Magnetism in zero dimensions – physics of magnetic molecules

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Contents for you today

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The beauty of magnetic molecules I

- 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
• 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 $T$.

$$H \approx DS_z^2$$

- Metastable magnetization and hysteresis;

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

$$H \approx DS_z^2 + E(S_x^2 - S_y^2)$$
[\text{Mn}^\text{III}_6\text{O}_2\text{(Et-sao)}_6\text{(O}_2\text{CPh(Me}_2\text{))}_2\text{(EtOH)}_6\text{]}:

- $S = 12$ 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).

“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 $H \sim DS^2$,. . . 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)


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$_6$Cr (1), Mn$_6$Fe (2), …

- Advantage: no $E$-terms, i.e. no (less) tunneling;

- Problem: exchange interaction sometimes antiferromagnetic.

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

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).

Antiferromagnetic Molecules III – Trend B

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).

Antiferromagnetic Molecules IV – Trend C

Soliton dynamics

- Theoretical realization of classical solitons on antiferromagnetic Heisenberg spin rings (1)

- Do quantum solitons exist and if, how do they look like? (2)

Molecules on Surfaces
Molecules on Surfaces I

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).

Molecules on Surfaces II

Rings on surfaces

- Sulfur-functionalized clusters Cr$_7$Ni 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)

Molecules on Surfaces III

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)

from (1)

"Backslash" on molecule

- How much of the deposited molecule survives?
- Study of a $\text{Mn}_6$ cluster grafted on a Polyoxometalate (POM) (1);
- Intra-molecular interactions change compared to free molecule (1).

from (1)

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)

Coherence Phenomena
Coherence Phenomena I

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.

Coherence Phenomena II

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;
- $\mu$s (!) can be reached. (1)

Up to date theory modeling
Model Hamiltonian (spin only)

\[ \hat{H} = \sum_{i,j} \vec{s}(i) \cdot J_{ij} \cdot \vec{s}(j) + \sum_{i,j} \vec{D}_{ij} \cdot \left[ \vec{s}(i) \times \vec{s}(j) \right] + \mu_B \vec{B} \sum_i g_i \vec{s}(i) \]

Exchange/Anisotropy  \hspace{1cm} \text{Dzyaloshinskii-Moriya}  \hspace{1cm} \text{Zeeman}

Isotropic Hamiltonian

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

Heisenberg  \hspace{1cm} \text{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:

- \[ \tilde{H} = - \sum_{i,j} J_{ij} \tilde{s}_i \cdot \tilde{s}_j + g\mu_B \tilde{S} \cdot \tilde{B} ; \]
- \[ \left[ H, \tilde{S}^2 \right] = 0, \left[ \tilde{H}, \tilde{S}_z \right] = 0 ; \]
- Irreducible Tensor Operator (ITO) approach, MAGPACK (1);
- Additional point group symmetries (2).

Reminder ITO

\[ H_{\text{Heisenberg}} = \sqrt{3} \sum_{i,j} J_{ij} T^{(0)}(\{k_i\}, \{\bar{k}_i\}|k_i = k_j = 1) \]

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, …
Advanced ITO & Point Groups II

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

Point Group Symmetry

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

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).

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);
Anisotropic magnetic molecules I – Theory

\[ H(\vec{B}) = -\sum_{i,j} J_{ij} \vec{S}(i) \cdot \vec{s}(j) + \sum_i d_i (\vec{e}_i \cdot \vec{s}(i))^2 + \mu_B \vec{B} \cdot \sum_i^N g_i \cdot \vec{s}(i) \]

- \( [H, \vec{S}^2] \neq 0, \ [H, \vec{S}_z] \neq 0; \)

- You have to diagonalize \( H(\vec{B}) \) for every field (direction and strength)!
  \( \Rightarrow \) Orientational average.

- If you are lucky, point group symmetries still exist. Use them!

- Easy: \( \text{dim}(\mathcal{H}) < 30,000 \); possible: \( 30,000 < \text{dim}(\mathcal{H}) < 140,000 \)

Anisotropic magnetic molecules II – Example

What can be achieved? \( \text{Mn}_3\text{Cr} \):

- Two couplings: \( J_1 \) to central Cr, \( J_2 \) between Mn; Mn: \( s=\frac{5}{2}, g=2.0 \); Cr: \( s=\frac{3}{2}, g=1.95 \)
- 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: \( J_1 = -0.29 \text{ cm}^{-1}, J_2 = -0.08 \text{ cm}^{-1} \),
  \( d_{\text{Mn}} = -1.21 \text{ cm}^{-1}, \vartheta_{\text{Mn}} = 22^\circ, d_{\text{Cr}} = +0.17 \text{ cm}^{-1} \).
- \textit{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:

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

cmp. (1,2).

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

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

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

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

- Yields eigenvalues for the shift operator $T$: \( \sim \)

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

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

- 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>
<thead>
<tr>
<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>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>1/2</td>
<td>0</td>
<td>4</td>
<td>8 $\equiv$ 0</td>
<td>12 $\equiv$ 4</td>
<td>16 $\equiv$ 0</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>-</td>
</tr>
<tr>
<td>9</td>
<td>1/2</td>
<td>0</td>
<td>5 $\equiv$ 4</td>
<td>10 $\equiv$ 1</td>
<td>15 $\equiv$ 3</td>
<td>20 $\equiv$ 2</td>
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<tr>
<td>9</td>
<td>1</td>
<td>0</td>
<td>5 $\equiv$ 4</td>
<td>10 $\equiv$ 1</td>
<td>15 $\equiv$ 3</td>
<td>20 $\equiv$ 2</td>
<td>25 $\equiv$ 2</td>
<td>30 $\equiv$ 3</td>
<td>35 $\equiv$ 1</td>
<td>40 $\equiv$ 4</td>
<td>45 $\equiv$ 0</td>
</tr>
</tbody>
</table>

No general, but partial proof yet.

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): $\tilde{H}^{\text{eff}} = -2J^{\text{eff}} \, \vec{S}_A \cdot \vec{S}_B$;


- 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

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

- \(|1\rangle = s^{-}(1)|\uparrow\uparrow\uparrow\ldots\rangle\) 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.

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 $M$ \( \Rightarrow (T = 0) \) 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).

(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
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.

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.

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.

Thank you very much for your attention.
Molecular Magnetism Web

www.molmag.de