A short introduction into magnetic molecules

Jürgen Schnack

Fachbereich Physik - Universität Osnabrück
http://obelix.physik.uni-osnabrueck.de/~schnack/

International Max Planck Research School for “Dynamical Processes in Atoms, Molecules and Solids”
Dresden, October 6th 2005
In late 20th century people coming from transport theory, general relativity, nuclear physics, and Zener diodes were triggered by a “magnetic” enthusiast.
Meanwhile a big collaboration has been established

- M. Luban, P. Kögerler, D. Vaknin (Ames Lab, USA); J. Musfeldt (U. of Tennessee, USA); N. Dalal (Florida State, USA);
- Chr. Schröder (FH Bielefeld & Ames Lab, USA);
- H. Nojiri (Tohoku University, Japan);
- R.E.P. Winpenny (Man U); L. Cronin (U. of Glasgow);
- J. Richter, J. Schulenburg, R. Schmidt (U. Magdeburg);
- S. Blügel, A. Postnikov (FZ Jülich); A. Honecker (Uni Braunschweig).
- E. Rentschler (U. Mainz); U. Kortz (IUB); A. Tennant (HMI Berlin).
... and various general results could be achieved

1. The suspects: magnetic molecules
2. The thumbscrew: Heisenberg model
3. Extension of Lieb, Schultz, and Mattis: $k$–rule for odd rings
4. Rotational bands in antiferromagnets
5. Giant magnetization jumps in frustrated antiferromagnets
6. Magnetization plateaus and susceptibility minima
7. Enhanced magnetocaloric effect
8. Hysteresis without anisotropy
9. A special triangular molecule-based spin tube
The beauty of magnetic molecules

- Macro molecules (polyoxometalates etc.): consist of constituents like Hydrogen (H), Carbon (C), Oxygen (O), and diamagnetic ions (e.g. Mo) as well as paramagnetic ions like Iron (Fe), Chromium (Cr), Copper (Cu), Nickel (Ni), Vanadium (V) or Manganese (Mn);

- Pure organic magnetic molecules: magnetic coupling between high spin units (e.g. free radicals);

- Single spin quantum number $\frac{1}{2} \leq s \leq \frac{7}{2}$;

- Intermolecular interaction relatively small, therefore measurements reflect the thermal behaviour of a single molecule.
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:

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:
  \[ H \approx -DS_z^2 + H', \quad [S_z, H'] \neq 0 \]

- Single molecule shows: metastable magnetization, hysteresis, ground state magnetization tunneling, thermally and phonon assisted tunneling.
The beauty of magnetic molecules IV

Why magnetic molecules?

- 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.
\{\text{Mo}_{72}\text{Fe}_{30}\} – a molecular brother of the kagome lattice and an archetype of geometric frustration

- Giant magnetic Keplerate molecule;
- Structure: Fe - yellow, Mo - blue, O - red;
- Antiferromagnetic interaction mediated by O-Mo-O bridges (1).

- Classical ground state of \{\text{Mo}_{72}\text{Fe}_{30}\}: three sublattice structure, coplanar spins (2);
- Quantum mechanical ground state \(S = 0\) can only be approximated, dimension of Hilbert space \((2s + 1)^N \approx 10^{23}\).

Hamiltonian and Tools
Model Hamiltonian – Heisenberg-Model

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

**Heisenberg**  **Zeeman**

The Heisenberg Hamilton operator together with a Zeeman term are used for the following considerations.

\( J < 0 \): antiferromagnetic coupling.

Very often additional terms – dipolar, anisotropic – are utterly negligible. If needed they can be cast in the form \( \sum_{i,j} \vec{s}(i) \cdot D_{ij} \cdot \vec{s}(j) \).
Decomposition into mutually orthogonal subspaces

If \[ [H, S_z] = 0 \], the Hilbert space \( \mathcal{H} \) can be decomposed into mutually orthogonal subspaces \( \mathcal{H}(M) \) (\( M \) is the quantum number belonging to \( S_z \))

\[
\begin{align*}
[H, S_z] &= 0 : \\
\mathcal{H} &= \bigoplus_{M=-S_{\text{max}}}^{+S_{\text{max}}} \mathcal{H}(M), \\
S_{\text{max}} &= Ns
\end{align*}
\]

\( \mathcal{H}(M) \) contains all states \( |m_1, \ldots, m_u, \ldots, m_N\rangle \) with \( \sum_i m_i = M \).

The Hamiltonian is diagonalized in all subspaces separately. The dimension of the largest subspace determines whether a Hamiltonian can diagonalized completely. If further symmetries apply this dimension will be further reduced.

For practical purposes

\[
\begin{align*}
\vec{s}(i) \cdot \vec{s}(j) &= s_z(i)s_z(j) + \frac{1}{2} \left[ s^+(i)s^-(j) + s^-(i)s^+(j) \right].
\end{align*}
\]
General Results
Rotational bands in antiferromagnets I

- Often minimal energies $E_{\text{min}}(S)$ form a rotational band: Landé interval rule (1);

- Most pronounced for bipartite systems (2,3), good approximation for more general systems;


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

- $| \text{localized magnon} \rangle = \frac{1}{2} ( |1\rangle - |2\rangle + |3\rangle - |4\rangle )$
- $|1\rangle = \sim^{-1}(1) |\uparrow \uparrow \uparrow \ldots\rangle$ etc.
- $H|1\rangle = J\{ |1\rangle + 1/2(|2\rangle + |4\rangle + |5\rangle + |8\rangle)\}$
- $H|2\rangle = J\{ |2\rangle + 1/2(|1\rangle + |3\rangle + |5\rangle + |6\rangle)\}$
- $H|3\rangle = J\{ |3\rangle + 1/2(|2\rangle + |4\rangle + |7\rangle + |6\rangle)\}$
- $H|4\rangle = J\{ |4\rangle + 1/2(|1\rangle + |3\rangle + |7\rangle + |8\rangle)\}$
- $\sim H|\text{localized magnon} \rangle \propto | \text{localized magnon} \rangle$

- Triangles trap the localized magnon, amplitudes cancel at outer vertices.
Giant magnetization jumps in frustrated antiferromagnets III
Kagome Lattice

- Non-interacting one-magnon states can be placed on various lattices, e.g. the kagome lattice;
- 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 $M \Rightarrow$ magnetization jump;
- Maximal number of independent magnons: $N/9$;
- Jump is a macroscopic quantum effect!

Condensed matter physics point of view: Flat band

- Flat band of minimal energy in one-magnon space, i.e. high degeneracy of ground state energy in $\mathcal{H}(M = Ns - 1)$;

- Localized magnons can be built from those eigenstates of the translation operator, that belong to the flat band;

- Sawtooth chain exceptional since degeneracy is $N/2$ (very high).

Enhanced magnetocaloric effect I

Basics

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

(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\(_x\)Ge\(_{1-x}\))\(_4\) 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 due to the condensation of independent magnons (3).

Enhanced magnetocaloric effect II
Simple $s = 1/2$ dimer

- Singlet-triplet level crossing causes a “quantum phase transition” (1) at $T = 0$ as a function of $B$.
- $M(T = 0, B)$ and $S(T = 0, B)$ not analytic as function of $B$.
- $C(T, B)$ varies strongly as function of $B$ for low $T$.

(1) If you feel the urge to discuss the term “phase transition”, please let’s do it during the coffee break. I will bring Ehrenfest along with me.
Enhanced magnetocaloric effect III

Entropy of antiferromagnetic $s = 1/2$ dimer

$S(T = 0, B) \neq 0$ at level crossing due to degeneracy

Enhanced magnetocaloric effect IV

Isentrops of $s = 1/2$ 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
Enhanced magnetocaloric effect V

Two molecular spin systems

- Graphics: isentrops of the frustrated cuboctahedron and a $N = 12$ ring molecule;

- Cuboctahedron features independent magnons and extraordinarily high jump to saturation;

- Degeneracy and $(T = 0)$–entropy at saturation field higher for the cuboctahedron;

- Adiabatic (de-) magnetization more efficient for the frustrated spin system.
Metamagnetic phase transition I

Hyteresis without anisotropy

- Normally hysteretic behavior of Single Molecule Magnets is an outcome of magnetic anisotropy.
- The classical AF Heisenberg Icosahedron exhibits a pronounced hysteresis loop.
- It shows a first order phase transition at $T = 0$ as function of $B$.
- The minimal energies are realized by two families of spin configurations.
- The overall minimal energy curve is not convex $\Rightarrow$ magnetization jump.

Metamagnetic phase transition II

- Quantum analog: Non-convex minimal energy levels ⇒ magnetization jump of \( \Delta M > 1 \).
- Lanczos diagonalization for various \( s \).
- True jump of \( \Delta M = 2 \) for \( s = 4 \).
- Polynomial fit in \( 1/s \) yields the classically observed transition field.

Summary

Geometric frustration of interacting spin systems is the driving force of a variety of fascinating phenomena in low-dimensional magnetism.

Therefore . . .
Frustrated, or not frustrated; that is the question:
Whether it’s nobler in the mind to suffer
The difficulties and pain of competing interactions,
Or to take arms against the intractable antiferromagnets?
And by diagonalizing the Hamiltonian? To know;
No more; and to say we understand
The gaps, the plateaus, and the giant jumps

...
Thank you very much for your attention.
Information

Advances and Prospects in Molecular Magnetism

362. Wilhelm und Else Heraeus-Seminar
Bad Honnef, 13. 11. 2005 - 16. 11. 2005

www.molmag.de
Buy now!

Quantum Magnetism

Lecture Notes in Physics, Vol. 645
Schollwöck, U.; Richter, J.; Farnell, D.J.J.; Bishop, R.F. (Eds.)
2004, XII, 478 p., Hardcover, 69,95 €
ISBN: 3-540-21422-4

Mikeska, Kolezhuk, One-dimensional magnetism
Richter, Schulenburg, Honecker, Q. Mag. in 2-D
Schnack, Molecular Magnetism
Ivanov, Sen, Spin Wave Analysis
Lafloréncie, Poilblanc, Low-Dim. Gapped Systems
Cabra, Pujol, Field-Theoretical Methods
Farnell, Bishop, Coupled Cluster Method
Klümper, Integrability of Quantum Chains
Sachdev, Mott Insulators
Lemmens, Millet, Spin Orbit Topology, a Triptych