Trends, questions and methods in molecular magnetism

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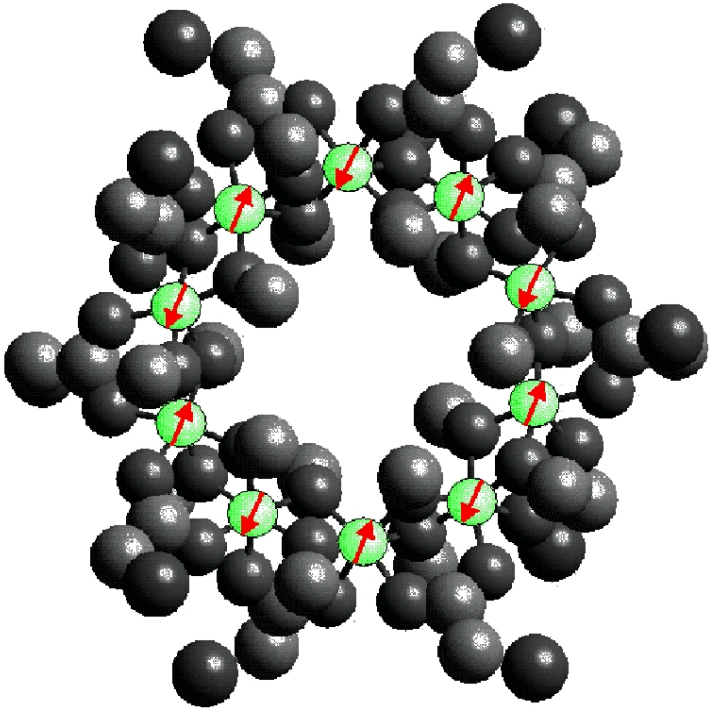
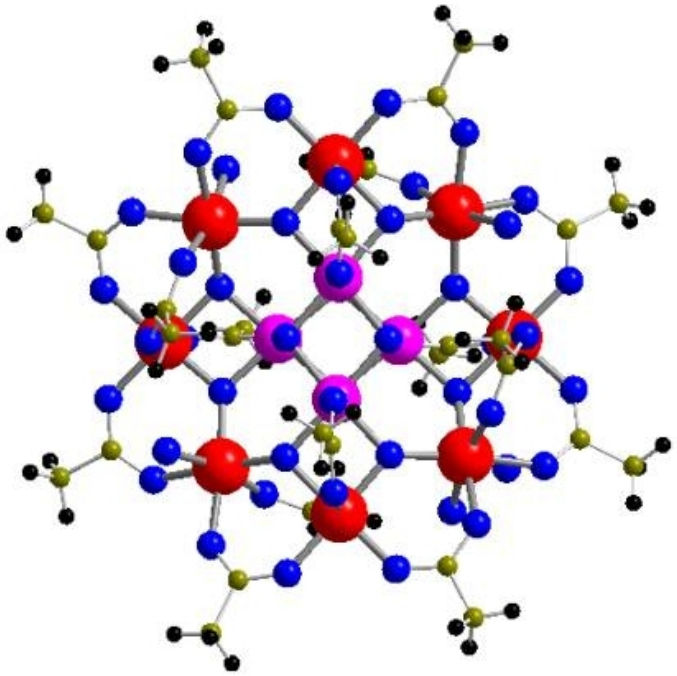
Contents for you today



Fe_{10}

1. The Beauty of Magnetic Molecules
2. Up to date theory modeling
3. Single Molecule Magnets
4. Coherence Phenomena
5. Molecules on Surfaces
6. Frustration effects

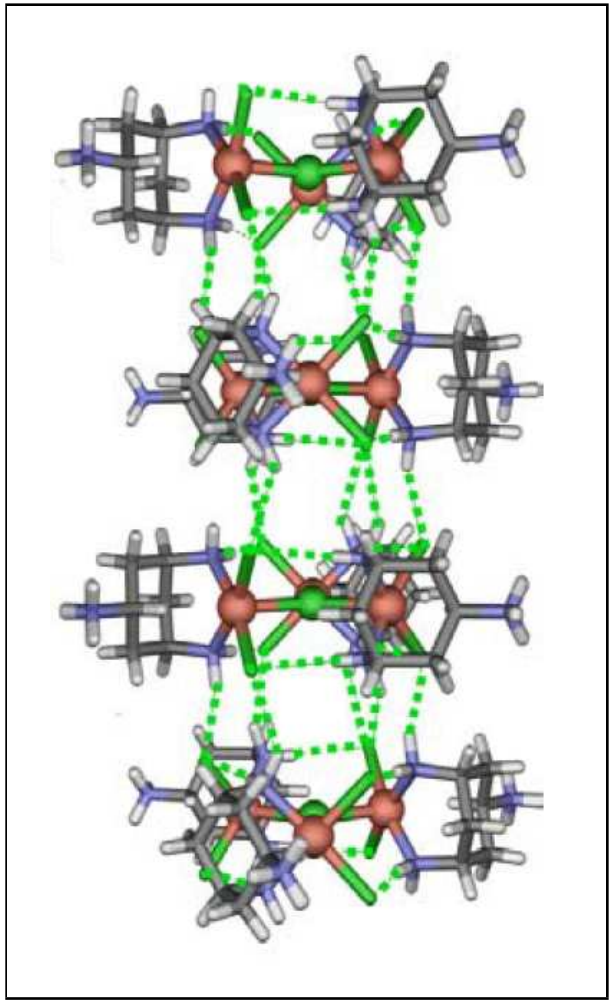
The beauty of magnetic molecules I



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:

  J. Schnack, H. Nojiri, P. Kögerler, G. J. T. Cooper, L. Cronin, Phys. Rev. B 70, 174420 (2004); Sato, Sakai, Läuchli, Mila, . . .

Up to date theory modeling

Model Hamiltonian (spin only)

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

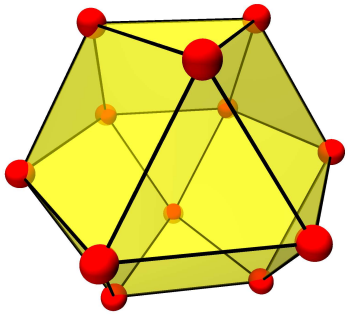
Exchange/Anisotropy Dzyaloshinskii-Moriya Zeeman

Isotropic Hamiltonian

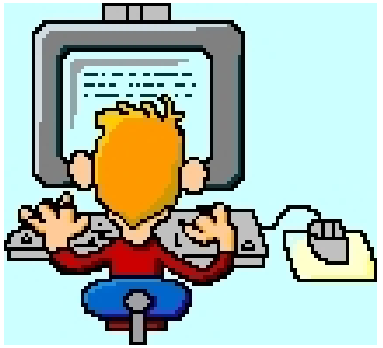
$$\underset{\sim}{H} = -\sum_{i,j} J_{ij} \vec{\underset{\sim}{s}}(i) \cdot \vec{\underset{\sim}{s}}(j) + g \mu_B B \sum_{i}^{N} \underset{\sim}{s}_z(i)$$

Heisenberg Zeeman

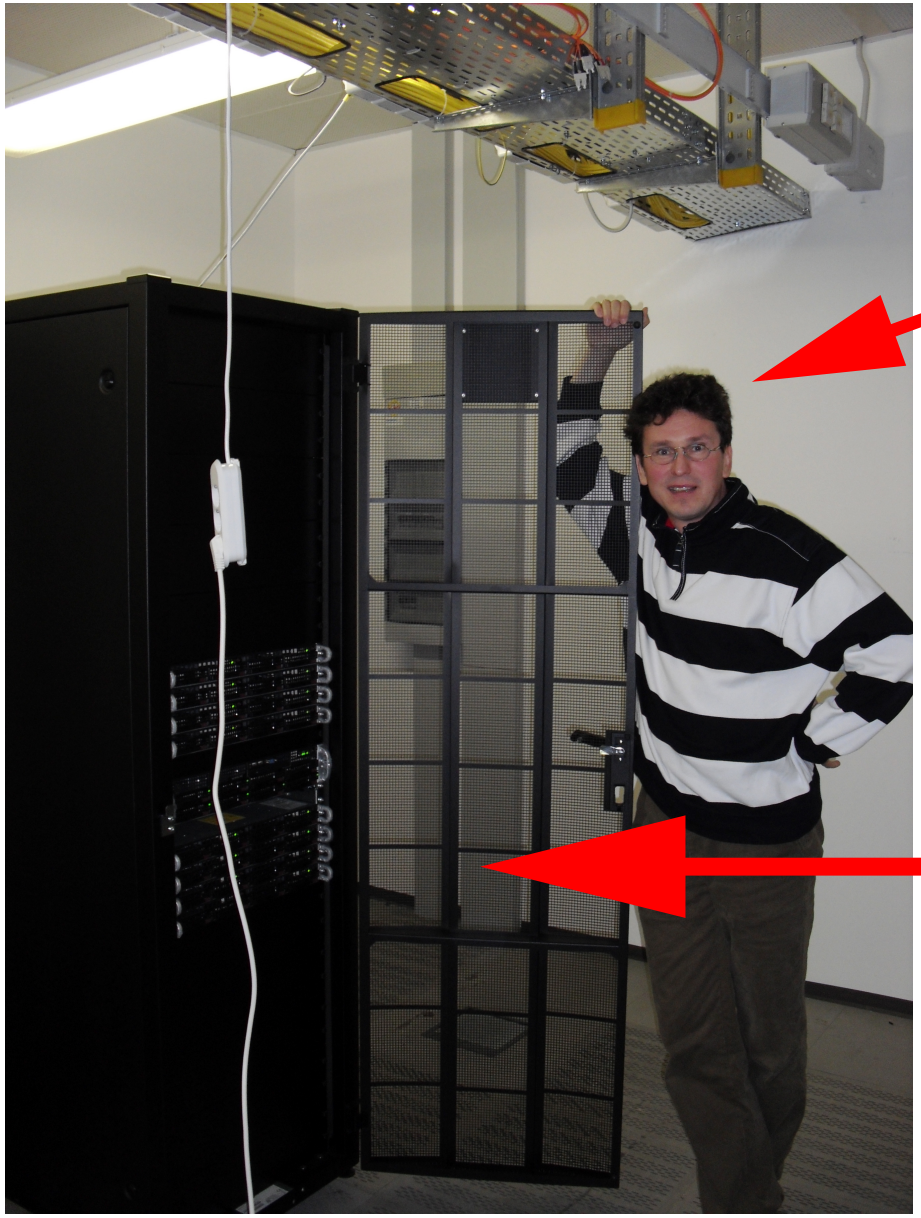
In the end it's always a big matrix!



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



Thank God, we have computers



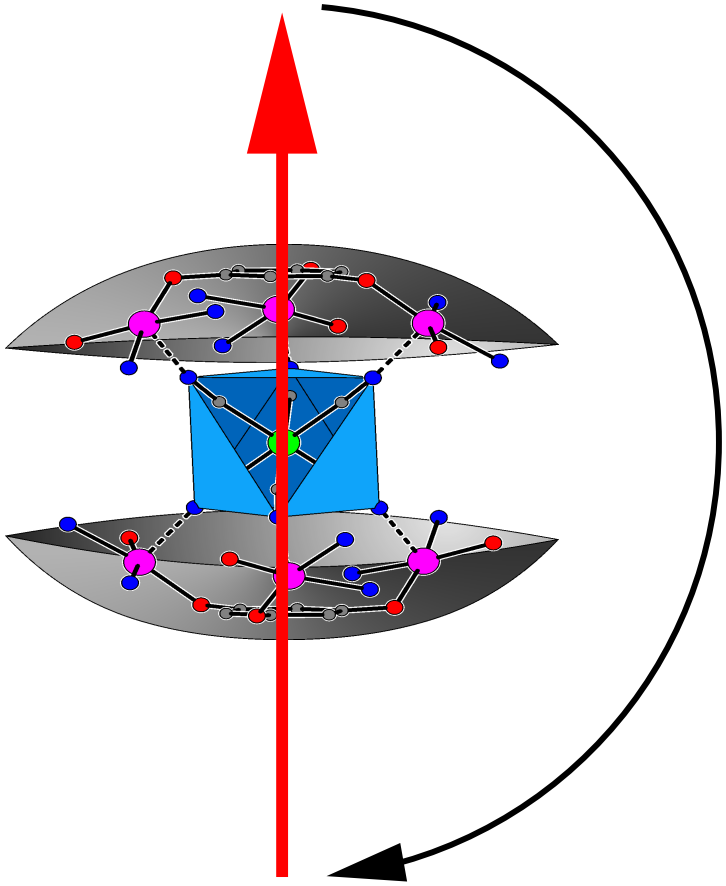
“cell professor”

128 cores, 384 GB RAM

. . . but that’s not enough!

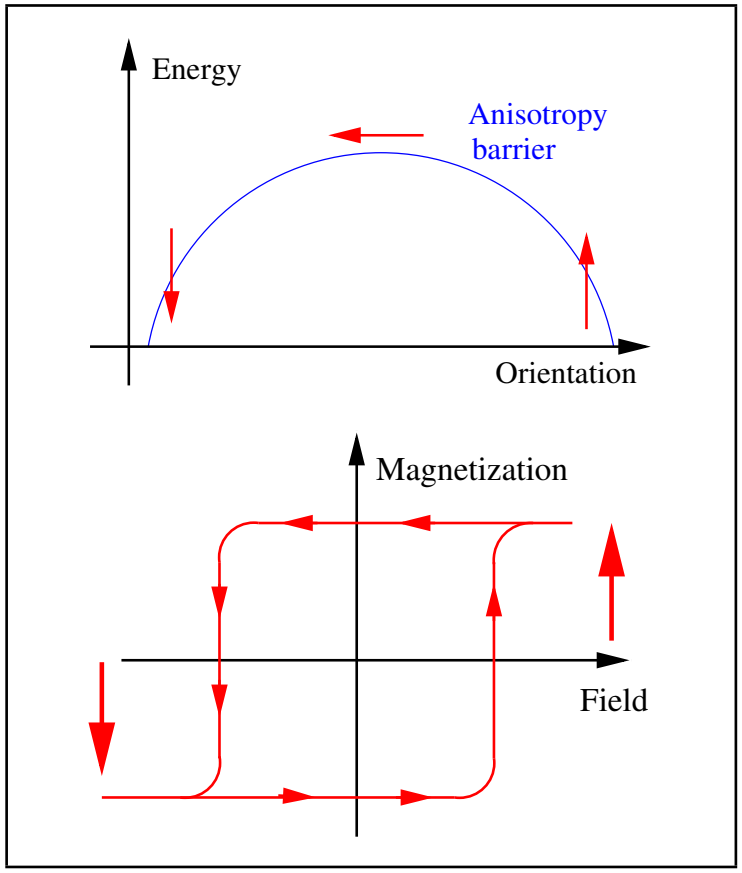
Single Molecule Magnets

Single Molecule Magnets I



- Magnetic Molecules may possess a large ground state spin, e.g. $S = 10$ for Mn_{12} or Fe_8;
- Ground state spin can be stabilized by anisotropy (easy axis).

Single Molecule Magnets II



- Single Molecule Magnets (SMM):
  large ground state moment;
  anisotropy barrier dominates at low T.

$$\underset{\sim}{H} \approx D\underset{\sim}{S}_z^2 + E(\underset{\sim}{S}_x^2 - \underset{\sim}{S}_y^2)$$

- Metastable magnetization and hysteresis;
- But also magnetization tunneling due to non-commuting terms, e.g. E, B_x, B_y.
- How can one increase the anisotropy barrier?

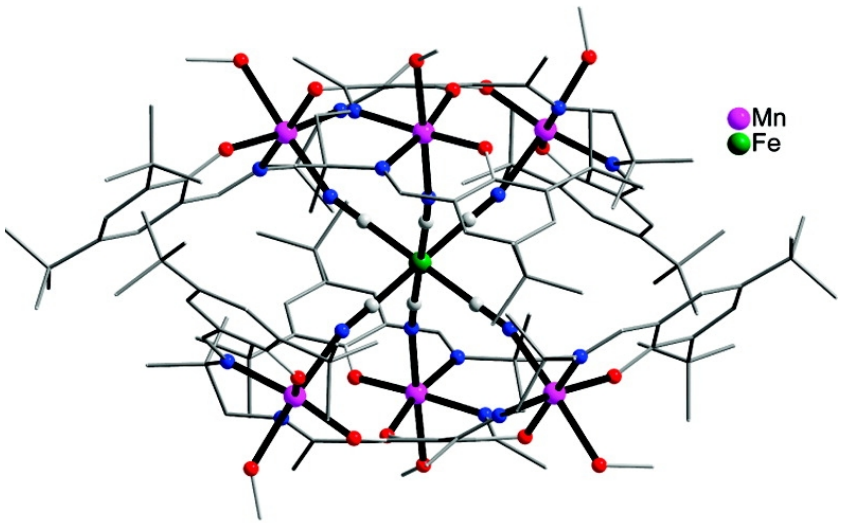
Anisotropic magnetic molecules I – Theory

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

- $\left[\underset{\sim}{H},\vec{\underset{\sim}{S}}^2\right]\neq 0$, $\left[\underset{\sim}{H},\vec{\underset{\sim}{S}}_z\right]\neq 0$;
- 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).

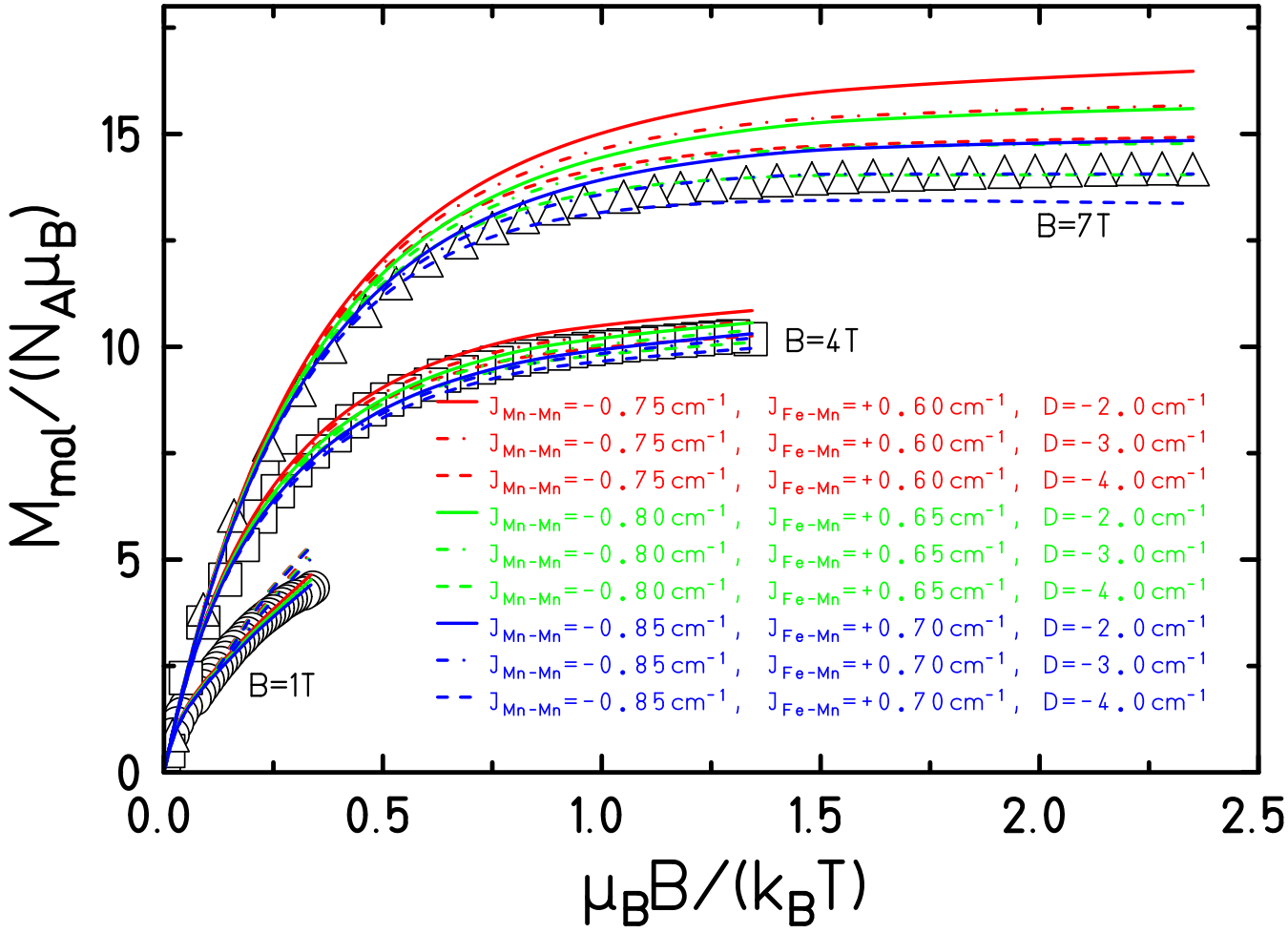
Mn$_6$Fe



- Idea of Thorsten Glaser (Bielefeld): Rational design of strict C_3 symmetric molecules: no E-term.
- Example 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.

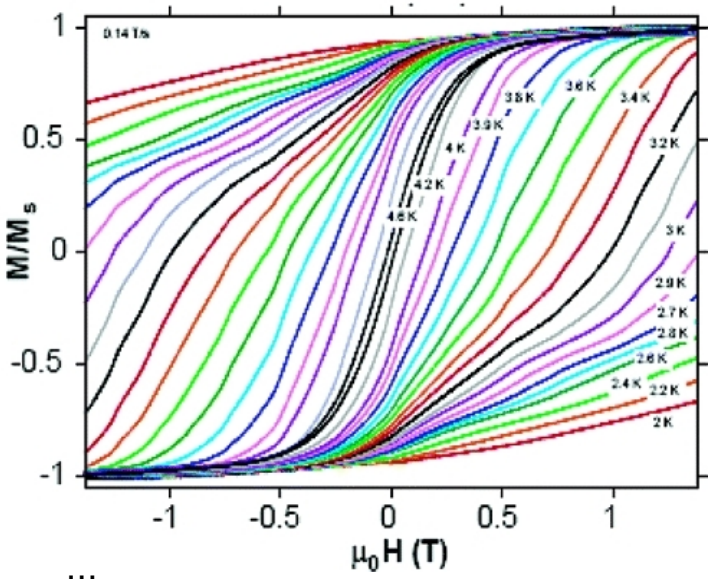
(1) T. Glaser, M. Heidemeier, T. Weyhermüller, R. D. Hoffmann, H. Rupp, P. Müller, Angew. Chem.-Int. Edit. **45**, 6033 (2006).
(2) T. Glaser, M. Heidemeier, E. Krickemeyer, H. Bögge, A. Stammler, R. Fröhlich, E. Bill, J. Schnack, Inorg. Chem. **48**, 607 (2009).

Mn$_6$Fe – Results



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

Single Molecule Magnets – Open Questions



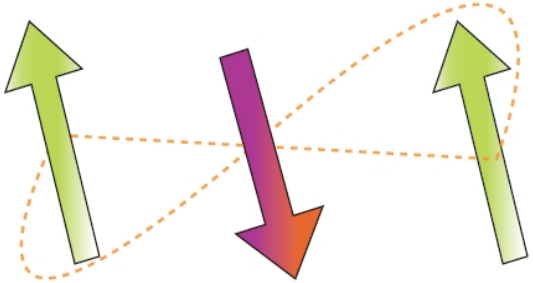
Mn_6^{III} ...
Euan Brechin (Edinburgh)
$U_{\text{eff}} = 86.4$ K

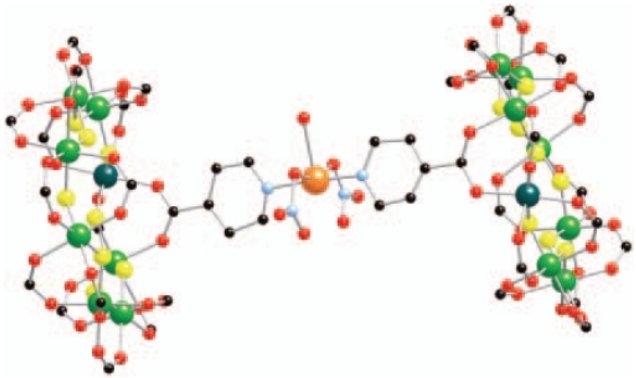
- Relaxations is a non-equilibrium process:
  (a) thermally over the barrier.
  (b) quantum tunneling between Zeeman eigenstates.
- Bath: phonons and nuclear spins.
- Complete description? So far only very rough quantum master equations.

Dante Gatteschi, Roberta Sessoli, Jacques Villain, *Molecular Nanomagnets: (Mesoscopic Physics and Nanotechnology)*, Oxford University Press (2006)

Coherence Phenomena

Coherence Phenomena I





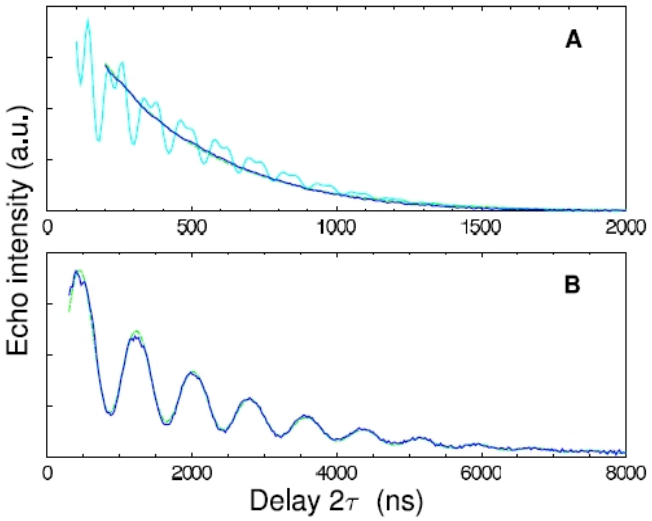
from (1)

Quantum computing

- Chemical realization through coupled molecules with switchable coupling;
- Original ideas, see e.g. (2);
- Molecular transistors; transport in weak or strong coupling regime (3).
- Needed: long coherence times.

(1) G. A. Timco *et al.*, Nature Nanotechnology (2009), accepted; R. E. P. Winpenny, Angew. Chem. Int. Ed. **47**, 7992 (2008); M. Affronte *et al.*, Dalton Transactions 2810 (2006); M. Affronte *et al.*, J. Magn. Magn. Mater. **310**, E501 (2007).
(2) M. N. Leuenberger and D. Loss, Nature **410**, 789 (2001).
(3) L. Bogani and W. Wernsdorfer, Nature Materials **7**, 179 (2008).

Coherence Phenomena II



from (1)

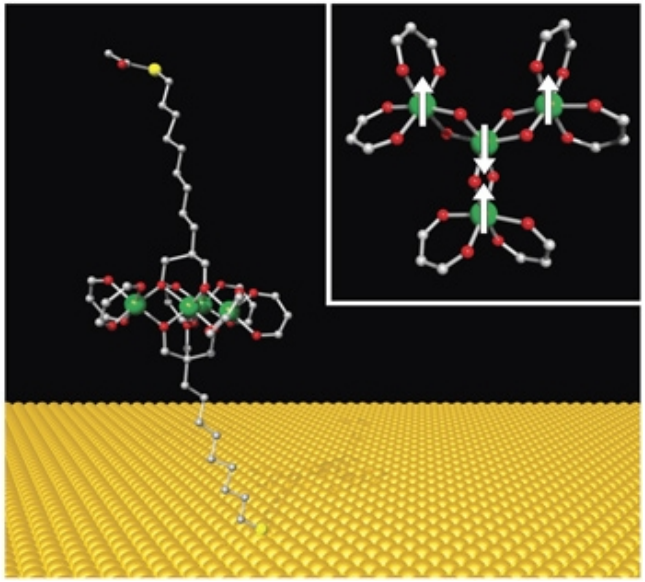
Spin relaxation times

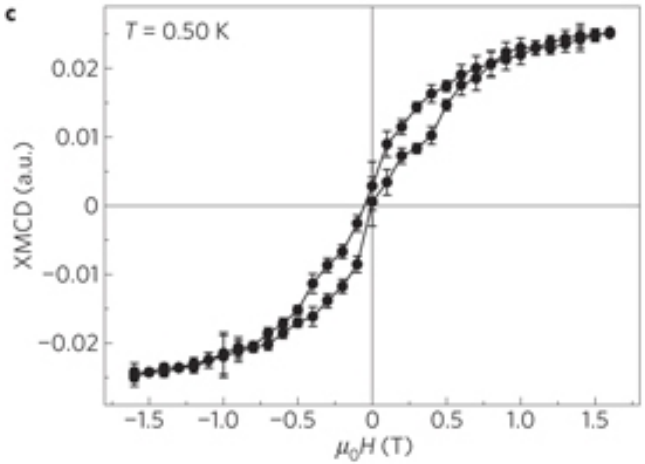
- EPR/NMR, Hahn echo techniques, T_1, T_2 times;
- Decoherence due to e.g. nuclei, phonons, dipolar interaction (**heat bath!**);
- Deuteration improves coherence times considerably;
- μs (!) can be reached. (1)

(1) A. Ardavan *et al.*, Phys. Rev. Lett. **98**, 057201 (2007).
(2) S. Bahr, K. Petukhov, V. Mosser, and W. Wernsdorfer, Phys. Rev. Lett. **99**, 147205 (2007);
W. Wernsdorfer, Nature Materials **6**, 174 (2007).
(3) S. Bertaina *et al.*, Nature **453**, 203 (2008).
(4) C. Schlegel *et al.*, Phys. Rev. Lett. **101**, 147203 (2008).

Molecules on Surfaces

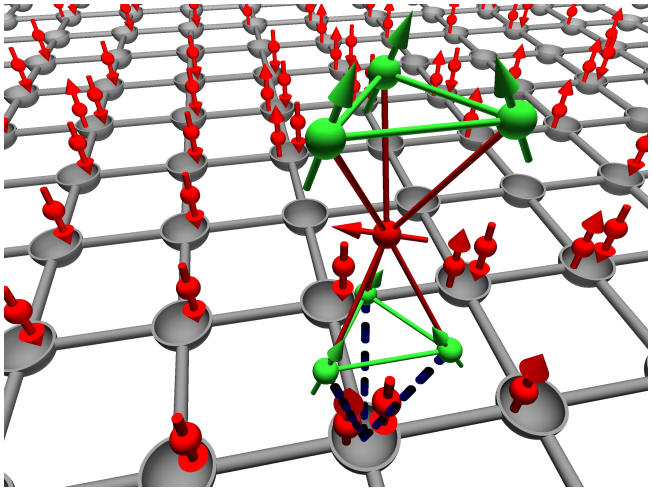
Molecules on Surfaces





- Deposited molecules interact with the (metallic) surface.
- How much molecular magnetism remains?
  M. Mannini, F. Pineider, P. Sainctavit, C. Danieli, E. Otero, C. Sciancalepore, A.M. Talarico, M.-A. Arrio, A. Cornia, D. Gatteschi, R. Sessoli, Nature Materials **8**, 194 (2009)
- Current induced tunnelling spectroscopy (CITS).
  M. Ruben, J. M. Lehn, and P. Müller, Chem. Soc. Rev. **35**, 1056 (2006).
- Transport theory through quantum dots: Schoeller, Wegewijs, Timm, Postnikov, Kortus,Blügel . . .

Molecules on Surfaces – NRG



- How to model the magnetism of deposited spin systems?

- Wilson's Numerical Renormalization Group method:

  (a) Spin system interacts with tight-binding electrons.

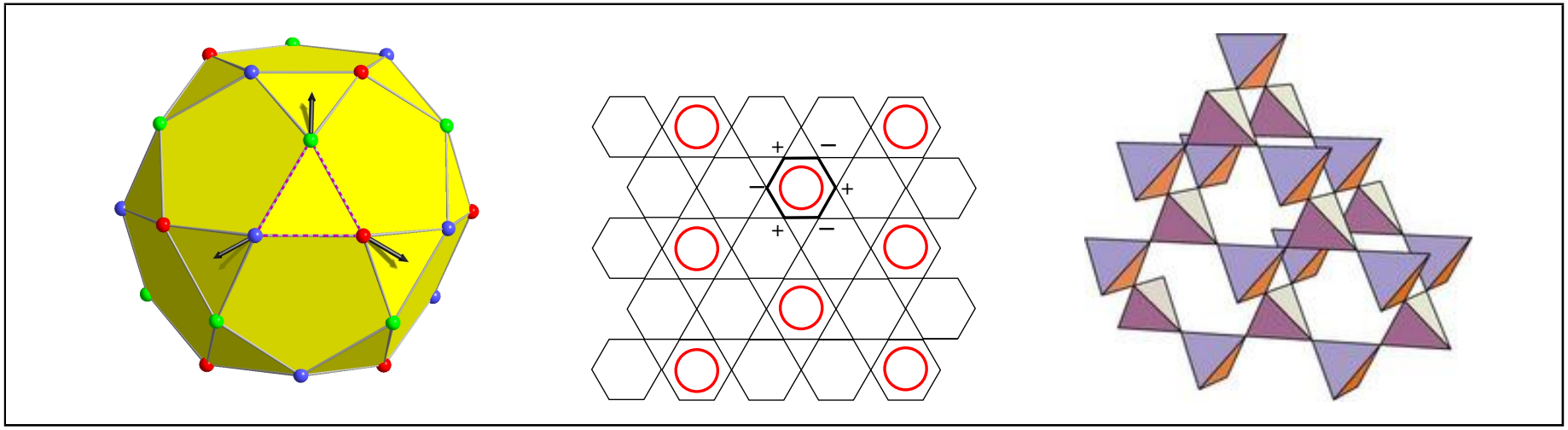
  (b) Tight-binding electrons are mapped onto a one-dimensional Wilson chain.

  (c) Iterative diagonalization and evaluation of observables.

(1) K. G. Wilson, Rev. Mod. Phys. **47**, 773 (1975).
(2) R. Bulla, T. A. Costi, and T. Pruschke, Rev. Mod. Phys. **80**, 395 (2008).

Frustration effects

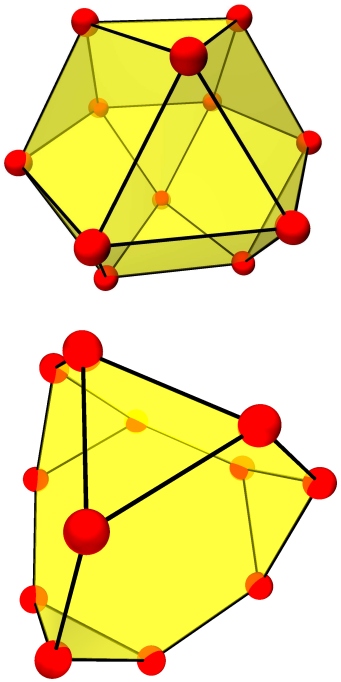
Frustrated spin systems



- Frustration: competing interactions – cannot be satisfied simultaneously;
- Example af systems: odd spin rings, cuboctahedron, icosahedron, icosidodecahedron, kagome lattice, pyrochlore lattice.
- Unusual magnetization: plateaus and jumps; large magnetocaloric effect; many singlets below first triplet.

J. Schnack, Dalton Trans. **39**, 4677 (2010).

Advanced ITO & Point Groups

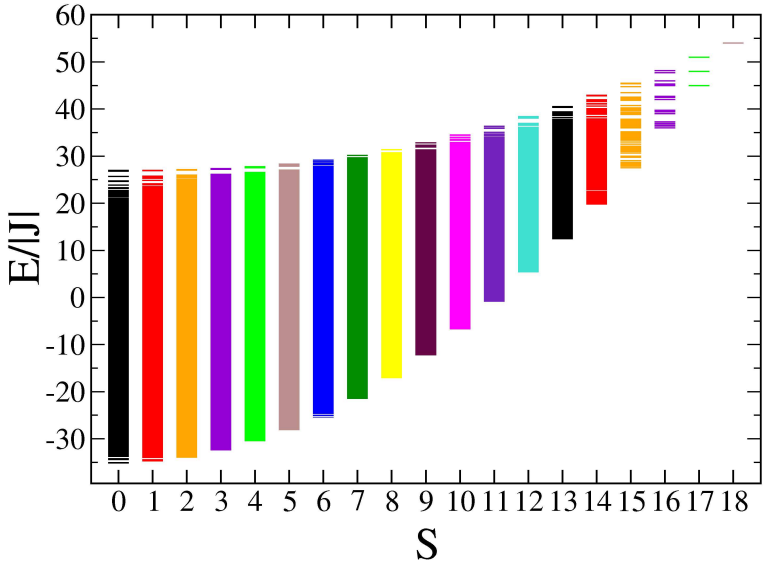


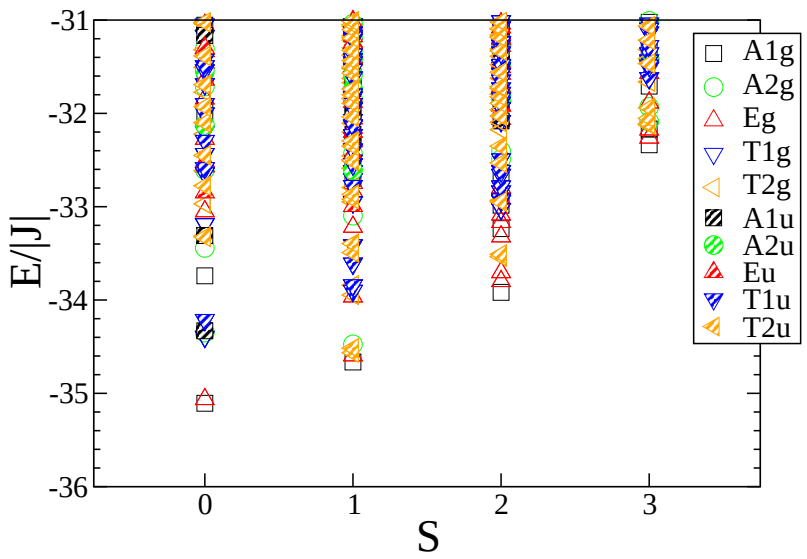
Group theory for highly symmetric molecules:

- $\underset{\sim}{H} = -\sum_{i,j} J_{ij}\ \underset{\sim}{\vec{s}}_i \cdot \underset{\sim}{\vec{s}}_j + g\mu_B \underset{\sim}{\vec{S}} \cdot \vec{B}$;
- $\left[\underset{\sim}{H}, \underset{\sim}{\vec{S}}^2\right] = 0,\ \left[\underset{\sim}{H}, \underset{\sim}{S}_z\right] = 0;$
- Irreducible Tensor Operator (ITO) approach (1);
- Additional point group symmetries (2,3).

(1) D. Gatteschi and L. Pardi, Gazz. Chim. Ital. **123**, 231 (1993); J. J. Borras-Almenar, J. M. Clemente-Juan, E. Coronado, and B. S. Tsukerblat, Inorg. Chem. **38**, 6081 (1999).
(2) O. Waldmann, Phys. Rev. B **61**, 6138 (2000); V. E. Sinitsyn, I. G. Bostrem, and A. S. Ovchinnikov, J. Phys. A-Math. Theor. **40**, 645 (2007); R. Schnalle and J. Schnack, Phys. Rev. B **79**, 104419 (2009);
(3) R. Schnalle, J. Schnack, Int. Rev. Phys. Chem. **29** (2010) 403-452.

Cuboctahedron



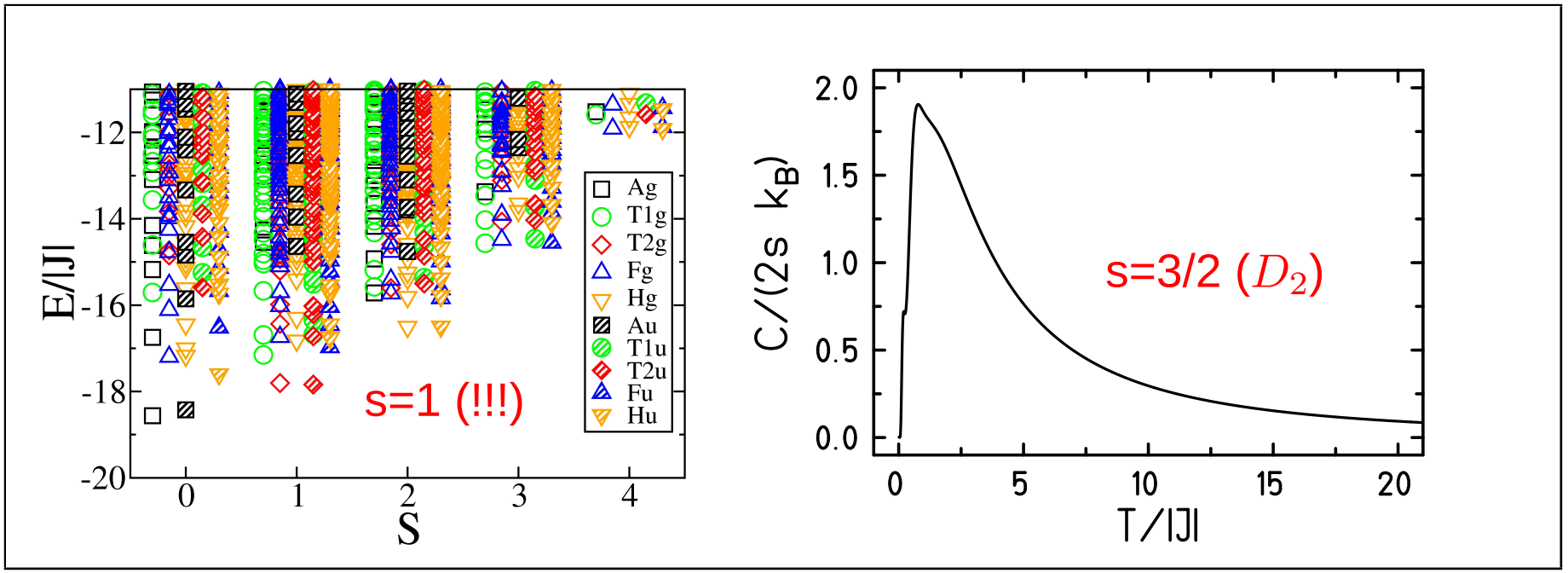


Cuboctahedron, $s = 3/2$, Hilbert space dimension 16,777,216; symmetry O_h (1).
Low-lying singlets, magnetization plateau, and jump (1,2).

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

R. Steinigeweg, Roman Schnalle , *Projection operator approach to spin diffusion in the anisotropic Heisenberg chain at high temperatures*, Phys. Rev. E 82, 040103(R) (2010).

Icosahedron

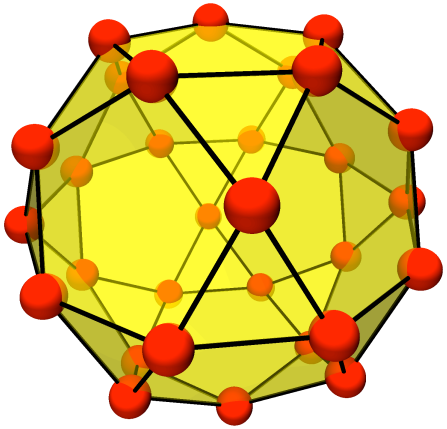


Icosahedron, $s = 3/2$, Hilbert space dimension 16,777,216; symmetry I_h
Very unusual heat capacity (1).

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

Finite-temperature Lanczos for The icosidodecahedron $s = 1/2$

DIMENSION = 1,073,741,824



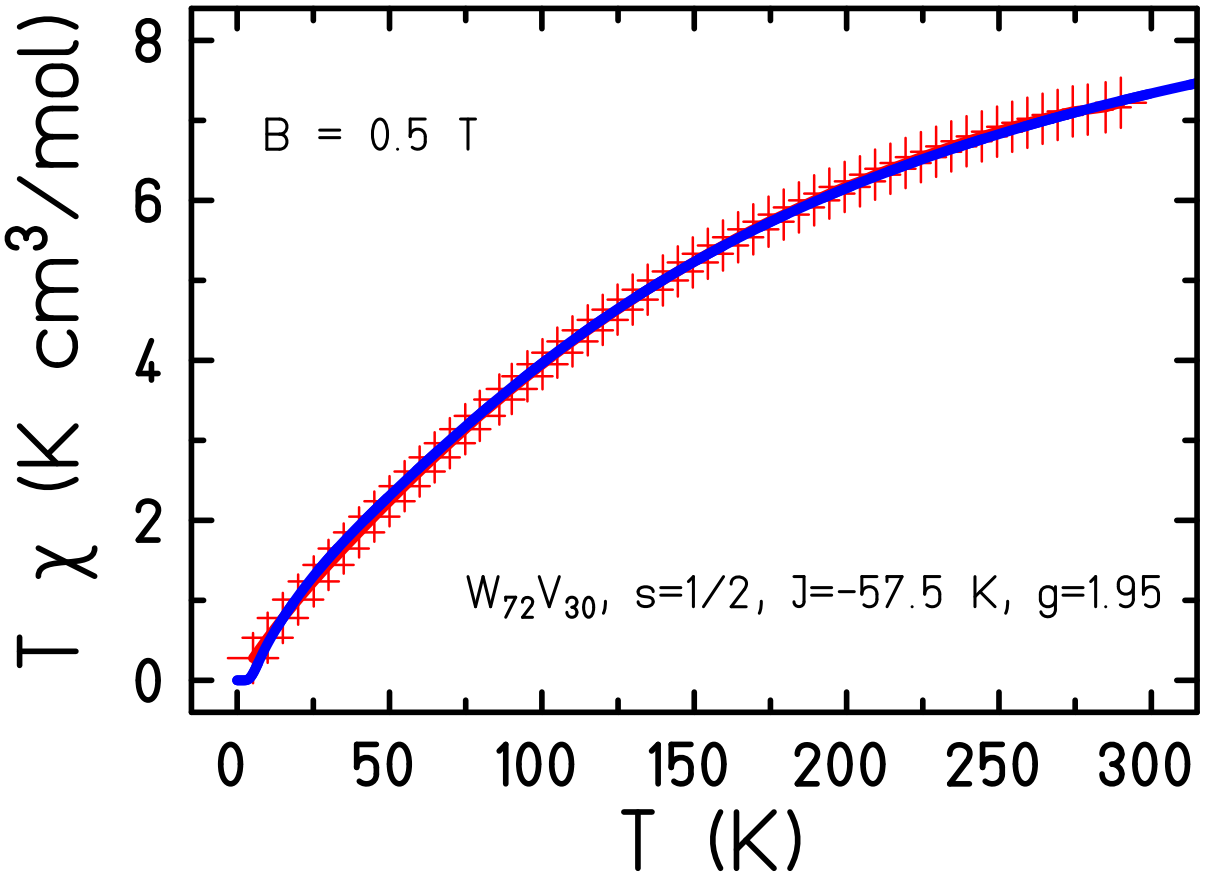
The idea of thermal Lanczos

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

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

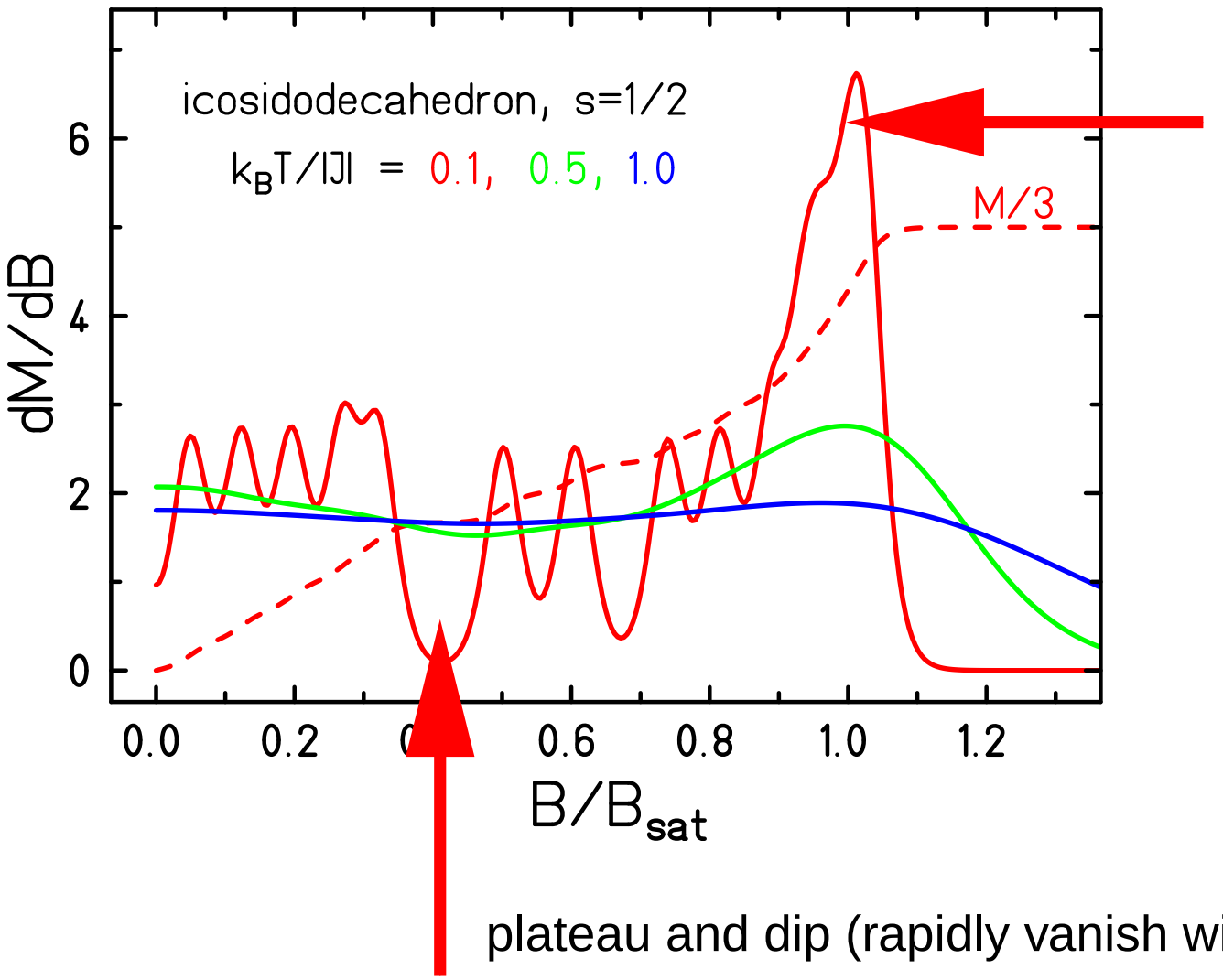
J. Jaklic and P. Prelovsek, Phys. Rev. B **49**, 5065 (1994).

Icosidodecahedron $s = 1/2$

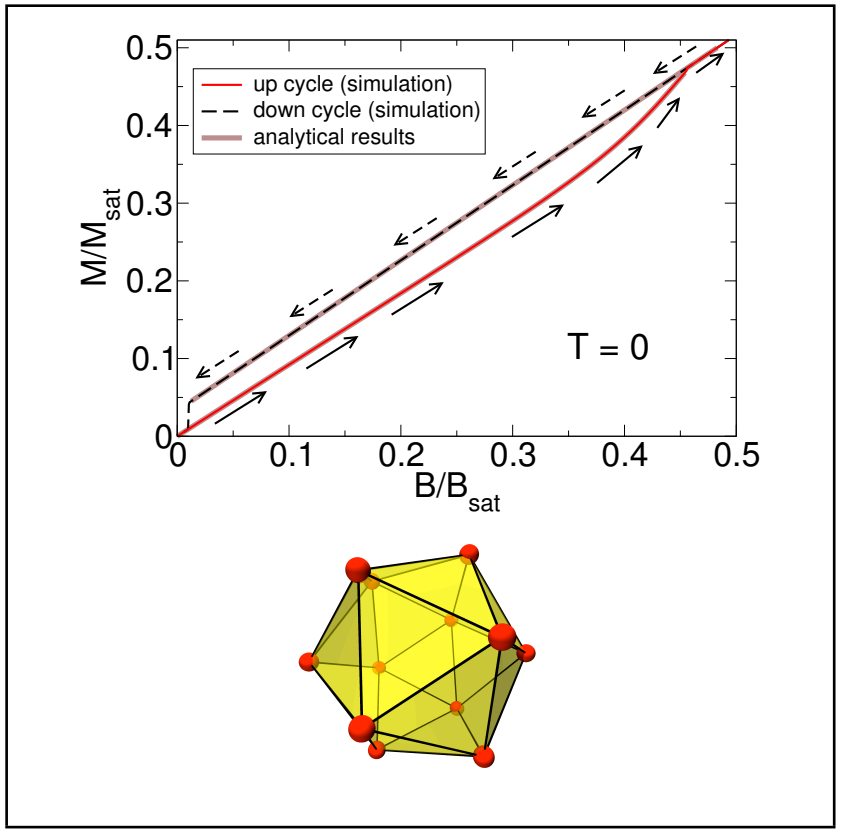


exp. data: A. M. Todea, A. Merca, H. Bögge, T. Glaser, L. Engelhardt, R. Prozorov, M. Luban, A. Müller, Chem. Commun. (2009) 3351.

Icosidodecahedron $s = 1/2$



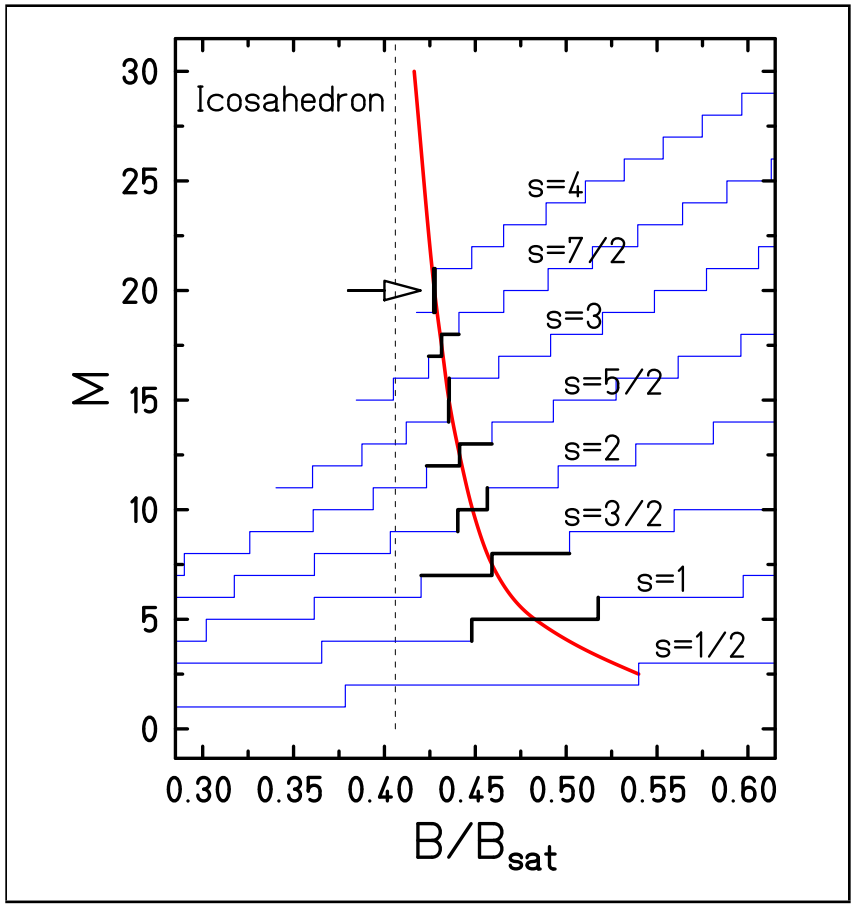
Metamagnetic phase transition I
Hysteresis without anisotropy



- Heisenberg model with isotropic nearest neighbor exchange
- Hysteresis behavior of the classical icosahedron in an applied magnetic field.
- Classical spin dynamics simulations (thick lines).
- Analytical stability analysis (grey lines).
- Movie.

C. Schröder, H.-J. Schmidt, J. Schnack, M. Luban, Phys. Rev. Lett. **94**, 207203 (2005)

Metamagnetic phase transition III
Quantum icosahedron



- Quantum analog:
  Non-convex minimal energy levels
  $\Rightarrow$ magnetization jump of $\Delta M > 1$.
- Lanczos diagonalization for various s vectors with up to 10^9 entries.
- True jump of $\Delta M = 2$ for $s = 4$.
- Polynomial fit in $1/s$ yields the classically observed transition field.

C. Schröder, H.-J. Schmidt, J. Schnack, M. Luban,
Phys. Rev. Lett. **94**, 207203 (2005)

Thank you very much for your attention.

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