QUANTUM SPIN DYNAMICS OF RARE-EARTH IONS

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Collaborations with other groups
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Nanometer scale

S = 10

1 nm  2 nm  3 nm  20 nm

Single Molecule  Magnetic Protein  Cluster  Nanoparticle

S = \frac{10^3}{10^6}
The molecules are regularly arranged in the crystal.
Mn(III) $S=2$

Mn(IV) $S=3/2$

Total Spin = 10
SINGLE MOLECULE « MAGNET »
Energy barrier in zero field (symmetrical)
\[ H = -D S_z^2 - B S_z^4 - E(S_+^2 + S_-^2) - C(S_+^4 + S_-^4) \]

If applied field // \(-M\)

Thermally activated tunneling

Ground state tunneling

Molecular magnets (S. Miyashita)
large spins give extremely small splittings

Tunneling probability:
\[ P_{LZ} = 1 - \exp\left[-\frac{\pi(\Delta/\hbar)^2}{\gamma c}\right] \]
\[ c = \frac{dH}{dt} \]
Tunneling of magnetization in Mn$_{12}$-ac:

« Technical » hysteresis loop + resonant tunneling

Steps at $H_n = 450 \text{ mT}$

ICM'94 Barbara et al, JMMM (1995); NATO-ASI, QTM'94 ed. Gunther and Barbara;
Thomas et al Nature (1996); Friedman et al, PRL (1996);

... Slow quantum spin dynamics of molecule magnets....
Crossover From Classical to Quantum Regime

\[(\text{Mn}_{12}-\text{ac})\]

Resonance width and tunnel window
Effects of magnetic couplings and hyperfine Interactions

Data points and calculated lines

Level Scheme

Inhomogeneous dipolar broadening and the electronic spin-bath

Homogeneous broadening of the tunnel window by nuclear spins:
Prokofiev and Stamp (1998)

Weak HF coupling:
Broadens the tunnel window (10^5)
Decoherence mechanisms

Landau-Zener model

For an ensemble of spins

\[ H = -D S_z^2 - B S_z^4 - E(S_z^2 + S_z^2) - C(S_z^4 + S_z^4) - g\mu_B S_z H \]

Tunneling probability:

\[ P_{LZ} = 1 - \exp\left[-\pi \frac{(\Delta / \hbar)^2}{\gamma c}\right] \]

\[ c = \frac{dH}{dt} \]

Single Molecule Magnets: large spins

very small tunnel splittings: \( \Delta \sim (E/D)^{-2S} \)

very small tunnel probabilities:

\[ P_{LZ} \sim \frac{\Delta^2}{c} \sim \frac{(E/D)^{4S}}{c} \]

\[ P_{PS} \sim \frac{(\Delta^2/\omega_0)}{e^{-\xi / \xi_0}} \]

Larger tunneling rate
Strong decoherence
$V_{15}$, a molecule with $S=1/2$
Dipolar interactions $10^3$ times smaller but $I=7/2$

Absorption of sub-centimetric waves

$W.~Wernsdorfer,~D.Mailly,~A.~Müller,~and~B.~Barbara,~EPL,~2004$
Gaussian absorption lines

\[ \Gamma_L = \frac{\pi}{4} (\gamma b)^2 f (\nu = \gamma B_L) \]

Important broadening by nuclear spins and other molecule spins

\[ P = \frac{(\gamma b)^2}{(\gamma B - \nu)^2 + (\gamma b)^2} \sin^2 \left\{ \frac{1}{2} \left[ (\gamma B - \nu)^2 + (\gamma b)^2 \right] t \right\} \]

\[ \Omega_R \sim \gamma b \sim 30 \text{ kHz} \ll 1/\tau_2 \sim \gamma \sigma \sim 0.2 \text{ GHz} \]

Rabi oscillations, require much larger \( b \).

\[ N = B_{\text{Max}}/2\pi \sigma = \gamma B \tau_2/2\pi \sim 20 \]

Precession \sim 20 \text{ turns}

W. Wernsdorfer, D. Mailly, A. Müller, and B. Barbara, EPL, 2004
Tunneling of the angular momentum of Isolated Rare-earths ions
(ensemble measurements of « paramagnetic » ions)

An extention of the slow quantum dynamics studies of SMM
to the cases of strong spin-orbit and hyperfine coupling

0.2 % Ho³⁺ in substitution of Y³⁺
In YLiF₄
Tetragonal symmetry (Ho in S4);
\( J = L+S = 8; \quad g_J=5/4 \)

Dipolar interactions

\(~ 20 \text{ mK} \ll 200 \text{ mK} \) (levels separation)
CF levels and energy barrier of $\text{Ho}^{3+}$ in $Y_{0.998}\text{Ho}_{0.002}\text{LiF}_4$

$$H_{CF} = B_2^0 O_2^0 + B_4^0 O_4^0 + B_6^0 O_6^0 + B_4^4 O_4^4 + B_6^4 O_6^4$$


$B_{20} = 0.606$ K, $B_{40} = -3.253$ mK, $B_{44} = -42.92$ mK, $B_{60} = -8.41$ mK, $B_{64} = -817.3$ mK

Sh. Gifeisman et al, Opt. Spect. (USSR) 44, 68 (1978);
Hysteresis loop of weakly interacting Ho$^{3+}$ ions in YLiF$_4$.
Quasi-Ising CF Ground-state + Hyperfine Interactions

$$H = H_{CF-Z} + A\{J_zI_z + (J^+ I^- + J^- I^+)/2\}$$

The ground-state doublet $\rightarrow 2(2 \times 7/2 + 1) = 16$ states

$$E(I, H_z)$$

$$g_J\mu_B H_n = nA/2$$

$$A = 38.6 \text{ mK, Linewidth } \sim 10 \text{ mK } \sim \text{Dip. Int.}$$

Avoided Level Crossings between $|\Psi^-, I_z\rangle$ and $|\Psi^+, I_z\rangle$ if $\Delta I = (I_z - I_z')/2 = \text{odd}$

Co-Tunneling of electronic and nuclear momenta:
**Electro-nuclear entanglement (2-bodies)**
Application of a transverse magnetic field:

(slow sweeping field: sample at the cryostat temperature)

Acceleration of quantum dynamics → the remanent magnetization vanishes
Quantum fluctuations destroy the local moment
Transition from « Classical » to Quantum Paramagnet (QPT)
Nature of the mixing: entangled electro-nuclear states
Additional steps at fields: $H_n = (23/2).n$ (mT)
(single Ho$^{3+}$ tunneling being at avoided level crossings at $H_n = 23.n$ mT)

Simultaneous tunneling of Ho$^{3+}$ pairs due to dipolar interactions (4-bodies entanglement)
Two Ho$^{3+}$ Hamiltonian avoided level crossings at $H_n = (23/2).n$

Giraud et al, PRL 87, 057203 1 (2001)
Ac susceptibility (SQUID measurements)

Single-ion and dipolar-bias Tunneling

Co-tunneling

Tunneling rates and ac measurement frequency

Single-ion level structure

\[ E_n = \Delta E \pm g \mu_B H_n \]

Tunneling:
\[ g \mu_B H_n = (n' - n) \frac{\alpha}{2} \]

Co-tunneling:
\[ g \mu_B H_n = (n' - n + 1/2) \frac{\alpha}{2} \]

(A = Ho hyperfine constant)

Two-ions Level structure

Electronic Spin-bath:
Co-tunneling
Bias tunneling
Diffusive tunneling

Nuclear spin-bath (Li, F, Y):
Linewidths

R. Giraud, A. Tkachuk, and B. Barbara
Ho-dimer satellites in the EPR signal in $^7$LiYF$_4$ (1% Ho): Bias-tunneling transitions only

Boris Malkin group, Kazan

In the $^7$Li 0.1% sample the width of single ions $\sim$3.5 mT and of dimers $\sim$2 mT

G. Shakurov, B. Malkin, B. Barbara, Appl. Magn. Res. 2005
Toy model of two coupled effective spins, with $g_z/g_x \gg 1$

$$H/J = \sum_{ij} S_i^z S_j^z + \alpha \sum_{ij} (S_i^+ S_j^- + S_j^+ S_i^-)/2 + \beta \sum_{ij} (S_i^+ S_j^+ + S_j^- S_i^-)$$

with

$$\alpha = (J_x + J_y)/4J \quad \beta = (J_x - J_y)/4J$$

This is why dipolar interactions induce co-tunneling.
Direct check of hyperfine sublevels from EPR
In Ho:YLiF₄ (B. Malkin group)

G. Shakurov, B. Malkin, B. Barbara, Appl. Magn. Res. 2005
Direct observation of levels repulsions
Hyperfine sublevels ($\Delta m=2$) in the EPR spectra

G. Shakurov, B. Malkin, B. Barbara, Appl. Magn. Res. 2005
Phenomenological fit:

\[ \frac{1}{T_1} = \frac{B^2 W}{[W^2 + (\omega_N - \Delta)^2]} \]

\[ \Delta = [1.3 \times 10^{18} (H-23n)^2 + \Delta_n^2]^{1/2} \]

with \( \Delta_n \sim 20 \text{ mK} \).

Levels broadening at crossing is extremely small (~ 2 mT):

Decoherence strongly suppressed: possible to measure directly level repulsion
Case of a metallic matrix: 

\( \text{Ho}^{3+} \) ions in \( Y_{0.999}\text{Ho}_{0.001}\text{Ru}_{2}\text{Si}_{2} \)

These steps come from tunneling transitions of \( J+I \) of single \( \text{Ho}^{3+} \) ions, in a sea of free electrons.

CONCLUSION

Molecular magnets

Coexistence of classical hysteresis loop and resonant quantum tunneling
  non-adiabatic Landau-Zener (single-ion picture)
  Observation of tunneling made possible by environmental spins (nuclear spins)
  Spin tunneling assisted by photons (photons bath)
  Strong decoherence by environmental spins (nuclear spins)

Highly diluted Ho$^{3+}$ in LiYF$_4$

Tunneling of the total angular momentum J = L+S of Ho$^{3+}$ single ions
  two-bodies entanglement
  Quasi-isolated Ho$^{3+}$ ions: J and I tunnel simultaneously (in a metal also: Ho in YSi$_2$Ru$_2$).
  Relevant quantum number of Ho$^{3+}$ is not J but I+J (Kramers, QPT…).

Co-tunneling, bias-tunneling, spin-diffusion in Ho$^{3+}$ dimmers
  four-bodies entanglements, Co-tunneling of dimmers is observed.
  Crucial role of the anisotropic character of dipolar interactions.
  Microscopic basis for the study of QPT (concentrated systems) and coherent quantum dynamics.

…. Molecular magnets with Rare-Earths

R-E Double-Deckers also show single-ion tunneling on electro-nuclear states
  (M. Ruben)
Some perspectives

Higher order many-body tunneling and decoherence by the environment (quantum phase transitions)

Spin-echo experiment and Rabi oscillations on electronic states of

- Molecular magnets
  (intra-molecules hyperfine interactions ~10 mK)

- Entangled E-N pairs of Ho\(^{3+}\)
  (dipolar interactions, hyperfine interactions ~1 mK)

Metallic systems: Decoherence by free carriers on spin tunneling in meta injection of polarized spins.

(Tunneling, Kondo, Heavy fermions, Spintronics)

Spin qubits manipulated by photons
Manipulating the exchange interactions between two spins

Qubit de spins coupled by the injection of an electron and manipulated by transfer of photo-electrons

Far infra-red: variations of charges (S)
Sub-centimeter: variations of spin projections (m_S)

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FOR

YOUR ATTENTION!
Mesoscopic Magnetism

Nano-magnetism

Tunneling of narrow DWs in highly anisotropic systems ($\text{Dy}_3\text{Al}_2$, $\text{SmCoCu}$)

Nanomagnetism on distributions (deposited clusters, $\text{BaFeO}$ nanoparticles...)

Single-particles nano-magnetism (micro-SQUIDs)
- nanoparticles, clusters (10 nm): thermally activated reversal (SW, NB models...)

Quantum nano-magnetism
- single molecule magnets (1 nm): reversal by tunneling, slow quantum dynamics with different environments: inhomogeneous and homogeneous baths (spin, phonon, radiation, free carriers...)

Sub-nanometer scale

Atomic magnets (Quantum)
- Rare-Earths ions (0.1 nm): Crucial role of nuclear spins