Int. Rev. Phys. Chem. **29**, 403-452 (2010).
FTLM: J. Schnack and O. Wendland, Eur. Phys. J. B **78**, 535-541 (2010).

Icosidodecahedron $s = 1/2$



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

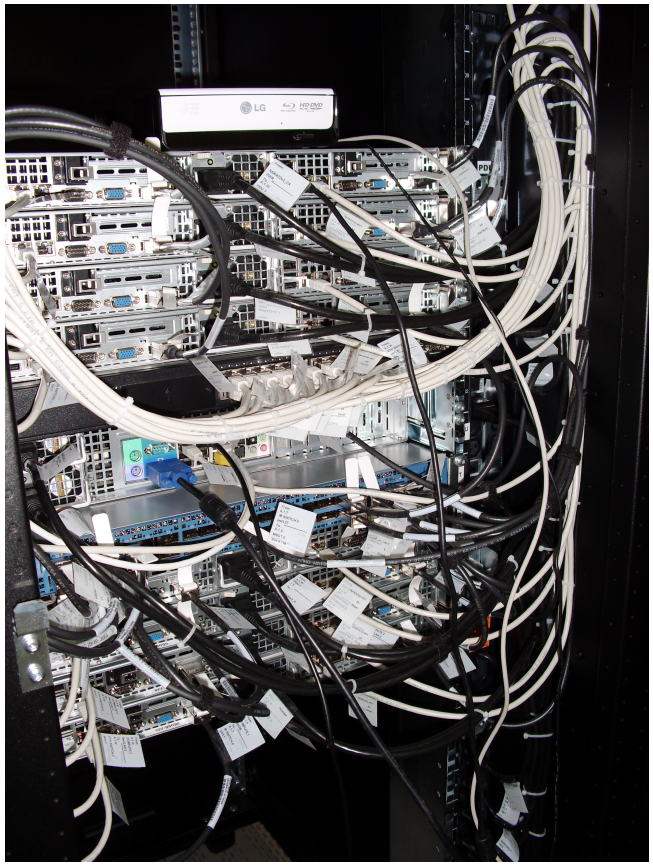
Icosidodecahedron $s = 1/2$



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

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

Summary



- 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 smaller than 10^{10}.
- I believe that this is the future.

Many thanks to my collaborators worldwide

- T. Englisch, T. Glaser, M. Höck, N.B. Ivanov, S. Leiding, A. Müller, S. Ratnabala, R. Schnalle, Chr. Schröder, J. Ummethum, O. Wendland (Bielefeld)
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- J. Richter, J. Schulenburg (Magdeburg); A. Honecker (Göttingen); U. Kortz (Bremen); A. Tennant, B. Lake (HMI Berlin); B. Büchner, V. Kataev, H.-H. Klauß (Dresden); P. Chaudhuri (Mühlheim); J. Wosnitza (Dresden-Rossendorf); J. van Slageren (Stuttgart); R. Klingeler (Heidelberg); O. Waldmann (Freiburg)

Thank you very much for your attention.

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