A bit of everything: how theoretical physicists treat magnetic molecules

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Seminar, Euan's group

Edinburgh, 20. 05. 2011

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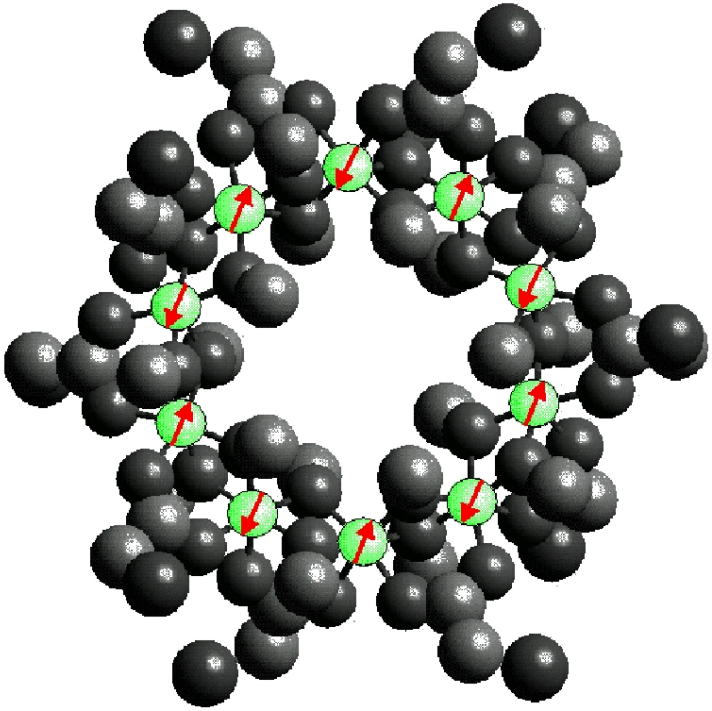
Contents for you today



Fe_{10}

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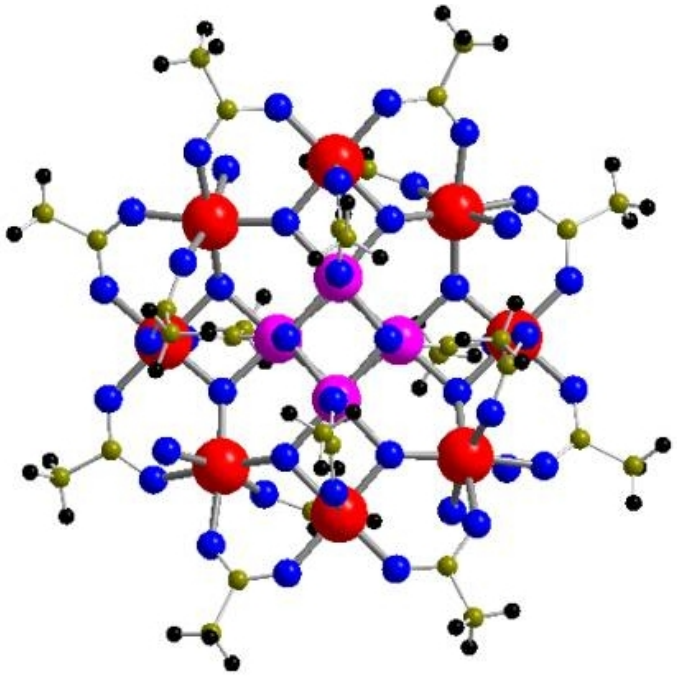
Magnetic Molecules

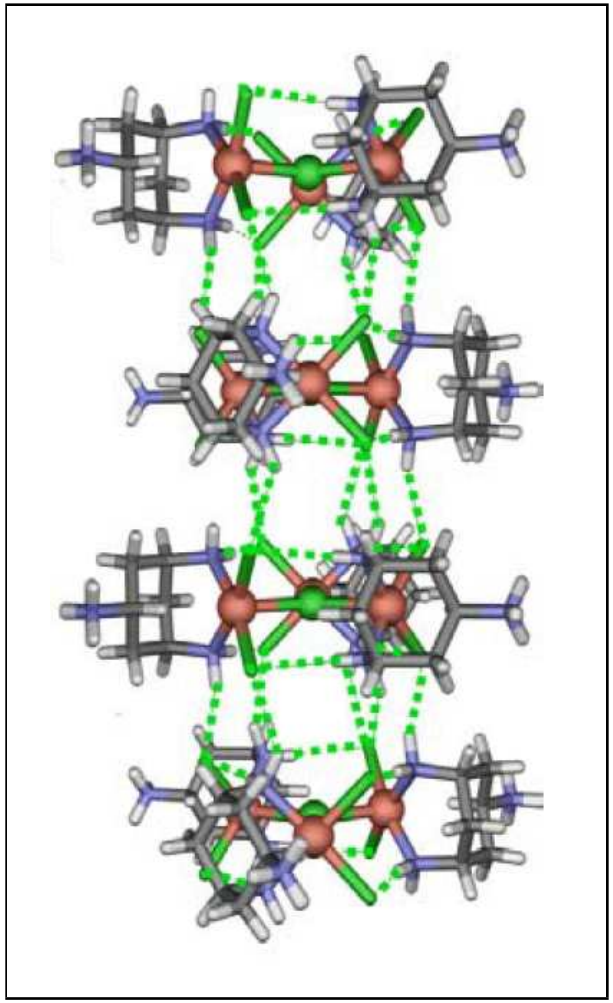
The beauty of magnetic molecules I



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)

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

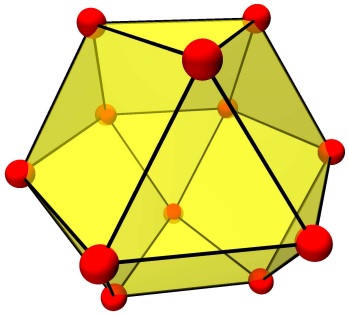
Exchange/Anisotropy — Dzyaloshinskii-Moriya — Zeeman

Isotropic Hamiltonian

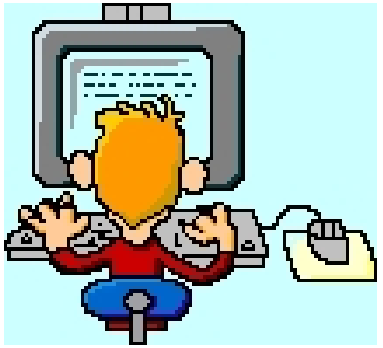
$$\underset{\sim}{H} = -2 \sum_{i<j} J_{ij} \vec{\underset{\sim}{s}}(i) \cdot \vec{\underset{\sim}{s}}(j) + g \mu_B B \sum_{i}^{N} \underset{\sim}{s}_z(i)$$

Heisenberg — Zeeman

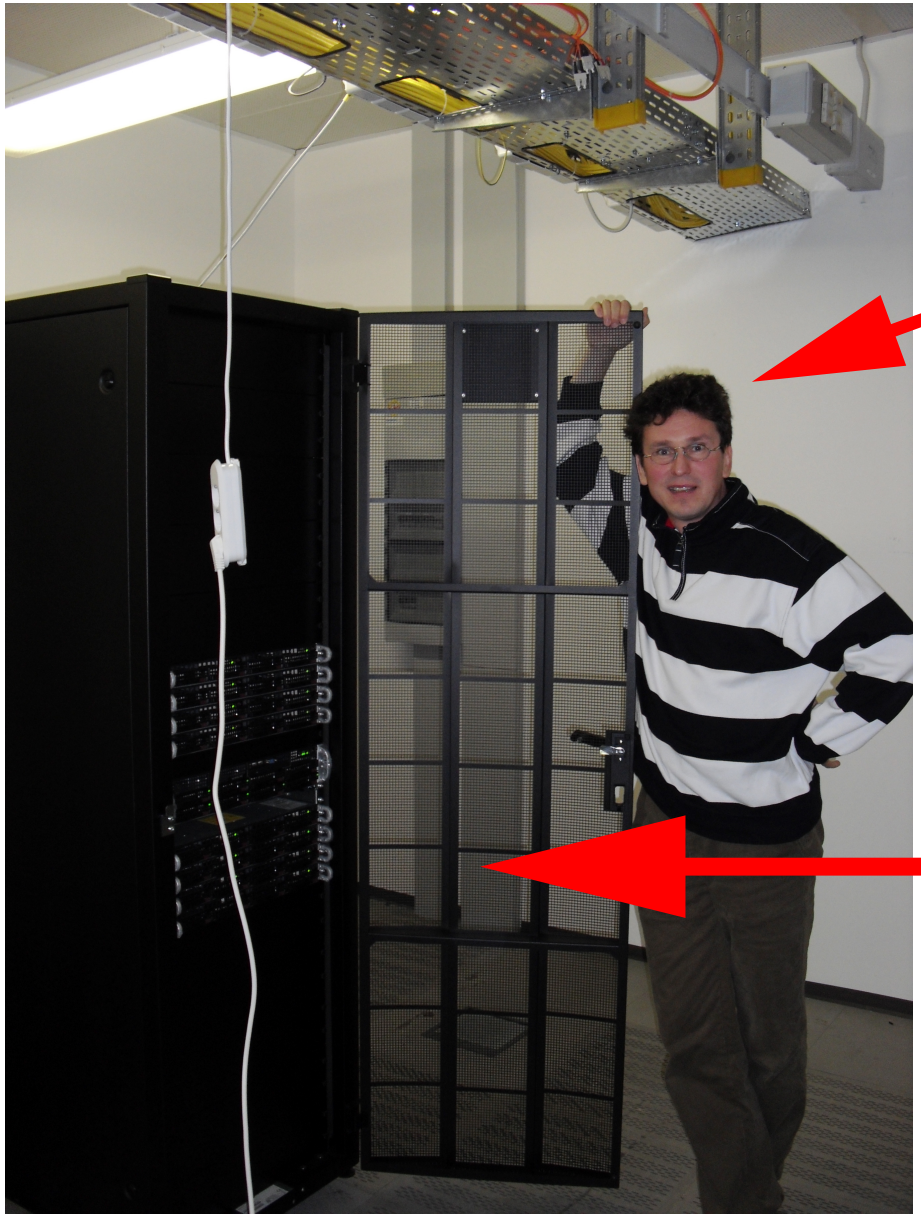
In the end it's always a big matrix!



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



Thank God, we have computers

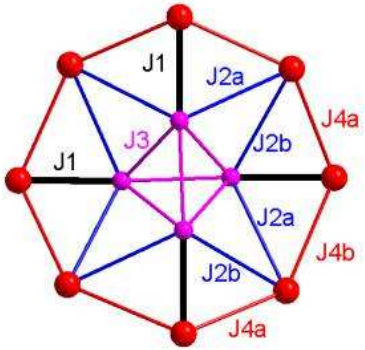


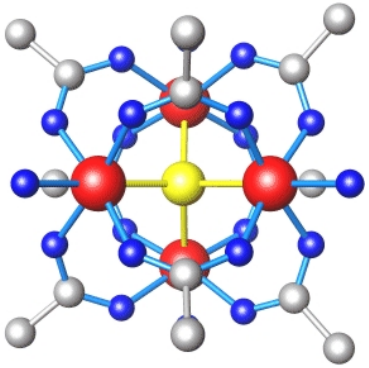
“cell professor”

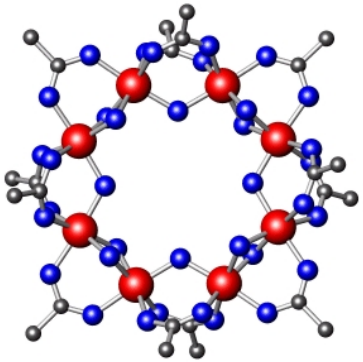
128 cores, 384 GB RAM

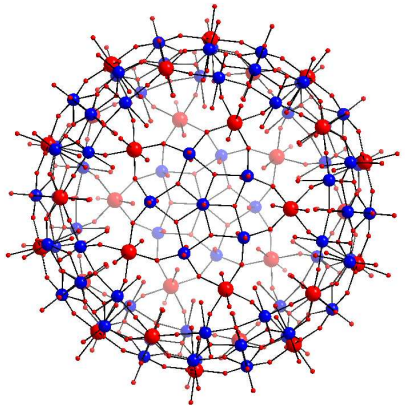
. . . but that’s not enough!

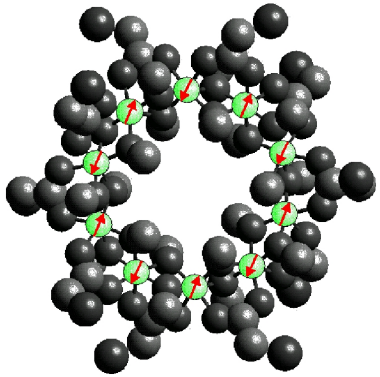
Magnetic Molecules











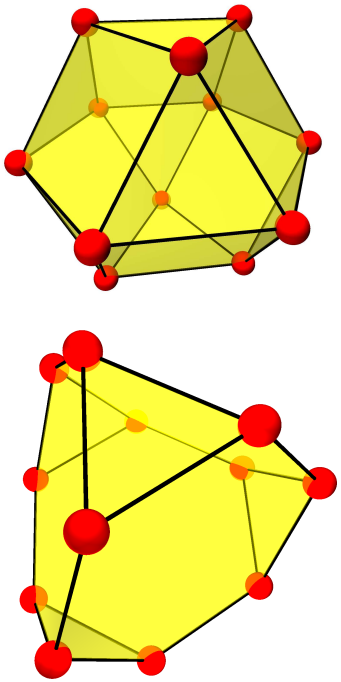
possess symmetries! Use them!

SU(2) 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).

Point group symmetry

(Ph.D. of Roman Schnalle)

Point Group Symmetry I

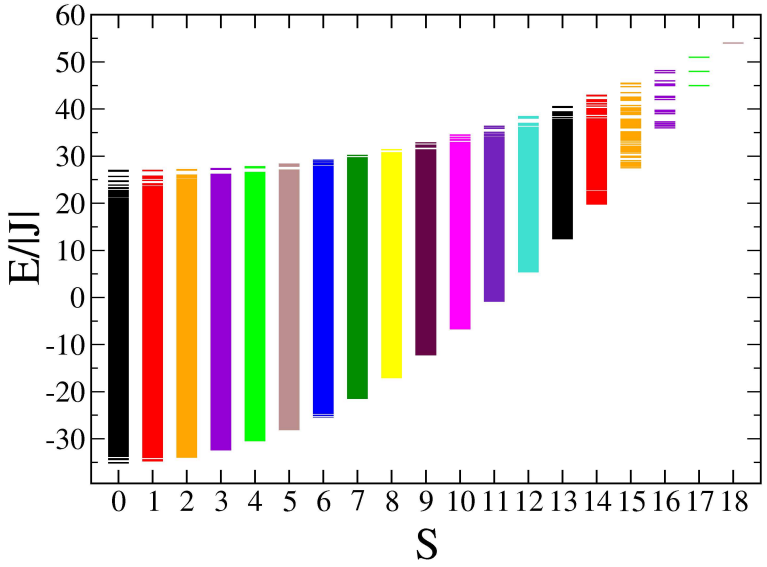
$$|\,\alpha'\,S\,M\,\Gamma\,\rangle = \mathcal{P}^{(\Gamma)}\,|\,\alpha\,S\,M\,\rangle = \left(\frac{l_\Gamma}{h}\sum_R \left(\chi^{(\Gamma)}(R)\right)^*\,\underset{\sim}{G}(R)\right)\,|\,\alpha\,S\,M\,\rangle$$

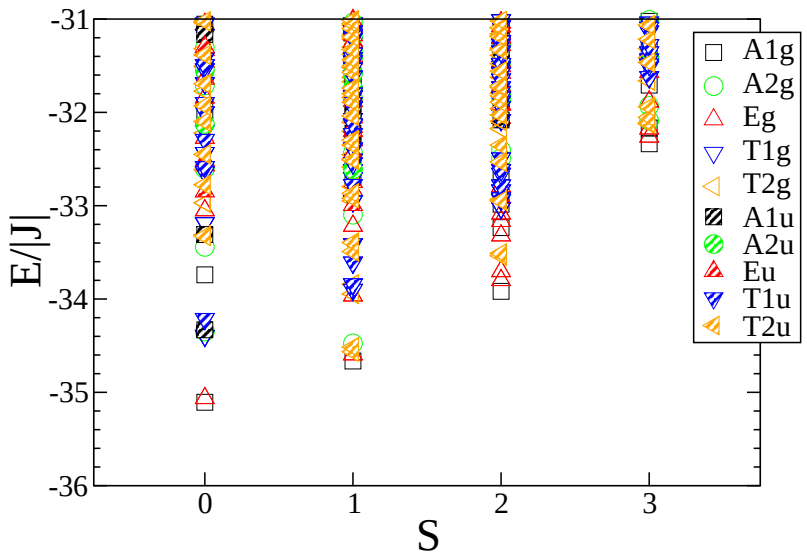
Point Group Symmetry

- 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.

Results I: Cuboctahedron

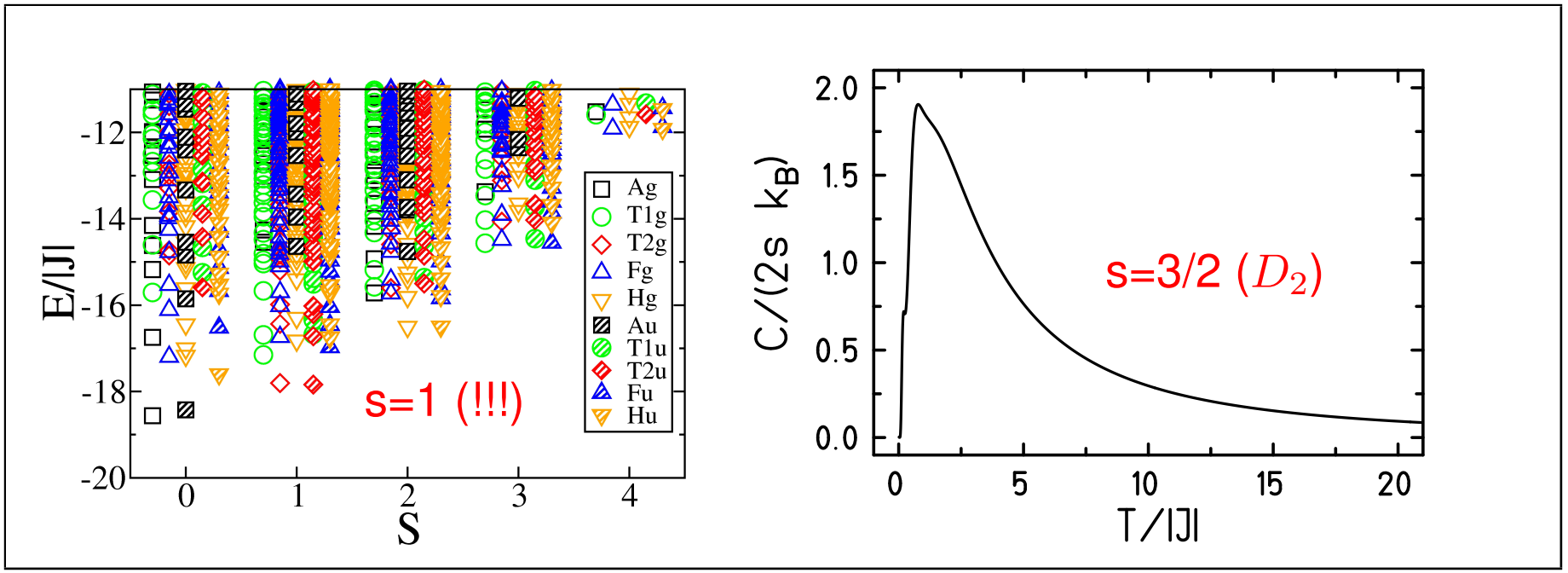




Cuboctahedron, $s = 3/2$, Hilbert space dimension 16,777,216; symmetry O_h (1).
Evaluation of recoupling coefficients very time consuming (1,2).

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

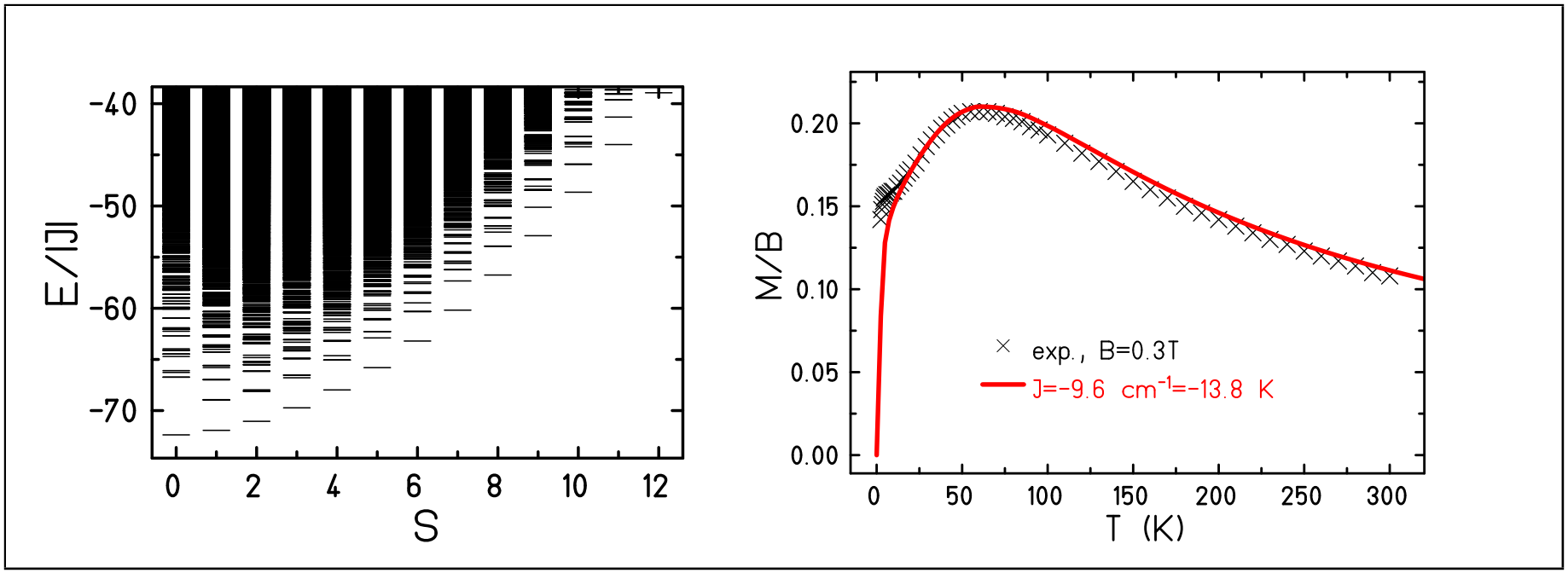
Results II: Icosahedron



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}



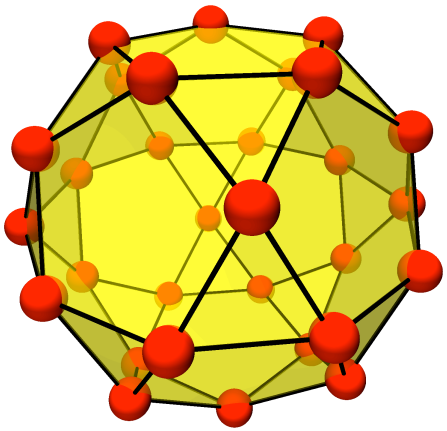
Spin ring, $N = 10$, $s = 5/2$, Hilbert space dimension 60,466,176; symmetry D_2
Symmetry C_{10} would lead to more complicated recoupling coefficients & complex representation (1).

(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



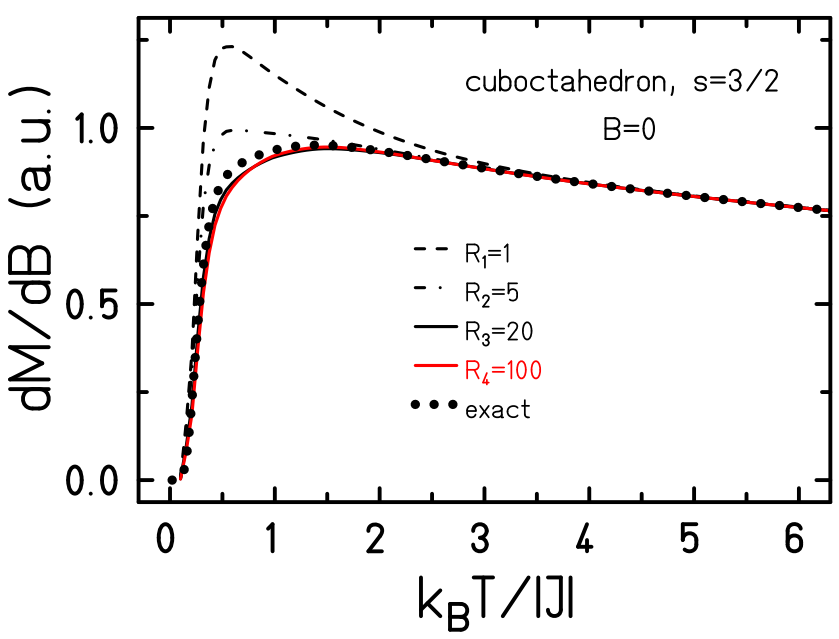
The idea of thermal Lanczos

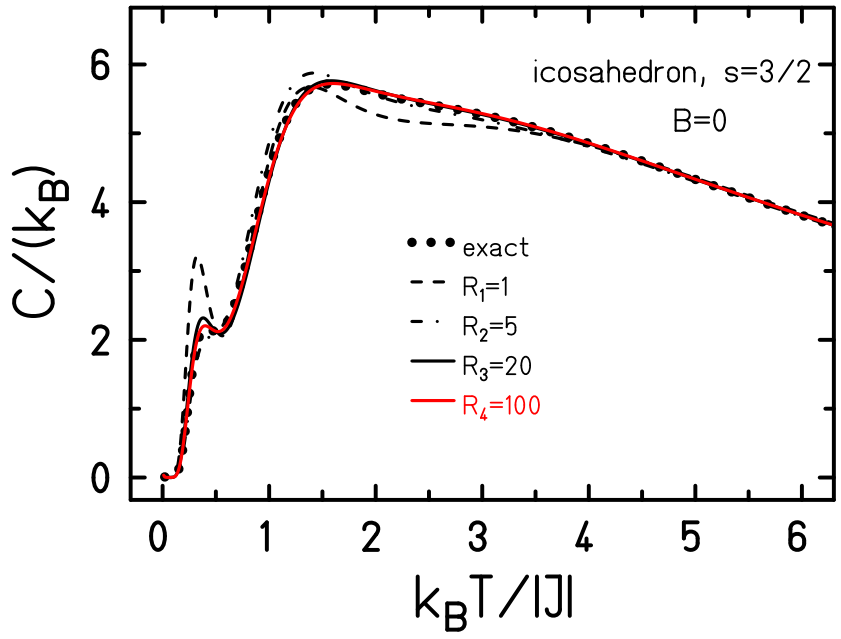
$$
\begin{aligned}
Z(T,B) &= \sum_{\nu} \langle\, \nu \,|\, \exp\left\{-\beta \underset{\sim}{H}\right\} \,|\, \nu \,\rangle \\
\langle\, \nu \,|\, \exp\left\{-\beta \underset{\sim}{H}\right\} \,|\, \nu \,\rangle &\approx \sum_{n} \langle\, \nu \,|\, n(\nu) \,\rangle \exp\left\{-\beta \epsilon_n\right\}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

- $|\, n(\nu) \,\rangle$ 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).

How good is thermal Lanczos?

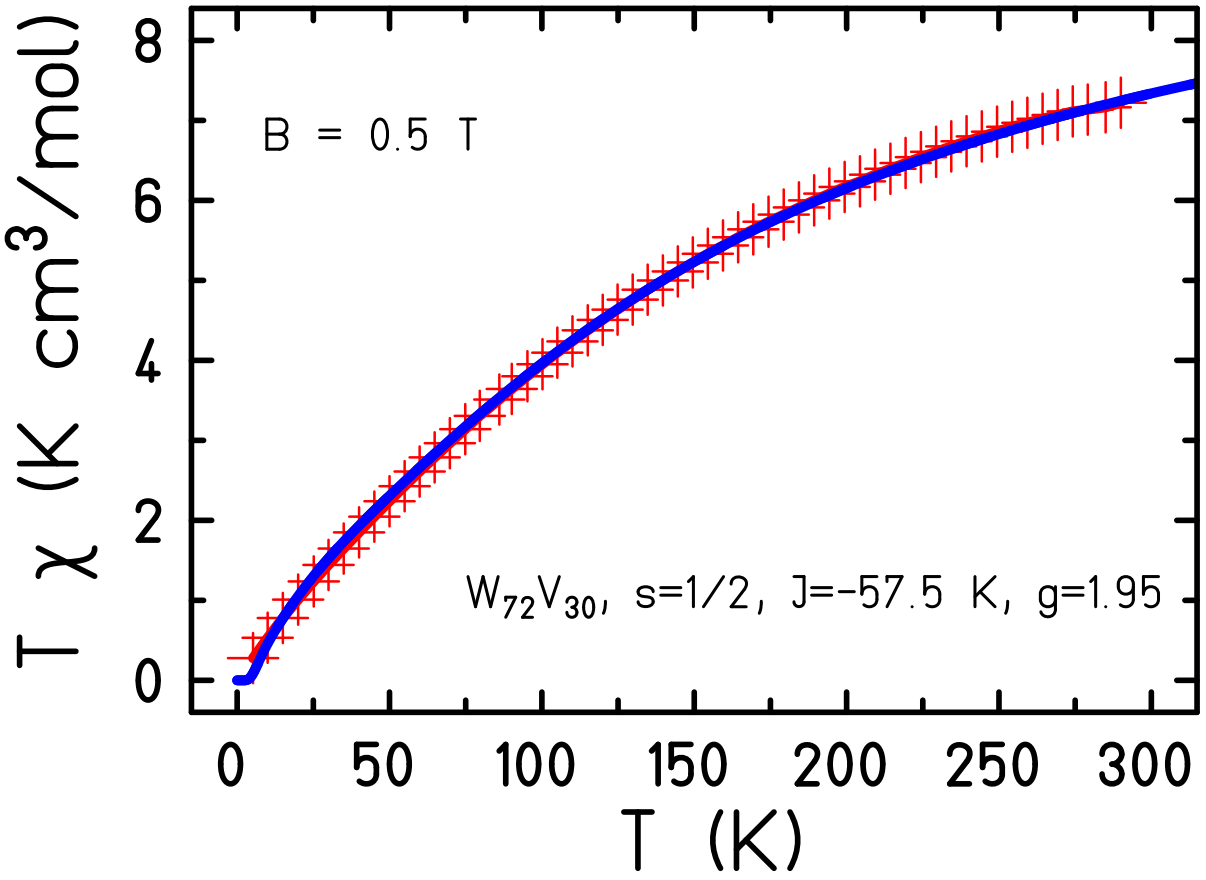




- Works very well, see e.g. cuboctahedron and icosahedron.
- $N = 12, s = 3/2$: Considered $< 100,000$ states instead of 16,777,216.

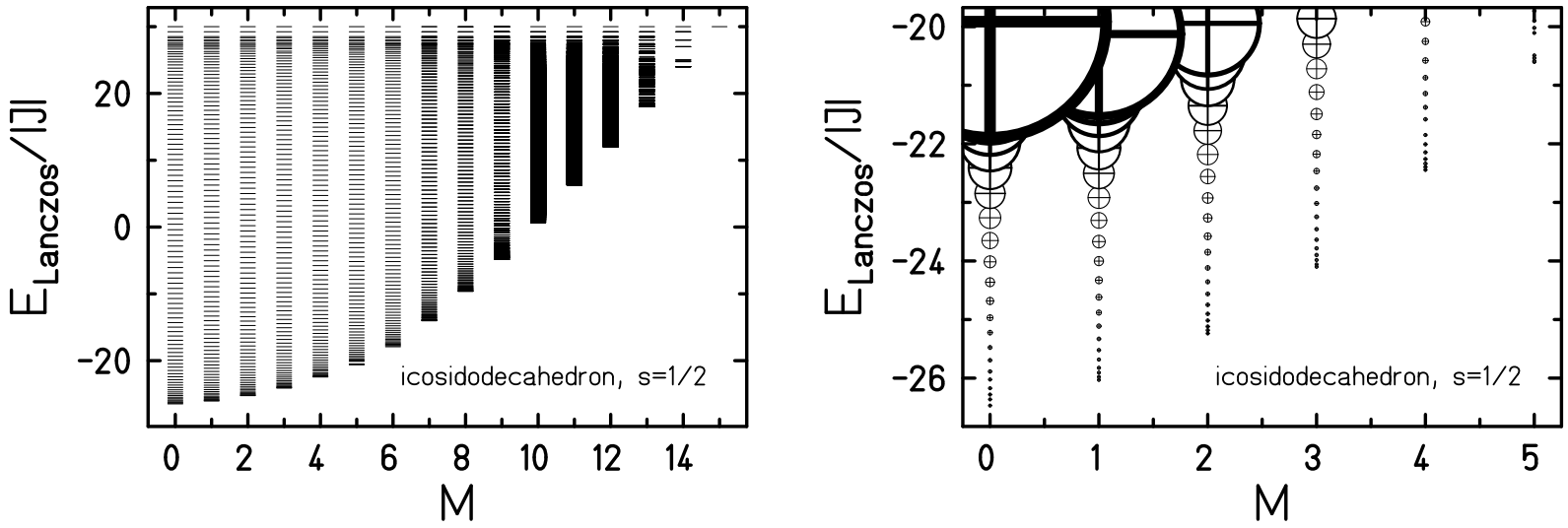
Exact results: R. Schnalle and J. Schnack, Int. Rev. Phys. Chem. **29** (2010) 403-452
TDLM: J. Schnack and O. Wendland, Eur. Phys. J. B **78** (2010) 535-541

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. (2009) 3351.

Icosidodecahedron $s = 1/2$



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

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

Anisotropic Magnetic Molecules

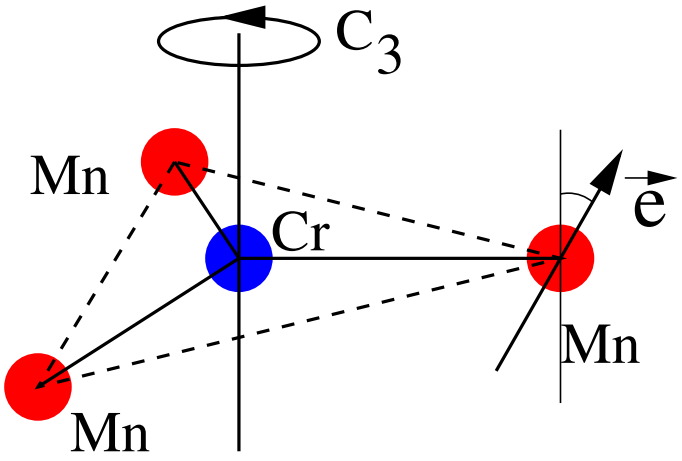
Anisotropic magnetic molecules I – Theory

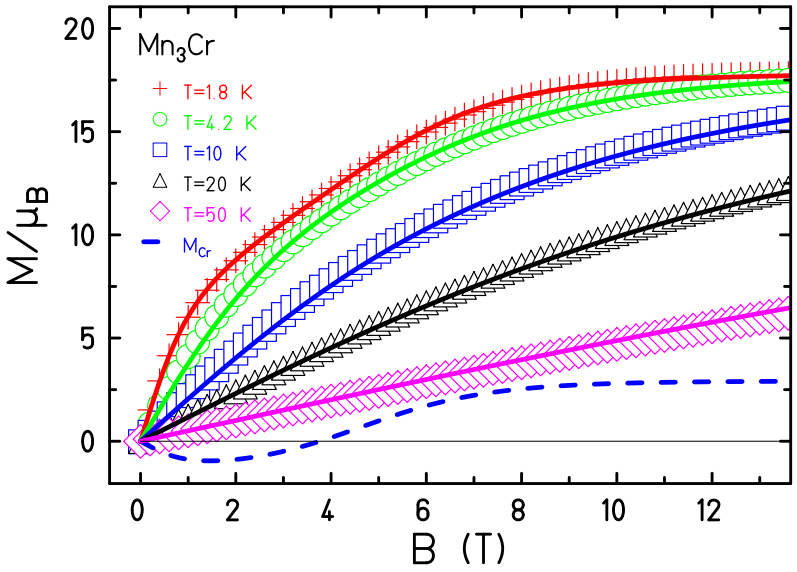
$$\underset{\sim}{H}(\vec{B}) \;=\; -\sum_{i,j} J_{ij}\,\underset{\sim}{\vec{s}}(i)\cdot\underset{\sim}{\vec{s}}(j) \;+\sum_{i} d_i\left(\vec{e}_i\cdot\underset{\sim}{\vec{s}}(i)\right)^2+ \;\mu_B\,\vec{B}\cdot\sum_{i}^{N}\mathbf{g}_i\cdot\underset{\sim}{\vec{s}}(i)$$

- $\left[\underset{\sim}{H},\underset{\sim}{\vec{S}}^2\right]\neq 0,\ \left[\underset{\sim}{H},\underset{\sim}{\vec{S}}_z\right]\neq 0$;
- You have to diagonalize $\underset{\sim}{H}(\vec{B})$ for every field (direction and strength)! Powder sample $\Rightarrow$ Orientational average.
- If you are lucky, point group symmetries still exist. Use them!

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

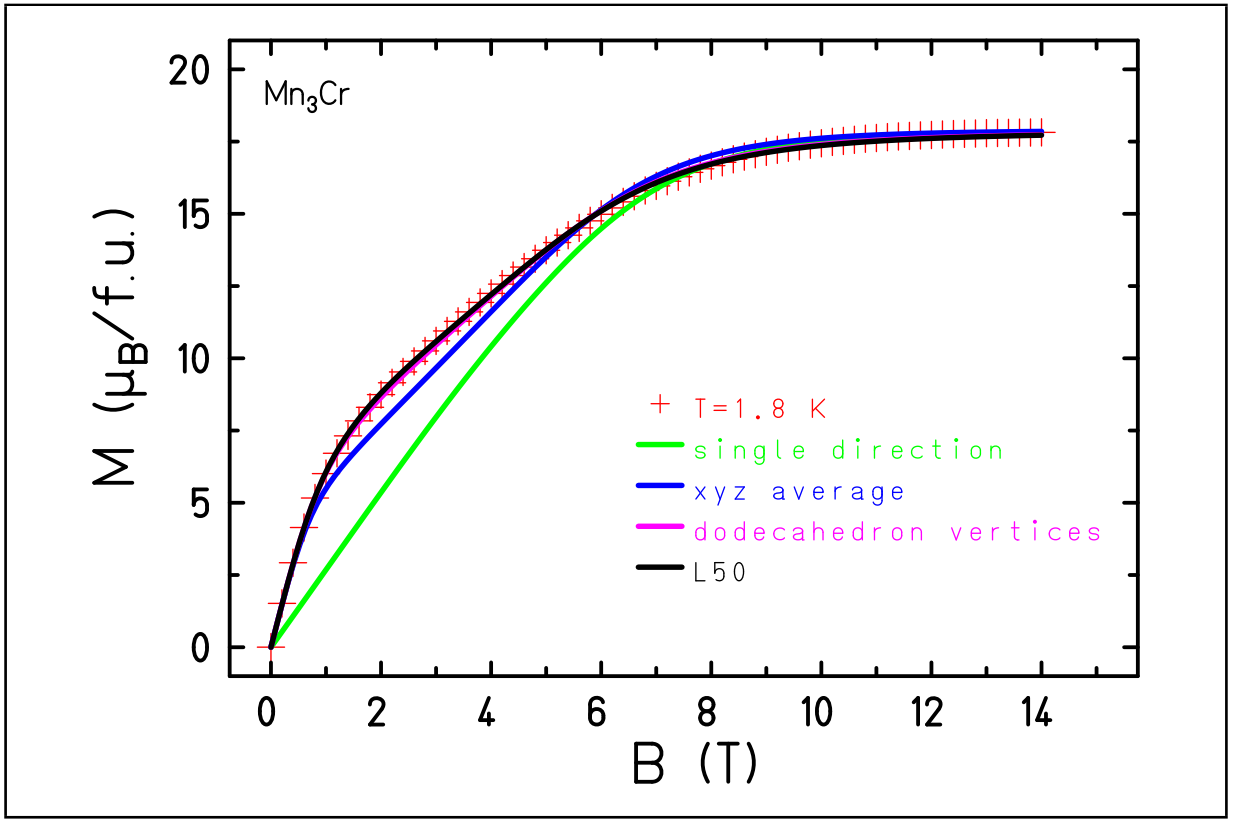
Anisotropic magnetic molecules II – Example





- 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 $\vec{e}(\vartheta, \phi)$.
  C_3: $\vartheta_{\text{Mn1}} = \vartheta_{\text{Mn2}} = \vartheta_{\text{Mn3}}$ ($\phi = 120°$).
  Model Cr anisotropy by local axis $\vec{e}(\vartheta = 0)$.
- Result: $J_1 = -0.29$ cm^{-1}, $J_2 = -0.08$ cm^{-1},
  $d_{\text{Mn}} = -1.21$ cm^{-1}, $\vartheta_{\text{Mn}} = 22°$,
  $d_{\text{Cr}} = +0.17$ cm^{-1}.
  M. Prinz *et al.*, Inorg. Chem. **49**, 607 (2010) 2093-2102.
- Can DFT (ab initio) determine non-collinear anisotropy tensors?
- Element-wise magnetization $\Rightarrow$ XMCD.

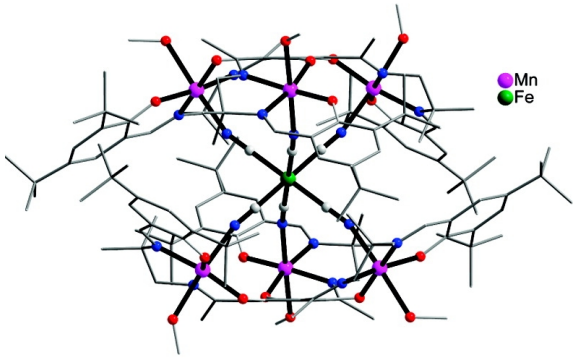
Mn$_3$Cr III – Angular averaging

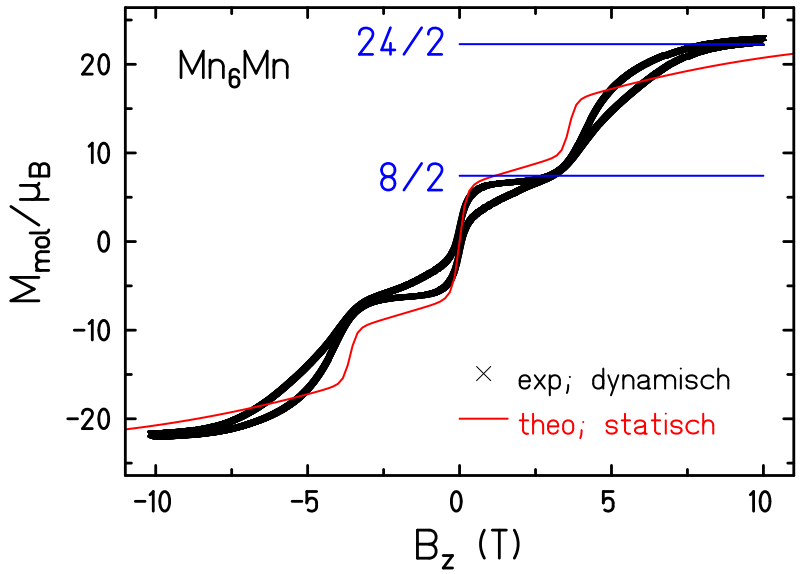


For a good fit you need several directions, at least 10.

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

Mn$_6$M

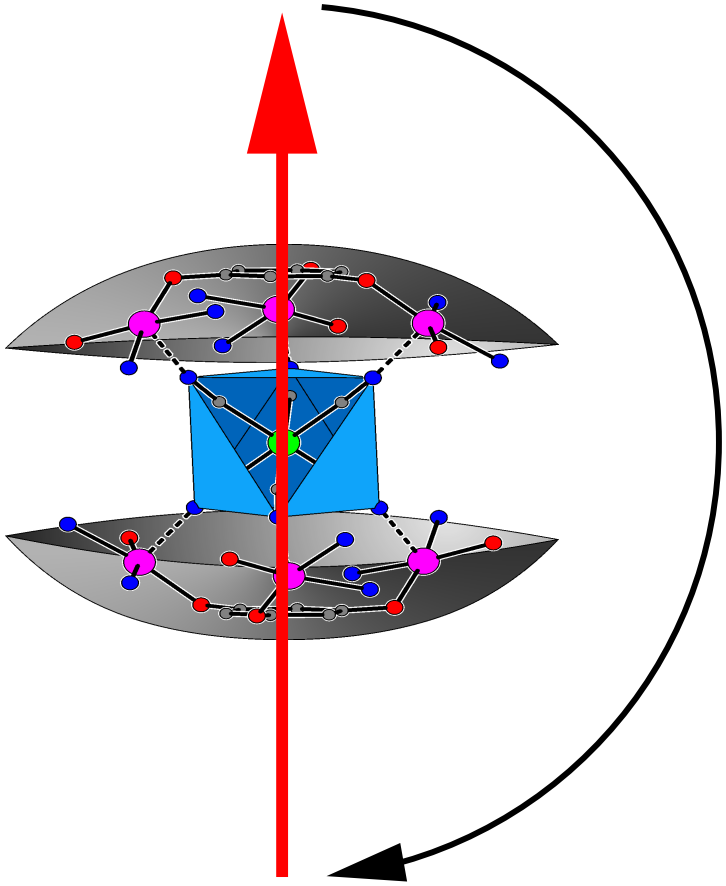




- Idea of Thorsten Glaser (Bielefeld): Rational design of strict C_3 symmetric molecules: no E-term, less tunneling.
- Examples: Mn$_6$Fe, Mn$_6$Co, Mn$_6$Mn, ...

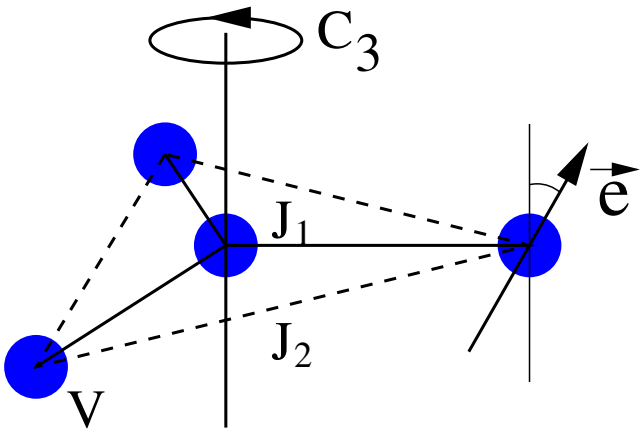
  (1) T. Glaser, M. Heidemeier, T. Weyhermüller, R. D. Hoffmann, H. Rupp, P. Müller,
  Angew. Chem.-Int. Edit. **45**, 6033 (2006).
  (2) T. Glaser, M. Heidemeier, E. Krickemeyer, H. Bögge, A. Stammler, R. Fröhlich, E. Bill, J. Schnack,
  Inorg. Chem. **48**, 607 (2009).
- Forschergruppe 945: investigations of Mn$_6$M-type molecules.

Some recent anisotropic magnetic molecules Ia



- Magnetic Molecules may possess a large ground state spin, e.g. $S = 10$;
- Ground state spin can be stabilized by anisotropy (easy axis).

V_4 I

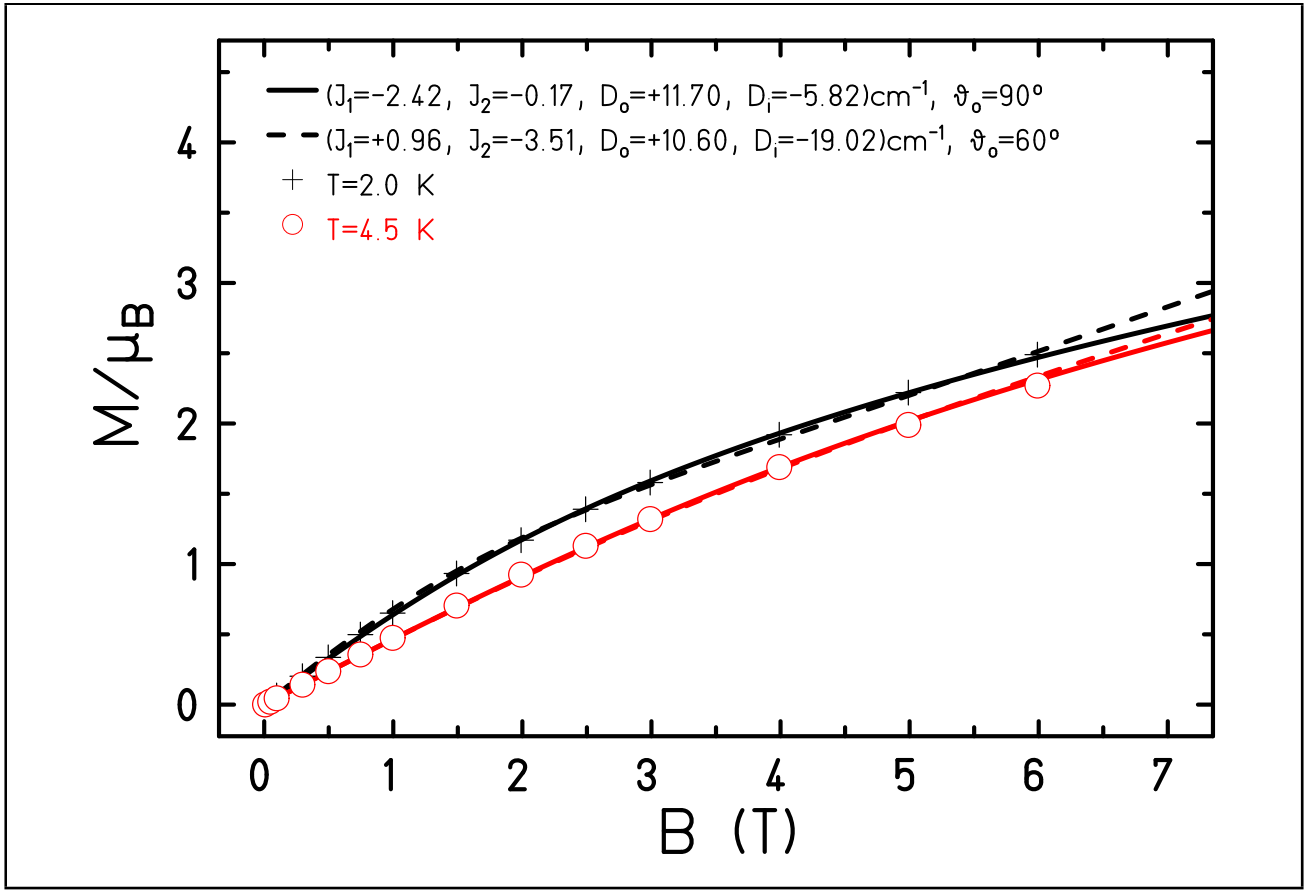


$[V_4^{III}Cl_6(thme)_2(bipy)_3]$

- 4 V_4^{III} 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.

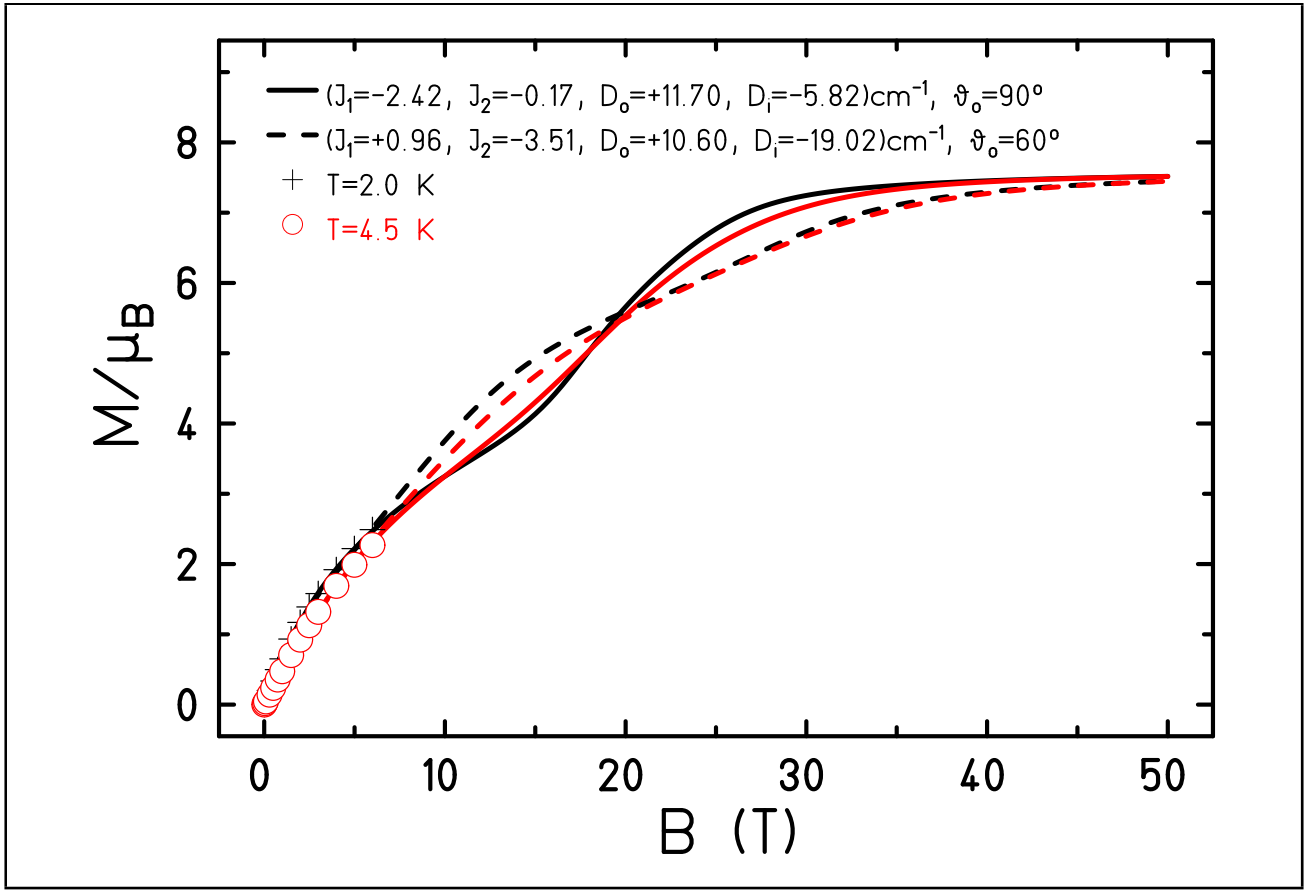
Ian S. Tidmarsh, Luke J. Batchelor, Emma Scales, Rebecca H. Laye, Lorenzo Sorace, Andrea Caneschi, Jürgen Schnack and Eric J.L. McInnes, Dalton Trans. (2009) 9402-9409

V_4 II



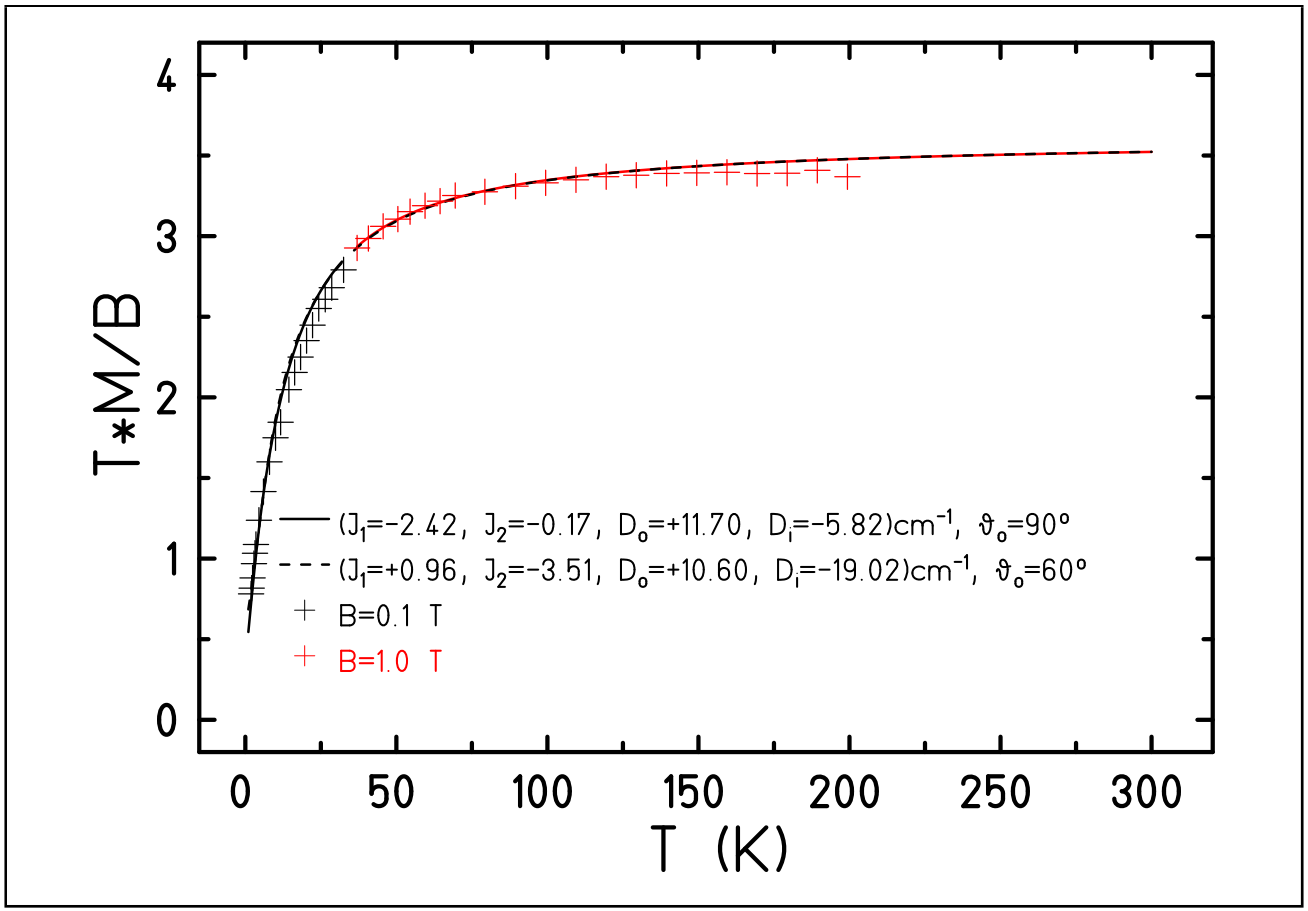
Two equally good parameter sets.

V_4 III



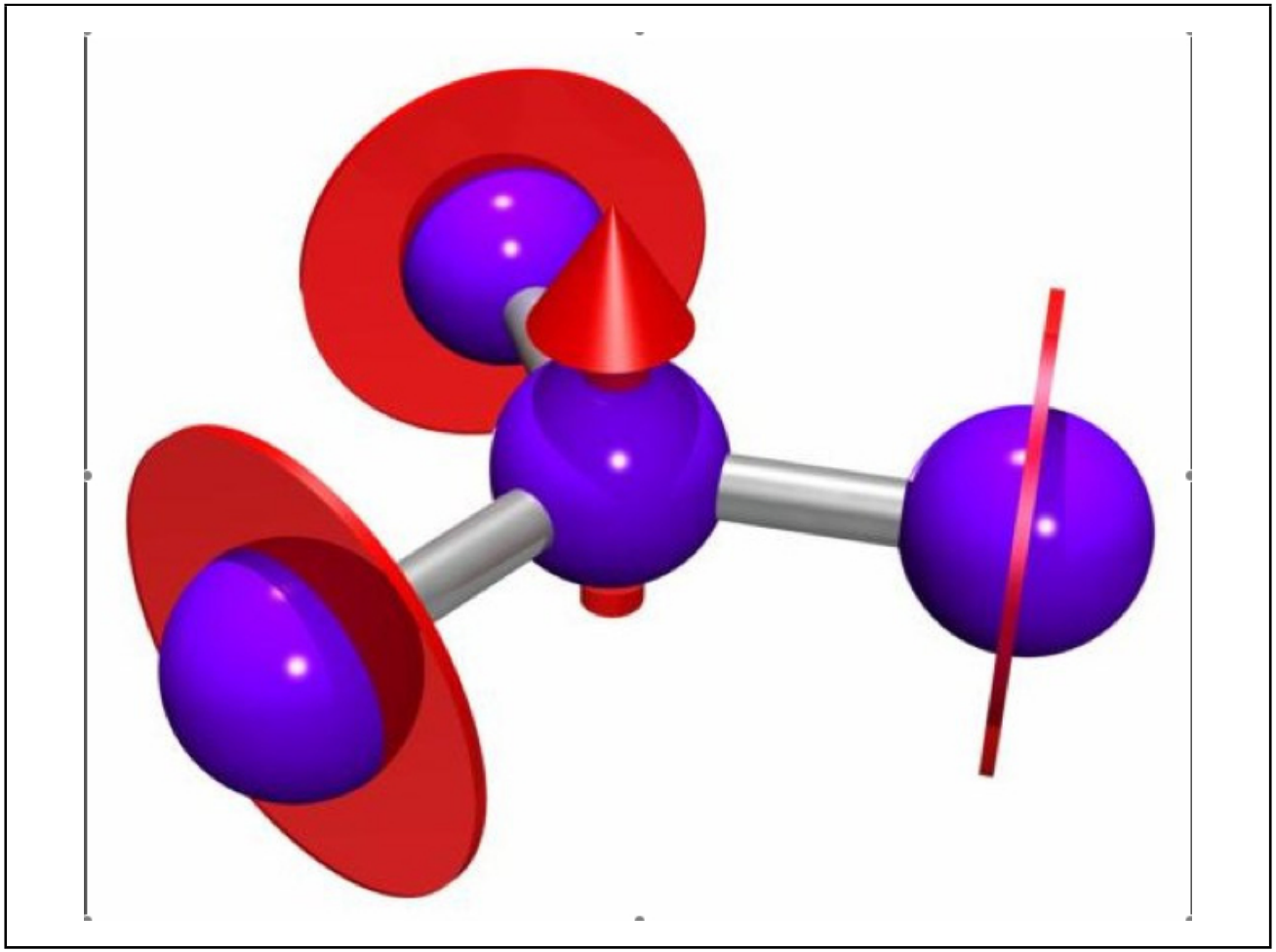
High fields could distinguish.

V_4 IV



Accuracy of measurement limits modeling.

V_4 – Anisotropy tensors

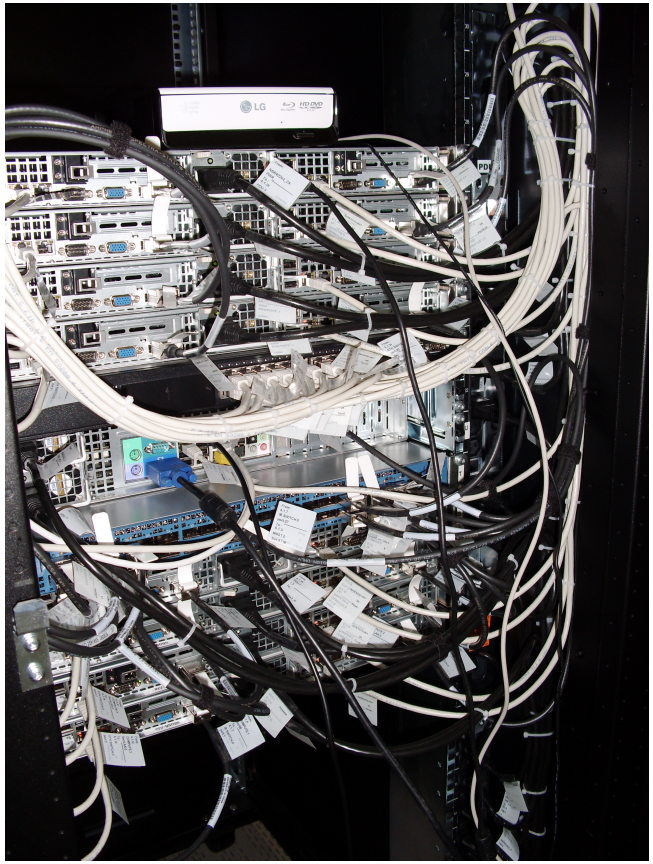


Cartoon of anisotropy tensors.

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)
- K. Bärwinkel, H.-J. Schmidt, M. Neumann (Osnabrück);
- M. Luban (Ames Lab, USA); P. Kögerler (Aachen, Jülich, Ames); J. Musfeldt (U. of Tennessee, USA); R.E.P. Winpenny, E.J.L. McInnes (Man U, UK); L. Cronin (Glasgow, UK); E. Brechin (Edinburgh, UK); H. Nojiri (Sendai, Japan); A. Postnikov (Metz, France)
- 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); K. Kuepper (Ulm)

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}.
- Anisotropic Hamiltonians with several parameters can be accurately treated today.
- Future developments: dynamical properties such as AC-susceptibility.

Thank you very much for your attention.

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