Magnetism in zero dimensions – physics of magnetic molecules

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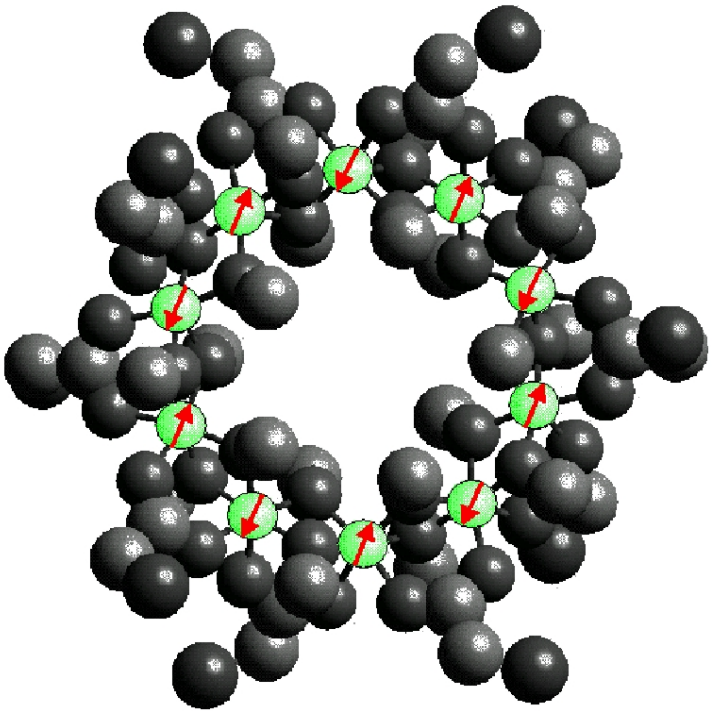
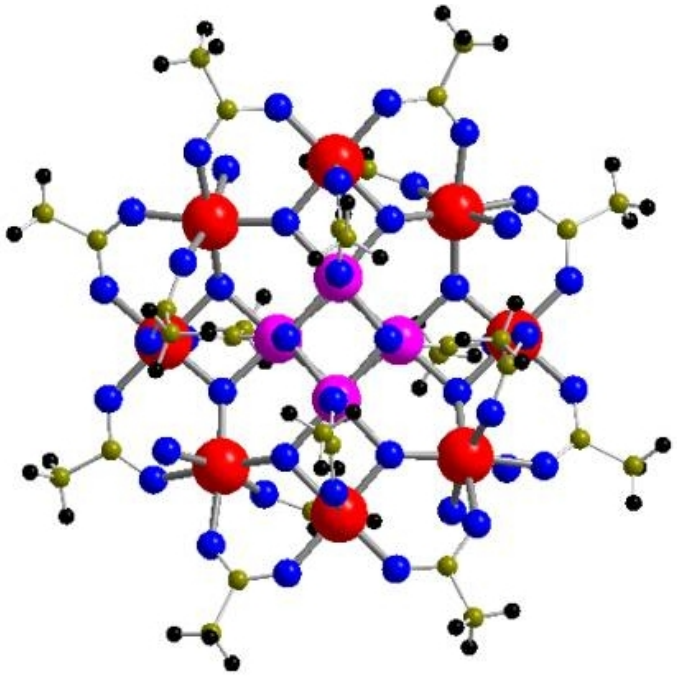
Contents for you today



Fe_{10}

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

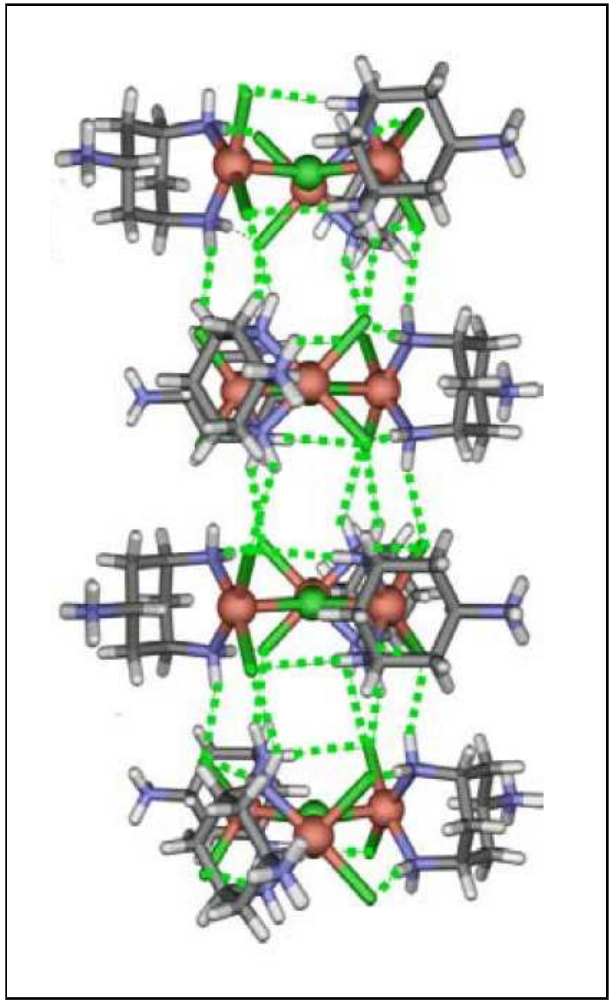
The beauty of magnetic molecules I



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

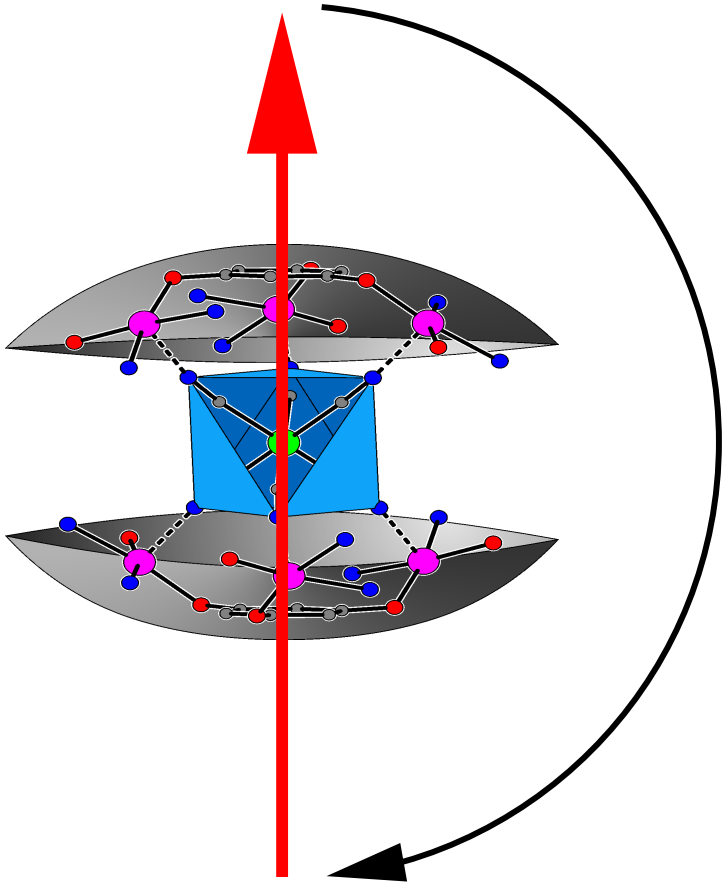


- Dimers (Fe_2), tetrahedra (Cr_4), cubes (Cr_8);
- Rings, especially iron and chromium rings
- Complex structures (Mn_{12}) – drosophila of molecular magnetism;
- “Soccer balls”, more precisely icosidodecahedra (Fe_{30}) and other macro molecules;
- Chain like and planar structures of interlinked magnetic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

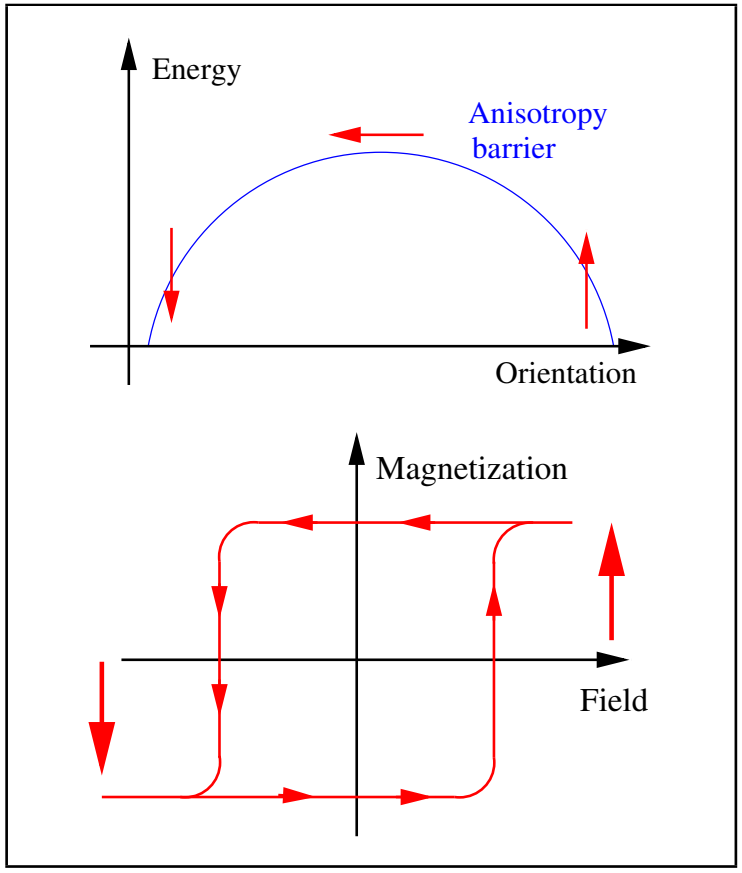
Single Molecule Magnets

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



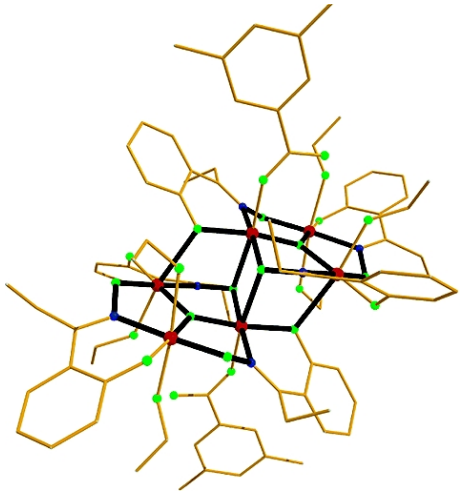
- Single Molecule Magnets (SMM): large ground state moment; anisotropy barrier dominates at low T.

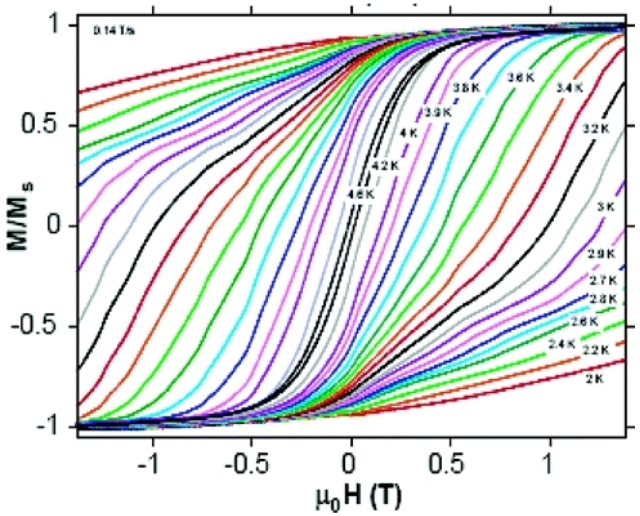
$$\underset{\sim}{H} \approx DS_z^2$$

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

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

Single Molecule Magnets III





$[Mn_6^{III}O_2(Et\text{-}sao)_6(O_2CPh(Me_2))_2(EtOH)_6]$:

- $S = 12$ 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)

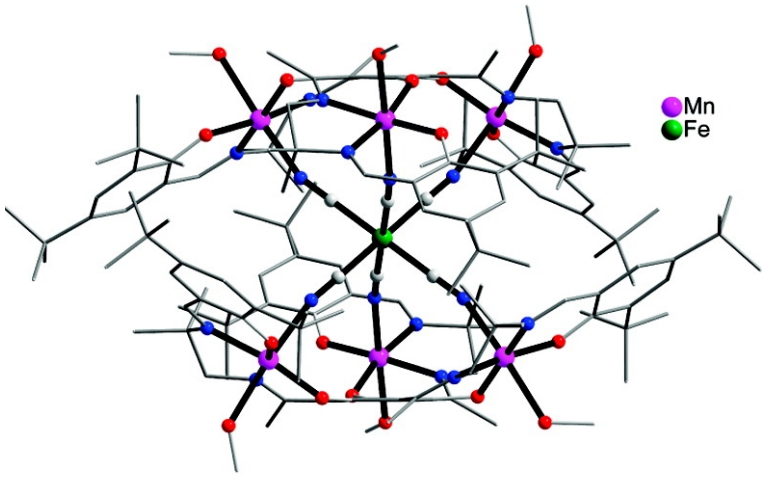
- "...the widely considered design rule to increase S is not as efficient as suggested by $\underset{\sim}{H} = DS^2$,...the increase is on the order of unity and not S^2."(2)

- "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



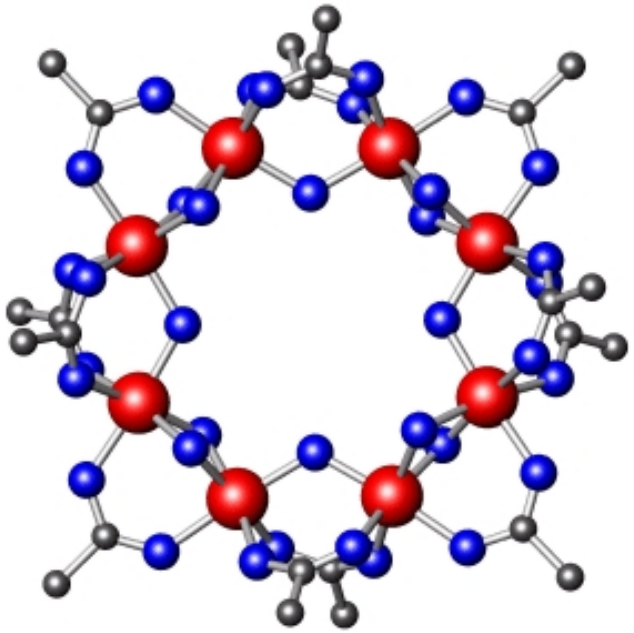
Rational design of strict C_3 symmetry:

- Idea of Thorsten Glaser:
  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

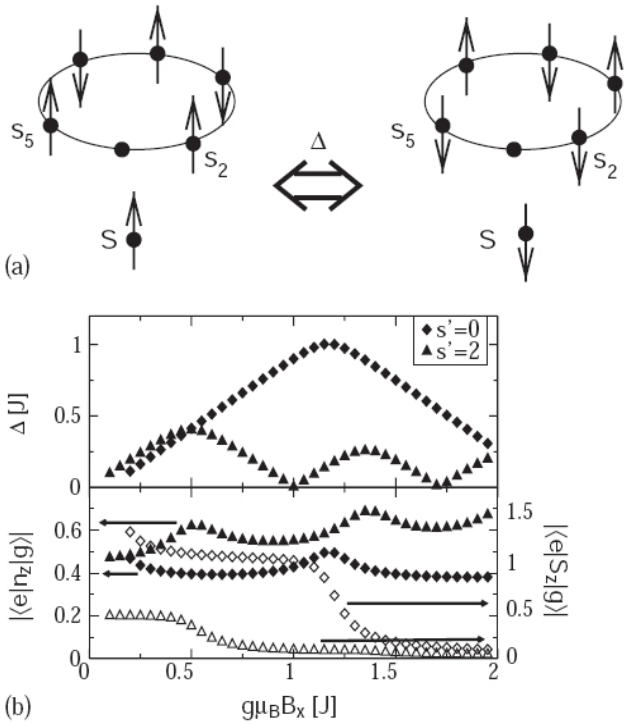
Antiferromagnetic Molecules I – Rings



- To date: many AF rings synthesized, e.g. Fe_6, Fe_{10}, Fe_{12}, ..., Cr_8, ...(1)
- 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 – Trend A



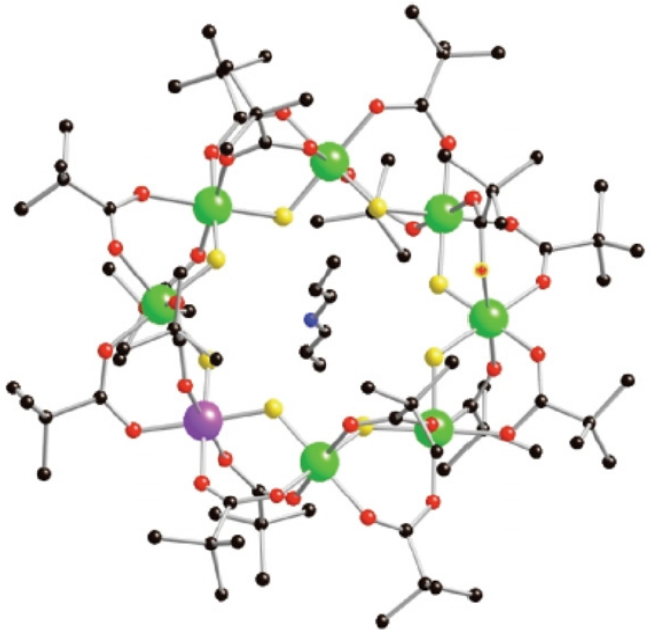
from (4)

Investigation of spin dynamics and coherent tunnelling

- Tunneling of the Neel vector at low lemperatures (1,2,3);
- Not very practical, no easy observable, since $S = 0$;
- Tunneling in doped af rings (4).

(1) O. Waldmann, Europhys. Lett. **60**, 302 (2002).
(2) A. Honecker, F. Meier, D. Loss, and B. Normand, Eur. Phys. J. B **27**, 487 (2002).
(3) F. Meier and D. Loss, Phys. Rev. Lett. **86**, 5373 (2001).
(4) F. Meier and D. Loss, Physica B **329-333**, 1140 (2003).

Antiferromagnetic Molecules III – Trend B



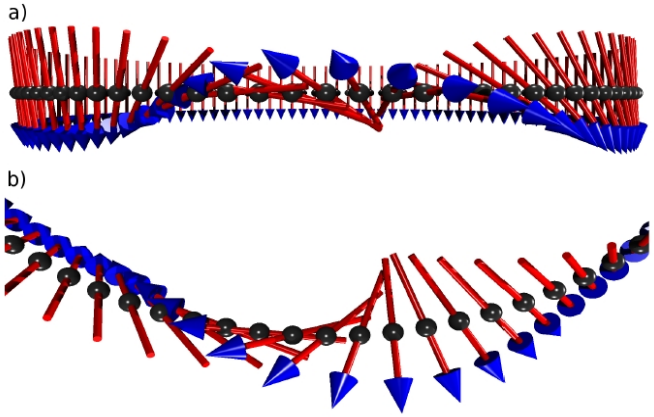
Cr_7Ni by Timco

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);
- Coupling of heterometallic rings for quantum computing (3).

(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 (2009), accepted.

Antiferromagnetic Molecules IV – Trend C



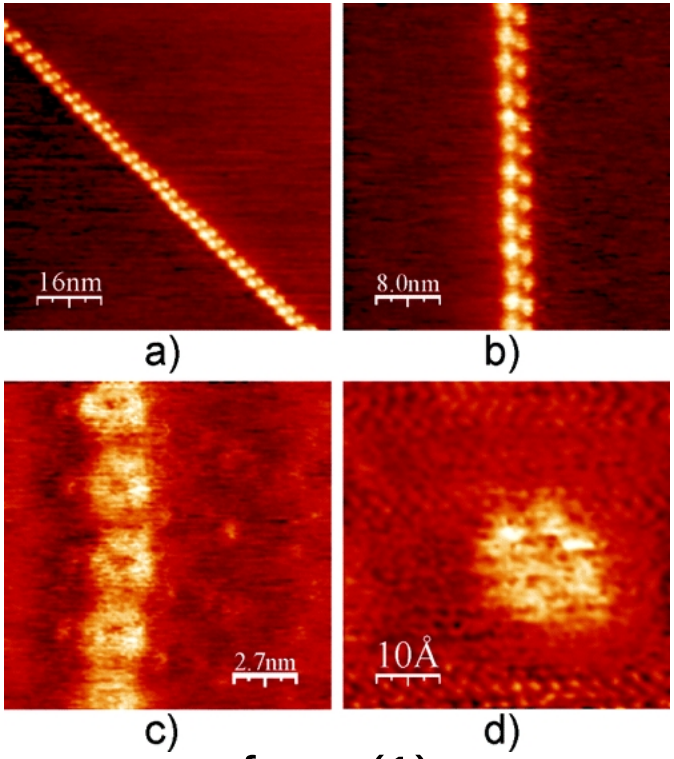
Soliton dynamics

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

(1) H.-J. Schmidt, C. Schröder, and M. Luban, cond-mat/0801.4262.
(2) J. Schnack and P. Shchelokovskyy, J. Magn. Magn. Mater. **306**, 79 (2006).

Molecules on Surfaces

Molecules on Surfaces I



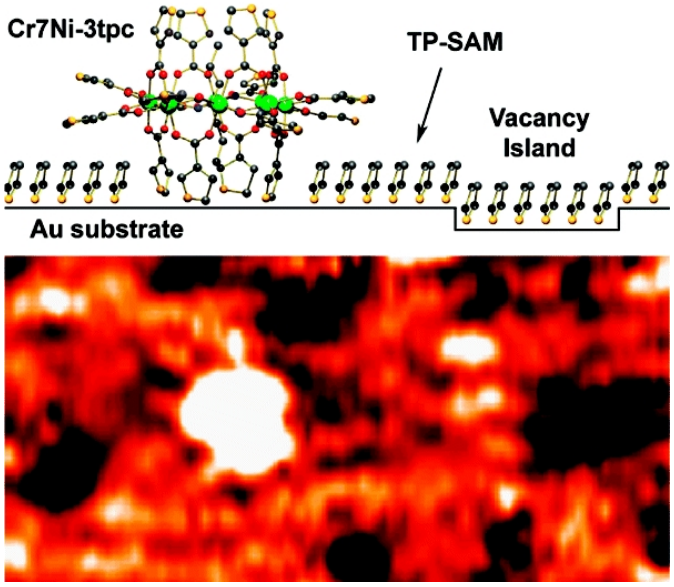
from (1)

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



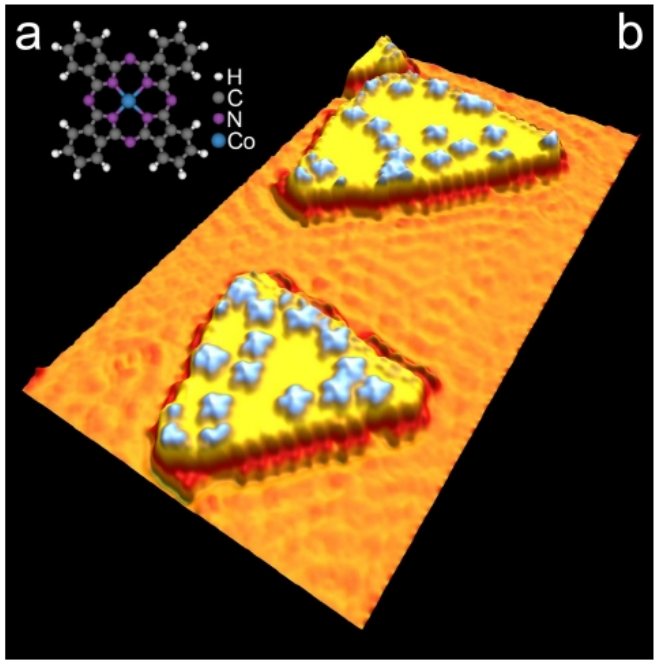
from (1)

Rings on surfaces

- 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). (2006).

Molecules on Surfaces III



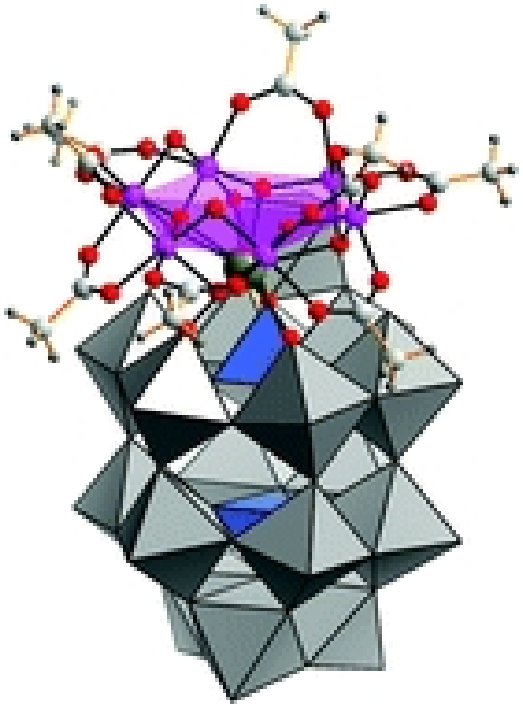
from (1)

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.*, Physical Review Letters **101**, 116602 (2008).

Molecules on Surfaces IV



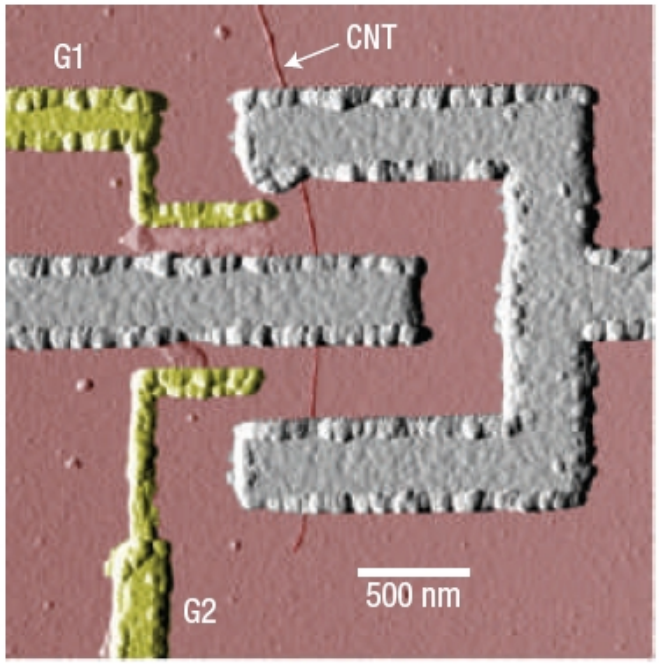
from (1)

“Backslash”on molecule

- How much of the deposited molecule survives?
- Study of a Mn_6 cluster grafted on a Polyoxometalate (POM) (1);
- Intra-molecular interactions change compared to free molecule (1).

(1) Xikui Fang and P. Kögerler, Chem. Commun. 3396 (2008).

Molecules on Surfaces V



from (1)

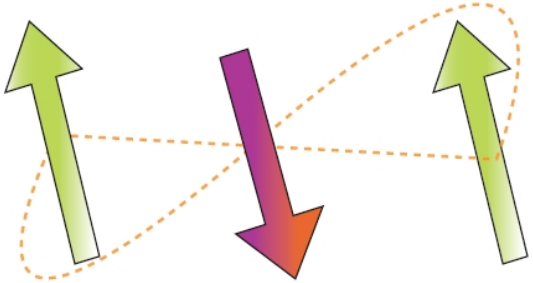
Carbon nanotube squid

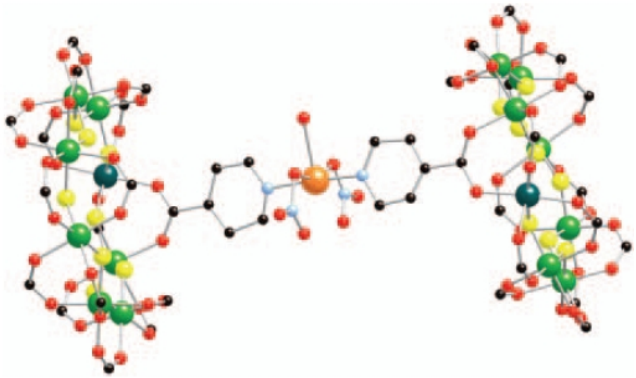
- Use of single-walled carbon nanotube (CNT) Josephson junctions;
- Discrete quantum dot (QD) energy level structure controlled by gates (1);
- CNT-SQUIDs sensitive local magnetometers to study the magnetization reversal of individual magnetic particles (1).

(1) J. P. Cleuziou *et al.*, Nature Nanotechnology **1**, 53 (2006).

Coherence Phenomena

Coherence Phenomena I





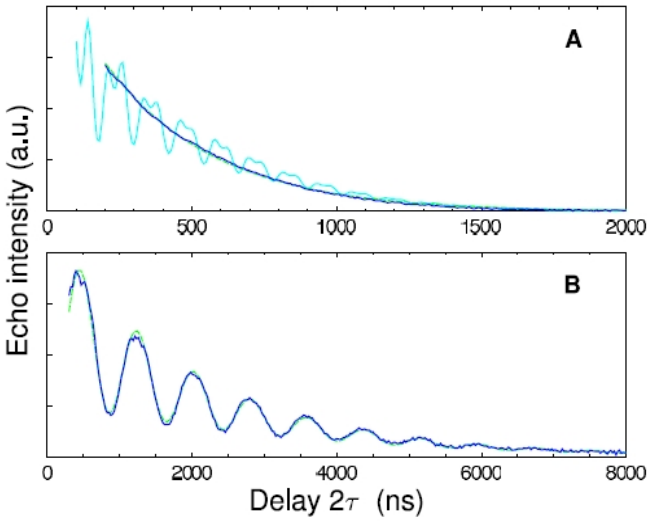
from (1)

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;
- 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).

Up to date theory modeling

Model Hamiltonian (spin only)

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

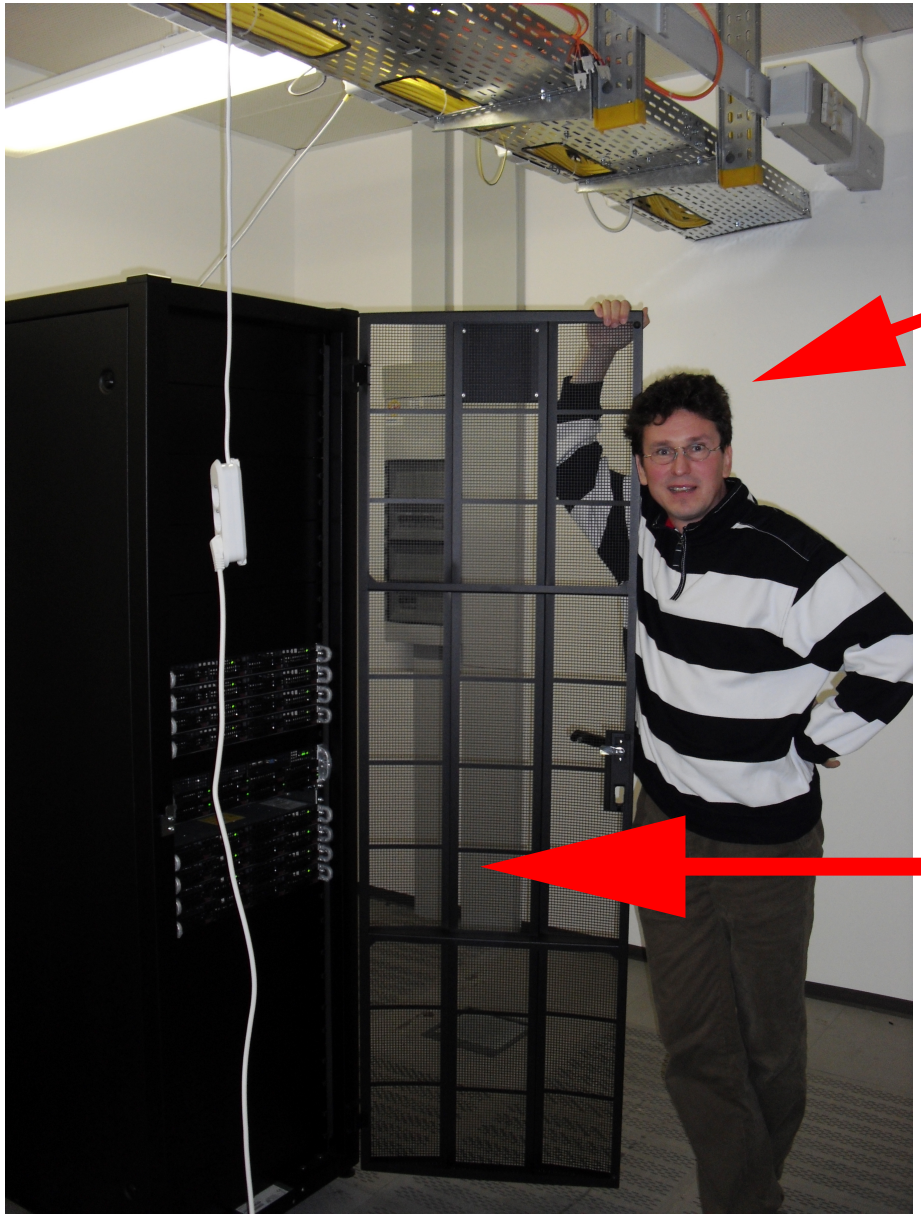
Exchange/Anisotropy — Dzyaloshinskii-Moriya — Zeeman

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

Thank God, we have computers

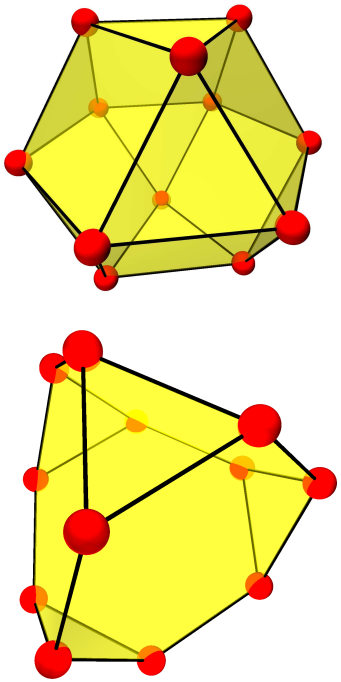


“cell professor”

128 cores, 384 GB RAM

. . . but that’s not enough!

Advanced ITO & Point Groups I



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, MAGPACK (1);
- Additional point group symmetries (2).

(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).

Reminder ITO

$$\underset{\sim}{H}_{\text{Heisenberg}} = \sqrt{3} \sum_{i,j} J_{ij} \, \underset{\sim}{T}^{(0)}(\{k_i\}, \{\overline{k}_i\} | k_i = k_j = 1)$$

Irreducible Tensor Operator approach

- Express spin operators and functions thereof as ITOs;
- Use vector coupling basis $|\, \alpha \; S \; M \,\rangle$ and recursive recoupling;
- Numerical implementation e.g. MAGPACK.

(1) Gatteschi, Tsukerblat, Coronado, Waldmann, ...
(2) R. Schnalle, Ph.D. thesis, Osnabrück University (2009)

Advanced ITO & Point Groups II

$$\mathcal{P}^{(n)} \mid \alpha\, S\, M \,\rangle = \left(\frac{l_n}{h} \sum_R \left(\chi^{(n)}(R) \right)^* \underset{\sim}{G}(R) \right) \mid \alpha\, S\, M \,\rangle$$

Point Group Symmetry

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

(1) O. Waldmann, Phys. Rev. B **61**, 6138 (2000).
(2) R. Schnalle, Ph.D. thesis, Osnabrück University (2009)

Advanced ITO & Point Groups III

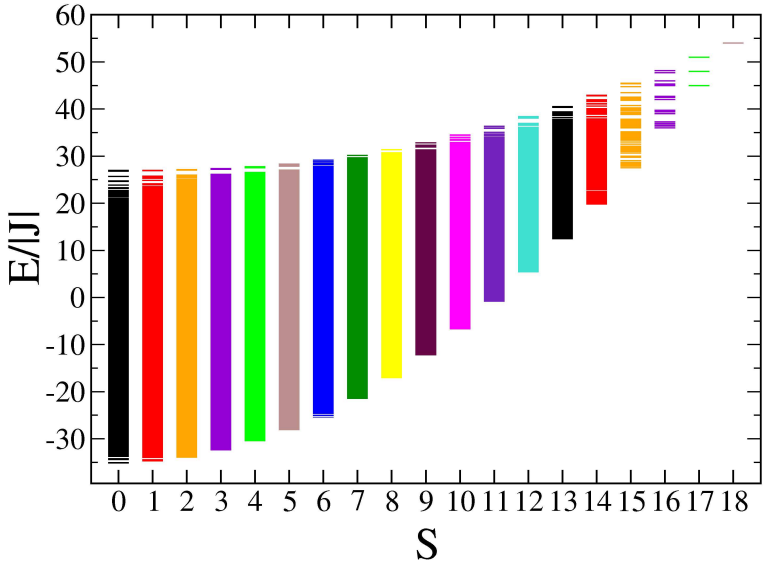
$$\underset{\sim}{G}(R)\,|\,\alpha\,S\,M\,\rangle_a = \sum_{\alpha'}\,|\,\alpha'\,S\,M\,\rangle_a\;{}_a\langle\,\alpha'\,S\,M\,|\,\alpha\,S\,M\,\rangle_b$$

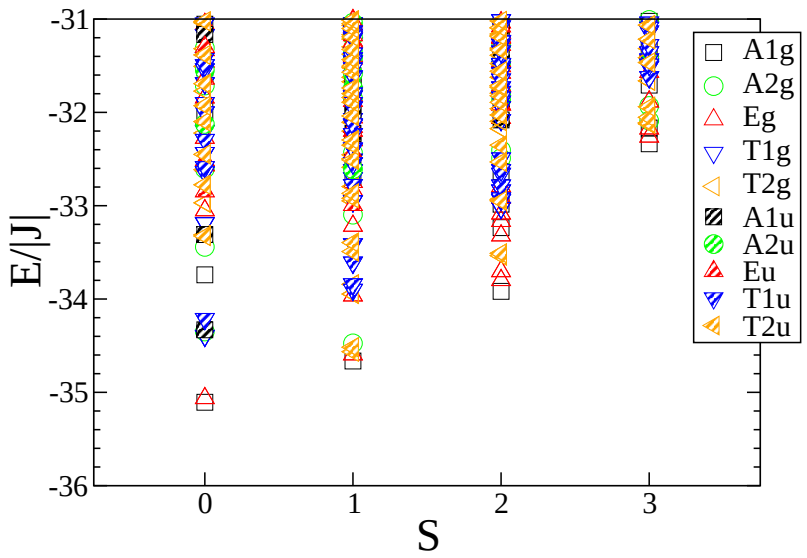
Serious problem: Recoupling

- So far: only point groups that are compatible with the coupling scheme are used (1);
- Problem: otherwise complicated basis transformation between different coupling schemes;
- Solution: implementation of graph-theoretical results to evaluate recoupling coefficients ${}_a\langle\,\alpha'\,S\,M\,|\,\alpha\,S\,M\,\rangle_b$ (2).

(1) O. Waldmann, Phys. Rev. B **61**, 6138 (2000).
(2) R. Schnalle, Ph.D. thesis, Osnabrück University (2009)

Advanced ITO & Point Groups IV





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).

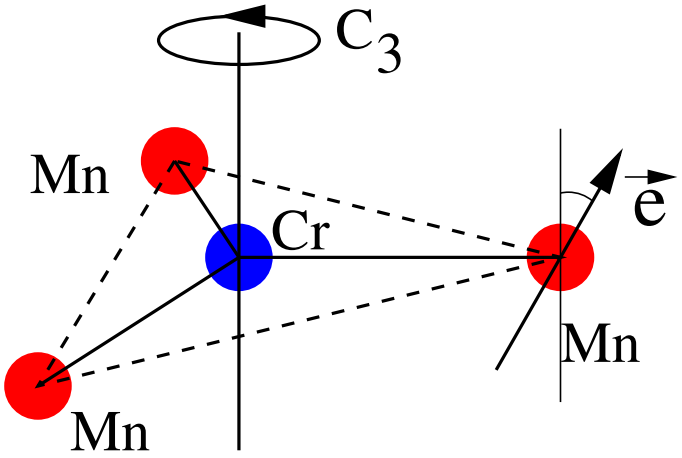
Anisotropic magnetic molecules I – Theory

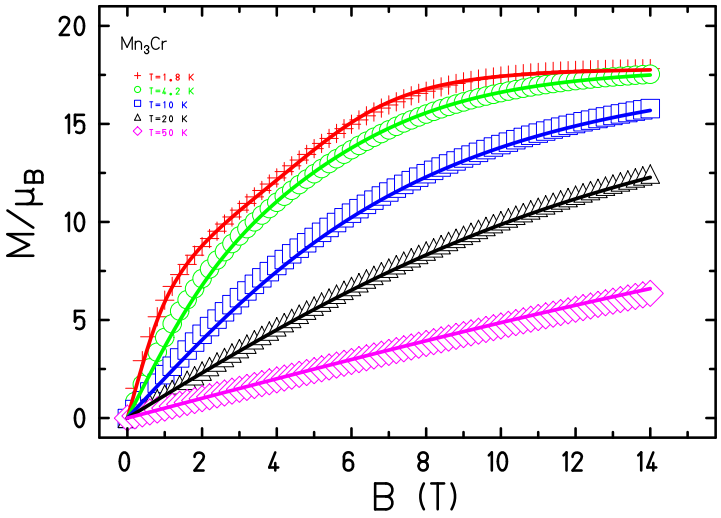
$$\underset{\sim}{H}(\vec{B}) \quad = \quad -\sum_{i,j} J_{ij}\, \vec{\underset{\sim}{s}}(i) \cdot \vec{\underset{\sim}{s}}(j) \quad + \sum_{i} d_i \left(\vec{e}_i \cdot \vec{\underset{\sim}{s}}(i)\right)^2 + \quad \mu_B\, \vec{B} \cdot \sum_{i}^{N} \mathbf{g}_i \cdot \vec{\underset{\sim}{s}}(i)$$

- $\left[\underset{\sim}{H}, \vec{\underset{\sim}{S}}^2\right] \neq 0$, $\left[\underset{\sim}{H}, \vec{\underset{\sim}{S}}_z\right] \neq 0$;
- You have to diagonalize $\underset{\sim}{H}(\vec{B})$ for every field (direction and strength)!
  $\Rightarrow$ 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



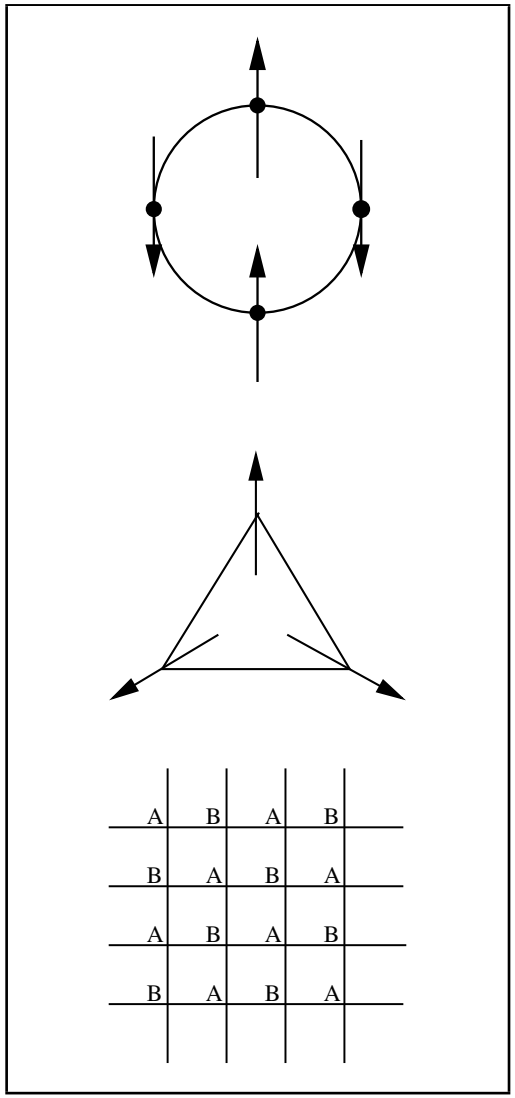


What can be achieved? Mn_3Cr:

- 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 $\phi = 120°$ 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: $J_1 = -0.29\ \text{cm}^{-1}$, $J_2 = -0.08\ \text{cm}^{-1}$, $d_{\text{Mn}} = -1.21\ \text{cm}^{-1}$, $\vartheta_{\text{Mn}} = 22°$, $d_{\text{Cr}} = +0.17\ \text{cm}^{-1}$.
- ab initio calculations needed.

Frustration effects

Definition of frustration

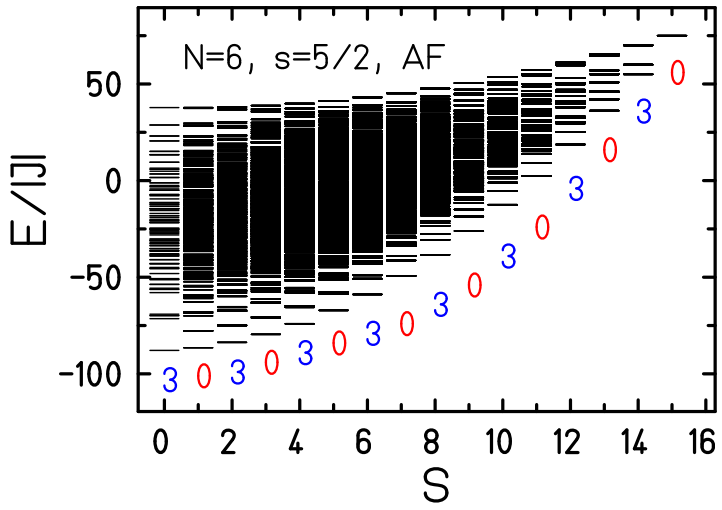


- Simple: An antiferromagnet is frustrated if in the ground state of the corresponding classical spin system not all interactions can be minimized simultaneously.

- Advanced: A non-bipartite antiferromagnet is frustrated. A bipartite spin system can be decomposed into two sublattices A and B such that for all exchange couplings:
  $J(x_A, y_B) \leq g^2$, $J(x_A, y_A) \geq g^2$, $J(x_B, y_B) \geq g^2$,
  cmp. (1,2).

(1) E.H. Lieb, T.D. Schultz, and D.C. Mattis, Ann. Phys. (N.Y.) **16**, 407 (1961)
(2) E.H. Lieb and D.C. Mattis, J. Math. Phys. **3**, 749 (1962)

Marshall-Peierls sign rule for even rings



- Expanding the ground state in $\mathcal{H}(M)$ in the product basis yields a sign rule for the coefficients

$$|\,\Psi_0\,\rangle = \sum_{\vec{m}} c(\vec{m})\;|\,\vec{m}\,\rangle \qquad \text{with} \sum_{i=1}^{N} m_i = M$$

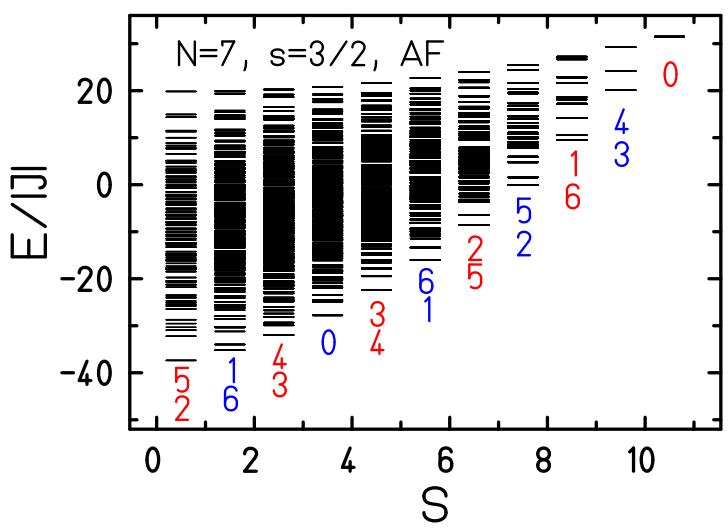
$$c(\vec{m}) = (-1)^{\left(\frac{Ns}{2} - \sum_{i=1}^{N/2} m_{2i}\right)} a(\vec{m})$$

All $a(\mathbf{m})$ are non-zero, real, and of equal sign.

- Yields eigenvalues for the shift operator $\underset{\sim}{T}$:
  $\exp\left\{-i\frac{2\pi k}{N}\right\}$ with $k \equiv a\,\frac{N}{2} \mod N\,, \quad a = Ns - M$

(1) W. Marshall, Proc. Royal. Soc. A (London) **232**, 48 (1955)

Numerical findings for odd rings



- 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):
  $k = \lfloor \frac{N+1}{4} \rfloor$ and $k = N - \lfloor \frac{N+1}{4} \rfloor$

- For the first excited state similar rules could be numerically established (3).

(1) K. Bärwinkel, H.-J. Schmidt, J. Schnack, J. Magn. Magn. Mater. **220**, 227 (2000)
(2) $\lfloor \cdot \rfloor$ largest integer, smaller or equal
(3) J. Schnack, Phys. Rev. B **62**, 14855 (2000)

k-rule for odd rings

- An extended k-rule can be inferred from our numerical investigations which yields the k quantum number for relative ground states of subspaces $\mathcal{H}(M)$ for even as well as odd spin rings, i.e. for all rings (1)

$$k \equiv \pm a \left\lceil \frac{N}{2} \right\rceil \mod N\,, \quad a = Ns - M$$

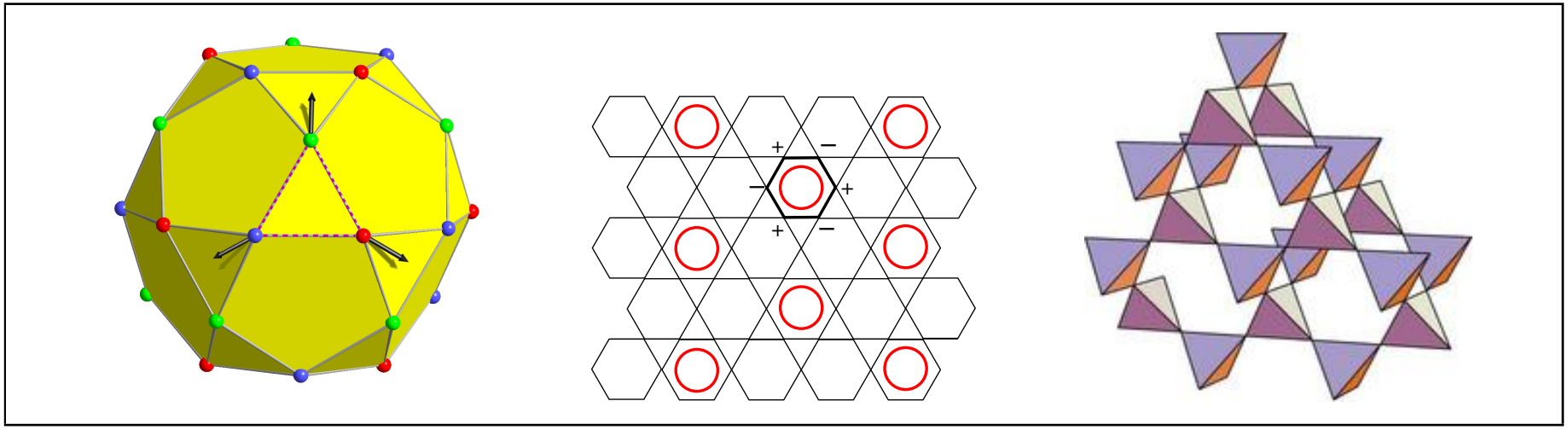
k is independent of s for a given N and a. The degeneracy is minimal ($N \neq 3$).

		a									
N	s	0	1	2	3	4	5	6	7	8	9
8	1/2	0	4	$8 \equiv 0$	$12 \equiv 4$	$16 \equiv 0$	-	-	-	-	-
9	1/2	0	$5 \equiv 4$	$10 \equiv 1$	$15 \equiv 3$	$20 \equiv 2$	-	-	-	-	-
9	1	0	$5 \equiv 4$	$10 \equiv 1$	$15 \equiv 3$	$20 \equiv 2$	$25 \equiv 2$	$30 \equiv 3$	$35 \equiv 1$	$40 \equiv 4$	$45 \equiv 0$

No general, but partial proof yet.

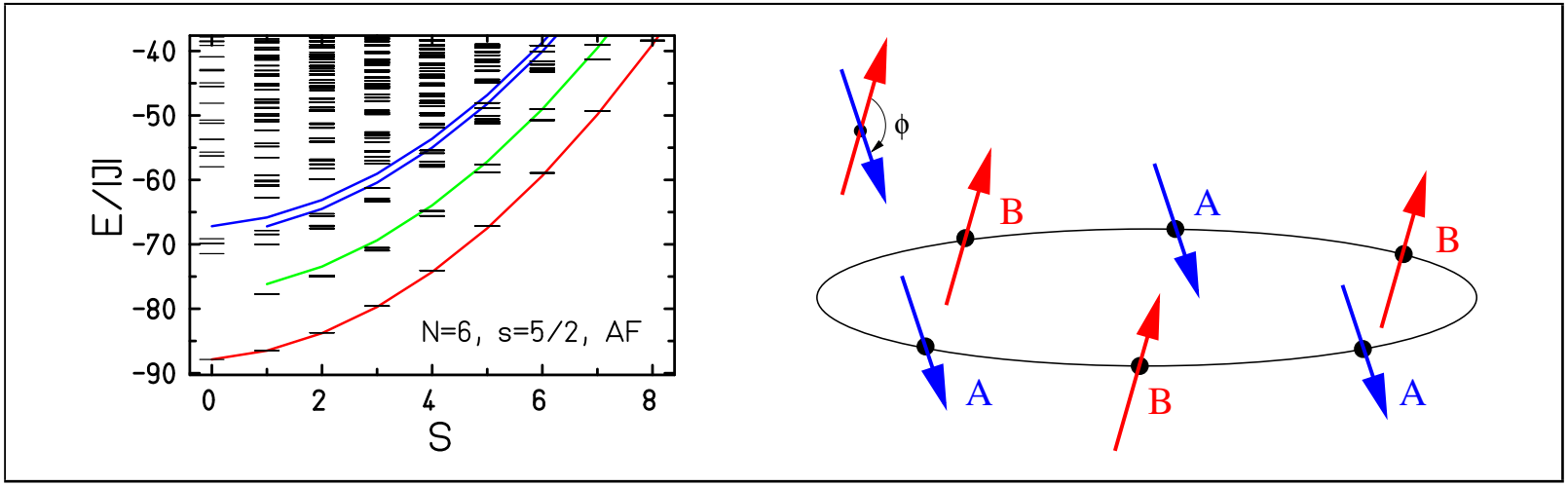
(1) K. Bärwinkel, P. Hage, H.-J. Schmidt, and J. Schnack, Phys. Rev. B **68**, 054422 (2003)

Fe_{30} and friends
Corner sharing triangles and tetrahedra



- Several frustrated antiferromagnets show an unusual magnetization behavior, e.g. plateaus and jumps.
- Example systems: icosidodecahedron, kagome lattice, pyrochlore lattice.

Rotational bands in non-frustrated antiferromagnets

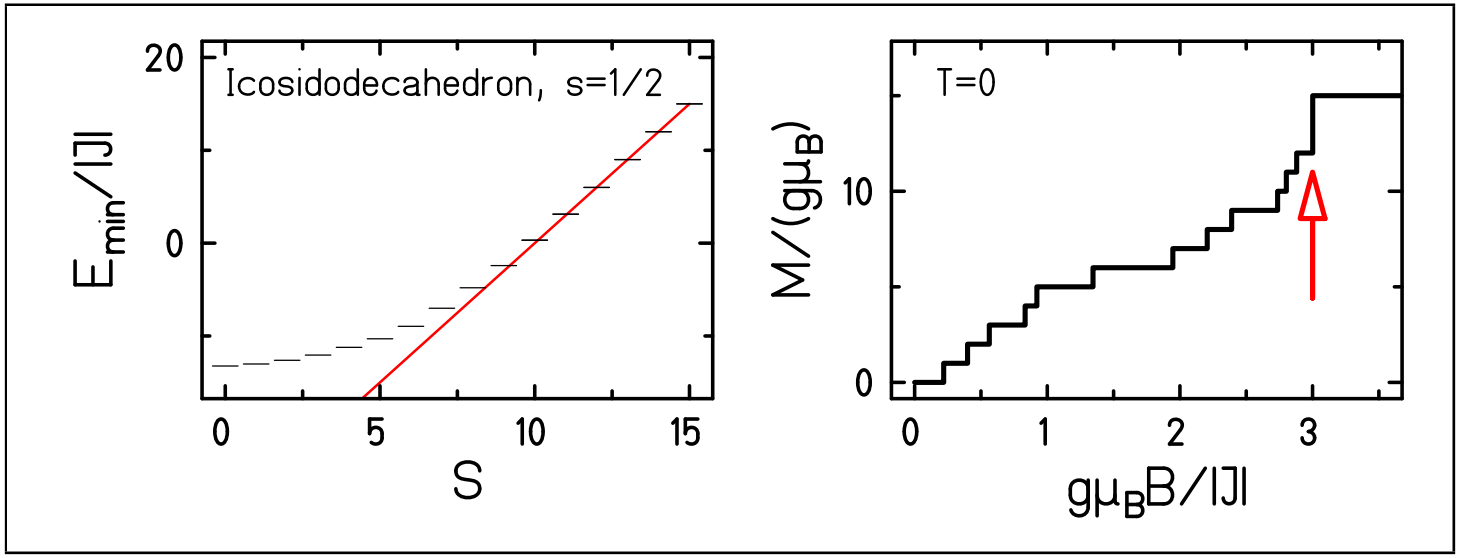


- Often minimal energies $E_{min}(S)$ form a rotational band: Landé interval rule (1);
- For bipartite systems (2,3): $\underset{\sim}{H}^{\text{eff}} = -2\, J_{\text{eff}}\, \underset{\sim}{\vec{S}}_A \cdot \underset{\sim}{\vec{S}}_B$;
- Lowest band – rotation of Néel vector, second band – spin wave excitations (4).

(1) A. Caneschi *et al.*, Chem. Eur. J. **2**, 1379 (1996), G. L. Abbati *et al.*, Inorg. Chim. Acta **297**, 291 (2000)
(2) J. Schnack and M. Luban, Phys. Rev. B **63**, 014418 (2001)
(3) O. Waldmann, Phys. Rev. B **65**, 024424 (2002)
(4) P.W. Anderson, Phys. Rev. B **86**, 694 (1952), O. Waldmann *et al.*, Phys. Rev. Lett. **91**, 237202 (2003).

Giant magnetization jumps in frustrated antiferromagnets I

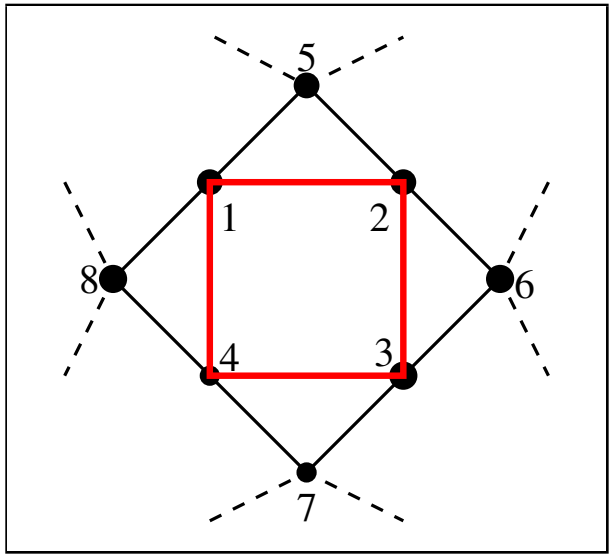
$\{Mo_{72}Fe_{30}\}$



- Close look: $E_{\text{min}}(S)$ linear in S for high S instead of being quadratic (1);
- Heisenberg model: property depends only on the structure but not on s (2);
- Alternative formulation: independent localized magnons (3);

(1) J. Schnack, H.-J. Schmidt, J. Richter, J. Schulenburg, Eur. Phys. J. B **24**, 475 (2001)
(2) H.-J. Schmidt, J. Phys. A: Math. Gen. **35**, 6545 (2002)
(3) J. Schulenburg, A. Honecker, J. Schnack, J. Richter, H.-J. Schmidt, Phys. Rev. Lett. **88**, 167207 (2002)

Giant magnetization jumps in frustrated antiferromagnets II
Localized Magnons

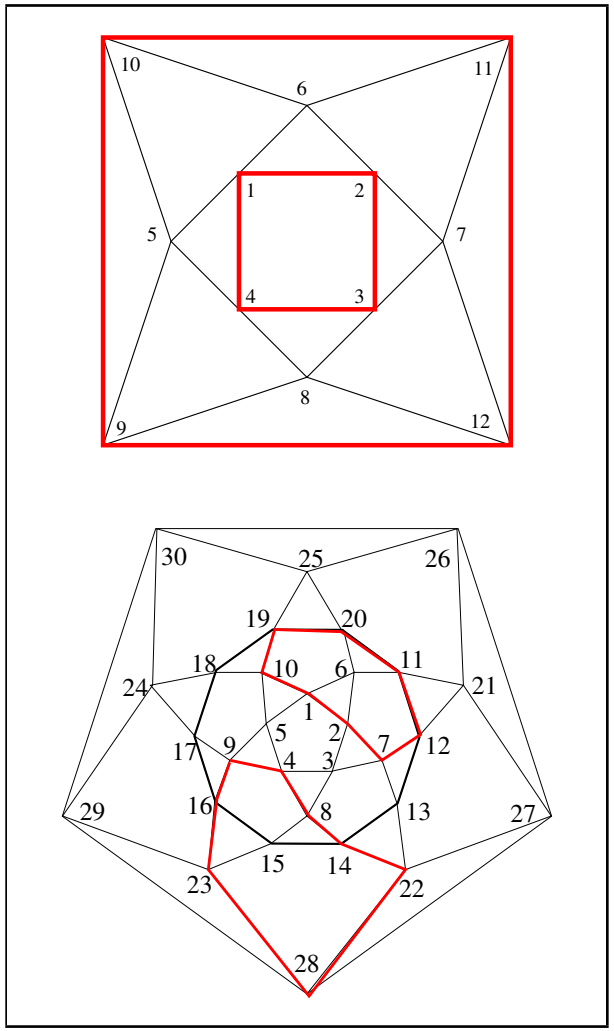


- $|\,\text{localized magnon}\,\rangle = \frac{1}{2}\left(|\,1\,\rangle - |\,2\,\rangle + |\,3\,\rangle - |\,4\,\rangle\right)$
- $|\,1\,\rangle = \underset{\sim}{s}^{-}(1)\,|\uparrow\uparrow\uparrow\ \ldots\rangle$ etc.
- $\underset{\sim}{H}\,|\,\text{localized magnon}\,\rangle \propto |\,\text{localized magnon}\,\rangle$
- Localized magnon is state of lowest energy (1,2).

- Triangles trap the localized magnon, amplitudes cancel at outer vertices.

(1) J. Schnack, H.-J. Schmidt, J. Richter, J. Schulenburg, Eur. Phys. J. B **24**, 475 (2001)
(2) H.-J. Schmidt, J. Phys. A: Math. Gen. **35**, 6545 (2002)

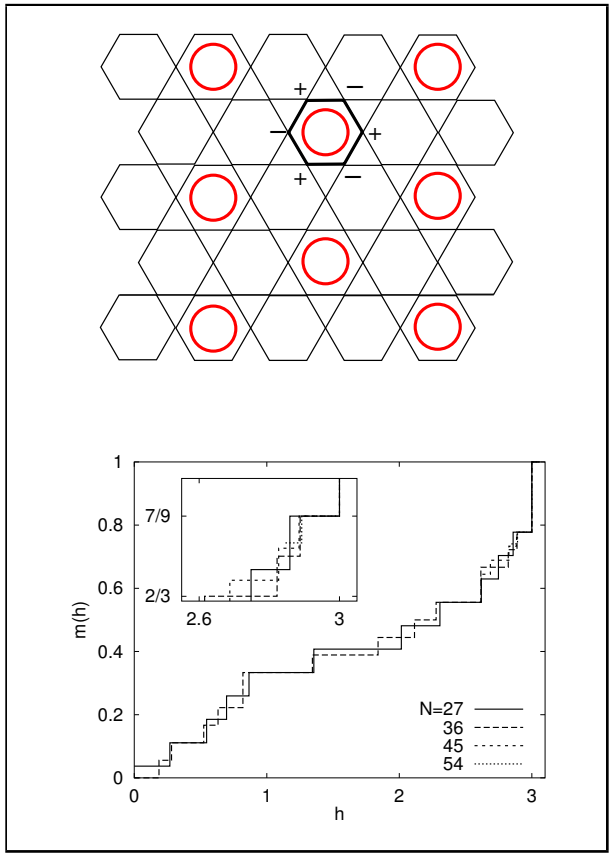
Giant magnetization jumps in frustrated antiferromagnets III



- Non-interacting one-magnon states can be placed on various molecules, e. g. 2 on the cuboctahedron and 3 on the icosidodecahedron (3rd delocalized);
- Each state of n independent magnons is the ground state in the Hilbert subspace with $M = Ns - n$;
- Linear dependence of E_{min} on M $\Rightarrow$ $(T = 0)$ magnetization jump;
- A rare example of analytically known many-body states!

J. Schnack, H.-J. Schmidt, J. Richter, J. Schulenburg, Eur. Phys. J. B **24**, 475 (2001)

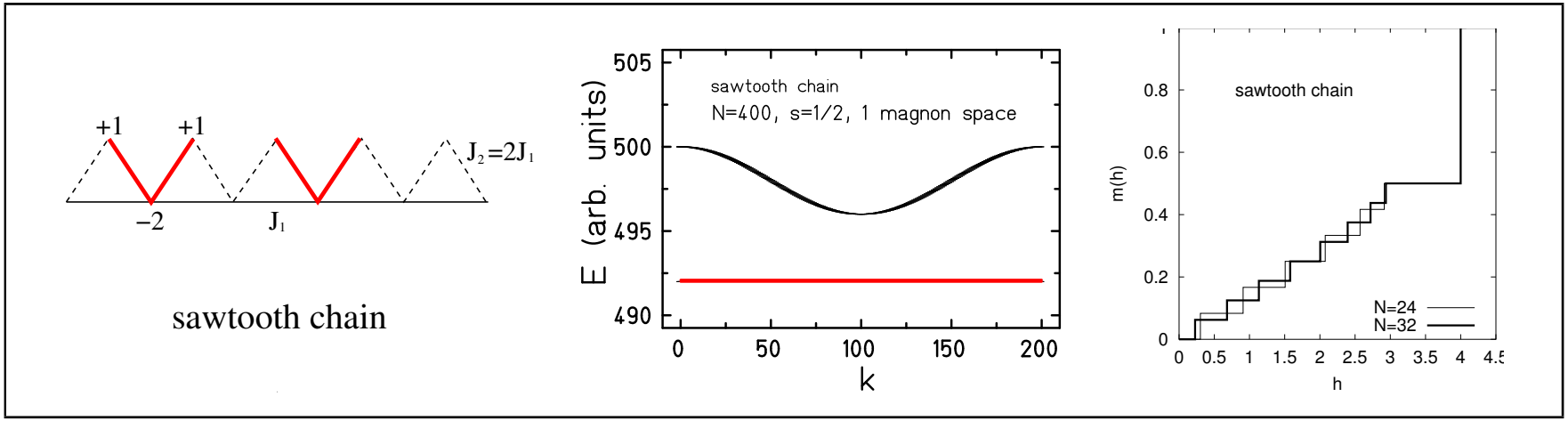
Giant magnetization jumps in frustrated antiferromagnets III
Kagome Lattice



- Non-interacting one-magnon states can be placed on various lattices, e. g. kagome or pyrochlore;
- Each state of n independent magnons is the ground state in the Hilbert subspace with $M = Ns - n$; Kagome: max. number of indep. magnons is N/9;
- Linear dependence of E_{min} on M $\Rightarrow$ $(T = 0)$ magnetization jump;
- Jump is a macroscopic quantum effect!
- A rare example of analytically known many-body states!

J. Schulenburg, A. Honecker, J. Schnack, J. Richter, H.-J. Schmidt, Phys. Rev. Lett. **88**, 167207 (2002)
J. Richter, J. Schulenburg, A. Honecker, J. Schnack, H.-J. Schmidt, J. Phys.: Condens. Matter **16**, S779 (2004)

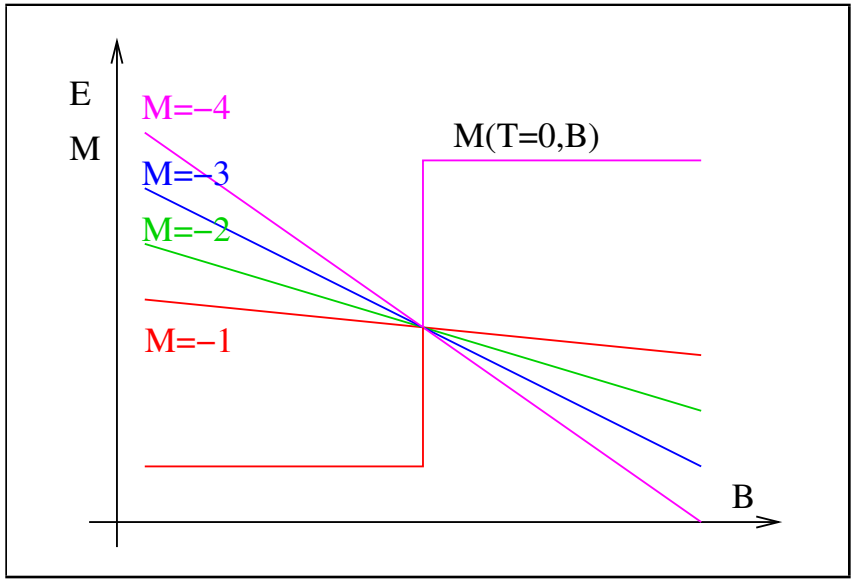
Condensed matter physics point of view: Flat band



- Flat band of minimal energy in one-magnon space; localized magnons can be built from delocalized states in the flat band.
- Entropy can be evaluated using hard-object models (1); universal low-temperature behavior.
- Same behavior for Hubbard model; flat band ferromagnetism (Tasaki & Mielke), jump of N with μ (2).

(1) H.-J. Schmidt, J. Richter, R. Moessner, J. Phys. A: Math. Gen. **39**, 10673 (2006)
(2) A. Honecker, J. Richter, Condens. Matter Phys. **8**, 813 (2005)

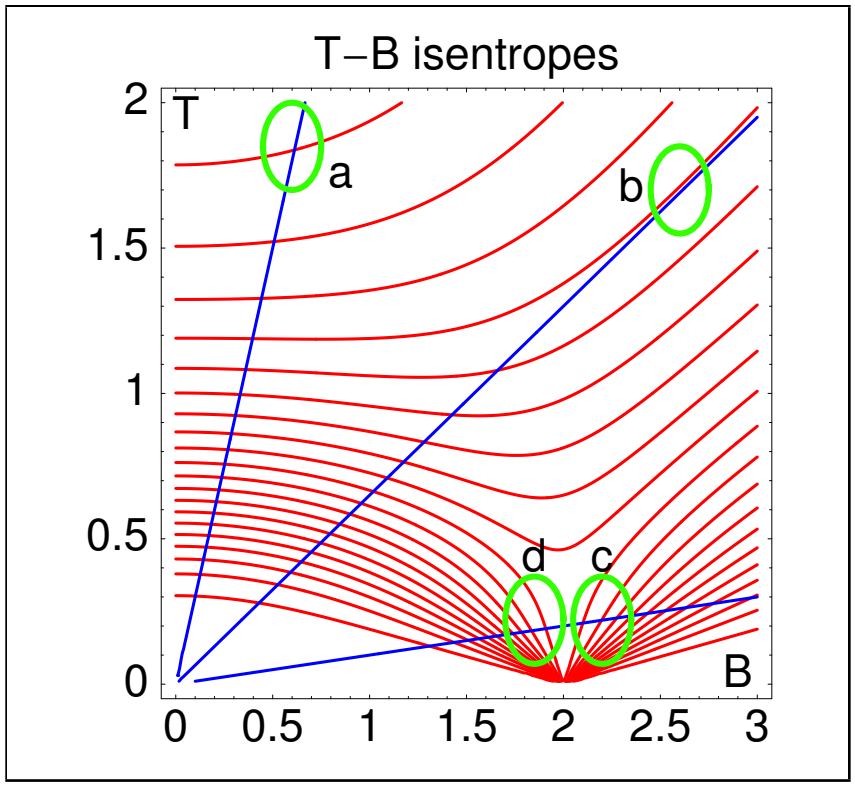
Magnetocaloric effect I
Giant jumps to saturation



- Many Zeeman levels cross at one and the same magnetic field.
- You know this for a giant spin at $B = 0$.
- High degeneracy of ground state levels $\Rightarrow$ large residual entropy at $T = 0$.
- $$\left(\frac{\partial T}{\partial B}\right)_S = -\frac{T}{C}\left(\frac{\partial S}{\partial B}\right)_T$$

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).

Magnetocaloric effect II
Isentrops of af $s = 1/2$ dimer



blue lines: ideal paramagnet, red curves: af dimer

Magnetocaloric effect:

(a) reduced,

(b) the same,

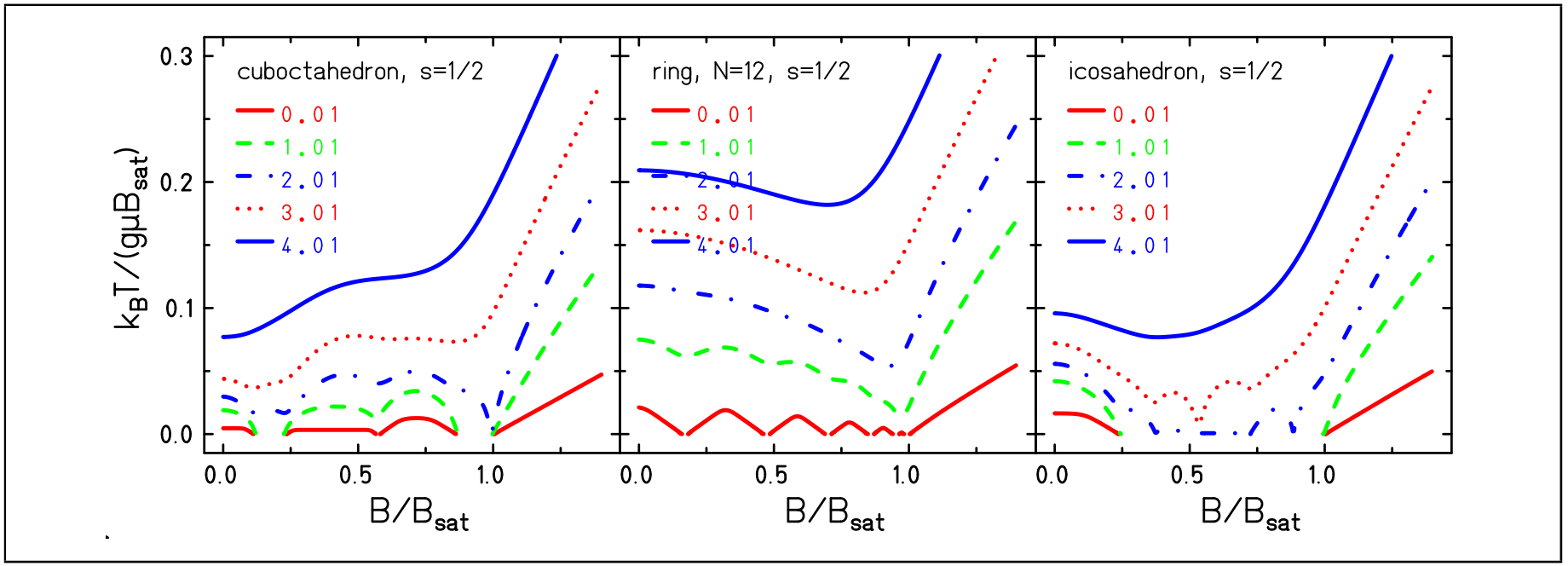
(c) enhanced,

(d) opposite

when compared to an ideal paramagnet.

Case (d) does not occur for a paramagnet.

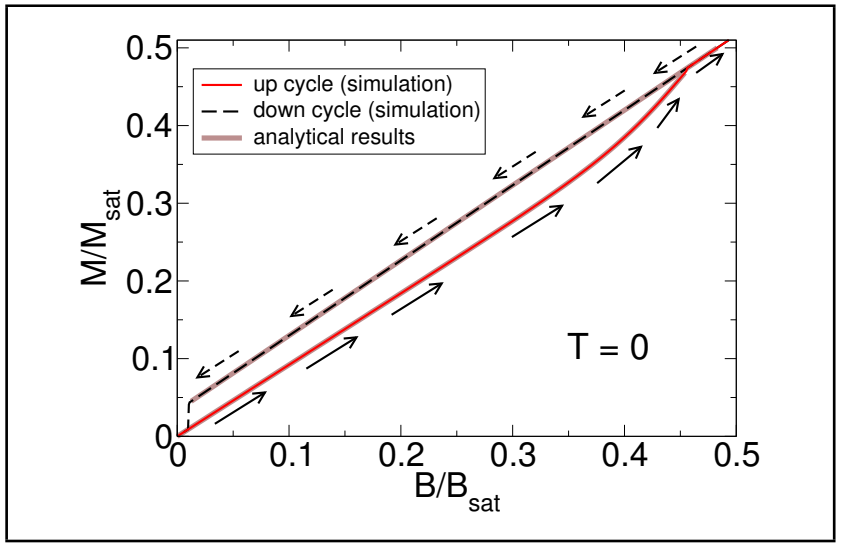
Magnetocaloric effect III – Molecular systems



- Cuboctahedron: high cooling rate due to independent magnons;
- Ring: normal level crossing, normal jump;
- Icosahedron: unusual behavior due to edge-sharing triangles, high degeneracies all over the spectrum; high cooling rate.

J. Schnack, R. Schmidt, J. Richter, Phys. Rev. B **76**, 054413 (2007)

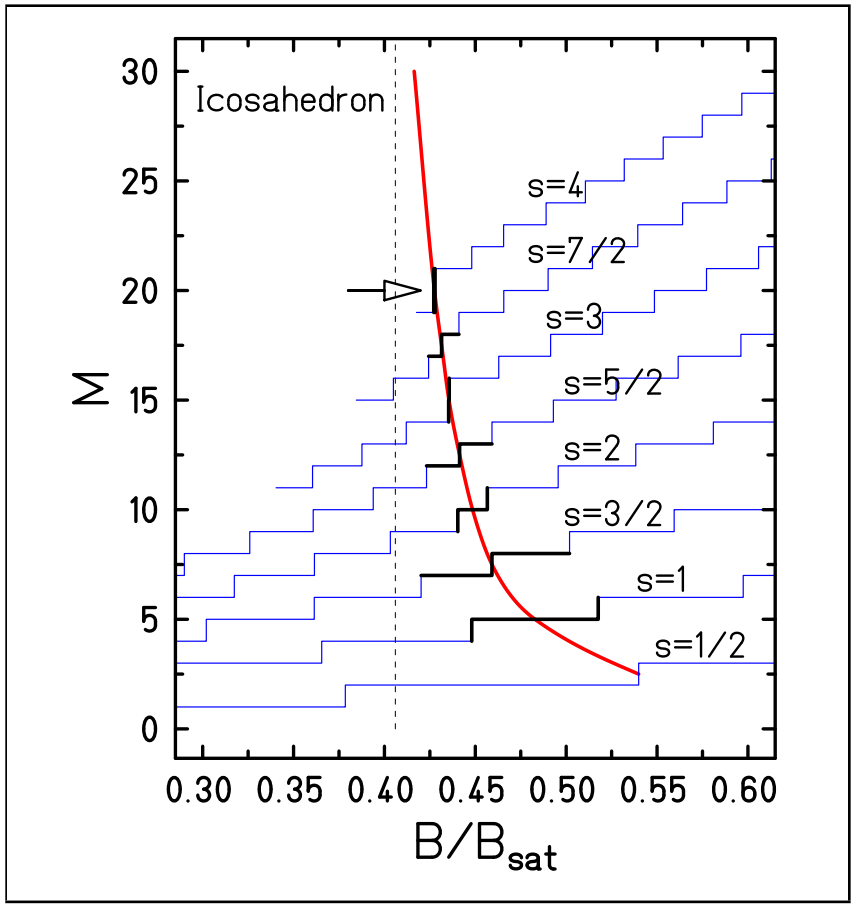
Metamagnetic phase transition I
Hysteresis without anisotropy



- 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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