Magnetism in zero dimensions – physics of magnetic molecules

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Contents for you today

1. Single Molecule Magnets
2. Antiferromagnetic Molecules
3. Molecules on Surfaces
4. Coherence Phenomena
5. Up to date theory modeling
6. Frustration effects
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 ($\text{Fe}_2$), 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:

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 $T$.

\[ H \sim DS_z^2 \]

- Metastable magnetization and hysteresis;

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

\[ H \sim DS_z^2 + E(S_x^2 - S_y^2) \]
Single Molecule Magnets III

\[
[Mn^{III}_6O_2(Et-sao)_6(O_2CPh(Me)_2)]_2(EtOH)_6]

- \( S = 12 \) 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).

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 $H \sim DS^2$, . . . 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\textsubscript{8} (2);

- Coupling of heterometallic rings for quantum computing (3).

(1) O. Cador \textit{et al.}, Angew. Chem. Int. Edit. 43, 5196 (2004);
H. C. Yao \textit{et al.}, Chem. Commun. 1745 (2006);
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)

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)

Molecules on Surfaces IV

“Backslash” on molecule

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

from (1)

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.

from (1)

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)

from (1)

Up to date theory modeling
Model Hamiltonian (spin only)

\[ H \sim = \sum_{i,j} \vec{s}(i) \cdot J_{ij} \cdot \vec{s}(j) + \sum_{i,j} \vec{D}_{ij} \cdot \left[ \vec{s}(i) \times \vec{s}(j) \right] + \mu_B B \sum_{i} ^N \vec{g}_i \vec{s}(i) \]

- Exchange/Anisotropy
- Dzyaloshinskii-Moriya
- Zeeman

Isotropic Hamiltonian

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

- 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:

- \( \tilde{H} = - \sum_{i,j} J_{ij} \tilde{s}_i \cdot \tilde{s}_j + g \mu_B \tilde{S} \cdot \tilde{B} \);

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

- 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

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

Point Group Symmetry

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

Advanced ITO & Point Groups III

\[ G(R) \mid \alpha S M \rangle_a = \sum_{\alpha'} \mid \alpha' S M \rangle_a a \langle \alpha' S M \mid \alpha S M \rangle_b \]

**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 \( a \langle \alpha' S M \mid \alpha S M \rangle_b \) (2).

Cuboctahedron, \( s = \frac{3}{2} \), 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

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

- \([\tilde{H}, \vec{S}^2] \neq 0, [\tilde{H}, \vec{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: \( \text{dim}(\mathcal{H}) < 30,000 \); possible: \( 30,000 < \text{dim}(\mathcal{H}) < 140,000 \)

Anisotropic magnetic molecules II – Example

What can be achieved? Mn₃Cr:

- 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 $\vartheta_{Mn1} = \vartheta_{Mn2} = \vartheta_{Mn3}$. Only relative $\phi = 120^\circ$ determined.

- Model Cr anisotropy by local axis $\vec{e}(\vartheta, \phi)$. Due to $C_3$ symmetry $\vartheta_{Cr} = 0$, $\phi_{Cr} = 0$.

- Result: $J_1 = -0.29 \text{ cm}^{-1}$, $J_2 = -0.08 \text{ cm}^{-1}$, $d_{Mn} = -1.21 \text{ cm}^{-1}$, $\vartheta_{Mn} = 22^\circ$, $d_{Cr} = +0.17 \text{ cm}^{-1}$.

- $ab$ initio calculations needed.
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

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

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

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

- Yields eigenvalues for the shift operator $T$:  

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

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

- 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)

$$k \equiv \pm a \left\lfloor \frac{N}{2} \right\rfloor \mod N, \quad a = Ns - M$$

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

<table>
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<th>$s$</th>
<th>0</th>
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</table>
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): $H_{\text{eff}} \approx -2J_{\text{eff}} \vec{S}_A \cdot \vec{S}_B$;


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

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

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

• 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 $M$ ⇒ $(T = 0)$ 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 $M$ ⇒ $(T = 0)$ magnetization jump;

- Jump is a macroscopic quantum effect!

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

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
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.

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