Spins Dynamics in Nanomagnets

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Lecture 1: Magnetic Interactions and Classical Magnetization Dynamics
Lecture 2: Spin Current Induced Magnetization Dynamics
Lecture 3: Quantum Spin Dynamics in Molecular Nanomagnets
Outline

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   Single molecule magnets
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   Crossover between regimes
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INTRODUCTION

Fig. I.1 Scale of size which goes from macroscopic down to nanoscopic sizes. The unit of this scale is the number of magnetic moments in a magnetic system (roughly corresponding to the number of atoms). The hysteresis loops are typical examples of magnetization reversal via nucleation, propagation and annihilation of domain walls (left), via uniform rotation (middle), and quantum tunneling (right).

Image from, W. Wernsdorfer, Advances in Chemical Physics 2001 and ArXiv:0101104
Quantum Tunneling of Magnetization in Small Ferromagnetic Particles

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(Received 29 October 1987)

The probability of tunneling of the magnetization in a single-domain particle through an energy barrier between easy directions is calculated for several forms of magnetic anisotropy. Estimated tunneling rates prove to be large enough for observation of the effect with the use of existing experimental techniques.

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

\[ \Gamma \sim e^{-B(0)} = e^{-U/k_{B}T_{c}} \]

\[ T_{c} = U/k_{B}B(0) \]

\[ T_{c} = U/k_{B}B(0) \]

also, Enz and Schilling, van Hemmen and Suto (1986)
Magnetic Bistability in a Molecular Magnet

Magnetic bistability in a metal-ion cluster

R. Sessoli*, D. Gatteschi*†, A. Caneschi*
& M. A. Novak†‡§ 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 Magnetization Tunneling in High-Spin Molecules

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(Received 1 November 1995)

We report the observation of steps at regular intervals of magnetic field in the hysteresis loop of a macroscopic sample of oriented Mn$_{12}$O$_{12}$(CH$_3$COO)$_{32}$H$_2$O$_8$ crystals. The magnetoc relaxation rate increases substantially when the field is tuned to a step. We propose that these effects are manifestations of thermally assisted, field-tuned resonant tunneling between quantum spin states, and attribute the observation of quantum-mechanical phenomena on a macroscopic scale to tunneling in a large (Avogadro’s) number of magnetically identical molecules.  [S0031-9007(96)00131-7]

![Graph of magnetization vs. magnetic field](image)

**FIG. 1.** Magnetization of Mn$_{12}$ as a function of magnetic field at six different temperatures, as shown (field sweep rate of 67 mT/min). The inset shows the fields at which steps occur.

Single Molecule Magnets

**Physics**
- Individual molecule can be magnetized and exhibit magnetic hysteresis 1993
- Quantum Tunneling of Magnetization 1995
- Quantum Phase Interference 1999
- Quantum Coherence 2008

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

**NYU**

**Mn$_{12}$**  $S = 10$

**Ni$_{12}$**  $S = 12$

**Mn$_{84}$**  $S = 6$

**Fe$_8$**  $S = 10$

Lis, 1980

Wippenny, 1999

Christou, 2004

Wiegert, 1984
First SMM: $\text{Mn}_{12}$-acetate

$[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CCH}_3)_{16}(\text{H}_2\text{O})_4].2\text{CH}_3\text{COOH}.4\text{H}_2\text{O}$

**Magnetic Core**

- 8 Mn$^{3+}$, $S=2$
- 4 Mn$^{4+}$, $S=3/2$

**Competing AFM Interactions**

- Ground state $S=10$

**Organic Environment**

- 2 acetic acid molecules
- 4 water molecules

**Single Crystal**

- $S_4$ site symmetry
- Tetragonal lattice $a=1.7$ nm, $b=1.2$ nm
- Strong uniaxial magnetic anisotropy ($\sim 60$ K)
- Weak intermolecular dipole interactions ($\sim 0.1$ K)
Intra-molecular Exchange Interactions

\[ H = \sum_{<ij>} J_{ij} \vec{S}_i \cdot \vec{S}_j + \sum_i \vec{S}_i \cdot D_i \cdot \vec{S}_i + ... \]

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

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

**Spin Hamiltonian**

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

\[ S_z |m > = m |m > \]

\[ E_m = -Dm^2 \]

[Ising-like] Uniaxial anisotropy

2S+1 spin levels
Relaxation processes in SMMs

Magnetic relaxation at high temperature

Thermal activation (over the barrier)

\[ U = U_0 (1 - H/H_o)^2 \]

\[ \Gamma \sim e^{-U/kT} \]
Resonant Quantum Tunneling of Magnetization

\[ H = -DS_z^2 - g\mu_B S_z H_z \]

\[ S_z |m > = m|m > \]

\[ E_m = -Dm^2 - g\mu_B H_z m \]

“Resonance” fields where antiparallel spin projections are coincident, \( H_k = kD/g\mu_B \), levels \( m \) and \( m' \); \( k=m+m' \)

\[ U = U_0(1-H/H_0)^2 \]

Anisotropy Field:

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

$H_L = kH_R$

$kH_R < H_L < (k+1)H_R$

$H_L = (k+1)H_R$

$\frac{M}{M_s}$

$H_L(T)$
Resonant Quantum Tunneling of Magnetization

Relaxation processes in SMMs

Magnetic relaxation at intermediate temperature

Thermally assisted tunneling

\[ U = U_0 (1 - H/H_0)^2 \]

\[ \Gamma_{TAT} = f(T) \]
Resonant Quantum Tunneling of Magnetization

Relaxation processes in SMMs

Magnetic relaxation at low temperature

Pure quantum tunneling

\[ U = U_0 (1 - H/H_0)^2 \]

\[ \Gamma_q \neq f(T) \]
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 \( \mathcal{H} = -DS_z^2 - H_x S_x \). The crossover from thermal to quantum regime for the escape rate can be either first \((H_x < SD/2)\) or second \((SD/2 < H_x < 2SD)\) order, that is, sharp or smooth, depending on the strength of the transverse field. This prediction can be tested experimentally in molecular magnets like Mn₁₂Ac. [S0031-9007(97)04645-0]

\[
U(x) = -x^2 + x^4 - x^2 \pm x^3
\]

\[
U(x) = -x^2 - x^4 \pm x^5
\]
Crossover between Thermally Assisted and Pure Quantum Tunneling in Molecular Magnet Mn$_{12}$-Acetate

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(Received 19 June 2000)

\[ \mathcal{H} = -DS_z^2 - BS_z^4 - g_z \mu_B S_z H_z + \mathcal{H}' \]

\[ H(n, m_{esc}) = nH_0 \{ 1 + B/D [m_{esc}^2 + (m_{esc} - n)^2] \} \]

\[ D = 0.548(3) \text{ K} \quad g_z = 1.94(1) \quad H_0 = D/g_z \mu_B = 0.42 \text{ T} \]

\[ B = 1.17(2) \times 10^{-3} \text{ K} \quad \text{(EPR: Barra et al., PRB 97)} \]
Experiments on the Crossover to Pure QTM in Mn12-acetate

\[ \frac{dM}{dH} \text{ versus } H_z \]

Schematic: dominant levels as a function of temperature

ADK et al. EPL 2000
L. Bokacheva, PRL 2001
K. Mertes et al. PRB 2001
W. Wernsdorfer et al. PRL 2006
Tunneling Selection Rules

\[ H = -D S_z^2 - g \mu_B S_z H_z + H_A \]

Form of \( H_A \) determined by the site symmetry of the molecule

\[
H_A = \begin{cases} 
E(S_x^2 - S_y^2) & \text{for } \text{C}_2\text{-site symmetry [rhombic]} \\
C(S_+^4 + S_-^4) & \text{for } \text{S}_4\text{-site symmetry [tetragonal]} 
\end{cases}
\]

Fe\textsubscript{8} \hspace{1cm} Mn\textsubscript{12}-acetate

C\textsubscript{2}\text{-site symmetry [rhombic]} \hspace{1cm} S\textsubscript{4}\text{-site symmetry [tetragonal]
Hysteresis Loops as a Function of Transverse Magnetic Field

Landau-Zener Transitions

\[ P = e^{-\epsilon} \]

\[ \epsilon = \pi \Delta^2 / (2\hbar v) \]

\[ v = 2Sg\mu_B dB_z / dt \]
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!


\[ H = -D S^2_\pm + E (S^2_+ + S^2_-) + C (S^4_+ + S^4_-) + g \mu_B S H \]

\[ D = 0.292 \text{K}, \quad E = 0.046 \text{K}, \quad C = -2.9 \times 10^{-5} \text{K} \]
Quantum Phase Interference in Fe$_8$

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

Quantum Phase Interference and Parity Effects in Magnetic Molecular Clusters

W. Wernsdorfer$^{1*}$ and R. Sessoli$^2$

An experimental method based on the Landau-Zener model was developed to measure very small tunnel splittings in molecular clusters of eight iron atoms, which at low temperature behave like a nanomagnet with a spin ground state of \( S = 10 \). The observed oscillations of the tunnel splittings as a function of the magnetic field applied along the hard anisotropy axis are due to topological quantum interference of two tunnel paths of opposite windings. Transitions between quantum numbers \( M = -S \) and \( (S - n) \), with \( n \) even or odd, revealed a parity effect that is analogous to the suppression of tunneling predicted for half-integer spins. This observation is direct evidence of the topological part of the quantum spin phase (Berry phase) in a magnetic system.
Micromagnetometry

**µ-Hall Effect**
- Based on Lorentz Force
- Measures magnetic field
  \[ V_H = \frac{\alpha I}{ne} M \]
- Large applied in-plane magnetic fields (>20 T)
- Broad temperature range
- Single magnetic particles
- Ultimate sensitivity \( \sim 10^2 \mu_B \)

**µ-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 \( \sim 1 \mu_B \)

Hall bars 1 to 10 \( \mu m \)

Josephson Junctions

Hall bars

1 \( \mu m \)

see, A. D. Kent et al., Journal of Applied Physics 1994

W. Wernsdorfer, JMMM 1995
Nano-SQUID

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