

# Magnetism in zero dimensions – physics of magnetic molecules

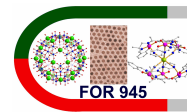
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Colloquium, Dresden Technical University

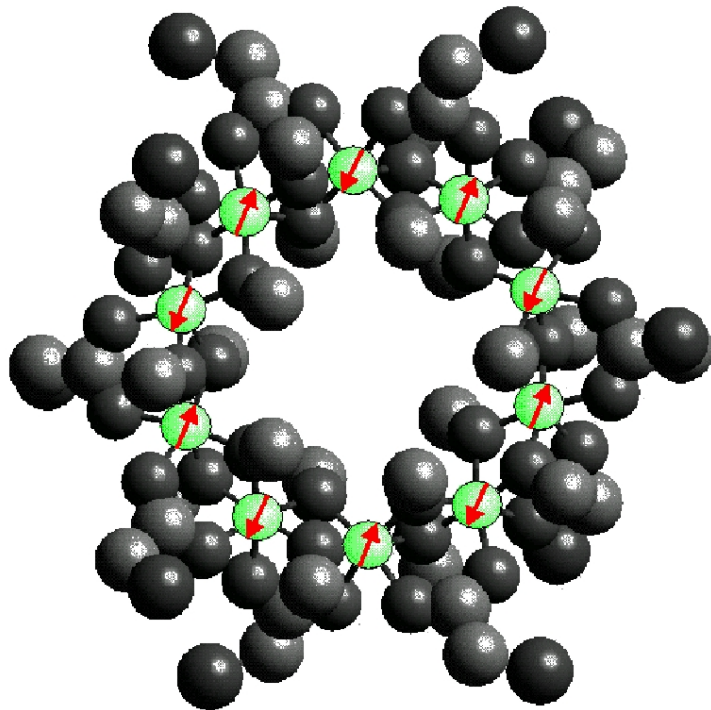
Dresden, January 6, 2010



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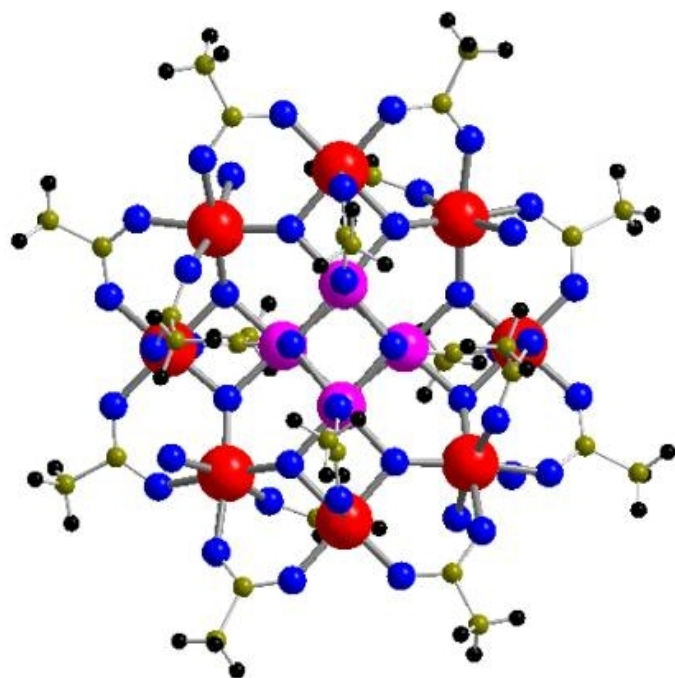
# Contents for you today



$\text{Fe}_{10}$

1. Single Molecule Magnets
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6. Frustration effects

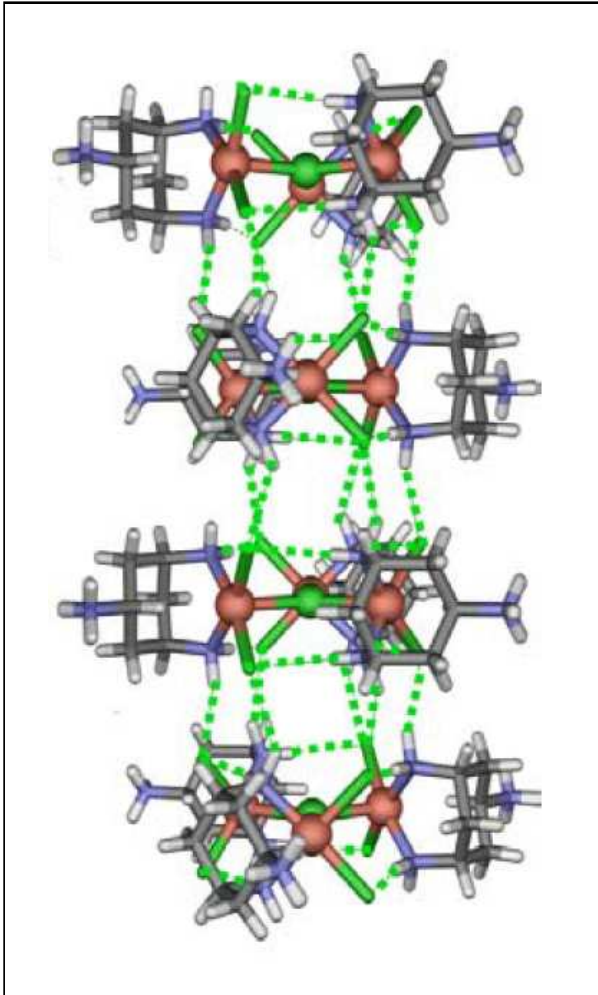
# The beauty of magnetic molecules I



Mn<sub>12</sub>

- 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

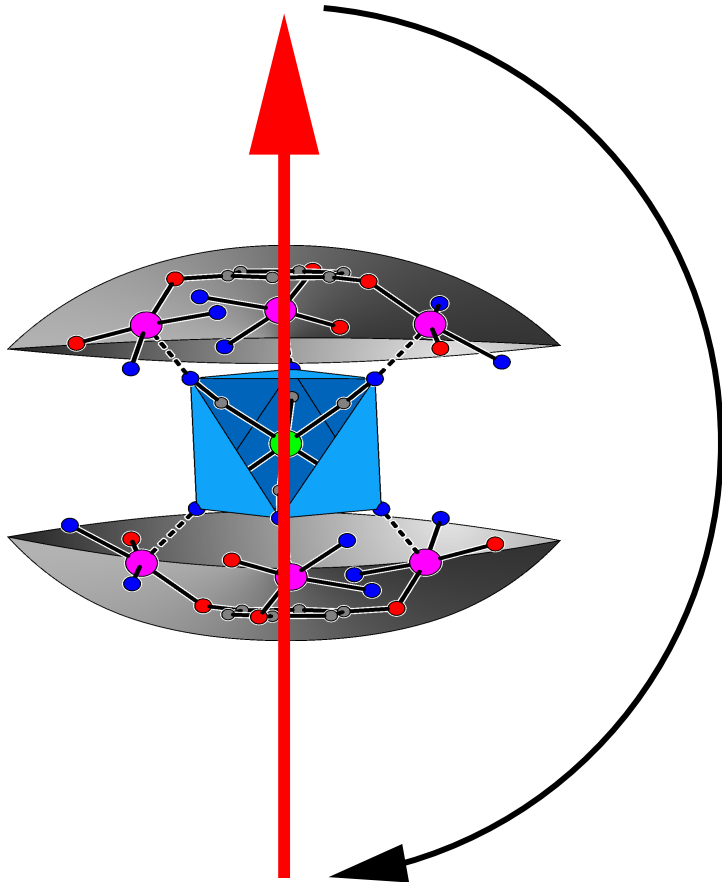


- Dimers ( $\text{Fe}_2$ ), tetrahedra ( $\text{Cr}_4$ ), cubes ( $\text{Cr}_8$ );
- Rings, especially iron and chromium rings
- Complex structures ( $\text{Mn}_{12}$ ) – drosophila of molecular magnetism;
- “Soccer balls”, more precisely icosidodecahedra ( $\text{Fe}_{30}$ ) and other macro molecules;
- 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, ...

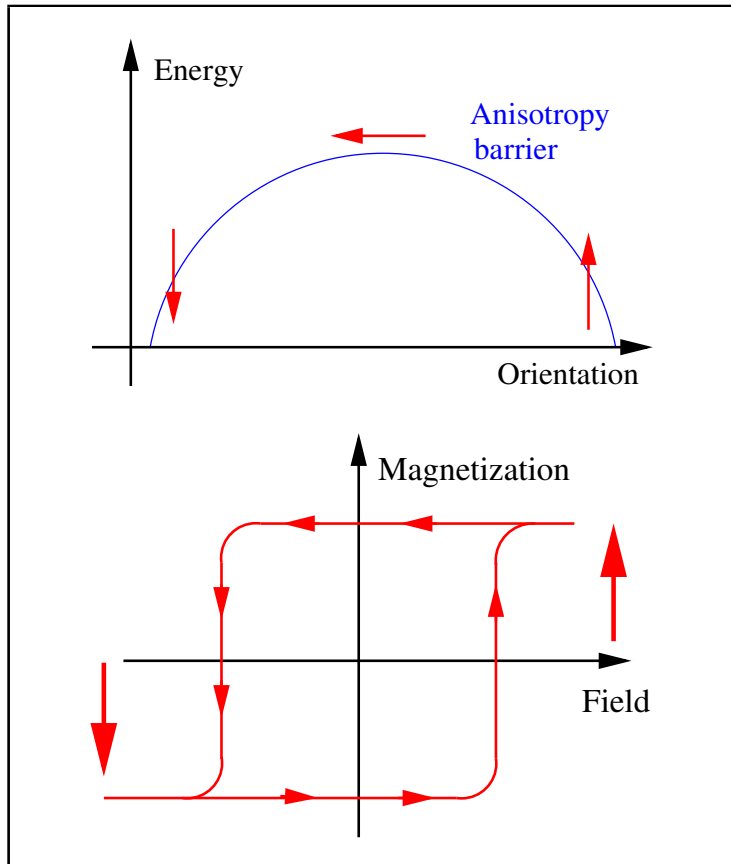
# Single Molecule Magnets

# Single Molecule Magnets I



- Magnetic Molecules may possess a large ground state spin, e.g.  $S = 10$  for  $\text{Mn}_{12}$  or  $\text{Fe}_8$ ;
- 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  $T$ .

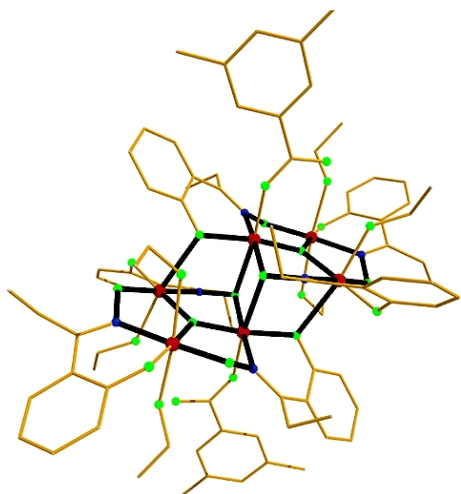
$$\tilde{H} \approx DS_z^2$$

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

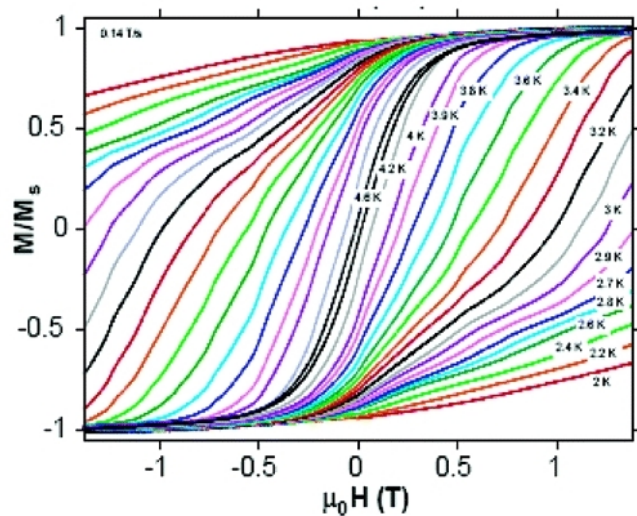
$$\tilde{H} \approx DS_z^2 + E(S_x^2 - S_y^2)$$



# Single Molecule Magnets III



- $S = 12$  ground state with  $D = -0.43 \text{ cm}^{-1}$
- $U_{\text{eff}} = 86.4 \text{ K}$  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

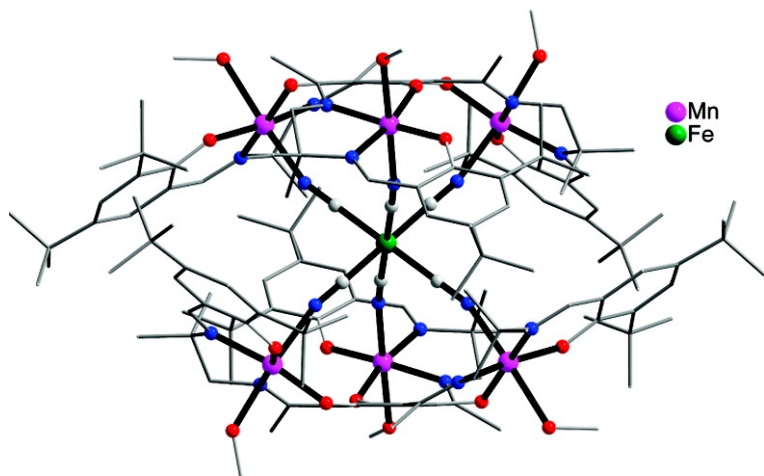
- “Magnitude of the anisotropy barrier is mainly determined by the strength of the spin-orbit coupling and cannot be engineered by independently optimizing  $D$  and  $S$ .”(1)
- “From this point of view systems with larger energy barriers should be obtained in the case of perfect alignment of the Jahn-Teller 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  $\tilde{H} = DS^2$ , . . . 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:



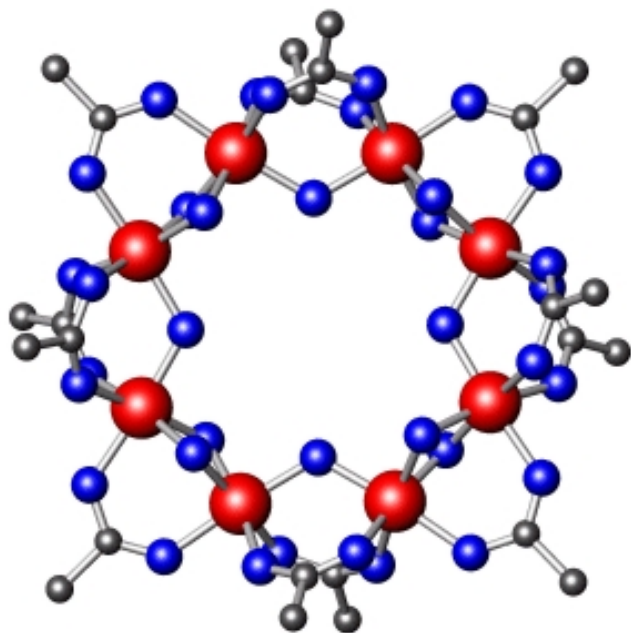
- Idea of Thorsten Glaser:  
 $C_3$  symmetric alignment of local easy axes  
(easy axis  $\equiv$  Jahn-Teller axis);
- Various ions could be used so far,  
e.g.  $Mn_6Cr$  (1),  $Mn_6Fe$  (2), ...
- Advantage: no  $E$ -terms, i.e. no (less) tunneling;
- Problem: exchange interaction sometimes antiferromagnetic.

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

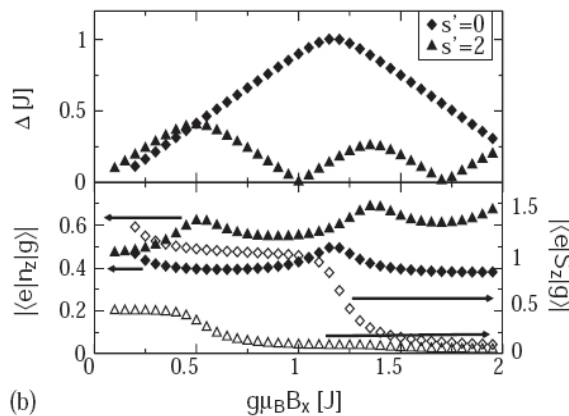
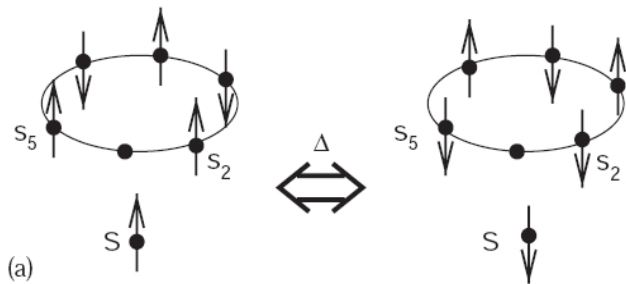


- To date: many AF rings synthesized, e.g.  $\text{Fe}_6$ ,  $\text{Fe}_{10}$ ,  $\text{Fe}_{12}$ , ...,  $\text{Cr}_8$ , ... (1)
- Theory: Exact diagonalization; Rotational band model; QMC; Classical (2)

(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 temperatures (1,2,3);
- Not very practical, no easy observable, since  $S = 0$ ;
- Tunneling in doped af rings (4).

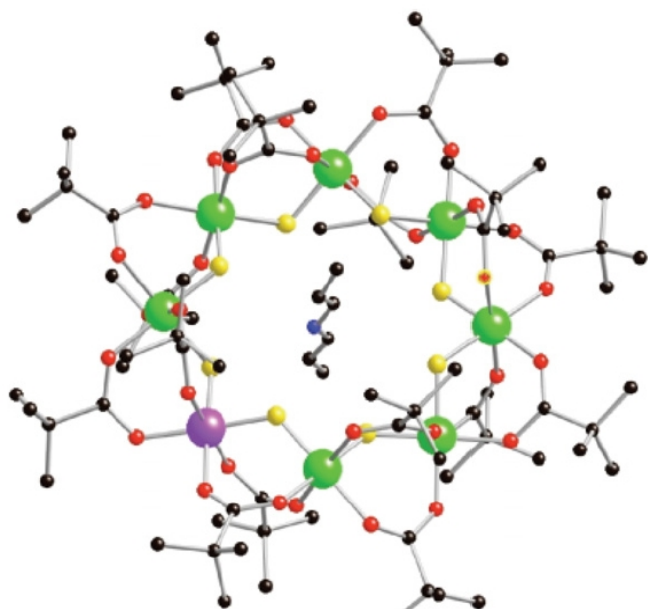
(1) O. Waldmann, Europhys. Lett. **60**, 302 (2002).

(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<sub>7</sub>Ni by Timco

### Synthesis of odd or heterometallic or coupled af spin rings

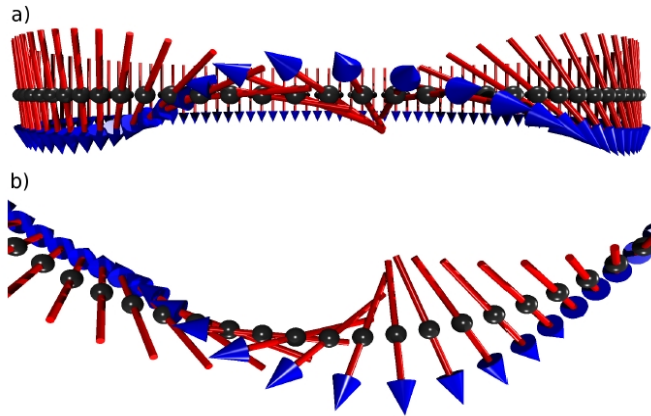
- Odd membered rings very rare; one reason: steric hindrance (1);
- Heterometallic rings derived from homometallic, especially from Cr<sub>8</sub> (2);
- Coupling of heterometallic rings for quantum computing (3).

(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.

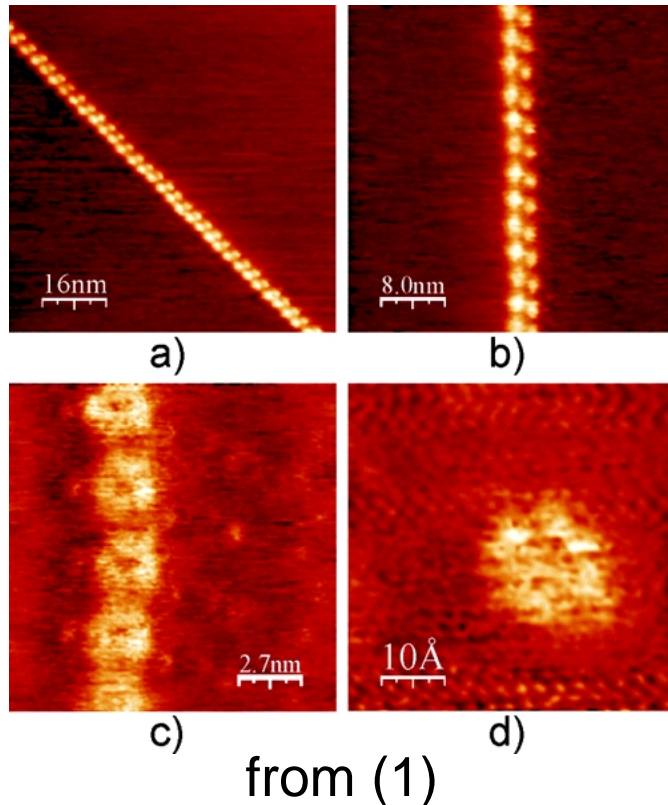
(2) J. Schnack and P. Shchelokovskyy, J. Magn. Magn. Mater. **306**, 79 (2006).



# Molecules on Surfaces

# Molecules on Surfaces I

## Early attempts by Paul Müller (Erlangen)



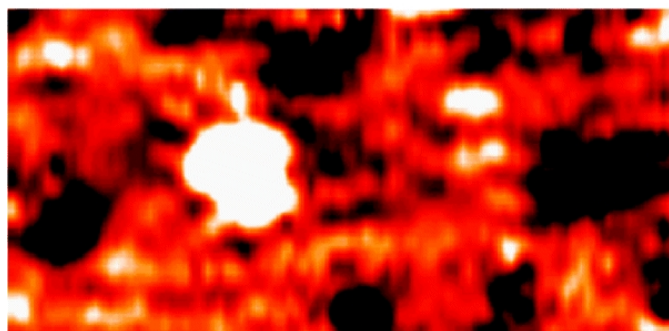
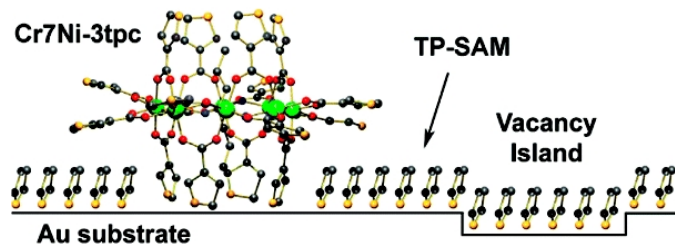
- $\text{Cu}_{20}$  on Highly Orientated Pyrolytic Graphite (HOPG) (1);
- Scanning tunnelling microscopy (STM) (2);
- Scanning tunnelling spectroscopy (STS) (2);
- Current induced tunnelling spectroscopy (CITS) (2).
- Theory: Schoeller, Wegewijs, Timm, Postnikov, Kortus.

(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

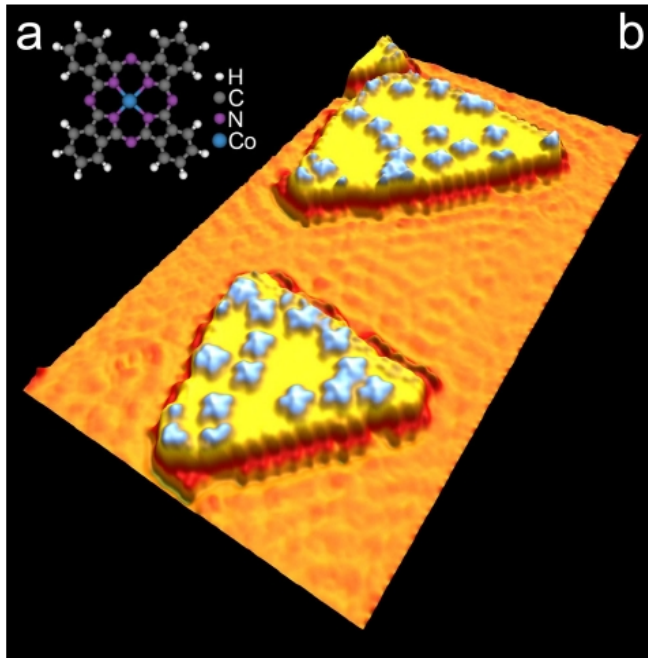


from (1)

- Sulfur-functionalized clusters  $\text{Cr}_7\text{Ni}$  on gold (1);
- Deposited from the liquid phase on  $\text{Au}(111)$ ;
- 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



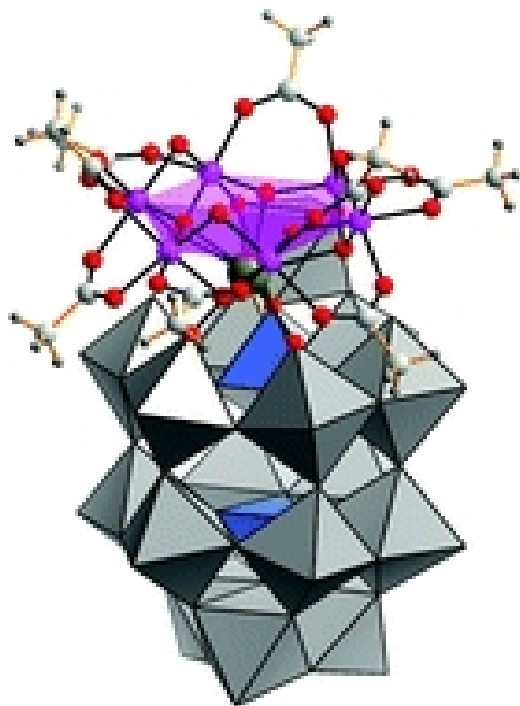
from (1)

## 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



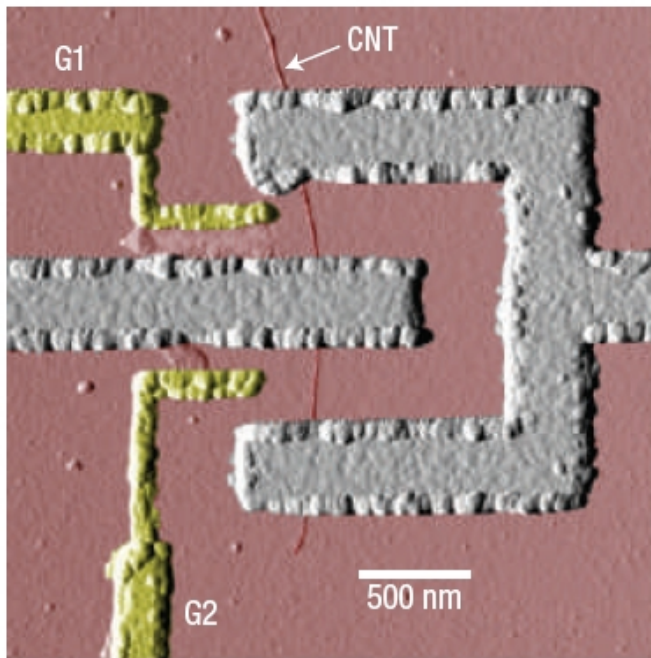
from (1)

## “Backslash” on molecule

- How much of the deposited molecule survives?
- Study of a Mn<sub>6</sub> 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



## Carbon nanotube squid

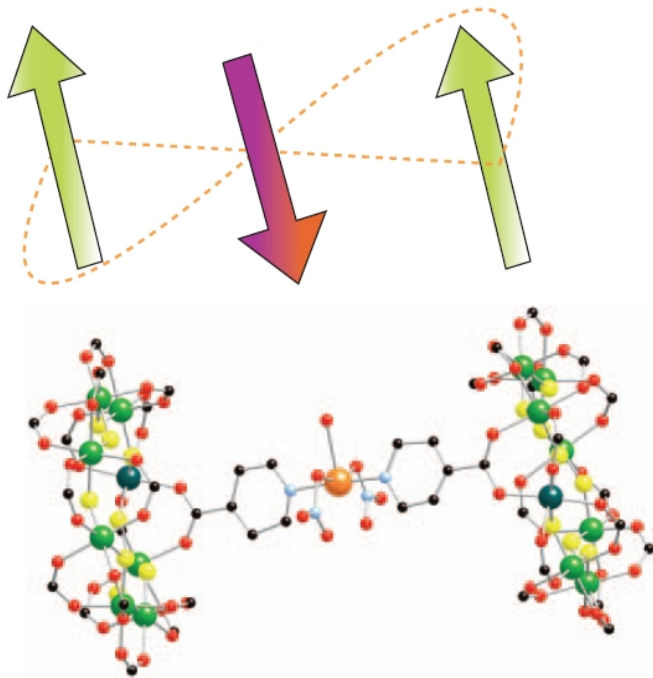
- Use of single-walled carbon nanotube (CNT) Josephson junctions;
- Discrete quantum dot (QD) energy level structure controlled by gates (1);
- CNT-SQUIDS sensitive local magnetometers to study the magnetization reversal of individual magnetic particles (1).

from (1)

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

# Coherence Phenomena

# Coherence Phenomena I



from (1)

## Quantum computing

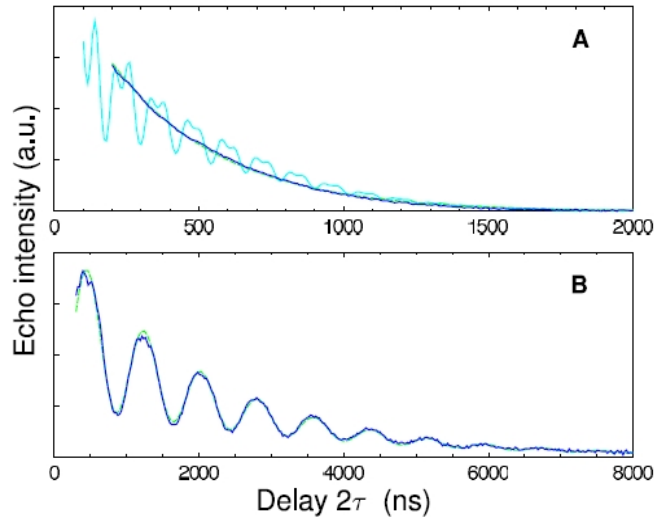
- Chemical realization through coupled molecules with switchable coupling;
- Original ideas, see e.g. (2);
- Molecular transistors; transport in weak or strong coupling regime (3).
- Needed: long coherence times.

(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

## Spin relaxation times



from (1)

- EPR/NMR, Hahn echo techniques,  $T_1$ ,  $T_2$  times;
- Decoherence due to e.g. nuclei, phonons, dipolar interaction;
- Deuteration improves coherence times considerably;
- $\mu\text{s}$  (!) 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)

$$\underline{H} = \sum_{i,j} \underline{\tilde{S}}(i) \cdot \mathbf{J}_{ij} \cdot \underline{\tilde{S}}(j) + \sum_{i,j} \vec{D}_{ij} \cdot [\underline{\tilde{S}}(i) \times \underline{\tilde{S}}(j)] + \mu_B \vec{B} \sum_i^N \mathbf{g}_i \underline{\tilde{S}}(i)$$

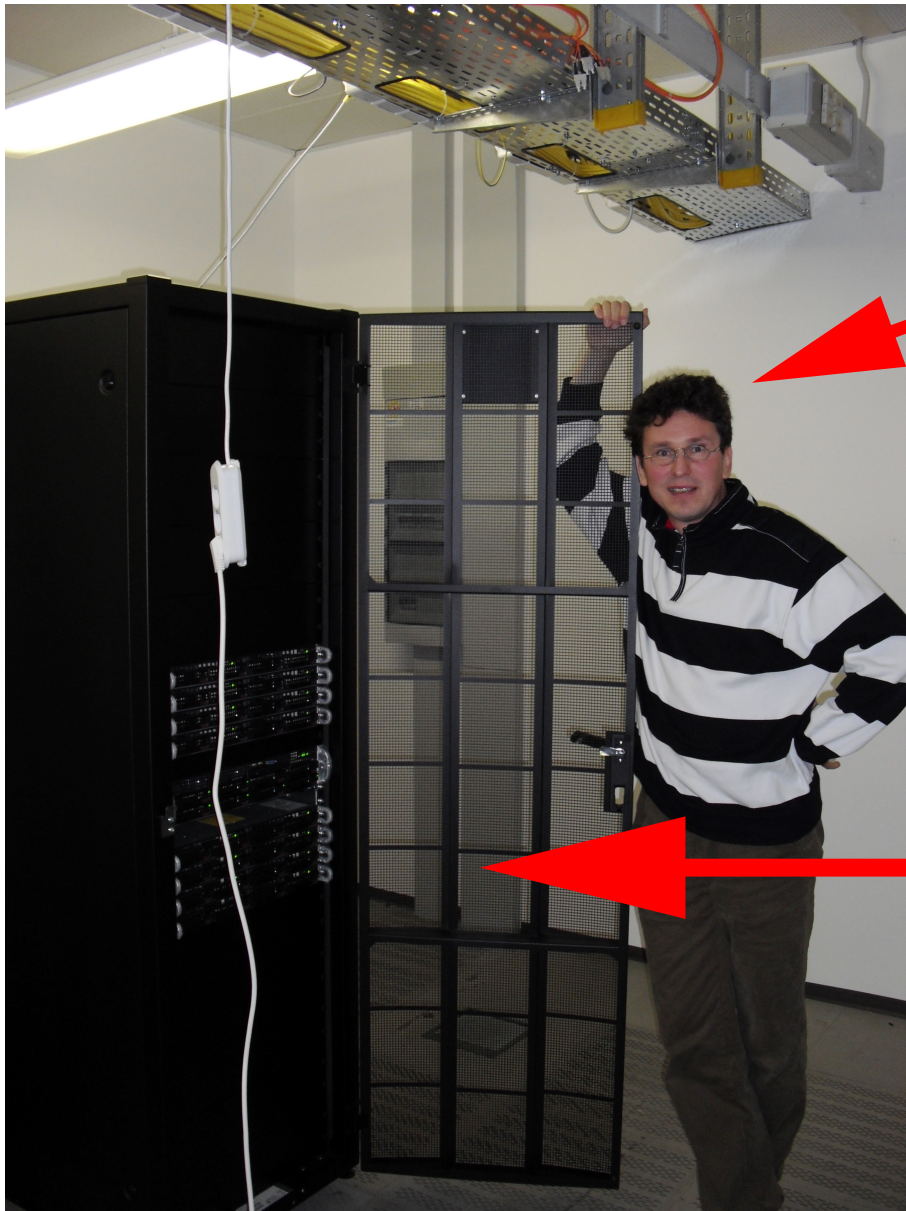
Exchange/Anisotropy
Dzyaloshinskii-Moriya
Zeeman

### Isotropic Hamiltonian

$$\underline{H} = - \sum_{i,j} J_{ij} \underline{\tilde{S}}(i) \cdot \underline{\tilde{S}}(j) + g \mu_B B \sum_i^N \tilde{S}_z(i)$$

Heisenberg
Zeeman

# Thank God, we have computers

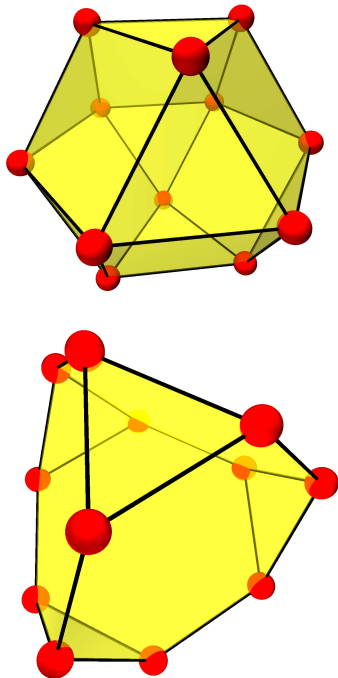


“cell professor”

128 cores, 384 GB RAM

... but that's not enough!

# Advanced ITO & Point Groups I



## Group theory for highly symmetric molecules:

- $\underline{H} = - \sum_{i,j} J_{ij} \underline{\vec{S}}_i \cdot \underline{\vec{S}}_j + g\mu_B \underline{\vec{S}} \cdot \vec{B}$  ;
- $[\underline{H}, \underline{\vec{S}}^2] = 0, [\underline{H}, \underline{S}_z] = 0;$
- 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. Borrás-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

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

## Irreducible Tensor Operator approach

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

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

# Advanced ITO & Point Groups II

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

## 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

$$\mathcal{G}(R) |\alpha S M\rangle_a = \sum_{\alpha'} |\alpha' S M\rangle_a {}_a\langle \alpha' S M | \alpha S M \rangle_b$$

## Serious problem: Recoupling

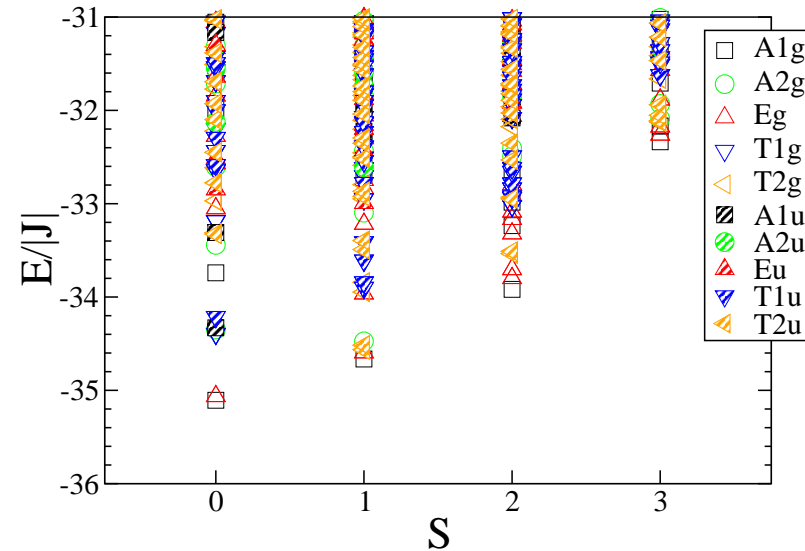
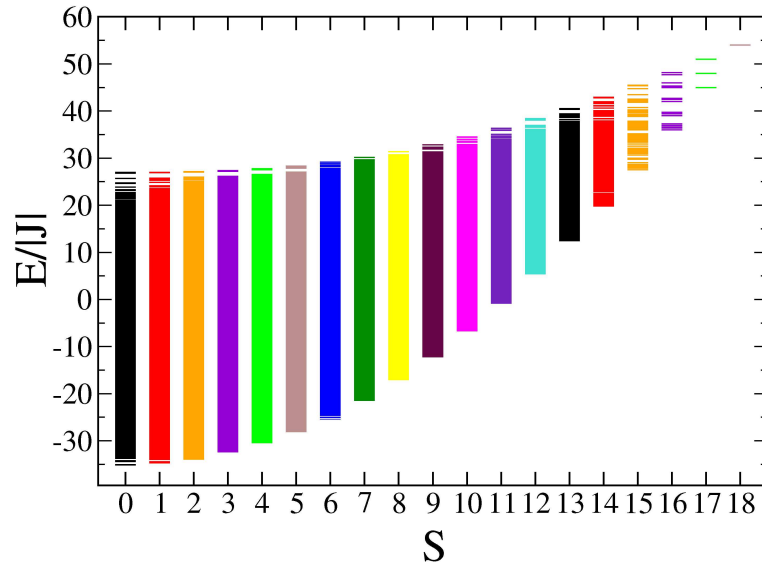
- So far: only point groups that are compatible with the coupling scheme are used (1);
- Problem: otherwise complicated basis transformation between different coupling schemes;
- Solution: implementation of graph-theoretical results to evaluate recoupling coefficients  ${}_a\langle \alpha' S M | \alpha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

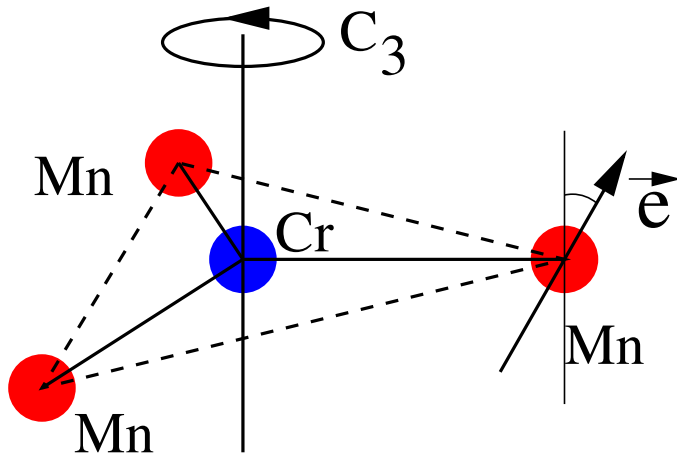
# Anisotropic magnetic molecules I – Theory

$$\tilde{H}(\vec{B}) = - \sum_{i,j} J_{ij} \vec{\tilde{S}}(i) \cdot \vec{\tilde{S}}(j) + \sum_i d_i (\vec{e}_i \cdot \vec{\tilde{S}}(i))^2 + \mu_B \vec{B} \cdot \sum_i^N \mathbf{g}_i \cdot \vec{\tilde{S}}(i)$$

- $[\tilde{H}, \tilde{S}^2] \neq 0, [\tilde{H}, \tilde{S}_z] \neq 0;$
- You have to diagonalize  $\tilde{H}(\vec{B})$  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:  $30,000 < \dim(\mathcal{H}) < 140,000$

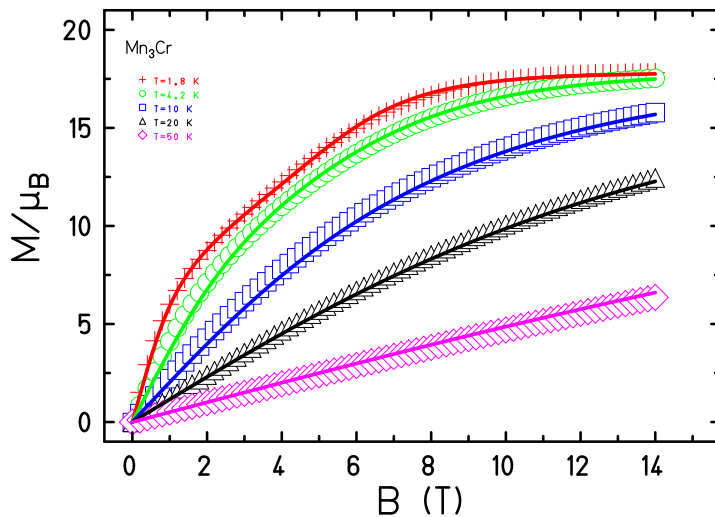
T. Glaser *et al.* et J. Schnack, Inorg. Chem. **48**, 607 (2009).

# Anisotropic magnetic molecules II – Example



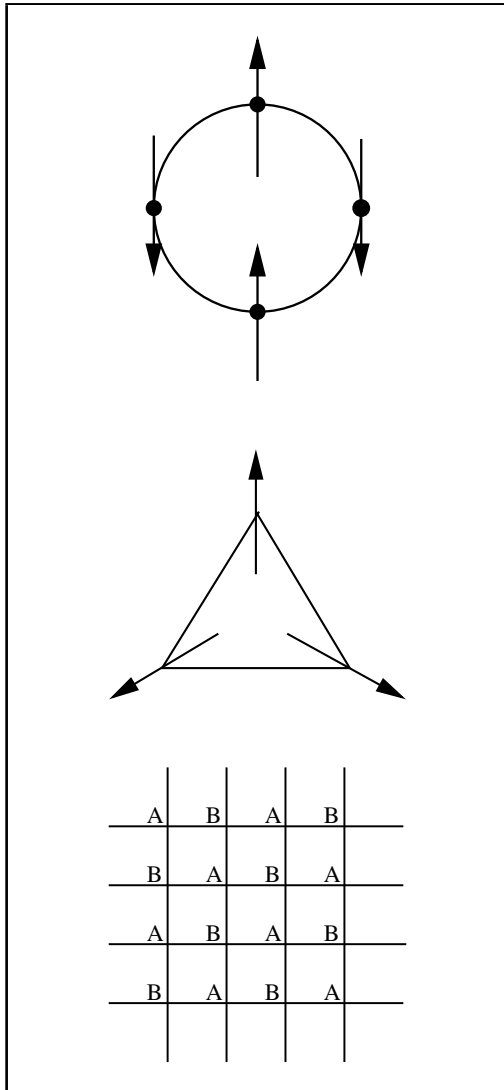
## What can be achieved? Mn<sub>3</sub>Cr:

- 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  $\vartheta_{\text{Mn}1} = \vartheta_{\text{Mn}2} = \vartheta_{\text{Mn}3}$ . 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:  $J_1 = -0.29 \text{ cm}^{-1}$ ,  $J_2 = -0.08 \text{ cm}^{-1}$ ,  $d_{\text{Mn}} = -1.21 \text{ cm}^{-1}$ ,  $\vartheta_{\text{Mn}} = 22^\circ$ ,  $d_{\text{Cr}} = +0.17 \text{ cm}^{-1}$ .
- ab initio calculations need.



# Frustration effects

# Definition of frustration



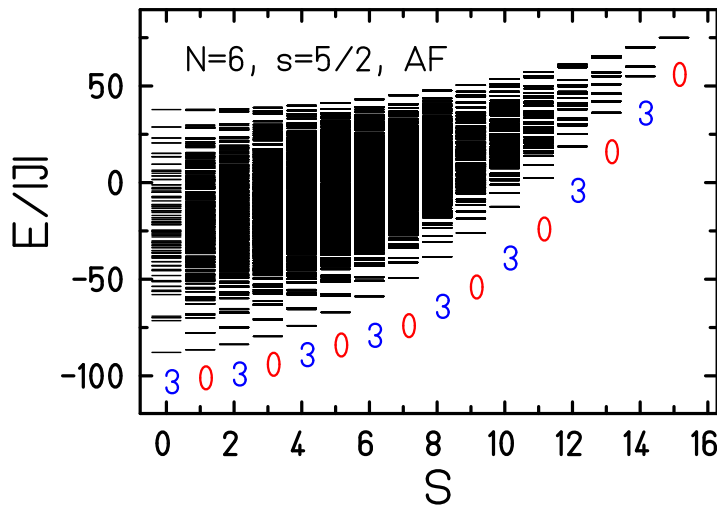
- **Simple:** An antiferromagnet is frustrated if in the ground state of the corresponding classical spin system not all interactions can be minimized simultaneously.

- **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:

$$J(x_A, y_B) \leq g^2, J(x_A, y_A) \geq g^2, J(x_B, y_B) \geq g^2, \text{ cmp. (1,2).}$$

- (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

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

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

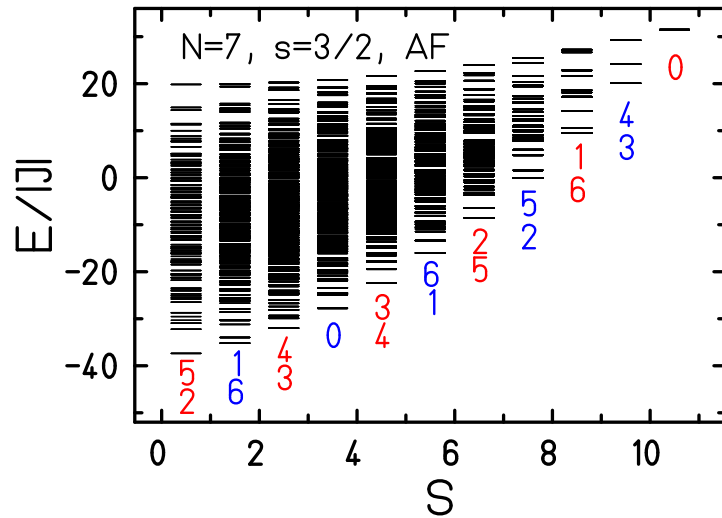
All  $a(\mathbf{m})$  are non-zero, real, and of equal sign.

- Yields eigenvalues for the shift operator  $\tilde{T}$ :

$$\exp\left\{-i\frac{2\pi k}{N}\right\} \quad \text{with} \quad k \equiv a\frac{N}{2} \pmod{N}, \quad a = N_s - M$$

(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.  $s = 1/2, 3/2, 5/2, \dots$  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):

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

- 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)

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

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

$N$	$s$	$a$									
		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	$5 \equiv 4$	$10 \equiv 1$	$15 \equiv 3$	$20 \equiv 2$	$25 \equiv 2$	$30 \equiv 3$	$35 \equiv 1$	$40 \equiv 4$	$45 \equiv 0$

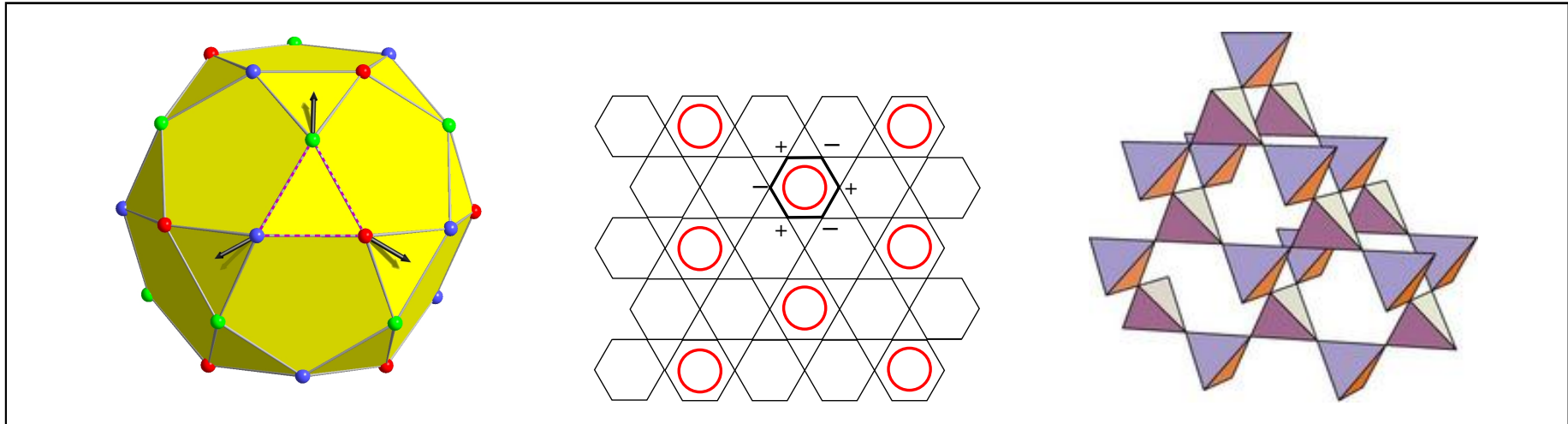
**No general, but partial proof yet.**

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



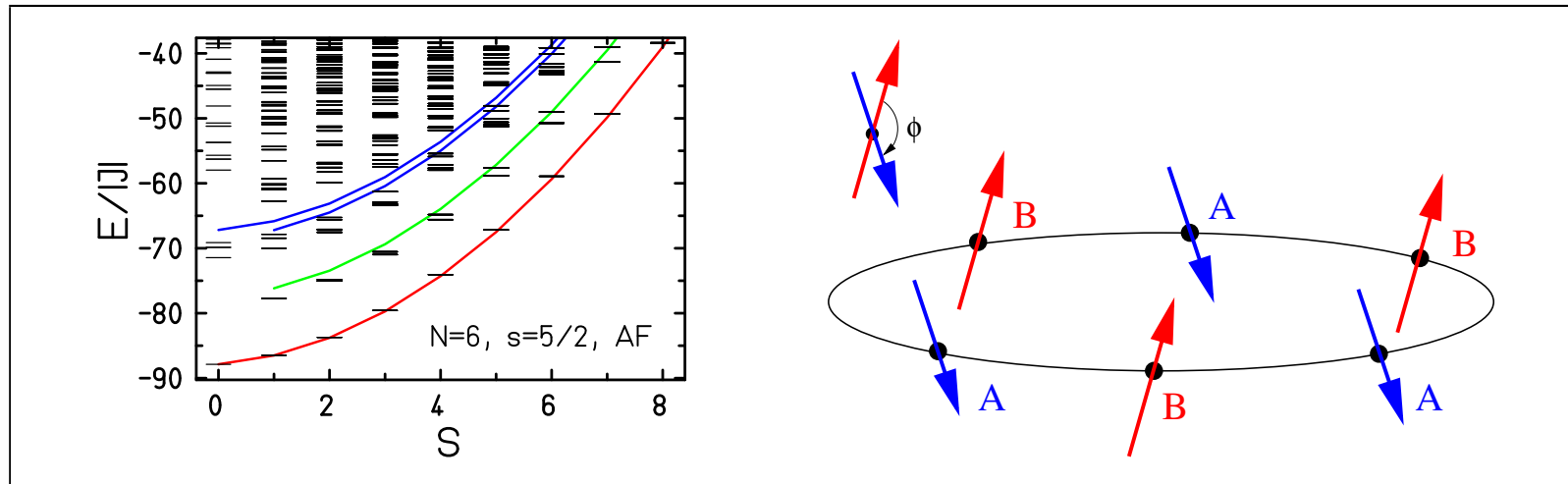
# Fe<sub>30</sub> and friends

## 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

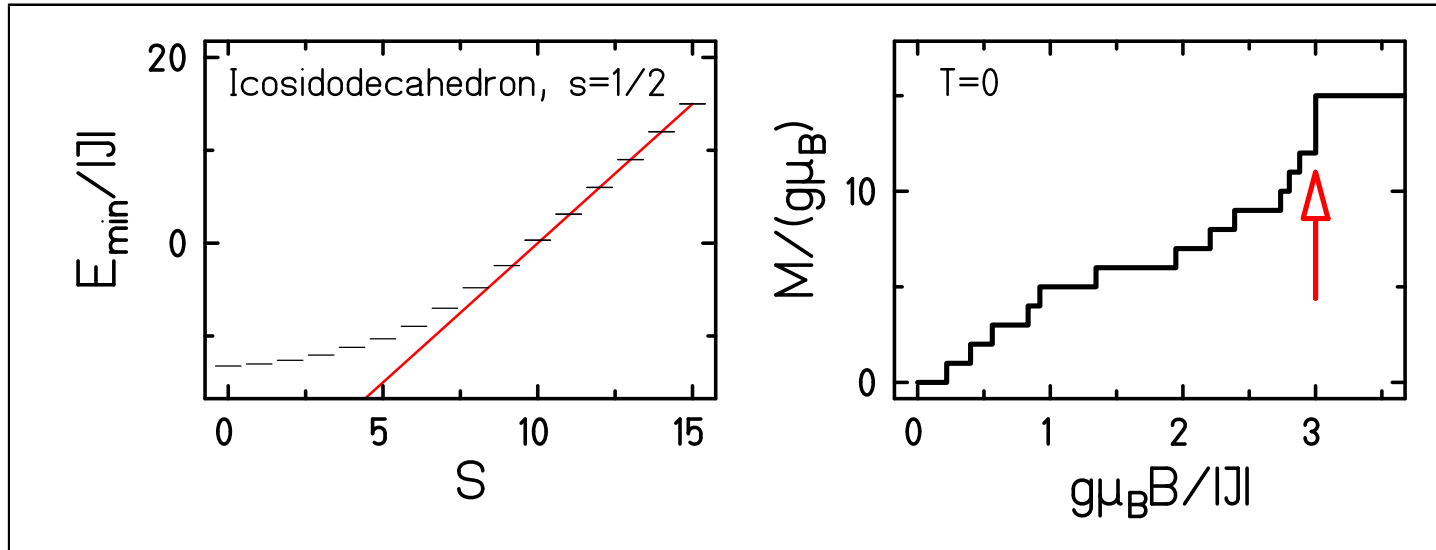


- Often minimal energies  $E_{min}(S)$  form a rotational band: Landé interval rule (1);
- For bipartite systems (2,3):  $\tilde{H}^{eff} = -2 J_{eff} \tilde{S}_A \cdot \tilde{S}_B$ ;
- Lowest band – rotation of Néel vector, second band – spin wave excitations (4).

(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<sub>72</sub>Fe<sub>30</sub>}



- Close look:  $E_{\min}(S)$  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);

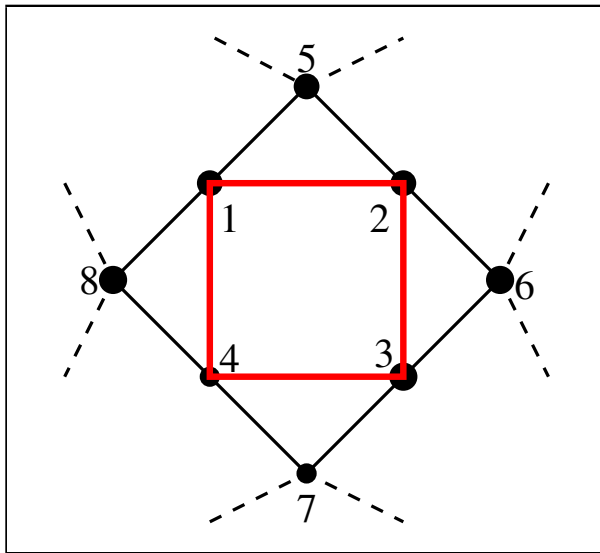
(1) J. Schnack, H.-J. Schmidt, J. Richter, J. Schulenburg, Eur. Phys. J. B **24**, 475 (2001)

(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



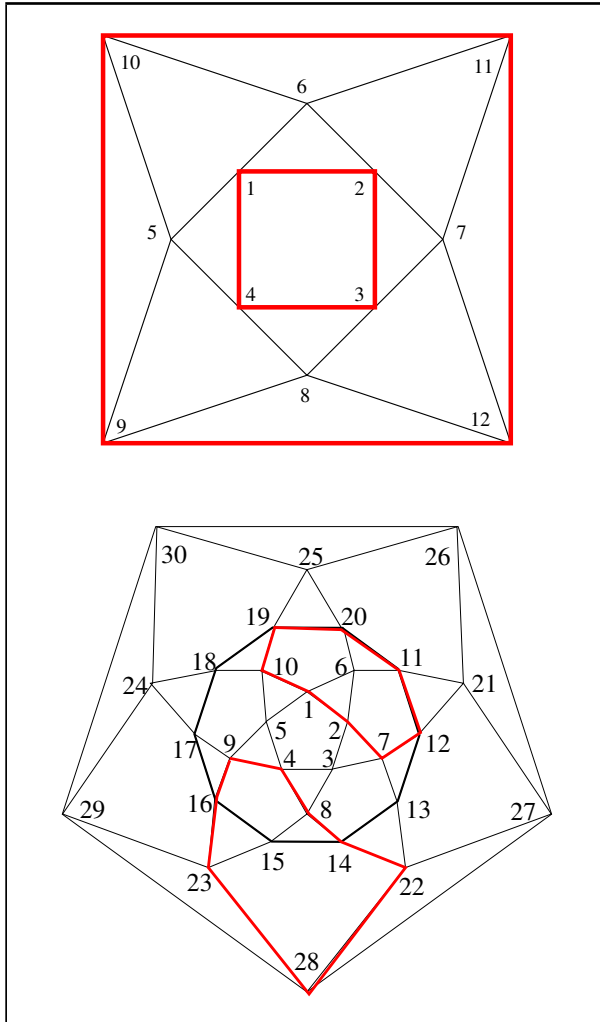
- $|\text{localized magnon}\rangle = \frac{1}{2} (|1\rangle - |2\rangle + |3\rangle - |4\rangle)$
- $|1\rangle = \tilde{s}^-(1) |\uparrow\uparrow\uparrow \dots\rangle$  etc.
- $\tilde{H} |\text{localized magnon}\rangle \propto |\text{localized magnon}\rangle$
- Localized magnon is state of lowest energy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

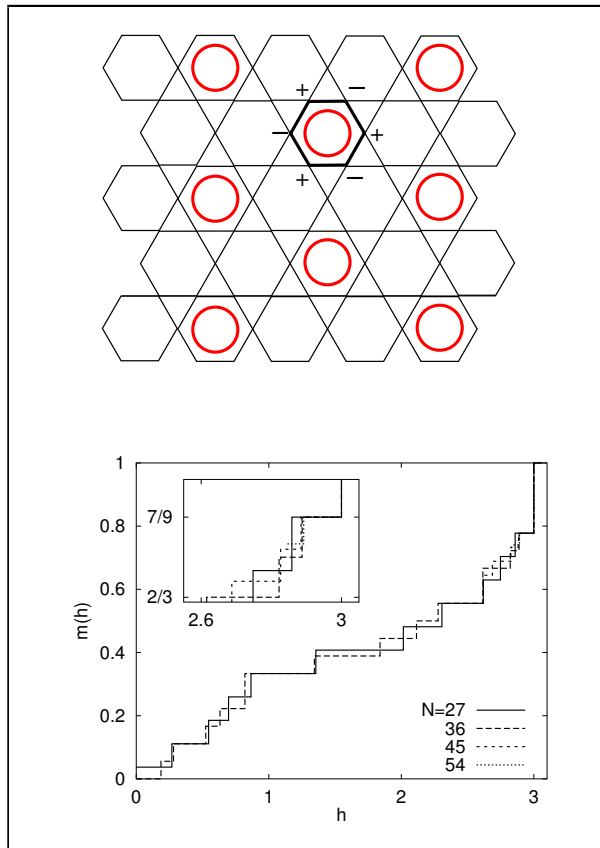


- Non-interacting one-magnon states can be placed on various molecules, e. g. 2 on the cuboctahedron and 3 on the icosidodecahedron (3rd delocalized);
- Each state of  $n$  independent magnons is the ground state in the Hilbert subspace with  $M = N_s - n$ ;
- Linear dependence of  $E_{\min}$  on  $M$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

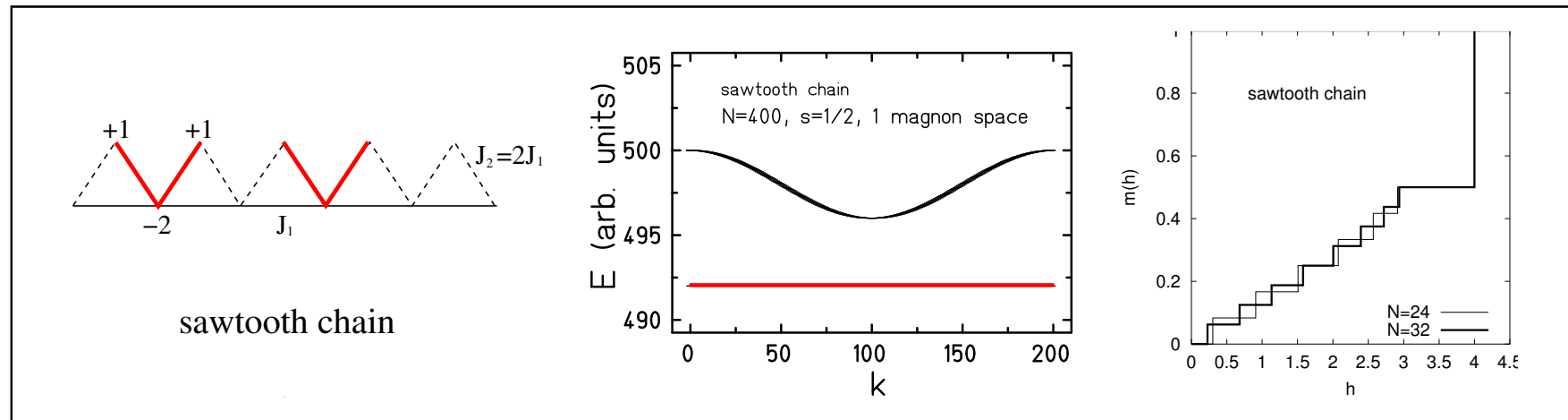


- Non-interacting one-magnon states can be placed on various lattices, e. g. kagome or pyrochlore;
- Each state of  $n$  independent magnons is the ground state in the Hilbert subspace with  $M = Ns - n$ ;  
Kagome: max. number of indep. magnons is  $N/9$ ;
- Linear dependence of  $E_{\min}$  on  $M$   
 $\Rightarrow$  ( $T = 0$ ) 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



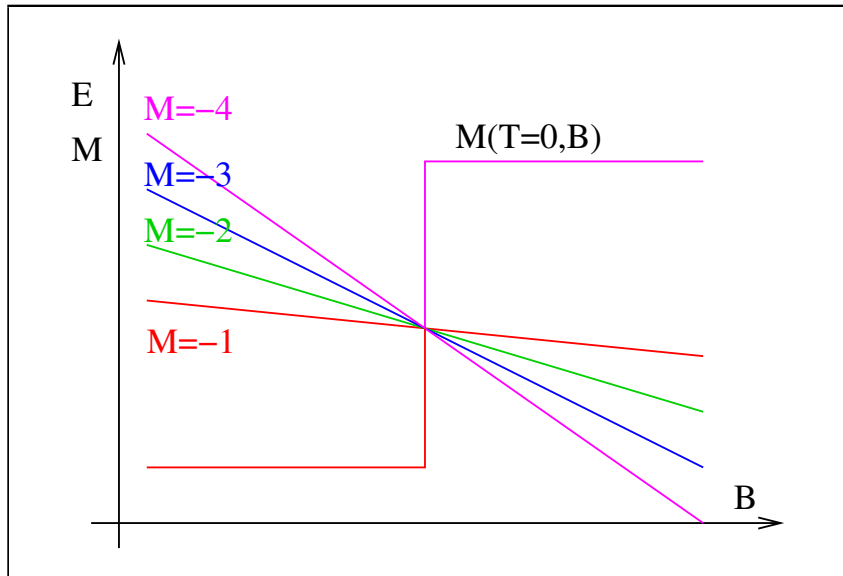
- Flat band of minimal energy in one-magnon space; localized magnons can be built from delocalized states in the flat band.
- Entropy can be evaluated using hard-object models (1); universal low-temperature behavior.
- Same behavior for Hubbard model; flat band ferromagnetism (Tasaki & Mielke), jump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

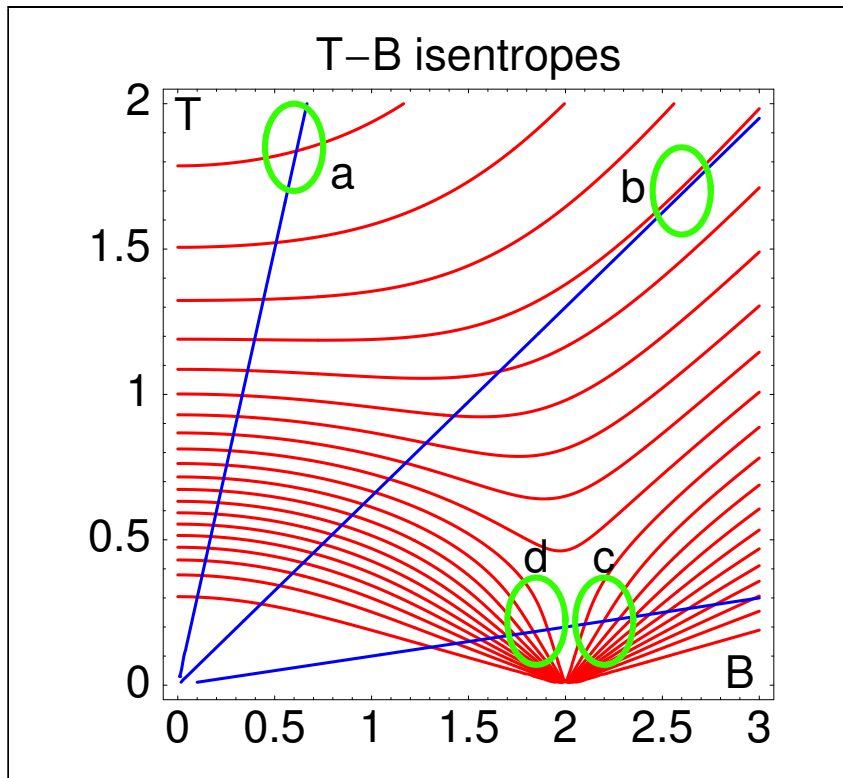
M. E. Zhitomirsky, *Phys. Rev. B* **67**, 104421 (2003).

M. E. Zhitomirsky and A. Honecker, *J. Stat. Mech.: Theor. Exp.* **2004**, P07012 (2004).



# Magnetocaloric effect II

## Isentropes of an $s = 1/2$ dimer



blue lines: ideal paramagnet, red curves: af dimer

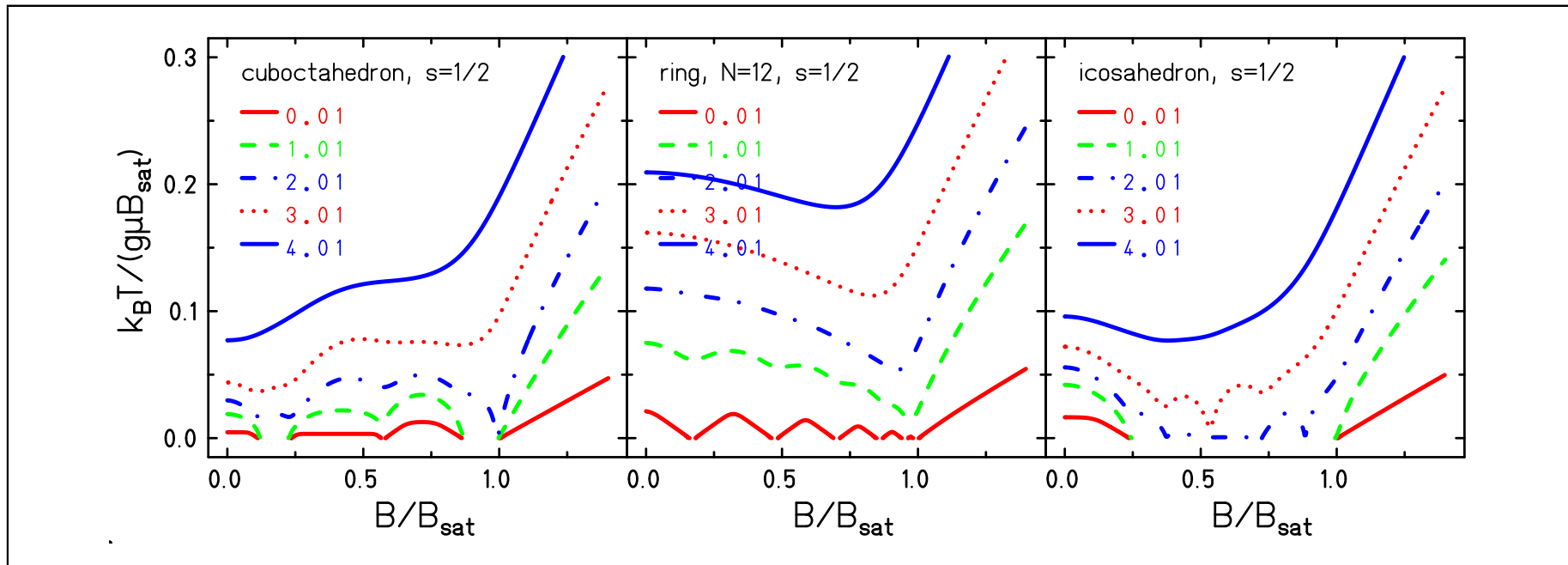
Magnetocaloric effect:

- (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

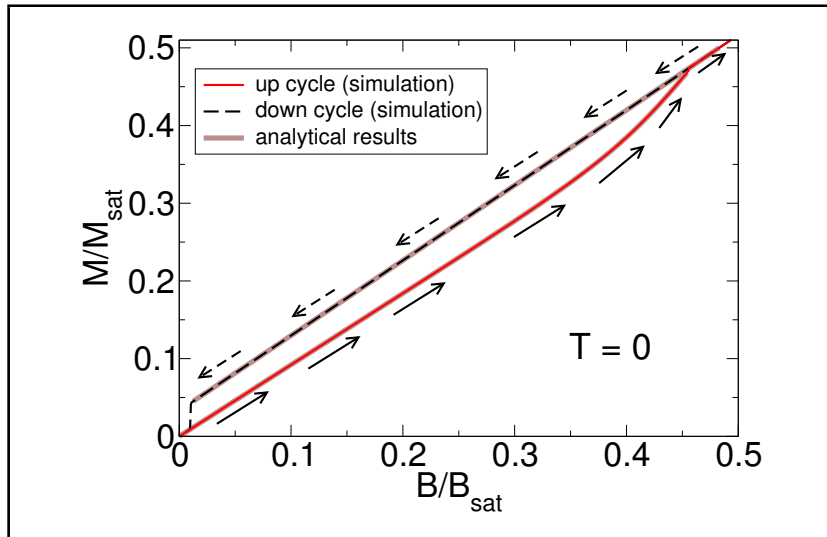


- Cuboctahedron: high cooling rate due to independent magnons;
- Ring: normal level crossing, normal jump;
- Icosahedron: unusual behavior due to edge-sharing triangles, high degeneracies all over the spectrum; high cooling rate.

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

# Metamagnetic phase transition I

## Hysteresis without anisotropy

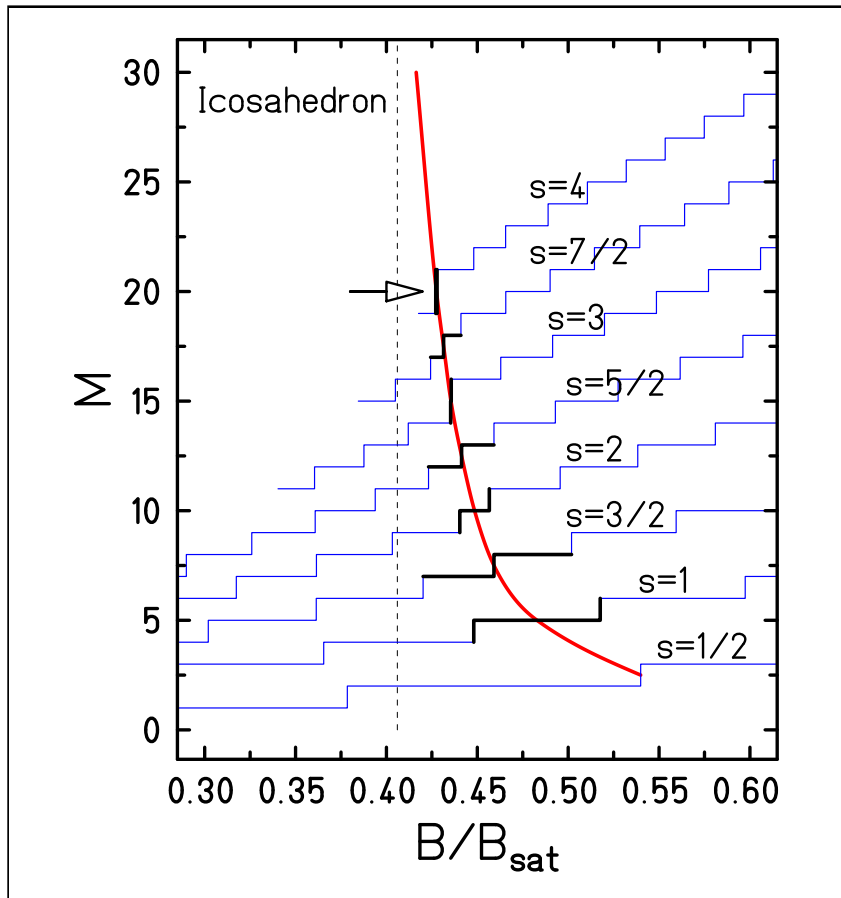


- Heisenberg model with isotropic nearest neighbor exchange
- Hysteresis behavior of the classical icosahedron in an applied magnetic field.
- Classical spin dynamics simulations (thick lines).
- Analytical stability analysis (grey lines).
- Movie.

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  
⇒ 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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