# Frustration-induced exotic properties of magnetic molecules, quantum antiferromagnets and correlated electron systems

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Condensed Matter Seminar, Ames Lab

Ames, May 5, 2008

Universität Bielefeld
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Deutsche
Forschungsgemeinschaft
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# Many thanks to my collaborators worldwide

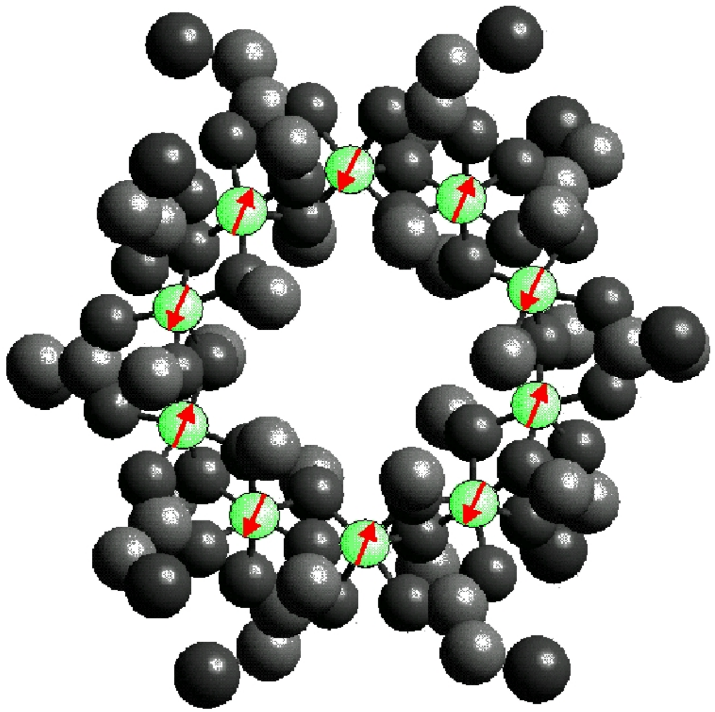
- T. Englisch, T. Glaser, M. Höck, S. Leiding, A. Müller, Chr. Schröder, B. Soleymanzadeh (Bielefeld)

- K. Bärwinkel, H.-J. Schmidt, M. Allalen, M. Brüger, D. Mentrup, D. Müter, M. Exler, P. Hage, F. Hesmer, K. Jahns, F. Ouchni, R. Schnalle, P. Shchelokovskyy, S. Torbrügge & M. Neumann, K. Küpper, M. Prinz (Osnabrück);

- M. Luban, D. Vaknin (Ames Lab, USA); P. Kögerler (RWTH, Jülich, Ames)
  J. Musfeld (U. of Tennessee, USA); N. Dalal (Florida State, USA);
  R.E.P. Winpenny (Man U, UK); L. Cronin (U. of Glasgow, UK);
  H. Nojiri (Tohoku University, Japan); A. Postnikov (U. Metz)

- J. Richter, J. Schulenburg, R. Schmidt (U. Magdeburg);
  S. Blügel (FZ Jülich); A. Honecker (U. Göttingen);
  E. Rentschler (U. Mainz); U. Kortz (IUB); A. Tennant, B. Lake (HMI Berlin);
  B. Büchner, V. Kataev, R. Klingeler, H.-H. Klauß (Dresden)

# Contents for you today

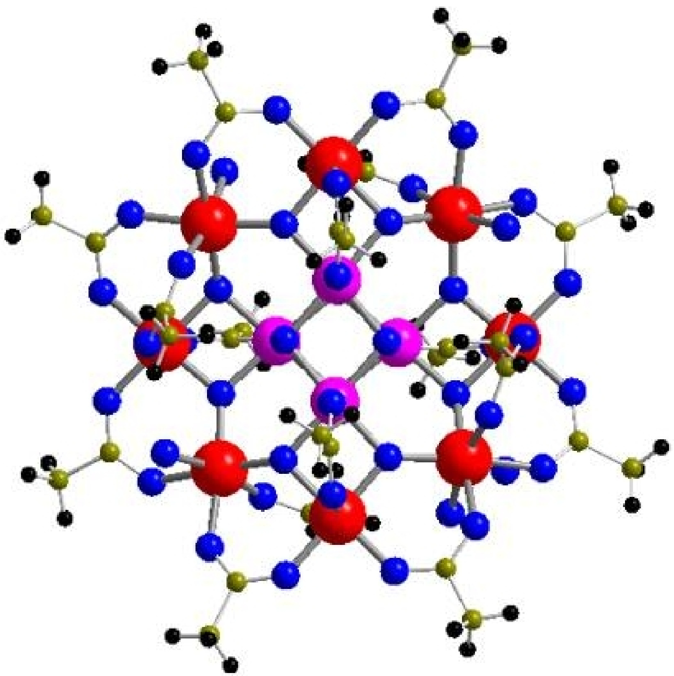


$Fe_{10}$

1. The suspects: magnetic molecules
2. Frustrated ring molecules
3. Corner-sharing triangles: $Fe_{30}$ and friends
4. Part II by Johannes Richter

# Magnetic Molecules

# The beauty of magnetic molecules I

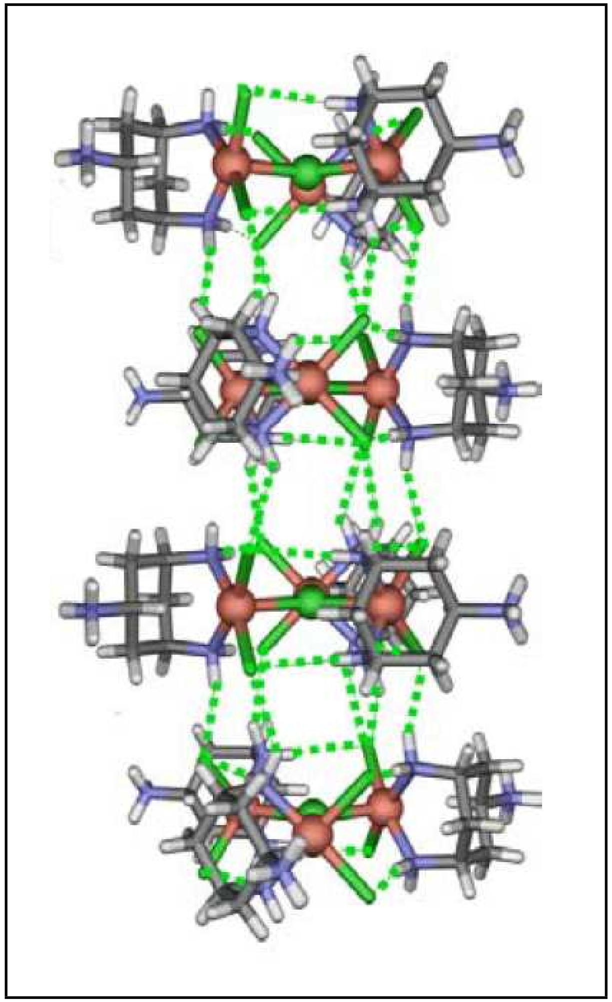


Mn$_{12}$

**Molecular materials:**

- 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

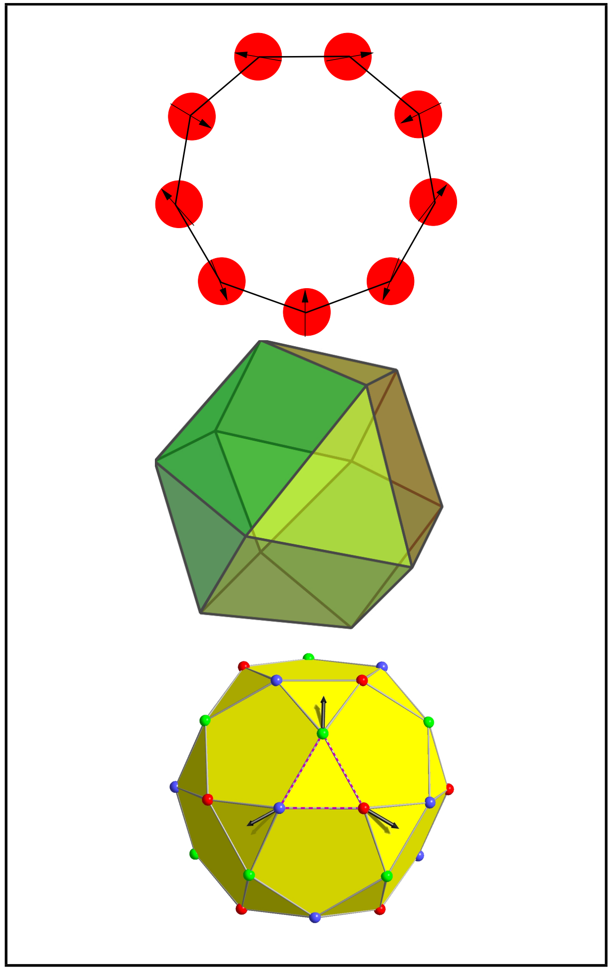


**Molecular structures:**

- 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, . . .

# The beauty of magnetic molecules III



## Frustrated AF molecular structures:

- Odd-membered rings (1);
- Cuboctahedra (corner-sharing triangles, 2);
- Icosidodecahedra (corner-sharing triangles, 3);
- Tetrahedra (edge-sharing triangles, 3);
- Icosahedra (edge-sharing triangles, 4).

(1) By G. Timco & R. Winpenny (Manchester) and H.C. Yao (Nanjing).
(2) By R. Winpenny (Manchester) and A. Powell (Karlsruhe).
(3) By A. Müller (Bielefeld) and P. Kögerler (Aachen & Ames).
(4) Almost (!) by R. Winpenny (Manchester).

# Model Hamiltonian – Heisenberg-Model

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

Heisenberg Zeeman

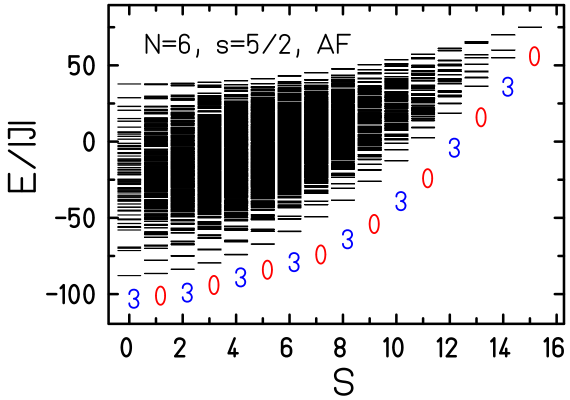
The Heisenberg Hamilton operator together with a Zeeman term are used for the following considerations; $J < 0$: antiferromagnetic coupling.

$$\left[\underset{\sim}{H}, \underset{\sim}{\vec{S}}^2\right] = 0 \qquad \& \qquad \left[\underset{\sim}{H}, \underset{\sim}{S}_z\right] = 0$$

$$\underset{\sim}{H}\,|\,\nu\,\rangle = E_\nu\,|\,\nu\,\rangle \quad \& \quad \underset{\sim}{\vec{S}}^2\,|\,\nu\,\rangle \; = \; S_\nu(S_\nu+1)\,|\,\nu\,\rangle \quad \& \quad \underset{\sim}{S}_z\,|\,\nu\,\rangle = M_\nu\,|\,\nu\,\rangle$$

# Frustrated ring molecules
# (a warm-up)

# 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

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

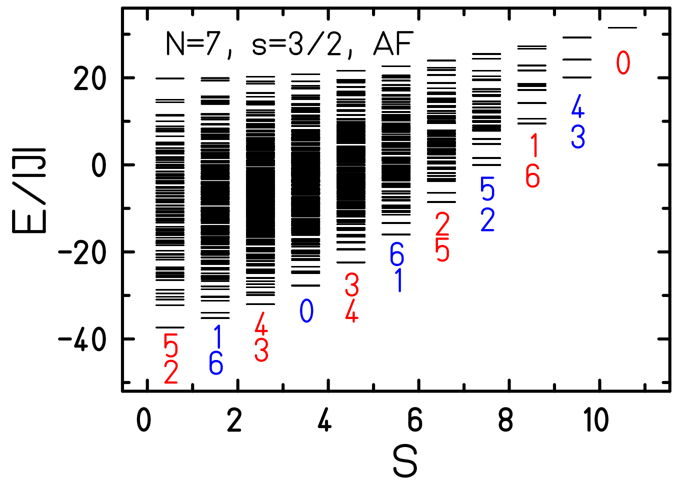
$$c(\vec{m}) = (-1)^{\left(\frac{Ns}{2} - \sum_{i=1}^{N/2} m_{2i}\right)} a(\vec{m})$$

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 ($N \neq 3$).

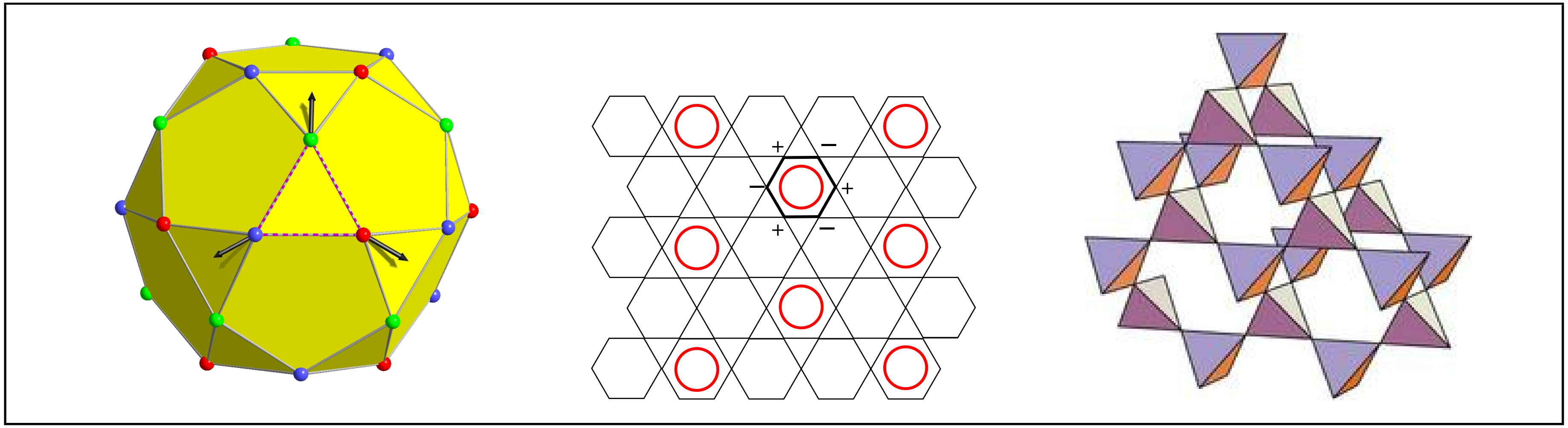
| $N$ | $s$ | $a$: 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 8 | 1/2 | 0 | 4 | $8 \equiv 0$ | $12 \equiv 4$ | $16 \equiv 0$ | - | - | - | - | - |
| 9 | 1/2 | 0 | $5 \equiv 4$ | $10 \equiv 1$ | $15 \equiv 3$ | $20 \equiv 2$ | - | - | - | - | - |
| 9 | 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 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)

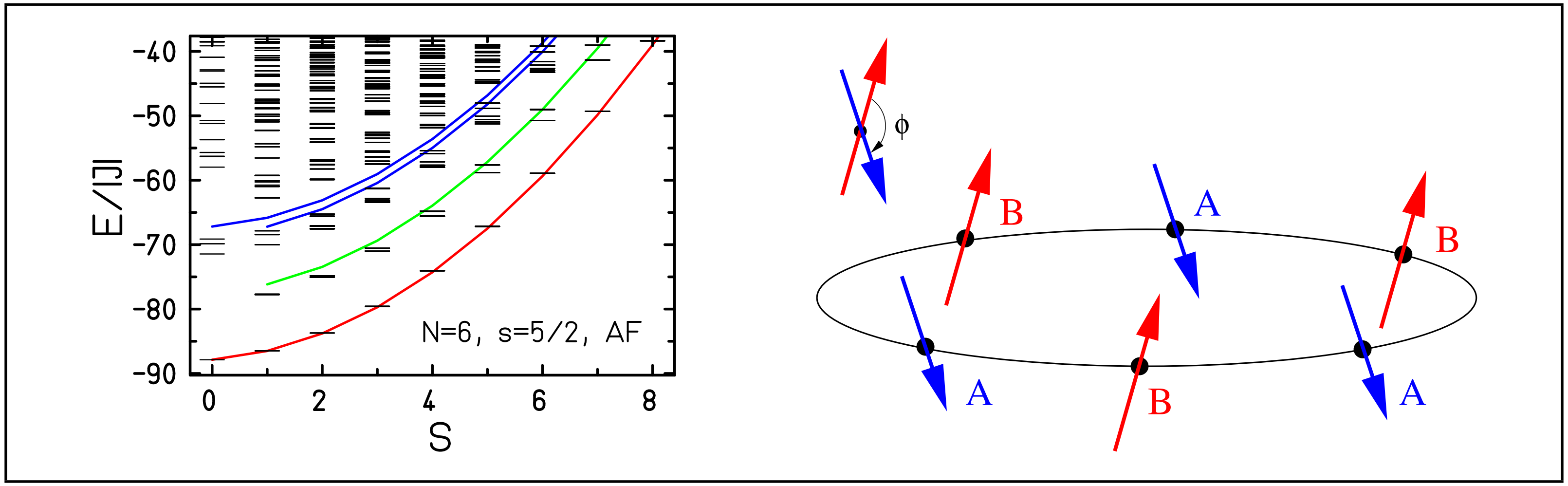
# $Fe_{30}$ and friends
# Corner sharing triangles and tetrahedra




- Several frustrated antiferromagnets show an unusual magnetization behavior, e.g. plateaus and jumps.

- Example systems: icosidodecahedron, kagome lattice, pyrochlore lattice.

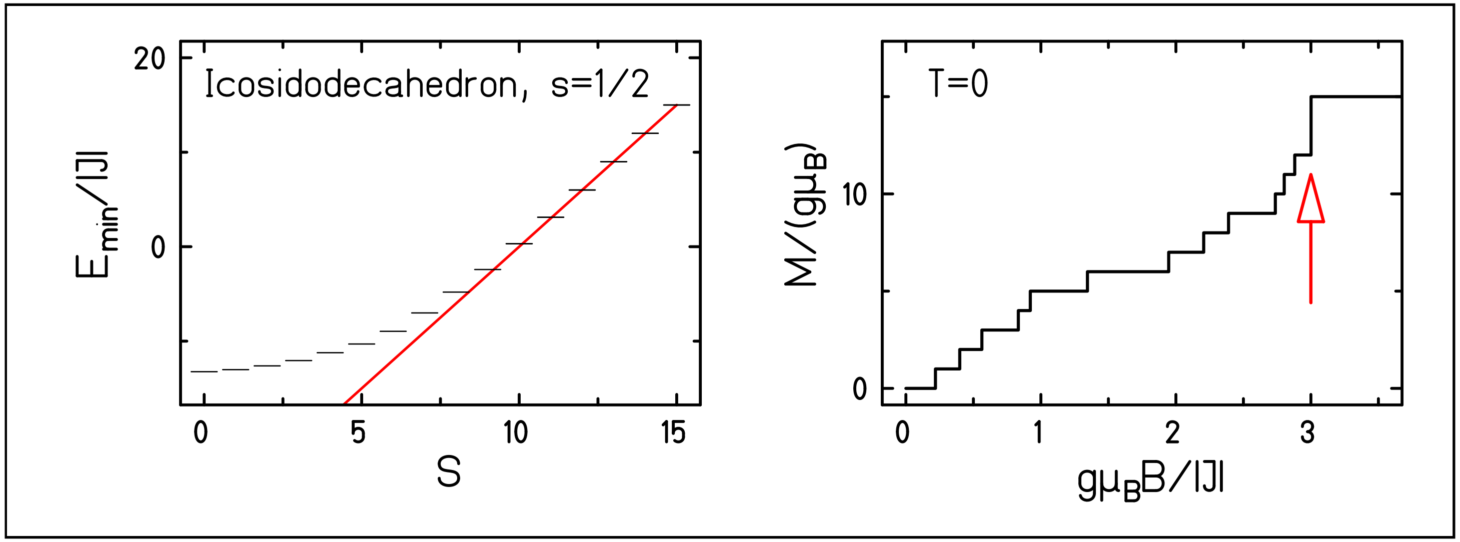
# Rotational bands in non-frustrated antiferromagnets




- Often minimal energies $E_{min}(S)$ form a rotational band: Landé interval rule (1);
- For bipartite systems (2,3): $\underset{\sim}{H}^{\text{eff}} = -2\, J_{\text{eff}}\, \vec{\underset{\sim}{S}}_A \cdot \vec{\underset{\sim}{S}}_B$;
- 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).

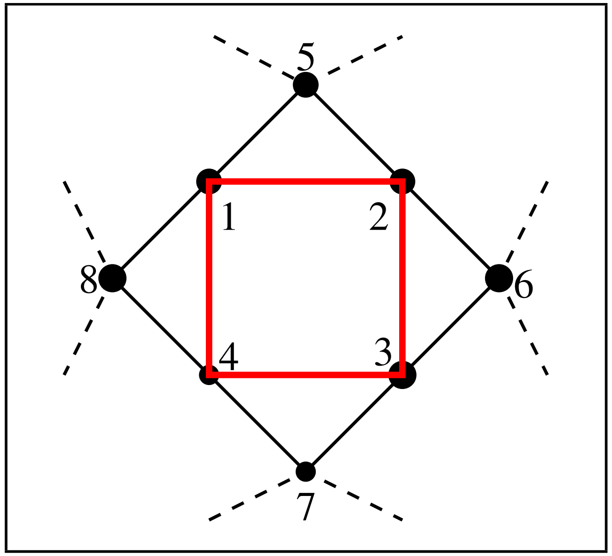
# Giant magnetization jumps in frustrated antiferromagnets I $\{$Mo$_{72}$Fe$_{30}\}$




- 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

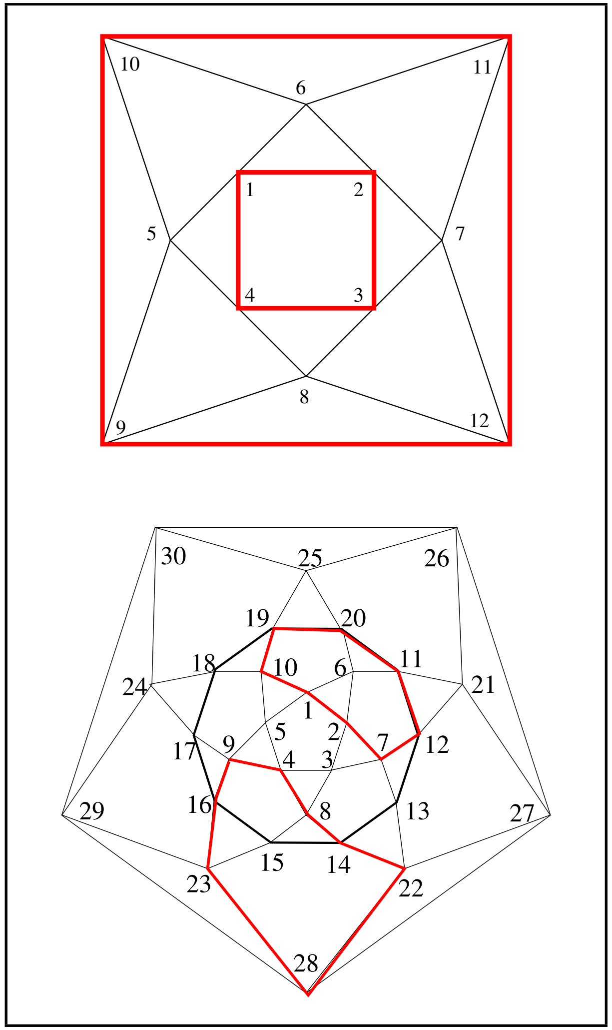



- $|\,\text{localized magnon}\,\rangle = \frac{1}{2}\left(\,|\,1\,\rangle - |\,2\,\rangle + |\,3\,\rangle - |\,4\,\rangle\right)$
- $|\,1\,\rangle = \underset{\sim}{s}^{-}(1)\,|\uparrow\uparrow\uparrow\,\dots\rangle$ etc.
- $\underset{\sim}{H}\,|\,\text{localized magnon}\,\rangle \propto |\,\text{localized magnon}\,\rangle$
- 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 $E_{\text{min}}$ on $M$ $\Rightarrow \quad (T = 0)$ magnetization jump;
- A rare example of analytically known many-body states!

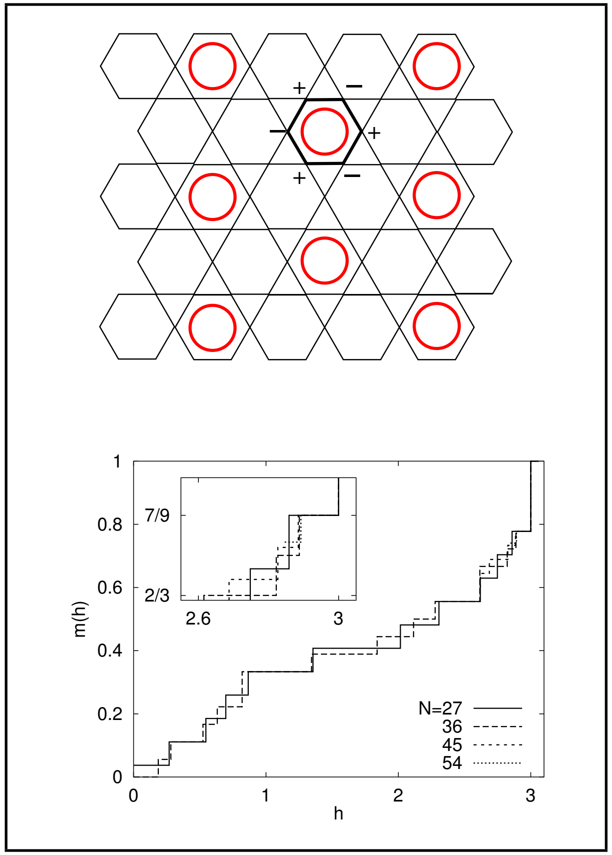
J. Schnack, H.-J. Schmidt, J. Richter, J. Schulenburg, Eur. Phys. J. B **24**, 475 (2001)

# Extended lattices and flat bands

More in Johannes Richter's talk
(next on this program)

CANCELED

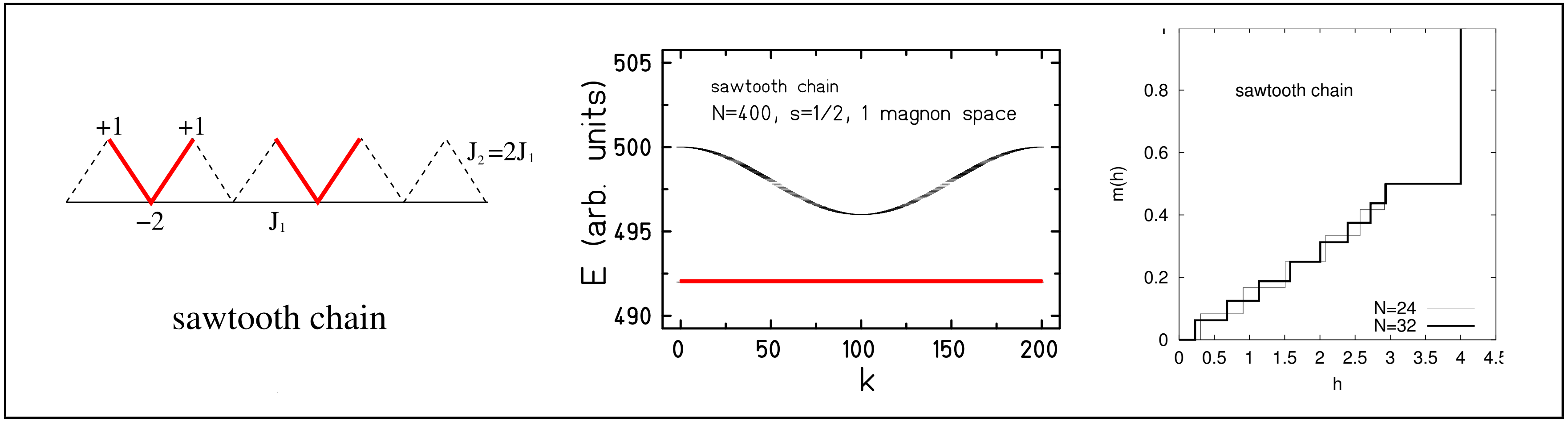
# Giant magnetization jumps in frustrated antiferromagnets III
# Kagome Lattice




- 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 $E_{\text{min}}$ on $M$ $\Rightarrow \quad (T = 0)$ 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)

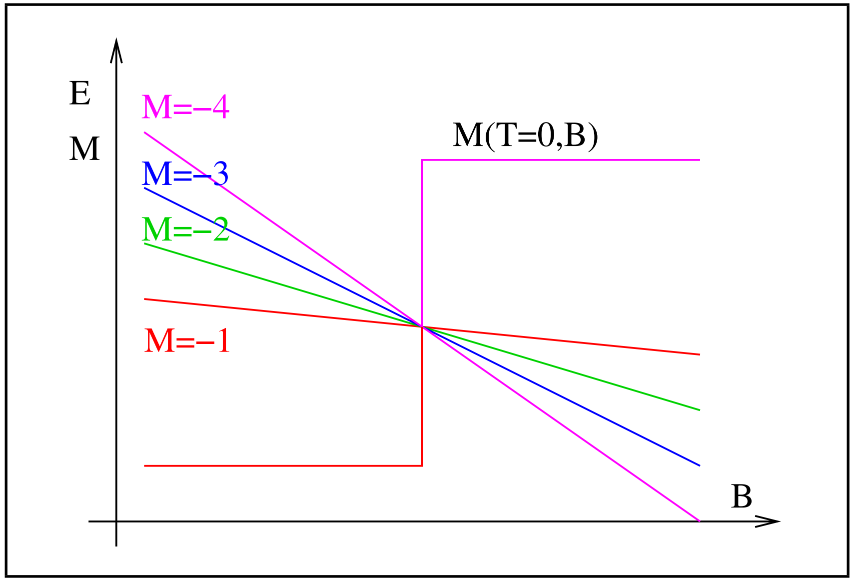
# Condensed matter physics point of view: Flat band




- 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; universal low-temperature behavior.
- Same behavior for Hubbard model; flat band ferromagnetism (Tasaki & Mielke), jump of $N$ with $\mu$ (1).

(1) 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.
- High degeneracy of ground state levels $\Rightarrow$ large residual entropy at $T = 0$.
- $$\left(\frac{\partial T}{\partial B}\right)_S = -\frac{T}{C}\left(\frac{\partial S}{\partial B}\right)_T$$

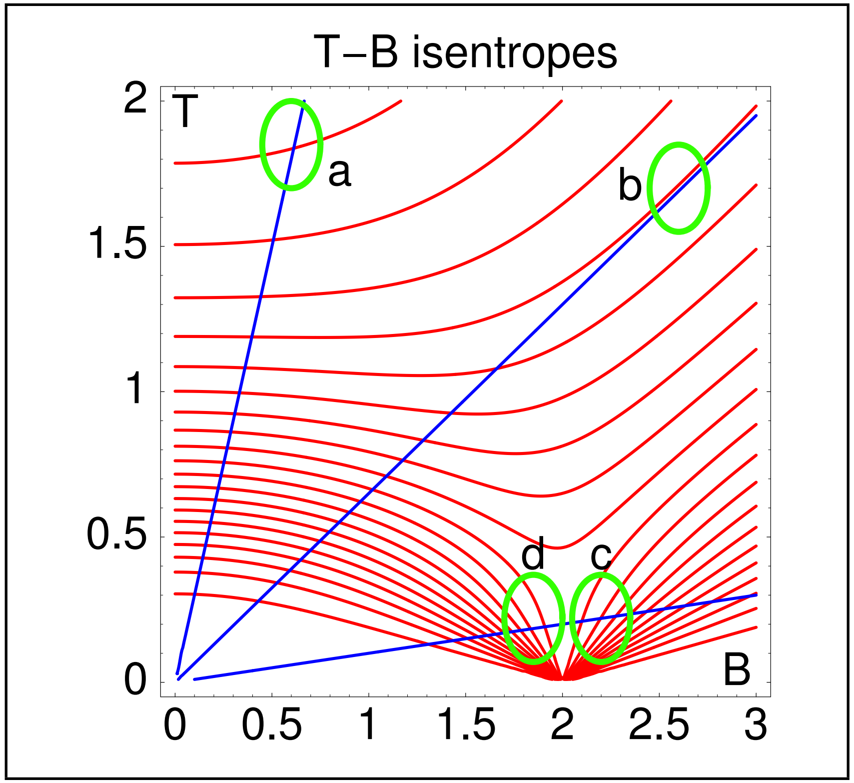
J. Schulenburg, A. Honecker, J. Schnack, J. Richter, H.-J. Schmidt, Phys. Rev. Lett. **88**, 167207 (2002)

A. Honecker, J. Richter, Condensed Matter Physics **8**, 813 (2005)

H.-J. Schmidt, J. Richter, R. Moessner, J. Phys. A: Math. Gen. **39**, 10673 (2006)

O. Derzhko, J. Richter, A. Honecker, H.-J. Schmidt, Low Temp. Phys. **33**, 745 (2007)

# 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,

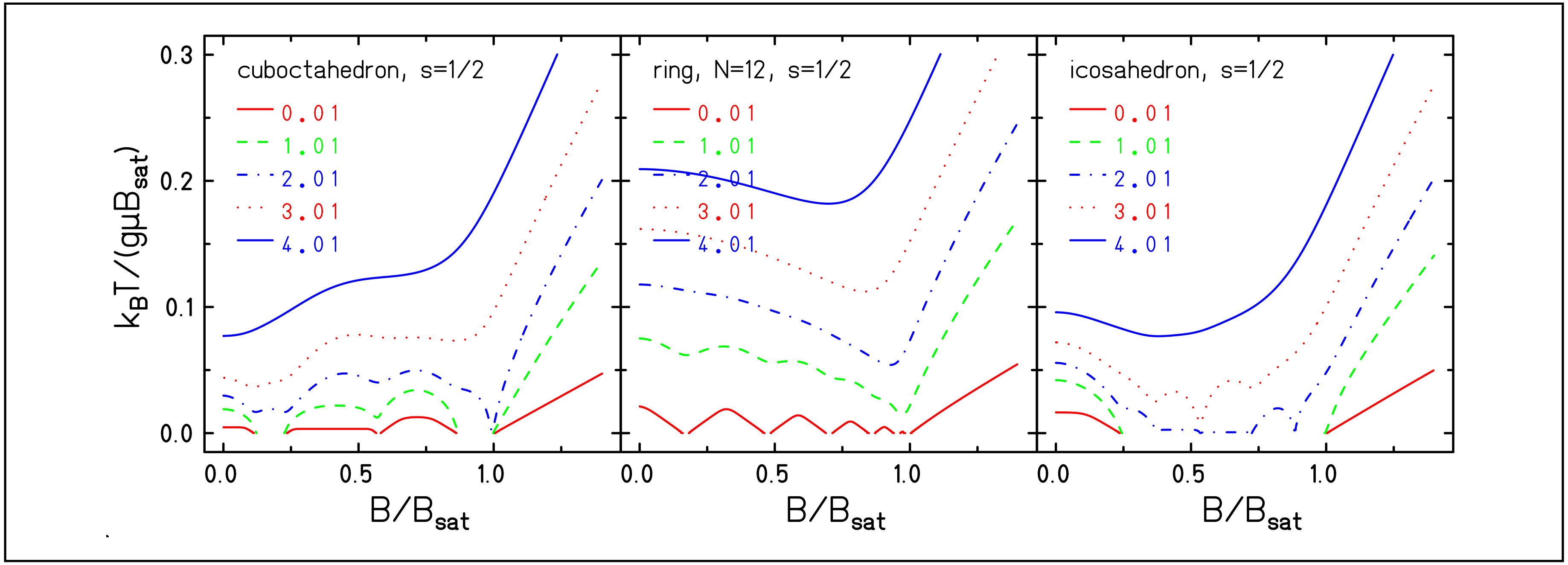
(c) enhanced,

(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)

# Thank you very much for your attention.

# German Molecular Magnetism Web

# www.molmag.de

Highlights. Tutorials. Who is who. DFG SPP 1137