Magnetism in zero dimensions: physics of magnetic molecules

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Vortrag

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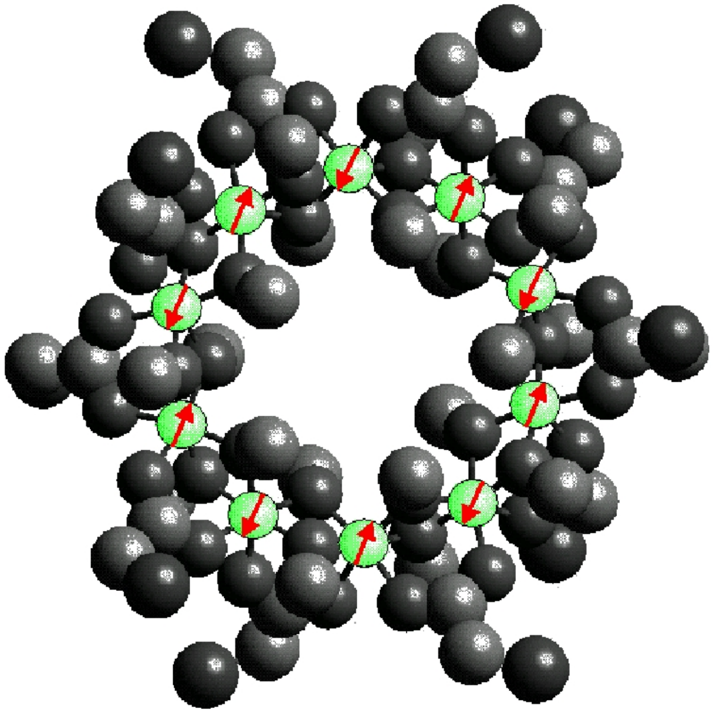
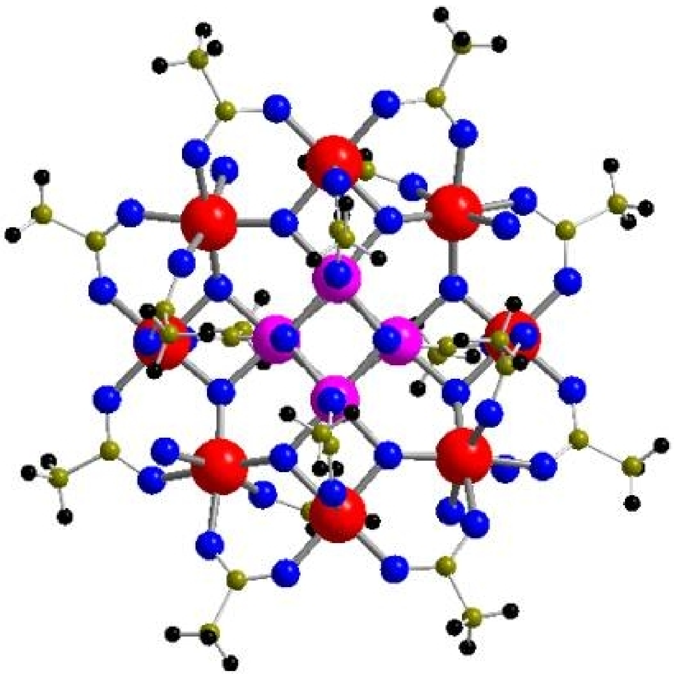


Fe_{10}

1. Beauty of Magnetic Molecules
2. Single Molecule Magnets
3. Antiferromagnetic Molecules
4. Molecules on Surfaces
5. Coherence Phenomena
6. Magnetocalorics
7. Put it into a tube
8. Medical Applications
9. Up to date theory modeling

Beauty of Magnetic Molecules

The beauty of magnetic molecules I

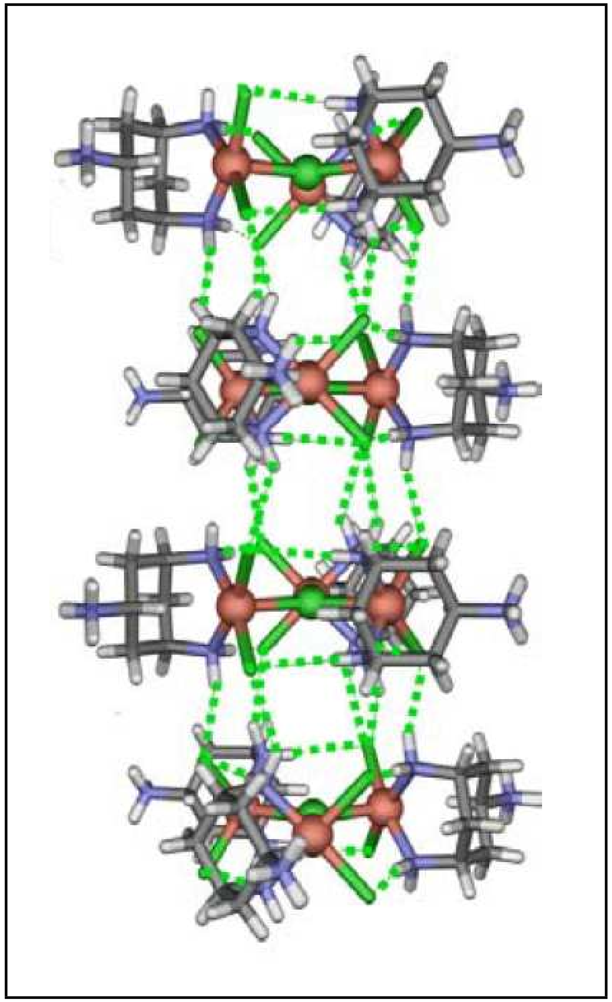


Mn_{12}

- Inorganic or organic macro molecules, e.g. polyoxometalates, 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);
- Single spin quantum number $1/2 \leq s \leq 7/2$;
- Intermolecular interaction relatively small, therefore measurements reflect the thermal behaviour of a single molecule.

Magnetism goes Nano, Ed. Stefan Blügel, Thomas Brückel, and Claus M. Schneider, FZ Jülich, Institute of Solid State Research, Lecture Notes **36** Jülich 2005

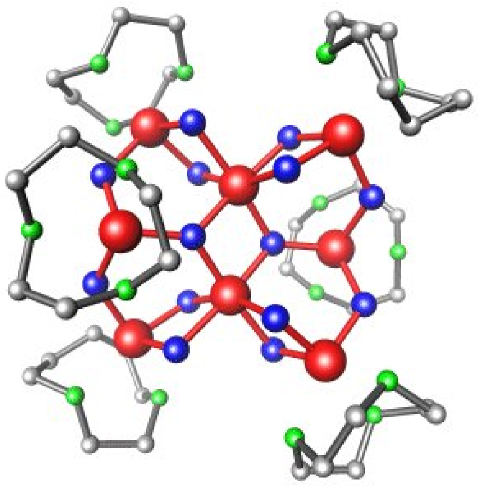
The beauty of magnetic molecules II

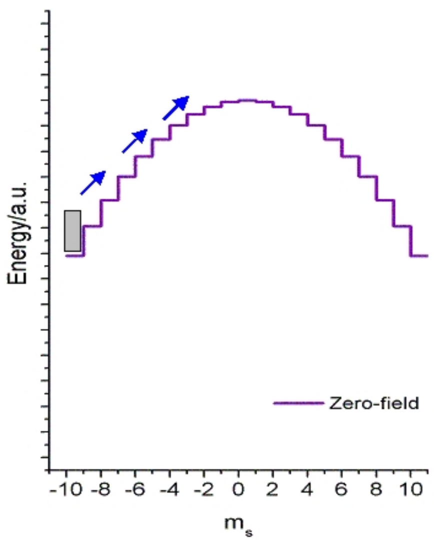


- Dimers (Fe_2), tetrahedra (Cr_4), cubes (Cr_8);
- Rings, especially iron rings (Fe_6, Fe_8, Fe_{10}, ...);
- Complex structures (Mn_{12}) – drosophila of molecular magnetism;
- “Soccer balls”, more precisely icosidodecahedra (Fe_{30}) and other macro molecules;
- Chain like and planar structures of 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)

The beauty of magnetic molecules III



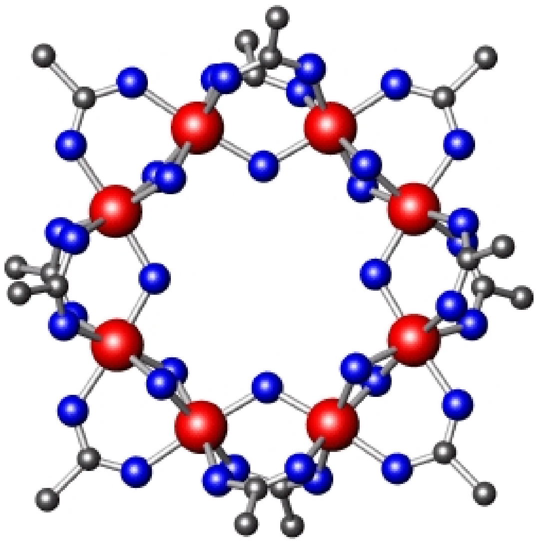


- Single Molecule Magnets (SMM): magnetic molecules with large ground state moment;
- Example: $S = 10$ for Mn_{12} or Fe_8;
- Anisotropy dominates approximate single-spin Hamiltonian:

$$\underset{\sim}{H} = -D \underset{\sim}{S}_z^2 + \underset{\sim}{H}' , \qquad \left[\underset{\sim}{S}_z , \underset{\sim}{H}' \right] \neq 0$$

- Single molecule shows: metastable magnetization, hysteresis, ground state magnetization tunneling, thermally and phonon assisted tunneling.
- Today's major efforts: improve stability of magnetization; investigate on surfaces.

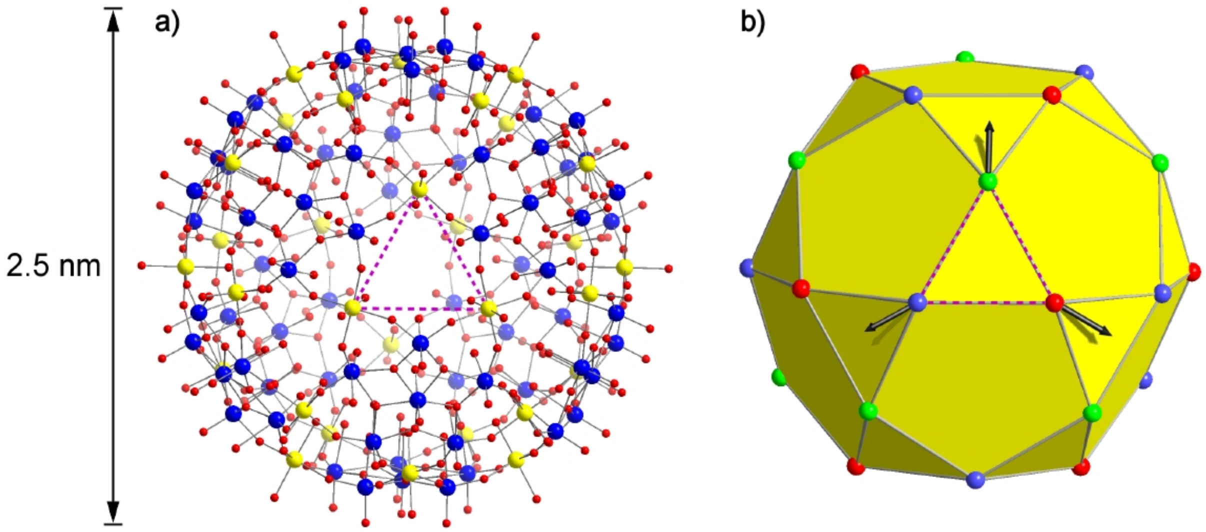
The beauty of magnetic molecules IV
Why magnetic molecules?



Cr_8

- Interacting spin system largely decoupled from remaining degrees of freedom;
- Transition few-spin system $\Rightarrow$ many-spin system, contribution to understanding of bulk magnetism;
- Transition quantum spin system ($s = 1/2$) $\Rightarrow$ classical spin system ($s_{\text{Fe}} = 5/2$, $s_{\text{Gd}} = 7/2$);
- Easy to produce, single crystals with $> 10^{17}$ identical molecules can be synthesized and practically completely characterized;
- Speculative applications: magnetic storage devices, magnets in biological systems, light-induced nano switches, displays, catalysts, qubits for quantum computers.

The beauty of magnetic molecules V
$\{Mo_{72}Fe_{30}\}$ – a giant magnetic Keplerate molecule

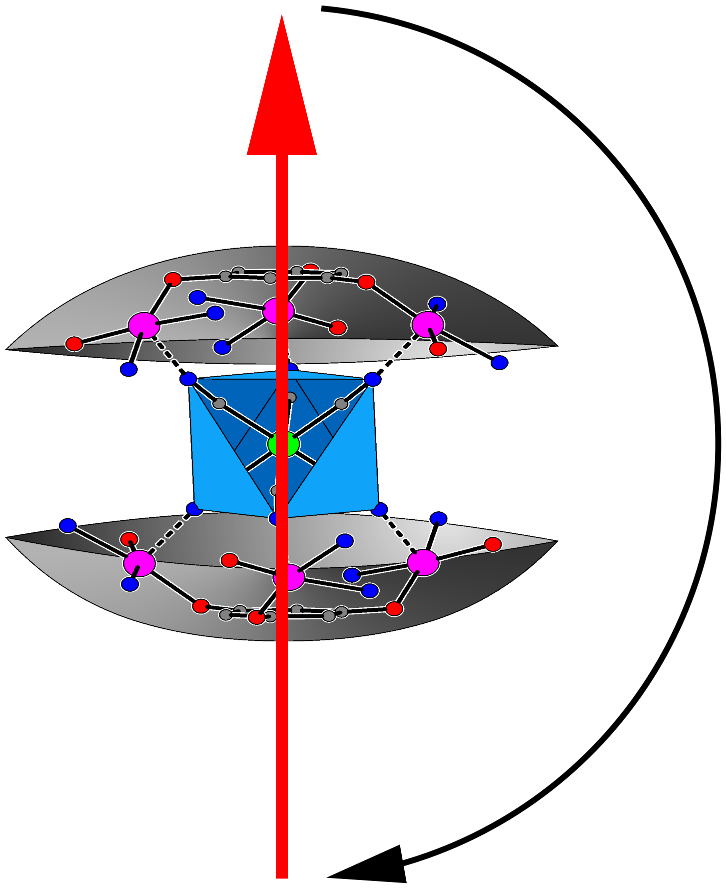


- Structure: Fe - yellow, Mo - blue, O - red;
- Exciting magnetic properties (1).
- Quantum treatment very complicated, dimension of Hilbert space $(2s+1)^N \approx 10^{23}$ (2).

(1) A. Müller *et al.*, Chem. Phys. Chem. **2**, 517 (2001) , (2) M. Exler and J. Schnack, Phys. Rev. B **67**, 094440 (2003)

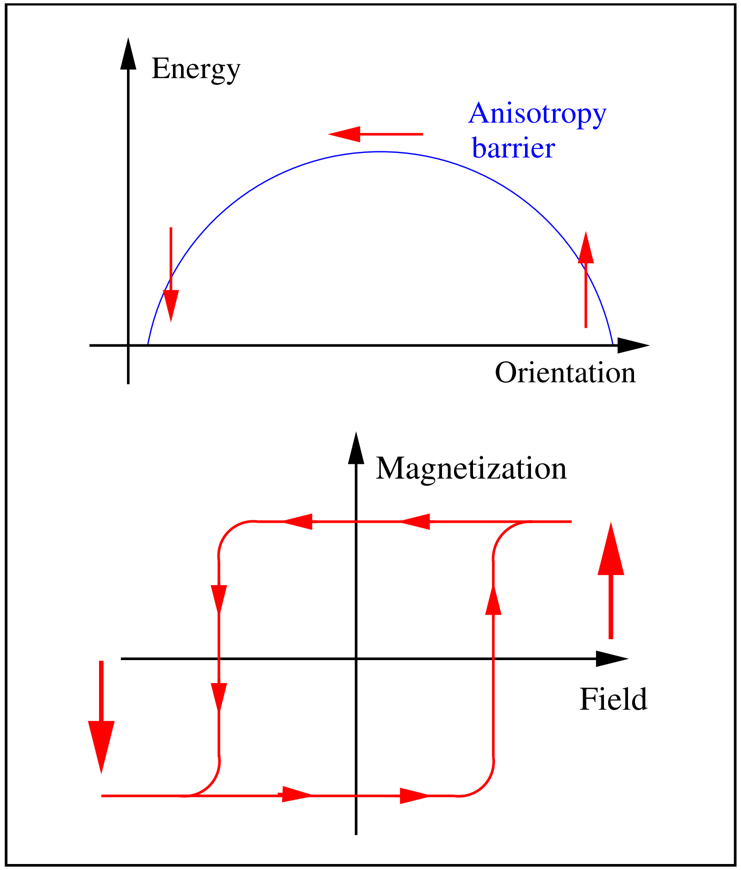
Single Molecule Magnets

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).
- Desired application as very small realization of a bit (up = 0, down = 1).

Single Molecule Magnets II



- Large ground state moment; anisotropy barrier dominates at low T.

$$\underset{\sim}{H} \approx D S_z^2$$

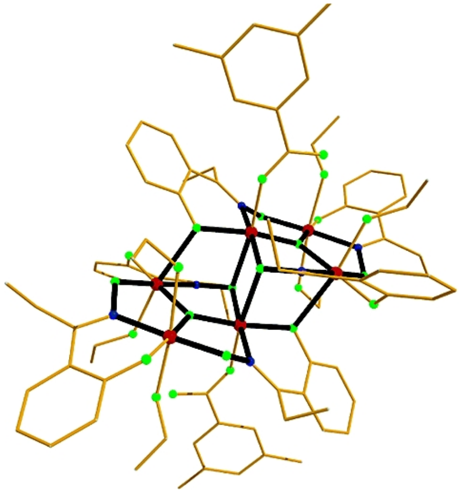
- Metastable magnetization and hysteresis;

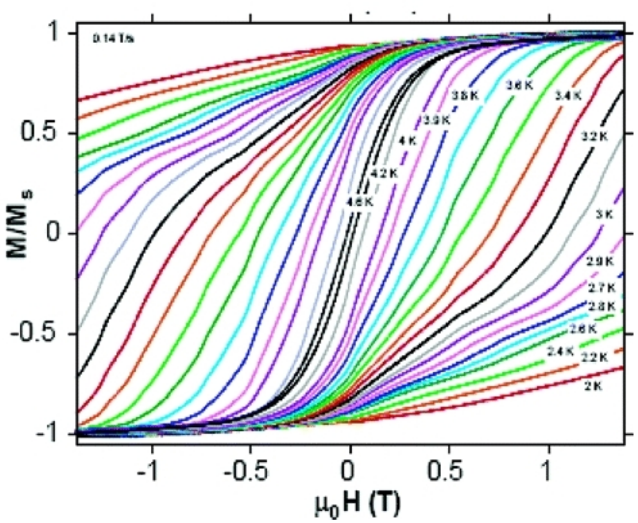
- But also magnetization tunneling due to non-commuting terms, e.g. E, B_x, B_y.

$$\underset{\sim}{H} \approx D S_z^2 + E(S_x^2 - S_y^2)$$

- Goal: S large, D large, $E = 0$. Impossible?

Single Molecule Magnets III





[$\mathrm{Mn}_6^{\mathrm{III}}\mathrm{O}_2$(Et-sao)$_6$($\mathrm{O}_2$CPh($\mathrm{Me}_2$))$_2$(EtOH)$_6$]:

- $S = 12$ ground state with $D = -0.43$ cm^{-1}
- $U_{\text{eff}} = 86.4$ K and a blocking temperature of about 4.5 K.
- A record molecule from the group of Euan Brechin (Edinburgh).

C. J. Milios *et al.*, J. Am. Chem. Soc. **129**, 2754 (2007)
S. Carretta *et al.*, Phys. Rev. Lett. **100**, 157203 (2008)

Single Molecule Magnets IV

- “Magnitude of the anisotropy barrier is mainly determined by the strength of the spin-orbit coupling and cannot be engineered by independently optimizing D and S.”(1)

- “From this point of view systems with larger energy barriers should be obtained in the case of perfect alignment of the Jahn-Teller axes . . .
However, the challenge here will be the control of the ferromagnetic exchange.”(1)

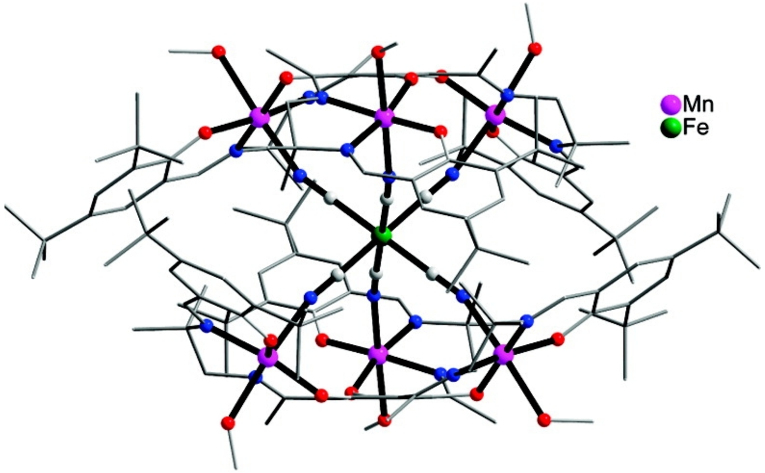
- “. . . the widely considered design rule to increase S is not as efficient as suggested by $\underset{\sim}{H} = DS^2$,. . . the increase is on the order of unity and not S^2.”(2)

- “For obtaining better SMMs, it hence seems most promising to work on the local ZFS tensors D_i or to work in a limit where the Heisenberg term is not dominant (i.e., to break the strong-exchange limit).”(2)

(1) E. Ruiz *et al.*, Chem. Commun. 52 (2008).

(2) O. Waldmann, Inorg. Chem. **46**, 10035 (2007).

Single Molecule Magnets V



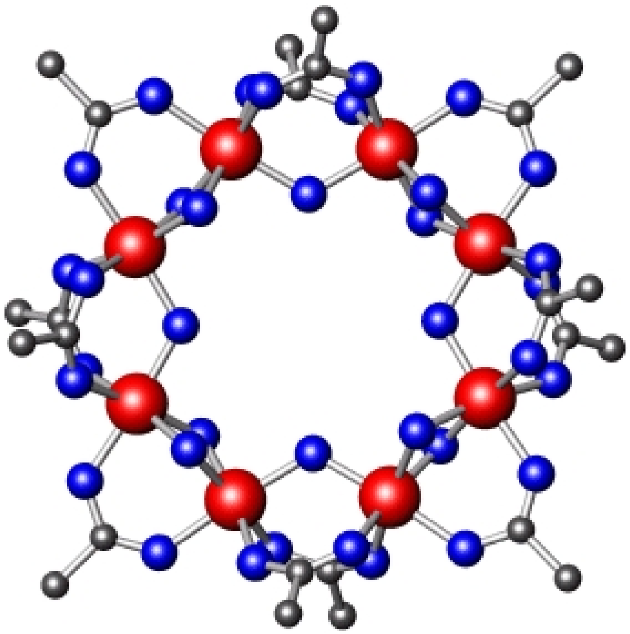
Rational design of strict C_3 symmetry:

- Idea of Thorsten Glaser (Bielefeld): C_3 symmetric alignment of local easy axes (easy axis $\equiv$ Jahn-Teller axis);
- Various ions could be used so far, e.g. Mn_6Cr (1), Mn_6Fe (2), . . .
- Advantage: no E-terms, i.e. no (less) tunneling;
- Problem: exchange interaction sometimes antiferromagnetic.

T. Glaser *et al.*, Angew. Chem.-Int. Edit. **45**, 6033 (2006).
T. Glaser *et al.*, Inorg. Chem. **48**, 607 (2009).

Antiferromagnetic Molecules

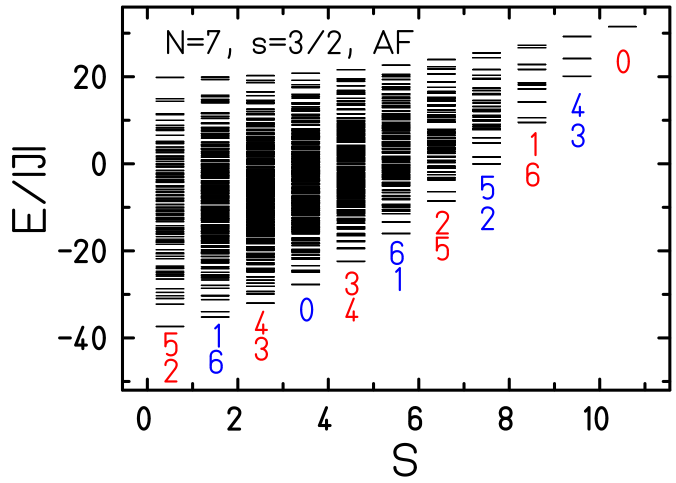
Antiferromagnetic Molecules I – Rings



- To date: many AF rings synthesized, e.g. Fe_6, Fe_{10}, Fe_{12}, . . . , Cr_8, . . . (1)
- Predominantly even rings.
- Theory: Exact diagonalization; Rotational band model; QMC; Classical (2)

(1) Taft, Delfs, Saalfrank, Rentschler, Winpenny, Timco, Timco, Timco, . . .
(2) Luban, Waldmann, Schnack, Schröder, Carretta, Engelhardt, . . .

Antiferromagnetic Molecules II



Extending theorems of Lieb, Schultz, and Mattis

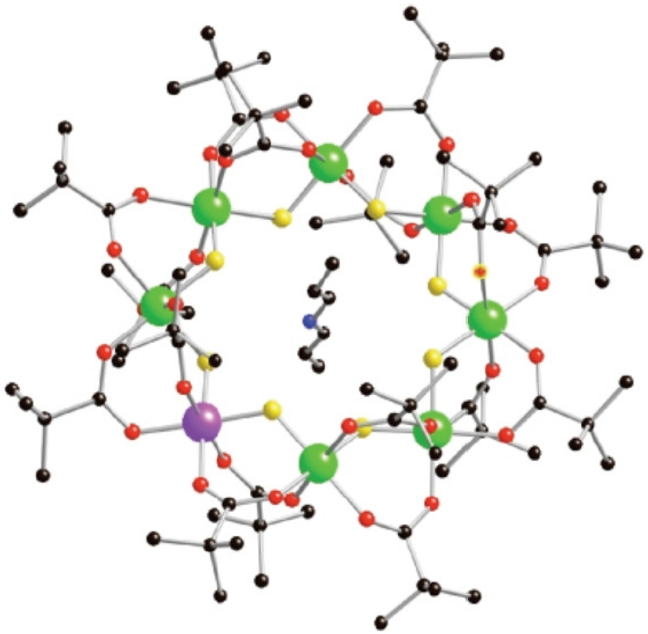
- For odd N and half integer s, i.e. $s = 1/2, 3/2, 5/2, \ldots$ we find that (1)
  - the ground state has total spin $S = 1/2$;
  - the ground state energy is **fourfold** degenerate.

- Reason: In addition to the (trivial) degeneracy due to $M = \pm 1/2$, a degeneracy with respect to k appears (2)

For all rings: $$k \equiv \pm a \left\lceil \frac{N}{2} \right\rceil \mod N \, , \quad a = Ns - M \, , \quad (4)$$

(1) K. Bärwinkel, H.-J. Schmidt, J. Schnack, J. Magn. Magn. Mater. **220**, 227 (2000)
(2) $\lceil \cdot \rceil$ largest integer, smaller or equal
(3) J. Schnack, Phys. Rev. B **62**, 14855 (2000)
(4) K. Bärwinkel, P. Hage, H.-J. Schmidt, and J. Schnack, Phys. Rev. B **68**, 054422 (2003)

Antiferromagnetic Molecules III



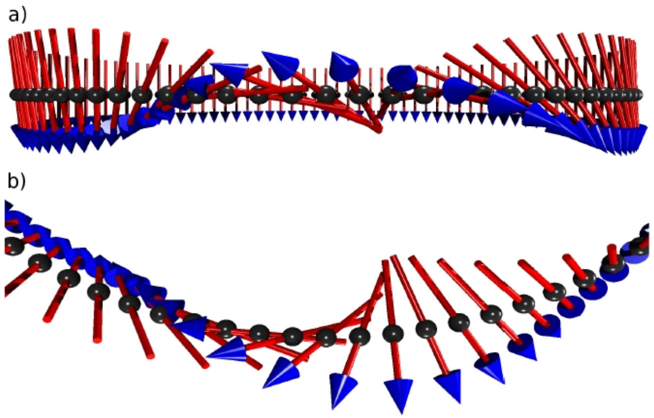
Cr_7Ni by Timco

Synthesis of odd or heterometallic or coupled af spin rings

- Odd membered rings very rare; one reason: steric hindrance (1);
- Heterometallic rings derived from homometallic, especially from Cr_8 (2); net ground state moment;
- Coupling of heterometallic rings for quantum computing (3, follows later).

(1) O. Cador *et al.*, Angew. Chem. Int. Edit. **43**, 5196 (2004);
H. C. Yao *et al.*, Chem. Commun. 1745 (2006);
(2) F. K. Larsen *et al.*, Angew. Chem. Int. Ed. **42**, 101 (2003); E. Micotti *et al.*, Phys. Rev. Lett. **97**, 267204 (2006); L. P. Engelhardt *et al.*, Angew. Chem. Int. Edit. **47**, 924 (2008), i.e. Timco, Timco, Timco, . . . ; (3) G. A. Timco *et al.*, Nature Nanotechnology **4**, 173 (2009).

Antiferromagnetic Molecules IV



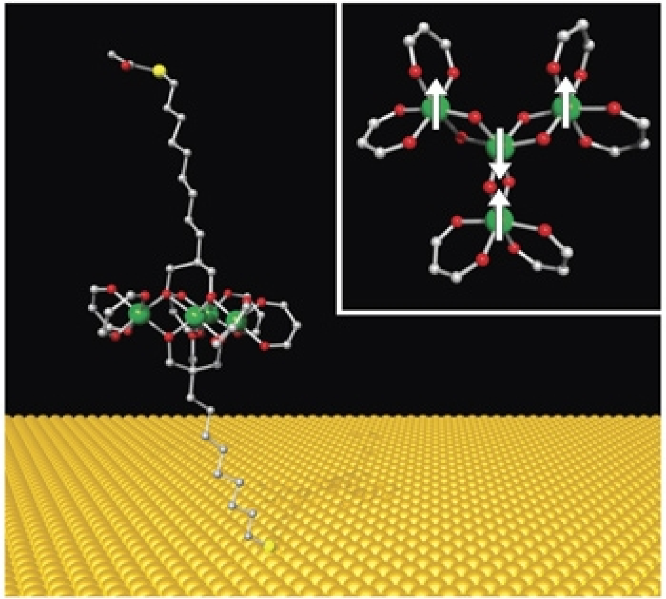
Soliton dynamics

- Theoretical realization of classical solitons on af Heisenberg spin rings (1)
- Do quantum solitons exist and if, how do they look like? (2)
- Can they be excited? Useful dynamics?

(1) H.-J. Schmidt, C. Schröder, and M. Luban, Journal of Physics: Condensed Matter **23**, 386003 (2011).
(2) J. Schnack and P. Shchelokovskyy, J. Magn. Magn. Mater. **306**, 79 (2006).

Molecules on Surfaces

Molecules on Surfaces



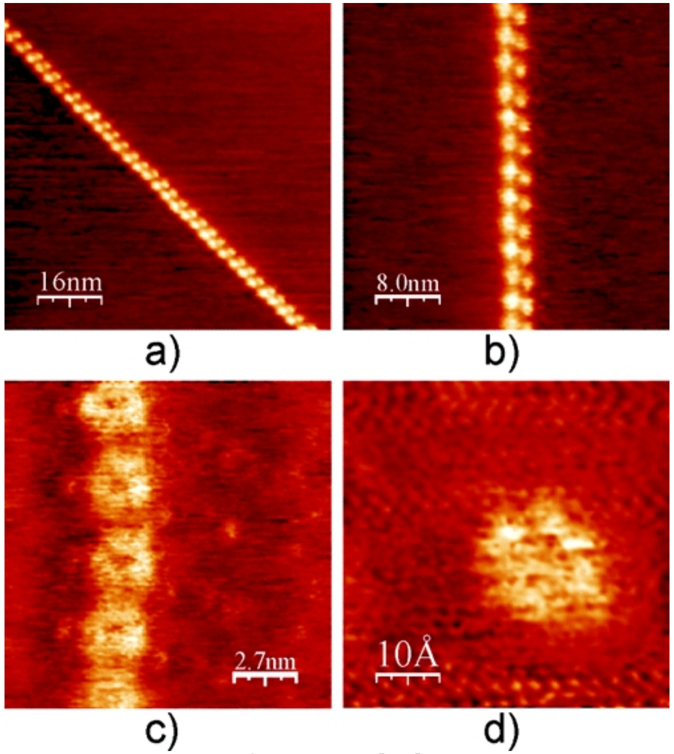
from (1)

What is the goal?

- Manipulation of single molecules only possible on surfaces;
- Deposition problematic;
- Possible chemical modification through surface.

(1) M. Mannini *et al.*, Nat. Mater. **8**, 194 (2009).

Molecules on Surfaces I



from (1)

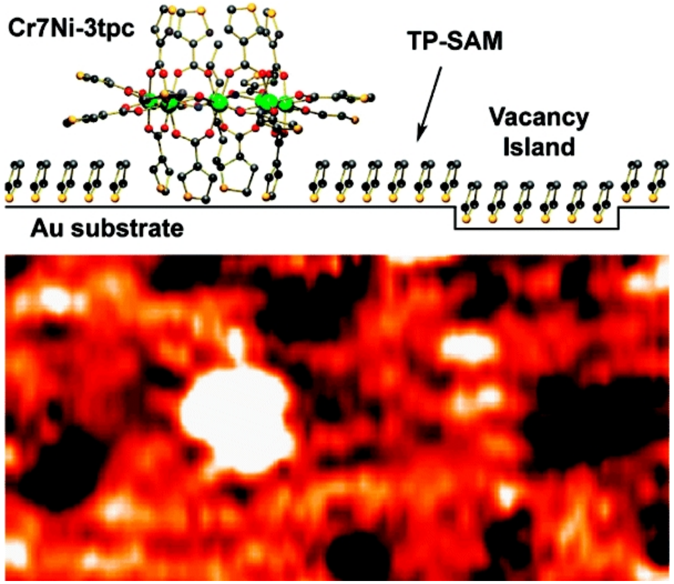
Early attempts by Paul Müller (Erlangen)

- Cu_{20} on Highly Orientated Pyrolytic Graphite (HOPG) (1);
- Scanning tunnelling microscopy (STM) (2);
- Scanning tunnelling spectroscopy (STS) (2);
- Current induced tunnelling spectroscopy (CITS) (2).
- Theory: Schoeller, Wegewijs, Timm, Postnikov, Kortus,Blügel.

(1) M. S. Alam *et al.*, Inorg. Chem. **45**, 2866 (2006).
(2) M. Ruben, J. M. Lehn, and P. Müller, Chem. Soc. Rev. **35**, 1056 (2006).

Molecules on Surfaces II

Rings on surfaces

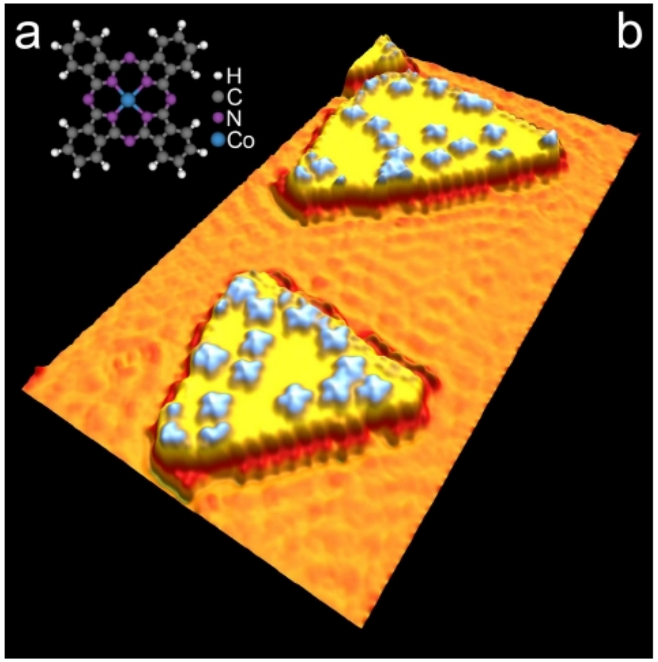


from (1)

- Sulfur-functionalized clusters Cr_7Ni on gold (1);
- Deposited from the liquid phase on Au(111);
- Scanning tunneling microscopy (STM) and X-ray photoemission spectroscopy (XPS);
- "The stoichiometric behavior of the core level intensities, which are the direct fingerprint of the ring, confirms that the ring integrity is preserved."(1)

(1) V. Corradini *et al.*, Inorg. Chem. **46**, 4937 (2007).

Molecules on Surfaces III



from (1)

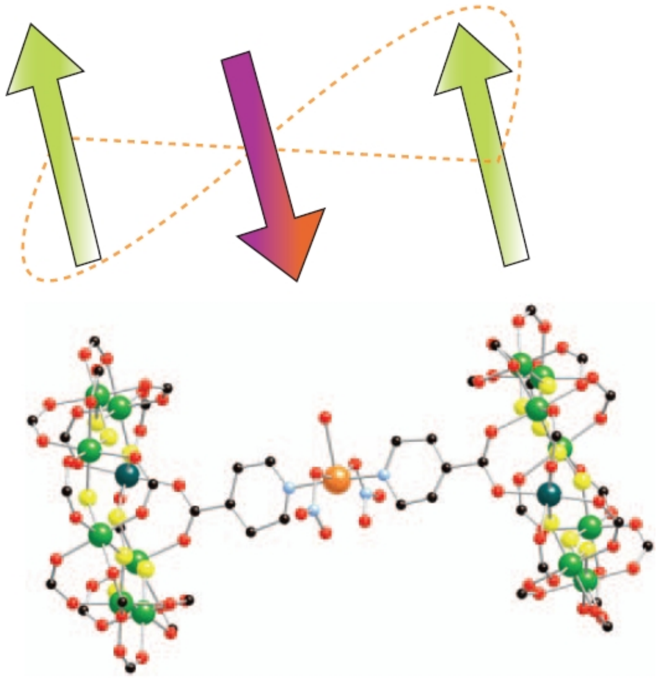
Spin-polarized measurements

- Cobalt-phthalocyanine molecules on cobalt islands (1);
- Spin-polarized STM and STS;
- Transport through polarized Co islands;
- Identification of ferromagnetic molecule-lead exchange interaction (1).

(1) C. Iacovita *et al.*, Phys. Rev. Lett. **101**, 116602 (2008).

Coherence Phenomena

Coherence Phenomena I



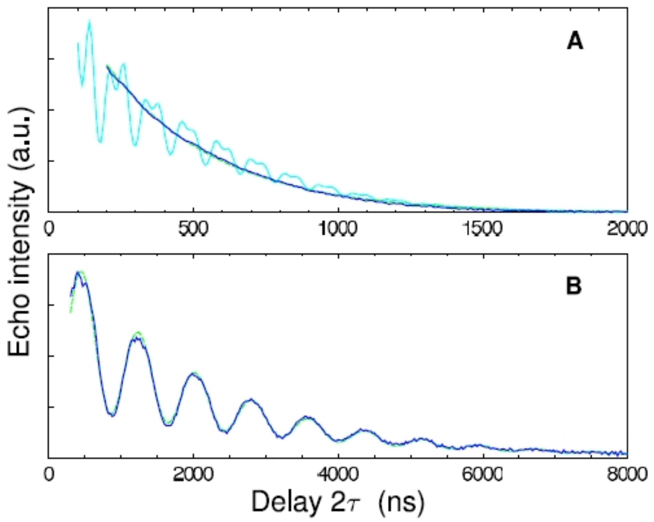
from (1)

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 **4**, 173 (2009); 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)

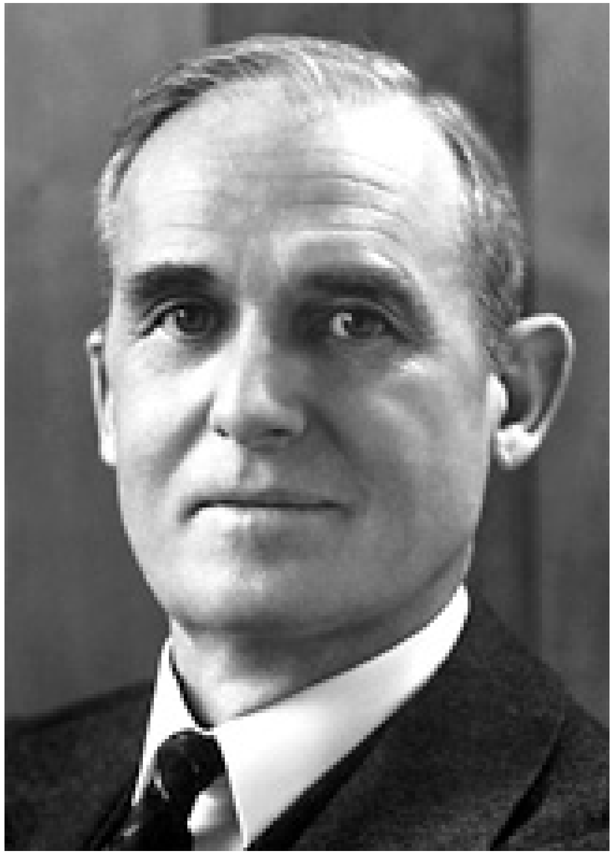
Spin relaxation times

- EPR/NMR, Hahn echo techniques, T_1, T_2 times;
- Decoherence due to e.g. nuclei, phonons, dipolar interaction;
- 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).

Magnetocalorics

Magnetocalorics I: Nobel Prize 1949



The Nobel Prize in Chemistry 1949 was awarded to William F. Giauque *for his contributions in the field of chemical thermodynamics, particularly concerning the behaviour of substances at extremely low temperatures*.

Magnetocalorics II

768 LETTERS TO THE EDITOR

Attainment of Temperatures Below 1° Absolute by Demagnetization of $Gd_2(SO_4)_3 \cdot 8H_2O$

We have recently carried out some preliminary experiments on the adiabatic demagnetization of $Gd_2(SO_4)_3 \cdot 8H_2O$ at the temperatures of liquid helium. As previously predicted by one of us, a large fractional lowering of the absolute temperature was obtained.

An iron-free solenoid producing a field of about 8000 gauss was used for all the measurements. The amount of $Gd_2(SO_4)_3 \cdot 8H_2O$ was 61 g. The observations were checked by many repetitions of the cooling. The temperatures were measured by means of the inductance of a coil surrounding the gadolinium sulfate. The coil was immersed in liquid helium and isolated from the gadolinium by means of an evacuated space. The thermometer was in excellent agreement with the temperature of liquid helium as indicated by its vapor pressure down to 1.5°K.

On March 19, starting at a temperature of about 3.4°K, the material cooled to 0.53°K. On April 8, starting at about 2°, a temperature of 0.34°K was reached. On April 9, starting at about 1.5°, a temperature of 0.25°K was attained.

It is apparent that it will be possible to obtain much lower temperatures, especially when successive demagnetizations are utilized.

W. F. Giauque
D. P. MacDougall

Department of Chemistry,
University of California,
Berkeley, California,
April 12, 1933.

W. F. Giauque and D. MacDougall, Phys. Rev. **43**, 768 (1933).

Magnetocalorics III

$$\left(\frac{\partial T}{\partial B}\right)_S = -\frac{T}{C}\left(\frac{\partial S}{\partial B}\right)_T$$

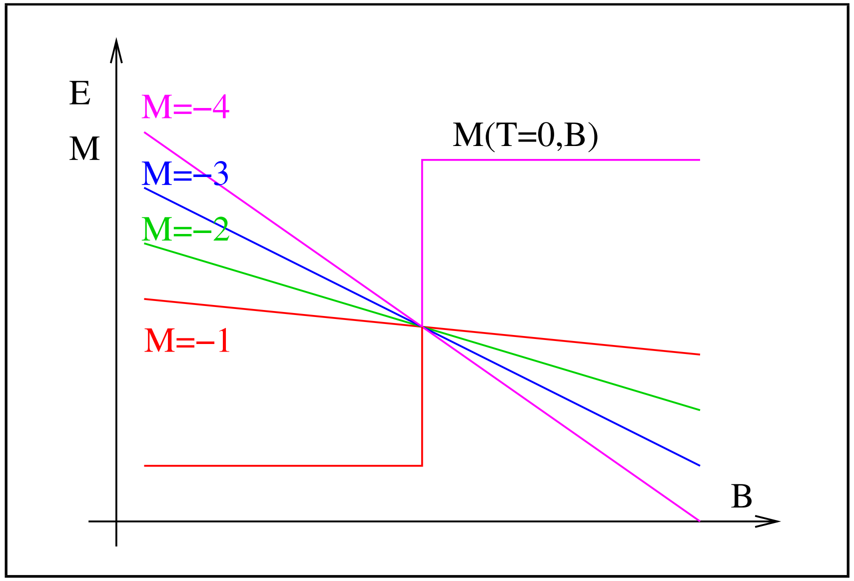
(adiabatic temperature change)

- Heating or cooling in a varying magnetic field. Discovered in pure iron by E. Warburg in 1881.
- Typical rates: $0.5 \ldots 2$ K/T.
- Giant magnetocaloric effect: $3 \ldots 4$ K/T e.g. in $Gd_5(Si_xGe_{1-x})_4$ alloys ($x \leq 0.5$).

- MCE especially large at large isothermal entropy changes, i.e. at phase transitions (1), close to quantum critical points (2), or at crossings of many magnetic levels (3).

(1) V.K. Pecharsky, K.A. Gschneidner, Jr., A. O. Pecharsky, and A. M. Tishin, Phys. Rev. B **64**, 144406 (2001).
(2) Lijun Zhu, M. Garst, A. Rosch, and Qimiao Si, Phys. Rev. Lett. **91**, 066404 (2003).
(3) J. Schnack, R. Schmidt, J. Richter, Phys. Rev. B **76**, 054413 (2007).

Magnetocalorics IV



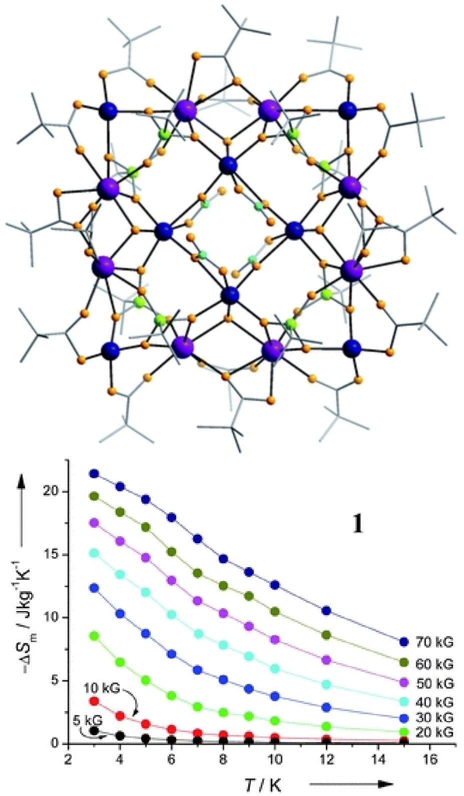
- High degeneracy of ground state levels $\Rightarrow$ large residual entropy at $T = 0$.

$$\left(\frac{\partial T}{\partial B}\right)_S = -\frac{T}{C}\left(\frac{\partial S}{\partial B}\right)_T$$

- This is for instance the case for a giant spin at $B = 0$.
- Good for sub-Kelvin cooling.

M. Evangelisti *et al.*, Appl. Phys. Lett. **87**, 072504 (2005).
J. Schulenburg, A. Honecker, J. Schnack, J. Richter, H.-J. Schmidt, Phys. Rev. Lett. **88**, 167207 (2002)
M. E. Zhitomirsky, Phys. Rev. B **67**, 104421 (2003).
M. E. Zhitomirsky and A. Honecker, J. Stat. Mech.: Theor. Exp. **2004**, P07012 (2004).

Magnetocalorics V



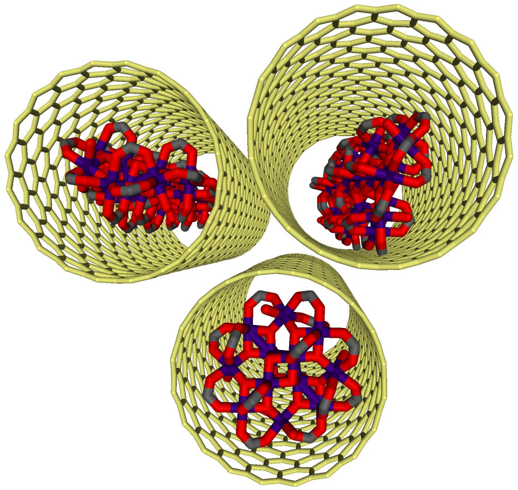
from (1)

- Gd compounds advantageous for magnetocaloric applications, since $s = 7/2$ large and exchange coupling small.
- Yields large density of states with large variation of magnetic quantum number.

(1) Y.-Z. Zheng, M. Evangelisti, and R. E. P. Winpenny, Chem. Sci. **2**, 99 (2011).
(2) Marco Evangelisti and Euan K. Brechin , Dalton Trans., **39**, 4672-4676 (2010).

Put it into a tube

Into a tube



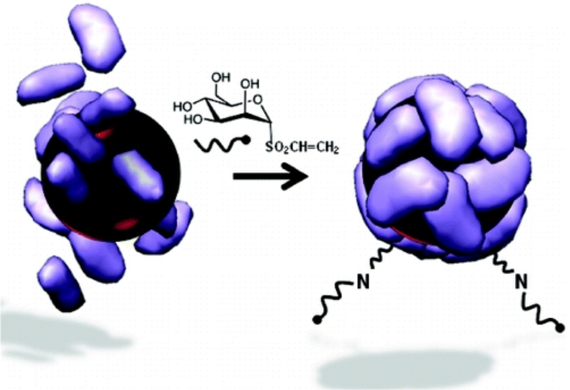
from (1)

- Idea 1: use carbon nano tube (CNT) to contact magnetic molecule electronically (1);
- Idea 2: CNTs filled with NMR active material can serve as local thermometers in biomedical applications (2).

(1) M. del Carmen Gimenez-Lopez *et al.*, Nat. Commun. **2**, 407 (2011).
(2) Anja U.B. Wolter, Rüdiger Klingeler, Bernd Büchner, Int. J. of Biomedical Nanoscience and Nanotechnology **2**, 99-111 (2011).

Medical Applications

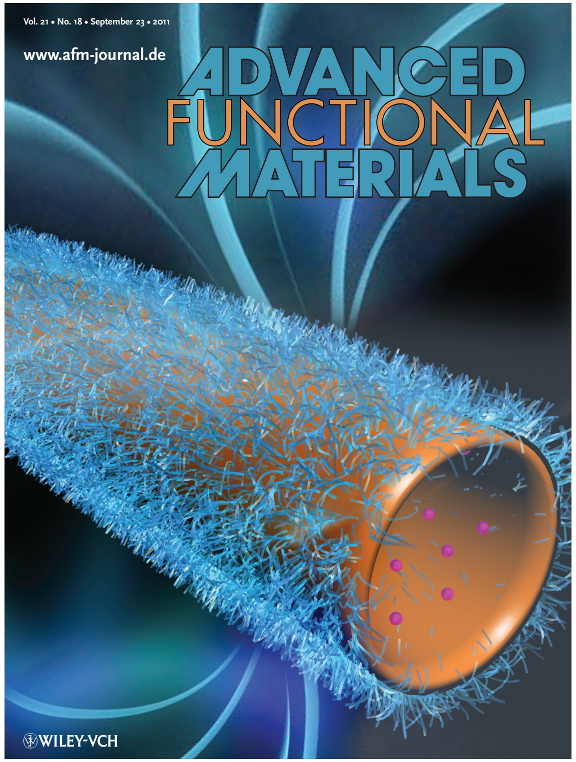
Medical applications I



- Chemical encapsulation of Maghemite nanoparticles;
- MRI performance comparable to Endorem (1).

(1) E. Valero *et al.*, J. Amer. Chem. Soc. **133**, 4889 (2011).

Medical applications II



- CNT filled with Co nanoparticles for hyperthermia (saturation magnetization of 106 emu/g and a coercivity $H_C = 250$ Oe);
- Co@CNT nanoparticles can at the same time be used for magnetic resonance imaging (MRI) with an efficiency comparable to commercially available T2 contrast agents.

(1) P. Lukanov *et al.*, Adv. Funct. Mater. **21**, 3583 (2011).

Up to date theory modeling

Model Hamiltonian (spin only)

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

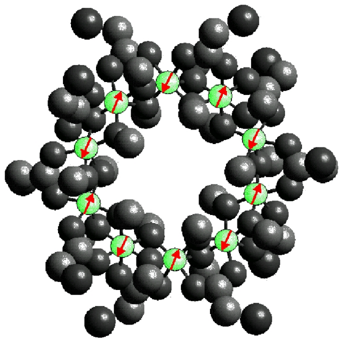
Exchange/Anisotropy   Dzyaloshinskii-Moriya   Zeeman

Isotropic Hamiltonian

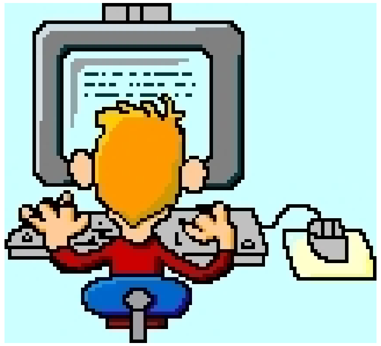
$$\underset{\sim}{H} = -\sum_{i,j} J_{ij} \, \underset{\sim}{\vec{s}}(i) \cdot \underset{\sim}{\vec{s}}(j) + g \, \mu_B \, B \sum_{i}^{N} \underset{\sim}{s}_z(i)$$

Heisenberg   Zeeman

In the end it's always a big matrix!



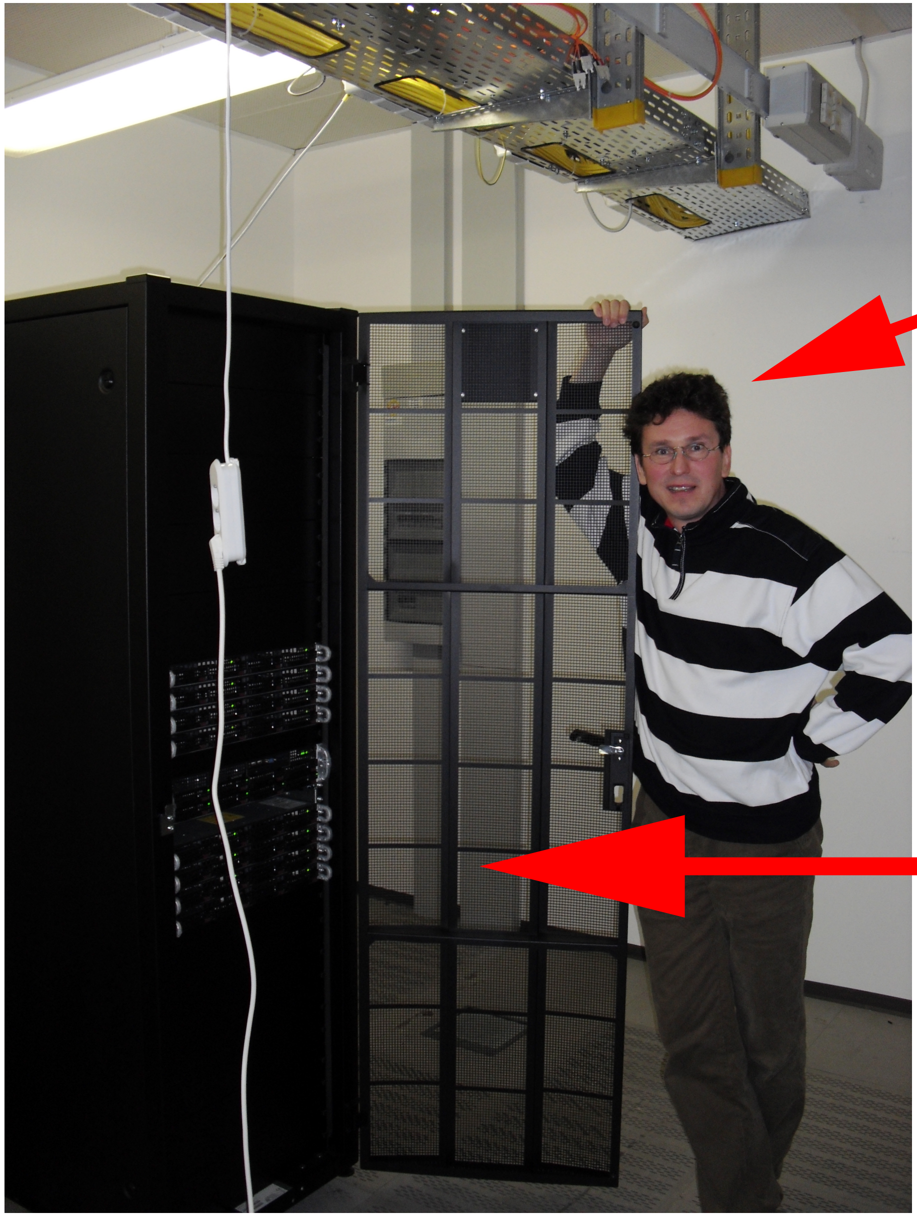
$$\Rightarrow \begin{pmatrix} -27.8 & 3.46 & 0.18 & \cdots \\ 3.46 & -2.35 & -1.7 & \cdots \\ 0.18 & -1.7 & 5.64 & \cdots \\ \vdots & \vdots & \vdots & \cdots \end{pmatrix} \Rightarrow$$



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

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

Thank God, we have computers

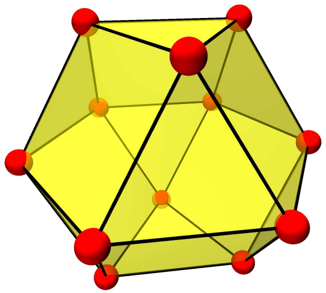


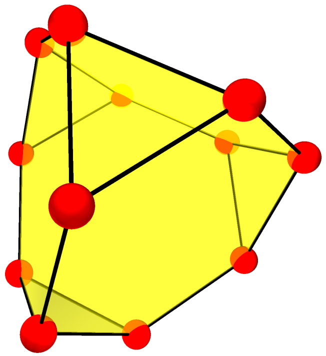
“cell professor”

128 cores, 384 GB RAM

. . . but that’s not enough!

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

$$\underset{\sim}{H}_{\text{Heisenberg}} = -2 \sum_{i<j} J_{ij}\, \underset{\sim}{\vec{s}}_i \cdot \underset{\sim}{\vec{s}}_j$$

$$= 2\sqrt{3} \sum_{i<j} J_{ij}\, \underset{\sim}{T}^{(0)}(\{k_i\}, \{\bar{k}_i\} | k_i = k_j = 1)$$

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 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.

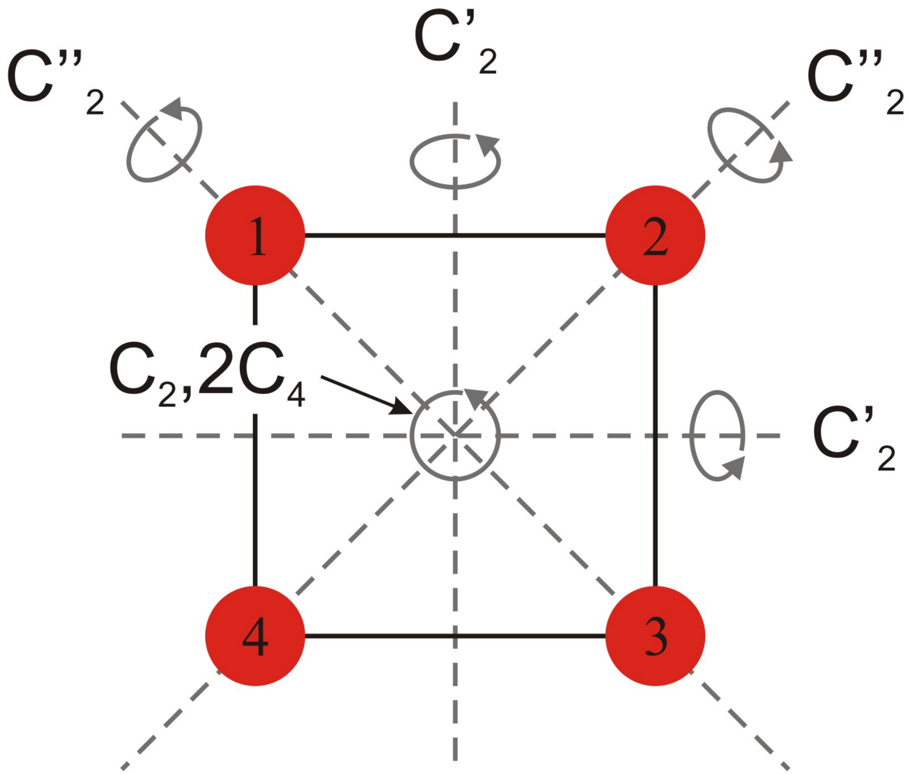
(1) M. Tinkham, *Group Theory and Quantum Mechanics*, Dover.
(2) D. Gatteschi and L. Pardi, Gazz. Chim. Ital. **123**, 231 (1993).
(3) O. Waldmann, Phys. Rev. B **61**, 6138 (2000).
(4) R. Schnalle and J. Schnack, Int. Rev. Phys. Chem. **29**, 403-452 (2010).

Point Group Symmetry II

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

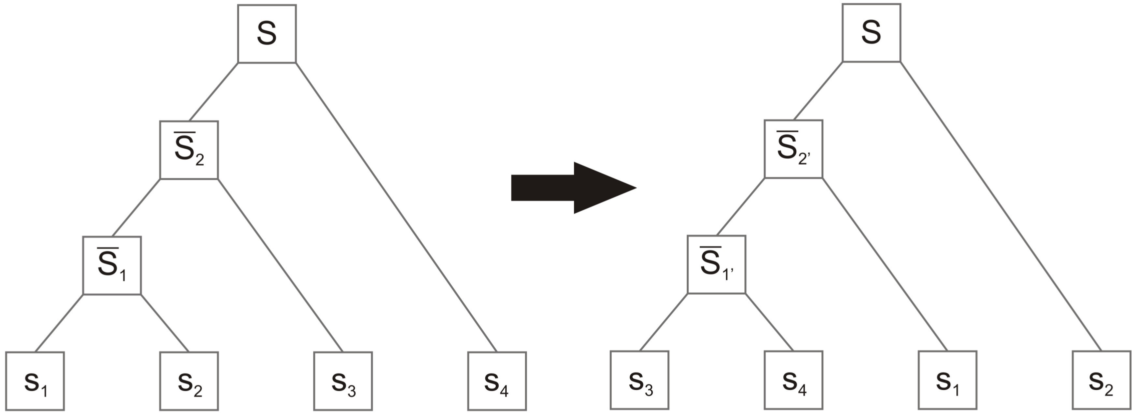
- Serious problem: application of $\underset{\sim}{G}(R)$, i.e. permutation of spins, leads to different coupling schemes: $a \Rightarrow b$;
- Solution: implementation of graph-theoretical results to evaluate recoupling coefficients ${}_a\langle\,\alpha'\,S\,M\,|\,\alpha\,S\,M\,\rangle_b$.

Point Group Symmetry III – example square



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

Point Group Symmetry IV – binary trees



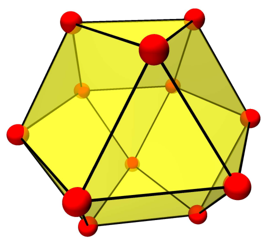
- Recoupling coefficient $\langle\, s_1 s_2 \overline{S}_1 s_3 \overline{S}_2 s_4 S M \mid s_3 s_4 \overline{S}_{1'} s_1 \overline{S}_{2'} s_2 S M \,\rangle$ can be evaluated by a graphical transformation of one binary tree into the other (1,2).

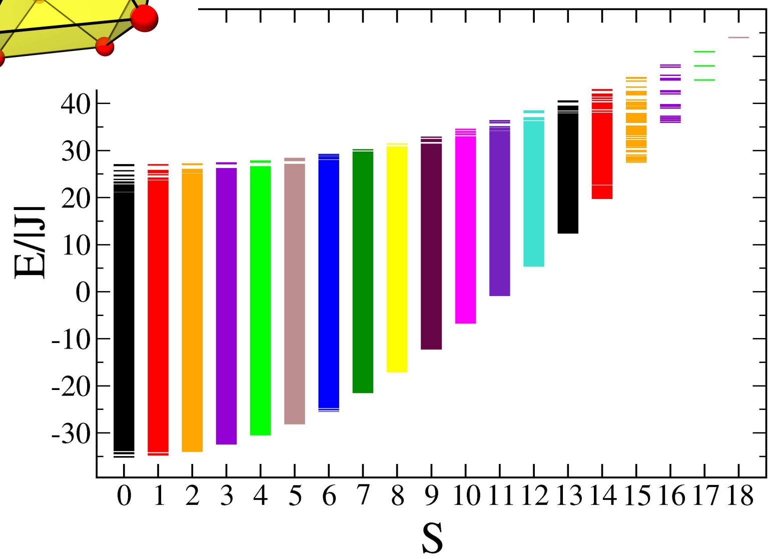
- Exchange and flop operations generate a recoupling formula consisting of square roots, Wigner-6J symbols, and sums over intermediate spins.

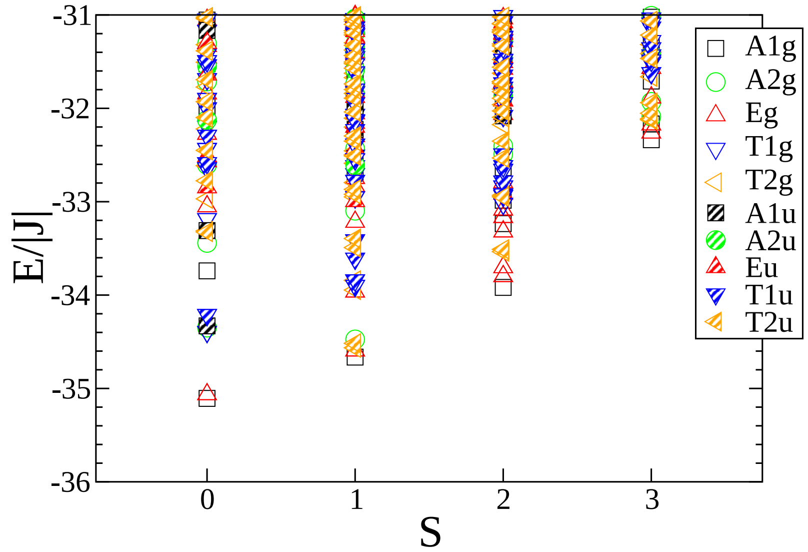
- Open question: optimal coupling for a given symmetry? (3)

(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 I: Cuboctahedron

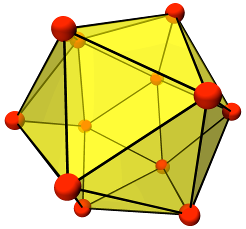




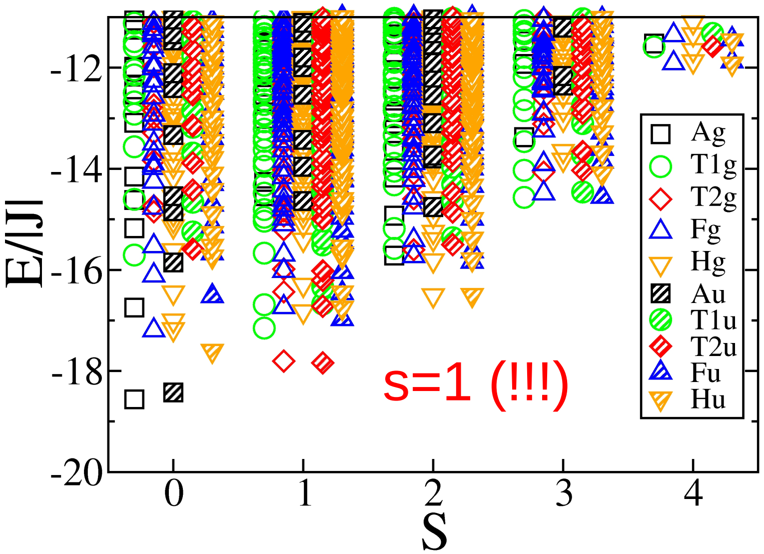


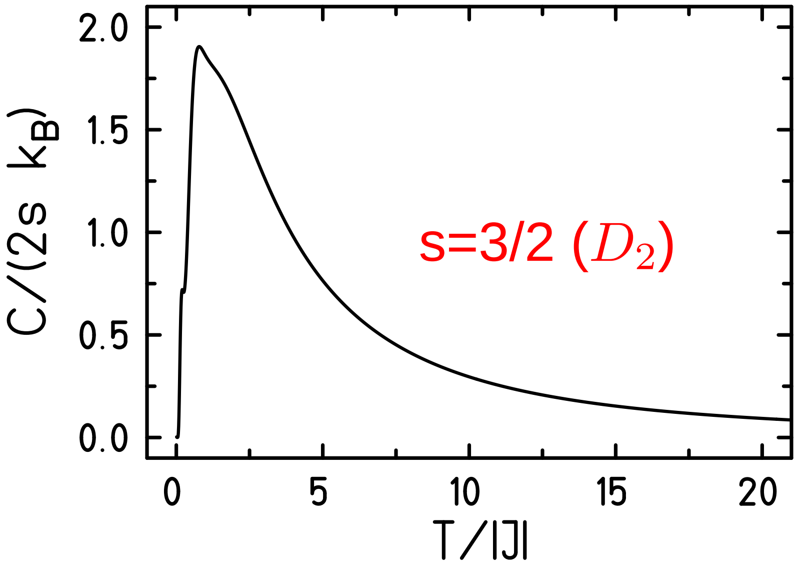
Cuboctahedron, $s = 3/2$, Hilbert space dimension 16,777,216; symmetry O_h (1).
Evaluation of recoupling coefficients very time consuming (1,2).

(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

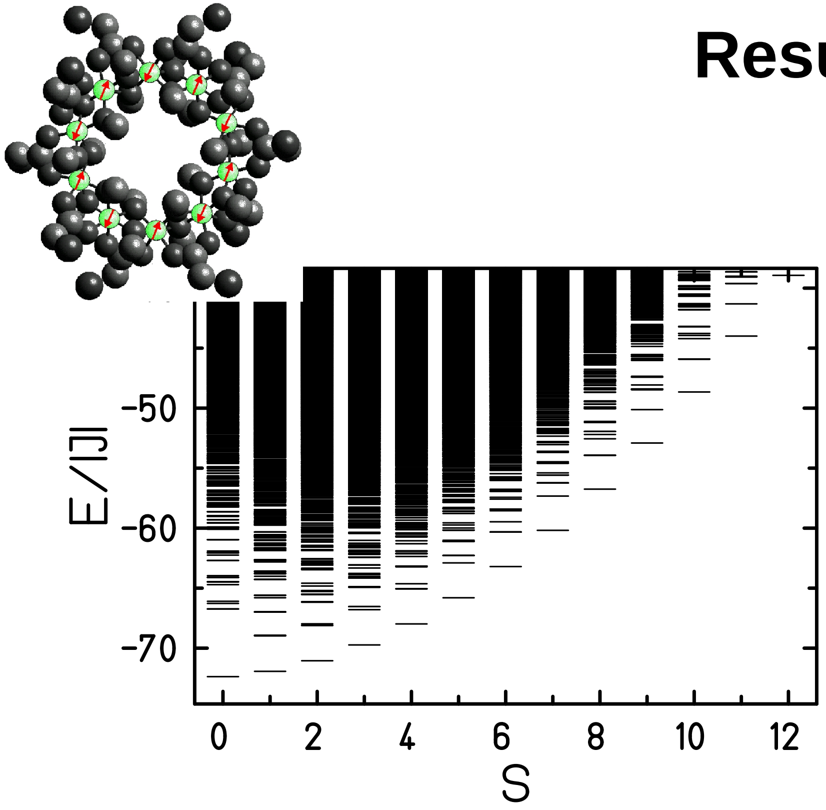


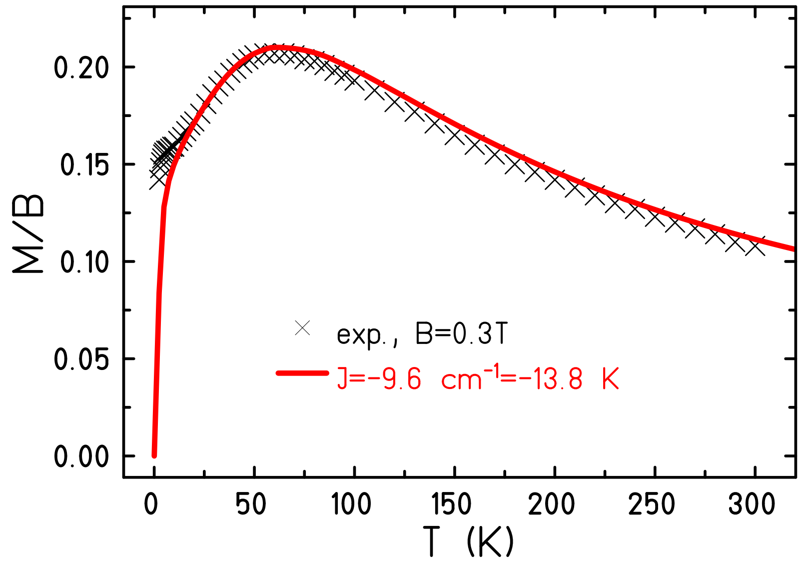


Icosahedron, $s = 3/2$, Hilbert space dimension 16,777,216; symmetry I_h;
Evaluation of recoupling coefficients for $s = 3/2$ in I_h **practically impossible** (1).

(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!

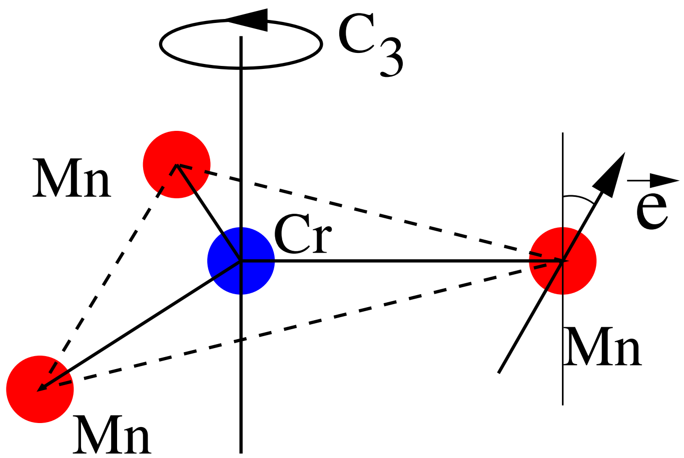
Anisotropic magnetic molecules I – Theory

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

- $\left[\underset{\sim}{H},\underset{\sim}{\vec{S}}^2\right] \neq 0$, $\left[\underset{\sim}{H},\underset{\sim}{S}_z\right] \neq 0$;
- 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: $30,000 < \dim(\mathcal{H}) < 140,000$

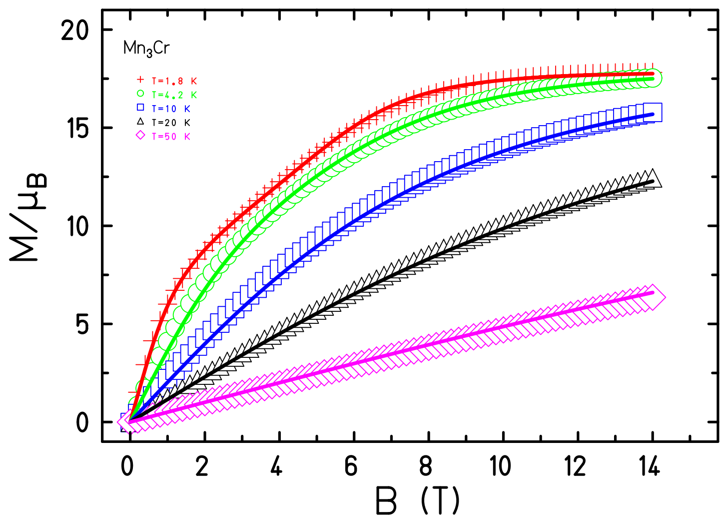
T. Glaser *et al.* *et* J. Schnack, Inorg. Chem. **48**, 607 (2009).

Anisotropic magnetic molecules II – Example



What can be achieved? 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}.
- ab initio calculations needed.



Further Reading

Further Reading

- Dalton Transactions, 2010, Issue 20, themed issue on molecular magnets
- CONDENSED MATTER PHYSICS, 2009, vol. 12, No. 3, special issue on spin systems
- Coordination Chemistry Reviews, 2009, Volume 253, Issues 19-20, DFG Molecular Magnetism Research Report
- Molecular Cluster Magnets (World Scientific Series in Nanoscience and Nanotechnology), Richard Winpenny (editor)
- Molecular Nanomagnets: (Mesoscopic Physics and Nanotechnology), Dante Gatteschi, Roberta Sessoli, Jacques Villain, Oxford University Press

Thank you very much for your attention.

Molecular Magnetism Web

www.molmag.de

Highlights. Tutorials. Who is who. Conferences.