Frustration-induced exotic properties of magnetic molecules

Jürgen Schnack

Department of Physics – University of Bielefeld – Germany
http://obelix.physik.uni-bielefeld.de/~schnack/

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The beauty of magnetic molecules

Huge variety of molecular structures:

- Dimers (Fe$_2$), tetrahedra (Cr$_4$), cubes (Cr$_8$);
- Rings, especially iron and chromium rings (order from The Manchester Magic Ring Factory, Brunswick Street, Manchester, M13 9PL, UK);
- SMMs such as Mn$_{12}$-acetate or Mn$_6$ (E. Brechin)
- “Soccer balls”, more precisely icosidodecahedra (Fe$_{30}$, Cr$_{30}$) and many other 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 II

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) E.g. by G. Timco & R. Winpenny and H.C. Yao.
(2) E.g. by R. Winpenny, L. Cronin and A. Powell.
(3) E.g. by A. Müller and P. Kögerler.
(4) Almost (!) by R. Winpenny.
Model Hamiltonian – Heisenberg-Model

\[
\widetilde{H} = -\sum_{i,j} J_{ij} \vec{s}(i) \cdot \vec{s}(j) + g \mu_B B \sum_{i} s_z(i)
\]

Heisenberg
Zeeman

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

\[
\begin{align*}
\left[ \widetilde{H}, \vec{S}^2 \right] &= 0 & & \left[ \widetilde{H}, S_z \right] &= 0 \\
\widetilde{H} | \nu \rangle &= E_\nu | \nu \rangle & & \vec{S}^2 | \nu \rangle &= S_\nu(S_\nu + 1) | \nu \rangle & & S_z | \nu \rangle &= M_\nu | \nu \rangle
\end{align*}
\]
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:

\[
J(x_A, y_B) \leq g^2, \quad J(x_A, y_A) \geq g^2, \quad J(x_B, y_B) \geq g^2,
\]

cmp. (1,2).

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

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

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

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

- Yields eigenvalues for the shift operator $T$:

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

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).

(2) $\lfloor \cdot \rfloor$ largest integer, smaller or equal
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 ($N \neq 3$).

<table>
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<th>$N$</th>
<th>$s$</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
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<td>12 ≡ 4</td>
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<td>-</td>
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<td>-</td>
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<tr>
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<td>1/2</td>
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<td>5 ≡ 4</td>
<td>10 ≡ 1</td>
<td>15 ≡ 3</td>
<td>20 ≡ 2</td>
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<td>30 ≡ 3</td>
<td>35 ≡ 1</td>
<td>40 ≡ 4</td>
<td>45 ≡ 0</td>
</tr>
</tbody>
</table>

No general proof yet.

Fe$_{30}$ and friends
(corner-sharing triangles)
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): $H^{\text{eff}} \sim -2 J^{\text{eff}} \vec{S}_A \cdot \vec{S}_B$;

Giant magnetization jumps in frustrated antiferromagnets I

\{ \text{Mo}_{72}\text{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);

Giant magnetization jumps in frustrated antiferromagnets II

Localized Magnons

- \[ |\text{localized magnon}\rangle = \frac{1}{2} (|1\rangle - |2\rangle + |3\rangle - |4\rangle) \]

- \[ |1\rangle \approx s^{-1}(1)|\uparrow\uparrow\uparrow \ldots\rangle \text{ etc.} \]

- \[ H |\text{localized magnon}\rangle \propto |\text{localized magnon}\rangle \]

- Localized magnon is state of lowest energy (1,2).

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

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 $E_{\text{min}}$ on $M$ \[ \Rightarrow (T = 0) \text{ magnetization jump}; \]

A rare example of analytically known many-body states!

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 $M$ $\Rightarrow$ ($T = 0$) magnetization jump;

- Jump is a macroscopic quantum effect!

- A rare example of analytically known many-body states!

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).

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(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 $T = 0$.

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

Magnetocaloric effect II

Isentrops of $af$ $s = 1/2$ 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.

blue lines: ideal paramagnet, red curves: af dimer
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.

Hysteresis without anisotropy (edge-sharing triangles) ⇒⇒⇒ see poster
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).

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.

Thank you very much for your attention.
German Molecular Magnetism Web

www.molmag.de

Highlights. Tutorials. Who is who. DFG SPP 1137