Molecular Magnetism

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Outline

- Introduction
- 0d Materials (Single Molecule Magnets)
  - Reversal of the magnetization: thermal process
  - Reversal of the magnetization: quantum process
  - Rational Design of SMMs
- 1d materials (Single Chain Magnets)
  - Addressing individual molecules
  - SMMs on surfaces
  - SMMs in transport experiments
Organic ferromagnets

Magnetism of $S=1/2$ for each molecule, not of “impurities”

the first one (1991)
$T_c = 0.6 \text{ K}$

the highest $T_c$
$T_c = 36 \text{ K}$
Magnetic Exchange in Molecular Materials

\[ H = S_A \cdot J \cdot S_B \]

\[ J = \begin{pmatrix} J_{xx} & J_{xy} & J_{xz} \\ J_{yx} & J_{yy} & J_{yz} \\ J_{zx} & J_{zy} & J_{zz} \end{pmatrix} \]

\[ H = J S_A \cdot S_B + S_A \cdot D_{AB} \cdot S_B + d_{AB} \cdot (S_A \times S_B)_A \]

Isotropic (Heisenberg)  
J = 1/3 Tr(J)

Anisotropic (traceless matrix)

Antisymmetric (Dzyaloshinsky-Moriya)

Favours AF interaction

Favours F interaction
Isotropic Exchange in a pair

\[ S = S_a + S_b \]

\[ S^2 = (S_a + S_b)^2 = S_a^2 + S_b^2 + 2S_a S_b \]

\[ S_a S_b = \frac{1}{2}(S^2 - S_a^2 - S_b^2) \]

\[ H = J_{\text{ex}}/2(S^2 - S_a^2 - S_b^2) \]

\[ E(S, S_a, S_b) = J_{\text{ex}}/2(S(S+1) - S_a(S_a+1) - S_b(S_b+1)) \]

**Lande’s rule** for the intervals: \( E(S) - E(S-1) = JS \)

\[ \chi_M = \frac{1}{3} \frac{N \mu_B^2 g^2}{kT} \frac{\sum_S S(S+1)(2S+1) \exp(-E(S)/kT)}{\sum_S (2S+1) \exp(-E(S)/kT)} \]
Beyond the pair of spins

\[ \mathcal{H} = \sum_{i,j \geq 1} J_{ij} S_i \cdot S_j \]

1) \( S_t^2 \) commutes with \( \mathcal{H} \),

2) \( S_{tz} \) commutes with \( \mathcal{H} \),

3) In zero field and zero anisotropy each \( S_t \) state is \((2S_t+1)\) degenerate

4) The base is defined by \( n-1 \) intermediate spin states plus \( S_t \)
e. g. : \( |S_a,S_b,S_c,S_{ab},S_t,M> \)

5) \( \mathcal{H} \) does not commute with intermediate spin states (e.g. \( S_{ab} \))
Magnetic anisotropy in molecular materials

The magnetic anisotropy is mainly associated to the asymmetry of the crystal field

\[ \mathcal{H}_{\text{CF}} = \sum_{N,k} B_N^k O_N^k \]

with \( N = 2, 4, 6, \ldots, 2S \)

and \(-N \leq k \leq +N\)

Stevens operators

The \( O_n^m \) operators are defined as:

\[ O_2^0 = 3S_z^2 - s(s + 1) \]

\[ O_2^2 = \frac{1}{2} (S_+^2 + S_-^2) \]

\[ O_4^0 = 35S_z^4 - [30s(s + 1) - 25]S_z^2 + 3s^2(s + 1)^2 - 6s(s + 1) \]

\[ O_4^2 = \frac{1}{4} [7S_z^2 - s(s + 1) - 5](S_+^2 + S_-^2) \]

\[ + \frac{1}{4} (S_+^2 + S_-^2)[7S_z^2 - s(s + 1) - 5] \]

\[ O_4^3 = \frac{1}{4} S_z (S_+^3 + S_-^3) + \frac{1}{4} (S_+^3 + S_-^3)S_z \]

\[ O_4^4 = \frac{1}{2} (S_+^4 + S_-^4). \]
Magnetic anisotropy in molecular materials

Alternative notations commonly used

\[ \mathcal{H}_{CF} = \mathbf{S} \cdot \mathbf{D} \cdot \mathbf{S} = D_{xx}S_x^2 + D_{yy}S_y^2 + D_{zz}S_z^2 \]

\[ D = D_{zz} - \frac{1}{2}D_{xx} - \frac{1}{2}D_{yy}; \quad E = \frac{1}{2}(D_{xx} - D_{yy}). \]

\[ \mathcal{H}_{CF} = D \left[ S_z^2 - \frac{1}{3}S(S + 1) \right] + E(S_x^2 - S_y^2). \quad \text{with} \quad -1/3 \leq E/D \leq +1/3. \]

\[ \mathcal{H}_{CF} = -D'S_z^2 + BS_x^2 \]

with \[ \tilde{B} = 2E \quad \text{and} \quad D' = -(D + B/2) \]
Single Domain Nanoparticles

![Graph showing energy and angular displacement.](image)

Energy vs. \( \theta \) with \( \Delta E \) indicated.
First evidences of Quantum Tunneling in nanosized magnetic particles
(difficulties due to size distribution)

Quantum Coherence in ferrihydrite confined in the ferritin mammalian protein
(inconclusive due to distribution of iron load)
• The continuum of levels within the potential wells breaks down and quantum size effects, like tunneling, are observed: this is the exciting region for new properties.
\[ H_{an} = D S_z^2 \]

\[
\begin{align*}
S_z | m \rangle & = m | m \rangle \\
E_m & = - |D| m^2
\end{align*}
\]

At equilibrium, the probability \( p_m^0 \) that the spin is in state \( | m \rangle \) is given by:

\[
p_m^0 = \left( \frac{1}{Z} \right) \exp\left[ -\beta (E_m) \right]
\]

Intuitively, it may be expected that the relaxation rate \( 1/\tau \) is proportional to the probability to be at the top of the barrier.

\[
1/\tau = (1/\tau_0) p_0^0 = \left( \frac{1}{Z} \right) (1/\tau_0) \exp( -\beta E_0 ) \approx
\]

\[
\approx (1/\tau_0) \exp[ -\beta (E_0 - E_s) ] \approx (1/\tau_0) \exp( -\beta |D| s^2 )
\]

\[
\tau = \tau_0 \exp(\Delta E/k_B T)
\]
Single Molecule Magnets: a school of physics

\[ \text{[Mn}_{12}\text{O}_{12}(\text{CH}_3\text{COO})_{16}(\text{H}_2\text{O})_{4}] \]

\( \text{Mn}^{\text{IV}} \)  
\( S=3/2 \)

\( \text{Mn}^{\text{III}}(S=2) \)

\( S_{\text{tot}}=10 \)

\( D \approx -0.7 \text{ K} \)

\( \Delta E/k_B \approx 65 \text{ K} \)

\( \tau = \tau_0 \exp(\Delta E/k_BT) \)

Sessoli et al. Nature 1993
Hysteresis loop of molecular origin

\[ T = 2.1 \text{ K} \]

Magnetization ($\mu_B$) vs. Magnetic Field (T)
Master equation and transition probability

The time evolution of the population of the $|m\rangle$ state is given by:

$$\frac{d}{dt} p_m(t) = \sum_q \left[ \gamma_q^m p_q(t) - \gamma_m^q p_m(t) \right]$$

Where $\gamma$ are the transition probabilities independent from each other (Markov process) and are related to spin-phonon interactions.

A trivial solution is that at equilibrium:

$$p_m^0 = \frac{1}{Z} \exp(-\beta E_m)$$

$$\sum_q \left[ \gamma_q^m p_q^0 - \gamma_m^q p_m^0 \right] = 0$$

The detailed balance principle tell us that also each term of the sum vanishes at equilibrium

$$\gamma_m^{m'} p_m^0 = \gamma_m^{m'} p_m^0$$

$$\gamma_m^{m'} / \gamma_m^{m} = p_m^0 / p_m^0 = \exp[\beta(E_m - E_{m'})]$$
In a more general case (biaxial anisotropy, transverse field)

\[ |m^*\rangle = \sum_{m'} \varphi_{m'}^{(m)} |m'\rangle \]

With \(k=0, 1, 2..., 2s\).
The population of each state varies exponentially:

\[ p_m(t) = \varphi_m^{(k)} \exp\left(\frac{-t}{\tau_k}\right) \]

And substituting in

\[
\frac{d}{dt} p_m(t) = \sum_q \left[ \gamma_q^m p_q(t) - \gamma_m^q p_m(t) \right]
\]

\[
\frac{1}{\tau_k} \varphi_m^{(k)} = \sum_q \left[ \gamma_q^m \varphi_q^{(k)} - \gamma_m^q \varphi_m^{(k)} \right] = \sum_q \left[ \gamma_q^m - \delta_q^m \sum_{q'} \gamma_m^{q'} \right] \varphi_q^{(k)}
\]

where the Kronecker symbol \(\delta_q^m\) (=1 if \(q = m\), while \(\delta_q^m = 0\) if \(q \neq m\)) has been introduced.
The Master matrix

\[ \frac{d \vec{N}}{dt} = \tilde{\Gamma} \vec{N} \]

\[ \tilde{\Gamma} = \begin{pmatrix}
-\sum_{m' \neq 1} \gamma_1^{m'} & \gamma_2^1 & \cdots & \gamma_{2s+1}^1 \\
\gamma_1^2 & -\sum_{m' \neq 2} \gamma_2^{m'} & \cdots & \gamma_{2s+1}^2 \\
\vdots & \ddots & \ddots & \ddots \\
\gamma_{2s+1}^1 & \gamma_{2s+1}^2 & \cdots & -\sum_{m' \neq s} \gamma_{2s+1}^{m'} 
\end{pmatrix} \quad \vec{N} = \begin{pmatrix} N_1 \\ N_2 \\ \vdots \\ N_{2S+1} \end{pmatrix} \]

There are 2s+1 solutions of \((\text{det} \Gamma - \lambda) = 0\)
One solution is \(\lambda = 0\), corresponding to \(\tau = \infty\) (the equilibrium)

The relaxation rate at low temperature is

\[ \tau = \max_{\lambda_i \neq 0} \left\{ -\frac{1}{\lambda_i} \right\} \]
Transition probabilities

The allowed transitions for spin-phonon coupling have 
\[ |m-m'|=1,2 \]

\[
\gamma_m^p = \frac{3}{2\pi\hbar^4 c^5} \frac{(E_p - E_m)^3}{\beta(E_p - E_m)} \left( g_a \left[ (S_+^2)_{mp} + (S_-^2)_{mp} \right] + g_b \left[ \{ S_+, S_z \}_{mp}^2 + \{ S_-, S_z \}_{mp}^2 \right] \right)
\]

When \((E_m-E_p)\) is small (which also corresponds to the top of the barrier) the transition probability is small because of the factor \((E_m-E_p)^3\), which mainly reflects the fact that there are few phonon states of very low energy.

\[
\tau=\tau_0 \exp(\Delta E/k_B T)
\]

\[
\tau_0(SMM) > \tau_0(MNP)
\]
Low temperature dynamics

Thermal activated quantum tunneling

\[ \frac{1}{T} \left( \frac{1}{K} \right) \]

\[ \ln \left( \frac{\tau}{\text{sec}} \right) \]

2 weeks

Mn12

Fe8

Quantum tunneling

Thermal activated

19
Tunnel mechanism & return to equilibrium

\[ H = 0 \]

\[ M = 10 \]

[Diagram showing the tunnel mechanism and return to equilibrium]
Resonant Quantum Tunneling of the Magnetization

\[ \mathcal{H}_{CF} = DS_z^2 + E(S_x^2 - S_y^2) \]

\[ E_m^{(0)} - E_{m'}^{(0)} = 0 \]

\[ g\mu_B H^{(mm')} = |D|(m + m') \]
Resonant Quantum Tunneling of the Magnetization

\[ \mathcal{H}_{CF} = D S_z^2 + E (S_x^2 - S_y^2) \]

\[ 2 \hbar \omega_{T^{(m,m')}} = \Delta_{(m,m')} \]
Two levels description

\[ \Delta = \frac{\langle m^* | \mathcal{H} | m^* \rangle - \langle m'^* | \mathcal{H} | m'^* \rangle}{2} \approx g \mu_B (m - m') \Delta H_z / 2 \]

Diagonal terms \( \propto S_z \)
Out of diagonal terms \( \propto S_{x,y} \)

\[
\left[ \begin{array}{cc}
E_{m^*} & \hbar \omega_T \\
\hbar \omega_T & E_{m'^*}
\end{array} \right]
\]

\[ \delta E = \pm \sqrt{\Delta^2 + \hbar^2 \omega_T^2} \]

\[
| \Phi_\ell \rangle = | m^* \rangle \cos \phi + | m'^* \rangle \sin \phi
\]

\[
| \Phi_L \rangle = -| m^* \rangle \sin \phi + | m'^* \rangle \cos \phi
\]

\[ | \tan \phi | = \frac{\hbar \omega_T}{\delta E \Delta^{1/3}} \]
Resonant Quantum Tunneling of the Magnetization

$H=0$

$\text{Mn}_{12}-ac$

Tunneling "on"

Tunneling "off"

Thomas et al., Nature 1996
Friedman et al., PRL 1996
Classical anisotropy potential

Axial    Rhombic    Tetragonal

\[ H = D \hat{S}_z^2 + E(\hat{S}_x^2 - \hat{S}_y^2) + \ldots \]

Fig. 2.2. The distance of the surface from the origin represents the classical potential energy of a spin experiencing a uniaxial crystal field with negative \( D \) (left), the same including a transverse second-order term (middle), or a transverse fourth-order term (right).
\[ \mathcal{H} = \mathcal{H}_0 + \delta \mathcal{H} \]
\[ \mathcal{H}_0 = -|D|S_z^2 + g\mu_B H_z \]

- Biaxial anisotropy (rhombic symmetry, \( x \neq y \neq z \))

\[ \delta \mathcal{H} = \left( \frac{B}{4} \right) (S_+^2 + S_-^2) \]

\[ \langle m | \mathcal{H} | m' \rangle \neq 0 \quad \text{only when } |m-m'| \text{ is even} \]

\[ | \Psi \rangle = \sum_p \varphi(s - 2p) | s - 2p \rangle \]

\[ | \Psi \rangle = \sum_p \varphi(s - 2p - 1) | s - 2p - 1 \rangle \]

\[ m - m' = 2k \]
Simulated relaxation time

Relaxation time for a Fe4 star: $S=5$ $D=-0.4$ cm$^{-1}$ $E=0.04$

- $H_x=100$ Oe
- $H_x=0$, $\theta=1^\circ$
- $H_x=0$
Tunneling and symmetry

\[ H = H_0 + \delta H \]
\[ H_0 = -|D|S_z^2 + g\mu_B H_z \]

- Uniaxial symmetry (e.g. tetragonal symmetry, \( x=y \neq z \))

\[ \delta H = C(S_+^4 + S_-^4) \]

\[ \langle m | H | m' \rangle \neq 0 \quad \text{only when } |m-m'| \text{ is } 4n \]

\[ \begin{align*}
|\Psi\rangle &= \sum_p \varphi(s - 4p) |s - 4p\rangle \\
|\Psi\rangle &= \sum_p \varphi(s - 4p - 1) |s - 4p - 1\rangle
\end{align*} \]

For any symmetry tunneling in zero field is not allowed for an half-integer spin state

The Karmers’ degeneracy
Relaxed selection rules

Thomas et al., *Nature* 1996
Friedman et al., *PRL* 1996

Mn_{12}-ac

Low temperature $H=0$ step is an artifact

$B_L (T)$

Tunneling "on"

Tunneling "off"
Relaxation time for a Fe₄ star: \( S = 5 \) \( D = -0.4 \text{ cm}^{-1} \) \( E = 0.04 \)

Simulated relaxation time

- \( H_x = 100 \text{ Oe} \)
- \( H_x = 0, \ \theta = 1^\circ \)
- \( H_x = 0 \)
Transverse field dependence of the tunnel-splitting

Fe$_8$ SMM
bixial symmetry

$\phi = 90^\circ$
$\phi = 50^\circ$
$\phi = 20^\circ$
$\phi = 7^\circ$
$\phi = 0^\circ$

$\phi = 0^\circ$
intermediate axis

$\phi = 90^\circ$
hard axis
A semiclassical picture

Easy axis

Clock-wise

Anti-Clock-wise

Hard axis
Destructive Topological Interferences

Destructive if

\[ A = k \pi / S \ (k \text{ odd}) \]

\[ \Delta H_x = \frac{2}{g \mu_B} \sqrt{2E(E-D)} \]

Destructive Topological Interferences

\[ H = D S_z^2 + E (S_x^2 - S_y^2) + C (S_+^4 - S_-^4) \]

experimental

calculated with \( D = -0.29, E = 0.046, C = -2.9 \times 10^{-5} \text{ K} \)
Parity effect on the topological interference

Tunnel resonance $|m_s=10\rangle \leftrightarrow |m_s=-10+n\rangle$

The effect of the transverse field is different for allowed and forbidden quantum resonances

Engineering Single Molecule Magnets

Why high order Spin Hamiltonian terms are important?

Tunnel splitting according to perturbation theory

\[ \mathcal{H} = \mathcal{H}_0 + \delta \mathcal{H} \]

\[ \mathcal{H}_0 = -D |S^2| + g \mu_B H_z \]

1. at order $2s$ if $\delta \mathcal{H}$ is $H_x$

\[ \hbar \omega_T = 4 |D| s^2 \left( \frac{g \mu_B H_x}{2 |D|} \right)^{2s} \frac{1}{(2s)!} \]

2. at order $s$ if $\delta \mathcal{H} = (B/4)(S^2_+ + S^2_-)$

\[ \hbar \omega_T = 4 |D| s^2 \left( \frac{B}{16 |D|} \right)^s \frac{(2s)!}{(s!)^2} \]

3. At order $s/2$ if $\delta \mathcal{H} = C(S^4_+ + S^4_-)$

\[ \hbar \omega_T = 4 |D| s^2 \left( \frac{C}{16 |D|} \right)^{s/2} \frac{(2s)!}{[(s/2)!]^2} \]

\[ s! \approx s^{s+1/2} e^{-s} \sqrt{2\pi}. \]
From the single spin to the pair

\[ \mathcal{H}_{SS} = -J_{12} S_1 \cdot S_2 \]

\[ |S_1 - S_2| \leq S \leq S_1 + S_2 \]

\[ W(S) = -(J_{12}/2)[S(S + 1) - S_1(S_1 + 1) - S_2(S_2 + 1)] \]

\[ g_S = c_1 g_1 + c_2 g_2 \]

\[ D_S = d_1 D_1 + d_2 D_2 + d_{12} D_{12} \]

\[ c_1 = (1 + c)/2; c_2 = (1 - c)/2 \]

\[ d_1 = (c_+ + c_-)/2; d_2 = (c_+ - c_-)/2 \]

\[ d_{12} = (1 - c_+)/2 \]

and

\[ c = \frac{S_1(S_1 + 1) - S_2(S_2 + 1)}{S(S + 1)} \]

\[ c_+ = \frac{3[S_1(S_1 + 1) - S_2(S_2 + 1)]^2 + S(S + 1)[3S(S + 1) - 3 - 2S_1(S_1 + 1) - 2S_2(S_2 + 1)]}{(2S + 3)(2S - 1)S(S + 1)} \]

\[ c_- = \frac{4S(S + 1)[S_1(S_1 + 1) - S_2(S_2 + 1)] - 3[S_1(S_1 + 1) - S_2(S_2 + 1)]}{(2S + 3)(2S - 1)S(S + 1)} \]
Non-collinearity is a key ingredient in molecular magnets
Non-collinearity of magnetic anisotropy

- High Order Transverse Anisotropy is a key factor in Quantum Tunneling of the Magnetization
- Its major source is the multispin nature of SMMs
- Non-collinearity of the anisotropy is necessary to observe transverse anisotropy in axial molecules

Why spin non-collinearity is so important in Molecular Magnetism?

- The use of organic ligand reduces the symmetry on the metal ion
- Most organic compounds crystallize in the monoclinic or orthorhombic systems
- If the symmetry of the magnetic center is lower than that of the space group INEVITABILY more than one non-magnetically equivalent center are present (metal ions not in special Wyckoff positions)
Mid-term goals:

- Increase the blocking temperature

- Total Spin (intra-molecular interactions)

- Axial Magnetic Anisotropy

- Transverse Magnetic Anisotropy

- Inter-molecular interactions

- Hyperfine interactions
Evolution of SMMs

$S=83/2$ !
(A. K. Powell)
Evolution of SMMs

Brechlin et al. JACS 2007

Mn₆ (S=12) (ΔE~80)

Mn₁₂

Mn₆R₆

Fe₈

Mn₁₉

Mn₂₅

Mn⁹Mo₆

Mn₆Cr
Why do SMMs work only at low temperature?

$\Delta E \sim |D|S_{tot}^2$

Increase $S_{tot}$ through ferromagnetic interaction:

$D = \sum_i c_i d_i$ but $c_i \propto \frac{1}{S_{tot}^2}$

$\Delta E$ does not increase with $S_{tot}$


Increase $S_{tot}$ by the $n^\circ$ of interacting spins:

$D = \sum_i c_i d_i$ but $c_i \propto \frac{1}{n_{spin}}$

$\Delta E$ increases as $S_{tot}$

Gatteschi et al. *Molecular Nanomagnets, OUP* 2006
Increase orbital contribution in 3d metal ions

Magnetic blocking in a linear iron(i) complex

Joseph M. Zadrozny, Dianne J. Xiao, Mihail Atanasov, Gary J. Long, Fernande Grandjean, Frank Neese and Jeffrey R. Long

Fe(I) in linear coordination

$J=7/2$

$U_{\text{eff}}=325 \text{ K}$

$H=1\text{kOe}$
Lanthanides: a source of magnetic anisotropy

Dalton Transactions

Cite this: DOI: 10.1039/c2dt31388j

www.rsc.org/dalton

Lanthanides in molecular magnetism: so fascinating, so challenging†

Javier Luzon\textsuperscript{a,b} and Roberta Sessoli\textsuperscript{a,c}

†Dedicated to the memory of Ian J. Hewitt.
Record Blocking Temperature in a RE SMM

\[
\left\{ \left[ \left( \text{Me}_3\text{Si} \right)_2\text{N}_2\text{Dy(THF)} \right)_2(\mu-\text{N}_2) \right\}^-
\]

\[
\text{N}_2^3^- \quad S=1/2
\]

\[
J(R-\text{Gd}) = 27 \text{ cm}^{-1}
\]

Anti-Ferromagnetic

\[
S_{\text{tot}} = 13/2
\]
From 0d to 1d: Single Chain Magnets

Molecular

Caneschi et al.

Angew. Chem. 2001

P. Gambardella et al.
Nature 2002

Figure 3 Magnetization of a monatomic wire array recorded at the L₃ edge, \( M \) as a function of the applied field at \( T = 45 \) K measured along the easy direction (filled squares) and at \( 80^\circ \) away from the easy direction (open circles) in the plane perpendicular...
Spin Dynamics in Single Chain Magnets

\[ \Delta E = 4J \]

\[ \Delta E = 2J \]

\[ \text{propagation} \]

\[ L > \xi \]

\[ L < \xi \]

\[ M(t) = M_{\text{sat}} \exp(t/\tau) \]

\[ \tau = \tau_0 \exp(4J/k_B T) \]

\[ \xi_{\text{Ising}} \propto (2J/k_B T) \]

The relaxation time diverges at low temperature as \( \xi^2 \)
High Coercitivity in SCMs

\[ \Delta E = 4S^2 J_{\text{intra}} \]

R = n-butyl

The role of diamagnetic defects in the dynamics

\[ \tau \propto \xi^2 \approx \exp\left(\frac{4J}{k_B T}\right) \text{ if } L \gg \xi_{th} \]

\[ \tau \propto \xi \approx \exp\left(\frac{2J}{k_B T}\right) \text{ if } L \ll \xi_{th} \]
The domain wall motion is a classical random walk: propagation \( \sim \frac{1}{N - 1} \).

\[
\lambda_1 \approx \frac{2q\alpha}{N - 1} \exp\left(-\frac{2J}{k_B T}\right)
\]

\[
\tau_1 \propto (N - 1) \exp\left(\frac{2J}{k_B T}\right)
\]

\( \tau_0 \) shifting
Finite size effects in SCMs

...taking into account multiple events...

\[ \Delta E = 2J \]
\[ \text{Prob} \sim q^5 \]

\[ \Delta E = 0 \]
\[ \text{Prob} \sim q^N \]

For short segments

the **UNDERBARRIER** process can become faster than any **thermally activated** mechanism

\[
\frac{1}{\tau(N)} = \frac{1}{\tau_1} + \alpha q^N
\]
If $q$ is temperature independent the cross-over to tunneling regime depends on the the length $L$. 

Transition from SCM to SMMs behavior
A perspective: switching from SCM to SMM

Perturbed state $\square$ short segments: the magnetization can reverse (collective reversal of the spins)

Unperturbed state $\square$ long segments: the magnetization is frozen (Glauber’s dynamics)
Dynamic control of magnetic nanowires by light-induced domain-wall kickoffs

Eric Heintze¹, Fadi El Hallak¹, Conrad Clauß¹, Angelo Rettori²³, Maria Gloria Pini⁴, Federico Totti⁵, Martin Dressel¹ and Lapo Bogani¹*
Why magnetic molecule @ surfaces?

- Electric field can be much more “local”
- Address individual molecules

Molecules in nano-junctions

Scanning Probe Microscopies
SP-STM Detection of Magnetic Bistability

Bistability in Atomic-Scale Antiferromagnets

Sebastian Loth,1,2,∗ Susanne Baumann,1,3 Christopher P. Lutz,1 D. M. Eigler,1 Andreas J. Heinrich1

Fig. 3. Thermal stability of AFM arrays. (A to C) STM images of (2×6) and (2×4) arrays of Fe atoms. (A) 1.2 K. Both arrays have stable Néel states. (B) 3.0 K. The smaller array switched rapidly during the image. (C) 5.0 K. Both arrays switched rapidly. Image size, 7.7 × 7.7 nm. Image was taken at 2 mV and 3 pA, and image acquisition time was 52 s. (D) Schematic of the atomic positions of Fe and Cu₂N substrate atoms in (2×n) and (1×n) arrays. Cu atoms, yellow; N atoms, light blue. Ball colors depict the spin alignment of one Néel state, with red being parallel and blue antiparallel with the tip’s spin. (E) Arrhenius plot of the switching rates for the arrays of (A) and a (1×8) and (1×6) chain (fig. S5). The determination of switching rates is explained in fig. S3. Magnetic field was 3 T. Fig. S4 shows comparison to a 1-T field. Fit parameters are given in table S1.

IBM Research Division, Almaden Research Center
TbPc$_2$: a single ion SMM

- Tb$^{3+}$
- $L=3$
- $S=3$
- $J=6$

- Thermally Evaporable
- Flat
- Large magnetic moment
- Large anisotropy
- High $T_B$

Kern et al., Nano Lett. 2008
Komeda et al. 2009
Hietschol et al. JACS 2011
Spintronics architectures based on TbPc$_2$

b) Candini et al. *Nanoletters* 2011
c) Urdampilleta et al. *Nature Materials* 2011
Spintronics architectures based on TbPc₂

Electronic read–out of a single nuclear spin using a molecular spin transistor

Romain Vincent¹, Svetlana Klyatskaya², Mario Ruben²,³, Wolfgang Wernsdorfer¹ & Franck Balestro¹
Challenges

- Chemical stability on surfaces
- Robustness of SMM behavior
• Element & valence selectivity

Chemical Selectivity:

atoms & valences (Mn²⁺, Mn³⁺, Mn⁴⁺)

• Surface sensitivity when absorption is detected as Total Electron Yield (b)

• a) absorption
  • b) T. E. Y
  • c) Fluorescence
The sunset of \( \text{TbPc}_2 \)
Terbium bis-phthalocyaninato

SMM behavior is sensitive to nanostructure

\( \text{TbPc}_2 \) thick film

Monolayer @ Au(111)

ESRF
Implanted probes ($^{8}$Li$^+$, $\mu^+$)

In muon spin relaxation, muons are employed like local probes of magnetic fields.

Muon: $S=1/2$

Muon decay (life time 2.2 $\mu$s)

$$\mu^+ \rightarrow e^+ + \nu_\mu + \nu_e$$

Positrons are preferentially emitted along muon spin.

Measuring the variation of the spatial distribution of positrons emitted in the time it’s possible to obtain information about the local magnetic fields experienced by the muons.
Implanted probes ($^8\text{Li}^+, \mu^+$)

Muon: $S=1/2$

Muon decay (life time 2.2 $\mu$s)

$\mu^+ \rightarrow e^+ + \nu_\mu + \nu_e$

Positrons are preferentially emitted along muon spin

Low energy muons

In collaboration with Zaher Salman @ PSI
Gradual increase of the relaxation time on increasing the distance from the Au substrate

Molecular packing is more important than electronic interaction with the substrate

Hofmann & al *ACS Nano*
doi:10.1021/nn3031673
**TbPc$_2$ on a magnetic substrate**

**Coupling Single Molecule Magnets to Ferromagnetic Substrates**


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**Graphs and Figures:**

- **Figure (a):**
  - Magnetic moment $M_{Ni}$ for Ni and Tb as a function of magnetic field $B$.
  - $\theta = 0^\circ$.

- **Figure (b):**
  - Schematic diagram of TbPc$_2$ on Ni/Cu substrate.
  - Magnetic interaction $B_{exc}$.

**Text:**

MODERATE AF INTERACTION
Magnetic molecules on a magnetic surface

Surface induced hysteresis @ 300 K

Fe octaethylporphyrin (OEP) chloride molecule
Sublimated on Co or Ni films on Cu(100)

Wende et al. Nature Materials VOL 6 JULY 2007, p. 516
Fe$_4$: another robust SMM

$S_T = 3 \times 5/2 - 5/2 = 5$

Lower $T_B$ than Mn$_{12}$
Fe₃M propellers

\[ S = 5 \quad D = -0.45 \text{ cm}^{-1} \quad \Delta E \sim 15 \text{ K} \]

\[ S = 6 \quad D = -0.16 \text{ cm}^{-1} \quad \Delta E \sim 8 \text{ K} \]

\[ S = 13/2 \quad D \sim -0.35 \text{ cm}^{-1} \quad \Delta E \sim 21 \text{ K} \]

100% pure

Small impurity of Fe₄
Adding remnant magnetization by chemical design

Zero Field Tunneling is less efficient for $S=13/2$

In collaboration with Dr. Carley Paulsen @ CNRS, Grenoble
Functionalization of Fe₄ clusters

- Functionalization by means of ligand exchange
- Two triol ligands take the place of six methoxides
- Sulphur-based functional groups make cluster bind to gold surfaces

Fe₄C₉SAc

By Andrea Cornia, University of Modena, Italy
Functionalization of Fe$_4$ clusters

By Andrea Cornia, University of Modena, Italy
Deposition of molecules on surfaces
French End-Station (TBT) setup by J.-P. Kappler (IPCMS, Strasbourg) & Ph. Sainctavit (IMPMC. Paris)

- UHV, bakeable
- $^3\text{He} - ^4\text{He}$ dilution refrigerator: $T \approx 500$ mK
- Superconducting coil: $-7 \, T < B < +75 \, T$
Magnetic hysteresis of Fe₄ wired to a gold surface

A. Monolayer

B. Bulk

C. T = 0.50 K

Magnetic hysteresis of Fe$_4$ wired to a gold surface

Control of the orientation on the surface

DFT calculations by Federico Totti
XNLD: An experimental technique sensitive to the orientation of molecules on the surface.
Angular Dependence of the Magnetic Hysteresis

Mannini et al. *Nature* 2010, 468, 417
**SMM: Quantum Master Matrix Approach**

\[
\frac{d \overrightarrow{N}}{dt} = \tilde{\Gamma} \overrightarrow{N}
\]

\[
\Gamma^m_q = \gamma^m_q - \delta^m_q \sum_{m'} \gamma^m_{m'}
\]

\[
\tilde{\Gamma} = \begin{pmatrix}
- \sum_{m' \neq 1} \gamma^m_{1} & \gamma^1_{2} & \ldots & \gamma^1_{2s+1} \\
\gamma^2_{1} & - \sum_{m' \neq 2} \gamma^m_{2} & \ldots & \gamma^2_{2s+1} \\
\vdots & \vdots & \ddots & \vdots \\
\gamma^{2s+1}_{1} & \gamma^{2s+1}_{2} & \ldots & - \sum_{m' \neq 2s+1} \gamma^m_{2s+1}
\end{pmatrix}
\]

\[
\overrightarrow{N} = \begin{pmatrix}
N_1 \\
N_2 \\
\vdots \\
N_{2S+1}
\end{pmatrix}
\]

\[
\gamma^p_q = \frac{3}{\pi \hbar^4 \rho c_s^5} \frac{(E_p - E_q)^3}{\left[ e^{(E_p - E_q)/k_B T} - 1 \right]} \left| \langle \phi_p | \mathcal{H}_{S-P_h} | \phi_q \rangle \right|^2
\]

\[
M(t) = \sum_m p_m(t) \frac{dE_m}{dH}
\]

\[
\frac{dp_m(t)}{dt} = \sum_q \left[ \gamma^m_q p_q(t) - \gamma^q_m p_m(t) \right]
\]
Numerical Simulation of the Magnetic Hysteresis

Zeeman Splitting of $S_T=5$

Metastable state

Quantum Master Matrix
Numerical Simulation of the Magnetic Hysteresis

Spin-Hamiltonian Matrix Calculation

Diagonalization

Eigen-Values & Pn(t=∞)

Integration over all permitted orientations

Eigen-Vectors 

Calculation of transition probabilities \( \gamma_{nq} \)

Calculation of the change in population

\[
\frac{d}{dt} p_m(t) = \sum_q \left[ \gamma^m_q p_q(t) - \gamma^q_m p_m(t) \right]
\]

Calculation of the magnetization

\[
M(t) = -\sum_m p_m(t) \frac{dE_m}{dH}
\]

Diagonalization of Master equation & Calculation of \( \tau \)

\( H' = H + dH \)

To have a statistical average: \( \gamma' = \gamma / 10000 \) and is cycled over \( n \) cycle

\( n \) & \( dH \) are chosen to correspond to experimental sweeping time
Numerical Simulation of the Magnetic Hysteresis

T=650 mK

Exp.

Calc.

\( \theta_D = 35^\circ \)

\( \Delta E_{QT} \sim 10 \ mK \)
UHV-Preparation & characterization facilities

- XPS, UPS, LEIS
- Surface treatment (sputtering, annealing)
- Evaporation of metal & molecules
- Variable temperature (20 K)
- STM & AFM
STM image of Fe$_4$Ph evaporated on Au(111)

Fe$_4$Ph is weakly bound to Au but does not form multilayer aggregates

Malavolti et al. in preparation
XMCD of Fe$_4$Ph evaporated on Au(111)

Fe$_4$@Au; Fe L$_2$edge

Angular dependent hysteresis
preferential orientation on the surface
XMCD of Fe₄Ph evaporated on Au(111)

Fe₄@Au; Fe L₂edge

Simulated Hysteresis using a 45° cone
Molecular Q-bit

Winpenny, Affronte
ACS Nano 2012
Evaporated @ CuN/Cu

The bias applied with an STM tip can change the spin state in a reversible way.
Magnetoresistance without magnetic electrodes

Fano-Resonance-Driven Spin-Valve Effect Using Single-Molecule Magnets

Kwangwoo Hong and Woo Youn Kim

DOI: 10.1002/anie.201208816
Further reading

SMM & Quantum Tunneling:
Molecular Nanomagnets
D. Gatteschi, R. Sessoli, J. Villain
Oxford University Press 2006

SMM & surfaces
Preparation of Novel Materials Using SMMs
Andrea Cornia¹ (✉) · Antonio Fabretti Costantino¹ · Laura Zobbi¹ ·
Andrea Caneschi² · Dante Gatteschi² · Matteo Mannini² · Roberta Sessoli²

Magnetism & surfaces
Magnetism and Synchrotron Radiation,
Springer Proceeding in Physics
Coulon, C.; Miyasaka, H.; Clerac, R.
Structure and Bonding; Springer:
University of Florence (Italy)

• Surface Science
  Dr. Matteo Mannini, Luigi Malavolti, Lorenzo Poggini, Valeria Lanzillotto, Brunetto Cortigiani

• Theory
  Dr. Federico Totti, Dr. Javier Luzon (now in Zaragoza)

University of Modena (Italy)
  Prof. Andrea Cornia & coworkers

University Pierre et Marie Curie, Paris (France)
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POST-DOCTORAL POSITION AVAILABLE

In the frame of an ERC Advanced Grant awarded to the University of Florence, Department of Chemistry, for the research project

**Molecular Nanomagnets at Surfaces:**
**Novel Phenomena for Spin Based Technologies**

![Molnanom@S](image_url)

A POST-DOCTORAL position (one year, renewable) is available for a highly motivated and talented young researcher with experience in the area of **surface science and magnetism** and/or **scanning probe microscopies**. Experience on molecular materials and/or cryogenics would be particularly appreciated. The applicant will work in the stimulating ambience of the Laboratory of Molecular Magnetic Materials ([http://www.unifi.it/lamm/index_English.html](http://www.unifi.it/lamm/index_English.html)) on a new UHV thermal deposition set-up equipped with a variable temperature **Omicron VT-STM/AFM** and all main facilities for in-situ preparation and characterization. **A low temperature – 9T magnetic field AFM-MFM** set-up is also available.

Please send your CV (with names of senior coworkers we could contact for recommendation) or contact Prof. Roberta Sessoli [roberta.sessoli@unifi.it](mailto:roberta.sessoli@unifi.it) for more information.