Lecture 1: Magnetic Interactions and Classical Magnetization Dynamics

Lecture 2: Spin Current Induced Magnetization Dynamics

Lecture 3: Quantum Spin Dynamics in Molecular Nanomagnets

Magnetic Nanostructures

Quantum Tunneling of Magnetization

Quantum Tunneling of Magnetization in Small Ferromagnetic Particles

The probability of tunneling of the magnetization in a single-domain particle through an energy barrier may be expressed as

\[ \Gamma \sim e^{-U/k_B T} \]

Where

\[ U = U_{\text{therm}} = U_{\text{quantum}} \]

\[ T = T_{\text{c}} = U / k_B B(0) \]

Thermal

Quantum

Also, Enz and Schilling, van Hemmen and Suto (1986)

Image from, W. Wernsdorfer, Advances in Chemical Physics 2001 and ArXiv:0101104
Magnetic Bistability in a Molecular Magnet

Magnetic bistability in a metal-ion cluster

R. Sessoli\(^*\), D. Gatteschi\(^{**}\), A. Caneschi\(^+\)
& M. A. Novak\(^\dagger\) Nature 1993, and Sessoli et al., JACS 1993

Magnetic hysteresis at 2.8 K and below (2.2 K)
S=10 ground state spin

Quantum Tunneling in Single Molecule Magnets

Macroscopic Measurement of Resonant Magneto- \textit{tunneling} Tuning in High-Spin Molecules

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We report the observation of steps in angular intervals of magnetic field in the hysteresis loop of a macroscopic sample of several Mn\(_{12}\)\textsubscript{acetate} \((\text{O}_2\text{CCH}_3)_{16}(\text{H}_2\text{O})_4\). The magnetization curve rises exponentially when the field is raised to a step. We propose that these effects are manifestations of tunneling between excited quantum states of the macroscopic sample.


Single Molecule Magnets

- Individual molecule can be magnetically \textit{hysteresis} 1993
- Quantum Tunneling of Magnetization
- Quantum Phase Interference
- Quantum Coherence

Magnetic Core
- Competing AFM interactions
- S=10

Organic Environment
- 2 acetic acid molecules
- 4 water molecules
- S\(_4\) site symmetry
- Tetragonal lattice \(a=1.7\) nm, \(b=1.2\) nm
- Strong uniaxial magnetic anisotropy (~60 K)
- Weak intermolecular dipole interactions (~0.1 K)

First SMM: Mn\(_{12}\)-acetate

\[[\text{Mn}_{12}\text{O}_{22}(\text{O}_2\text{CCH}_3)_{16}(\text{H}_2\text{O})_4]\_2\text{CH}_3\text{COOH}4\text{H}_2\text{O}\]

SMM Characteristics
- Molecules
- High spin ground state
- Uniaxial anisotropy
- Single crystals
- Synthesized in solution
- Modified chemically
- Peripheral ligands
- Oxidized/reduced
- Soluble
- Bonded to surfaces

\(8\) Mn\(^{3+}\) S=2
\(4\) Mn\(^{4+}\) S=3/2

Physics

NYU

2009 Boulder School, Lecture 3
Intra-molecular Exchange Interactions

\[ J_1 \sim 215 \text{ K} \]
\[ J_2, J_3 \sim 85 \text{ K} \]
\[ J_4 \sim 45 \text{ K} \]

\[ (2S_1+1)(2S_2+1)^4=10^8 \Rightarrow S=10 \text{ and } 2S+1=21 \]

Magnetic Anisotropy and Spin Hamiltonian

Spin Hamiltonian

\[ H = -D S_z^2 - g \mu_B \vec{S} \cdot \vec{H} \]

\[ S_z |m \rangle = m |m \rangle \]

\[ E_m = -D m^2 \]

[Ising-like] Uniaxial anisotropy

2S+1 spin levels

Resonant Quantum Tunneling of Magnetization

Relaxation processes in SMMs

Magnetic relaxation at high temperature

Thermal activation (over the barrier)

\[ \Gamma \sim e^{-U/kT} \]

Anisotropy Field:

\[ H_A = \frac{2DS}{g\mu_B} \]
Resonant Quantum Tunneling of Magnetization

Relaxation processes in SMMs

Resonant Quantum Tunneling of Magnetization

Crossover from Thermally Assisted to Pure QTM

\[ H = -D S_z^2 - g \mu_B S_z H_z - g \mu_B S_x H_x \]


Crossover: Chudnovsky & Garanin, PRL 1997
First- and Second-Order Transitions between Quantum and Classical Regimes for the Escape Rate of a Spin System

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(Received 7 July 1997)

We have found a novel feature of the bistable large-spin model described by the Hamiltonian \( \mathcal{H} = -DS_z^2 - \frac{1}{2} g \mu_B S_z H_z + \mathcal{H}' \). The crossover from thermal to quantum regime for the escape rate can be either first \((H_z < |D|/2)\) or second \((|D|/2 < H_z < 2|D|)\) order, that is, sharp or smooth, depending on the strength of the transverse field. This prediction can be tested experimentally in molecular magnets like Mn_{12}-acetate.

Crossover between Thermally Assisted and Pure Quantum Tunneling in Molecular Magnet Mn_{12}-Acetate

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\[ \mathcal{H} = -D S_z^2 - \frac{1}{2} g \mu_B S_z H_z + \mathcal{H}' \]

\[ H(n, m_{\text{esc}}) = n H_0 \left[1 + B/D \left( m_{\text{esc}}^2 + (m_{\text{esc}} - n)^2 \right) \right] \]

\[ D = 0.548(3) \text{ K} \quad g = 1.94(1) \quad H_m = D/2g\mu_B = 0.42 \text{ T} \]

B = 1.17(2) \times 10^{-3} \text{ K} (EPR: Barra et al., PRB 97)

Energy relative to the lowest level in the metastable well

K. Mertes et al. PRB 2001

Experiments on the Crossover to Pure QTM in Mn_{12}-acetate

Schematic: dominant levels as a function of temperature

ADK et al. EPL 2000
L. Bokacheva, PRL 2001
K. Mertes et al. PRB 2001
W. Weimersdorfer et al. PRL 2006

Tunneling Selection Rules

\[ \mathbf{H} = -D S_z^2 - g \mu_B S_z H_z + \mathbf{H}_A \]

Form of \( \mathbf{H}_A \) determined by the site symmetry of the molecule

Fe_{12}

Mn_{12}-acetate

\( C_{2v} \)-site symmetry (rhombic)
\( S_4 \)-site symmetry (tetragonal)

\[ \mathbf{H}_A = E(S_x^2 - S_y^2) \]
\[ \mathbf{H}_A = C(S_+^4 + S_-^4) \]
Hysteresis Loops as a Function of Transverse Magnetic Field

Landau-Zener Transitions

\[ P = e^{-\epsilon} \]
\[ \epsilon = \pi \Delta^2/(2\hbar v) \]
\[ v = 2Sg\mu_BdB_z/dt \]

Oscillations and Parity Effect in the Tunnel Splitting

Spin-parity effects in QTM: Loss et al., 1992
von Delft & Henley, 1992

Predicted for a biaxial system by Garg 1992!

Quantum Phase Interference in Fe_8

\[ H = -DS_x^2 + E(S_x^2 - S_y^2) - g\mu_B S_x H_x \]

Micromagnetometry

- **\(\mu\)-Hall Effect**
  - Based on Lorentz Force
  - Measures magnetic field
  - Large applied in-plane magnetic fields (>20 T)
  - Broad temperature range
  - Single magnetic particles
  - Ultimate sensitivity ~10^2 \(\mu_B\)

- **\(\mu\)-SQUID**
  - Based on flux quantization
  - Measures magnetic flux
  - Applied fields below the upper critical field (~1 T)
  - Low temperature (below T_c)
  - Single magnetic particles
  - Ultimate sensitivity ~1 \(\mu_B\)

see, A. D. Kent et al., Journal of Applied Physics 1994
W. Wernsdorfer, JMMM 1995
Summary

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