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Conference on Single Molecule Magnets and Hybrid Magnetic Nanostructures

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Electronic Transport in Single-Molecule Magnets on Metallic Surfaces

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Electronic Transport
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Acknowledgements

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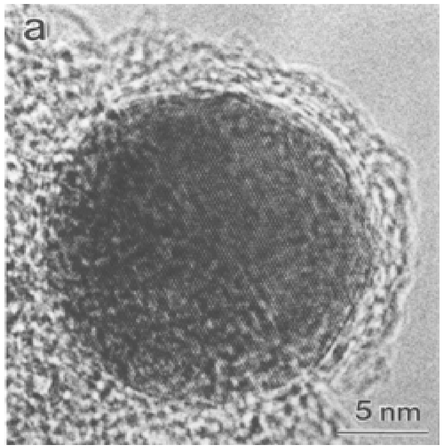
Outline

- System of interest and SMM
- Quantum spin tunneling and phase interference in Single-Molecule Magnet(SMM)
- Electronic transport in SMM
  - Previous experimental work
  - Electric Current: Fermi Golden Rule
  - Electric conductance
  - Tunneling probability of the SMM: two-level model
  - Example: Fe8
- Summary

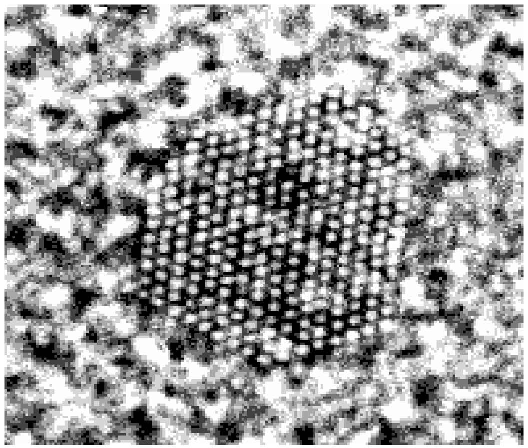
Systems of Interest

Nano-particle | **Ferritin** | **Single Molecule**

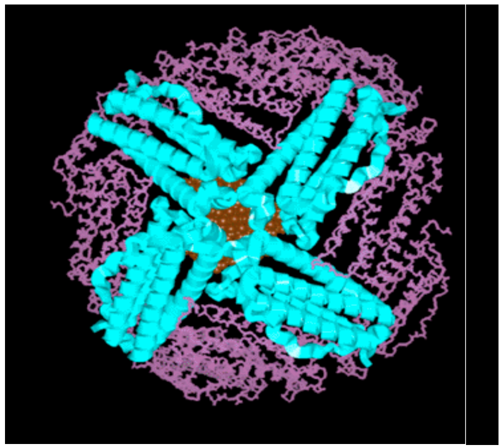
S = 10^6 — 10^3 — 10^2 — 10



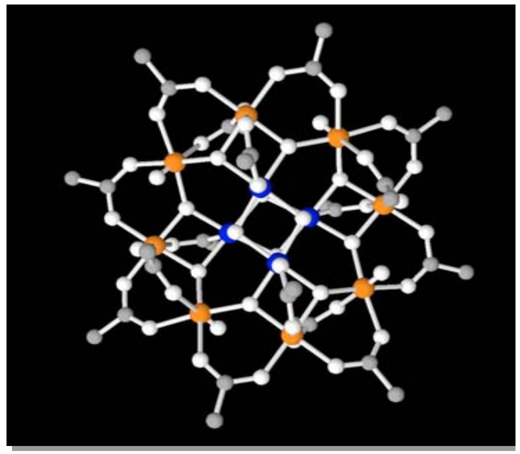
20nm



3nm

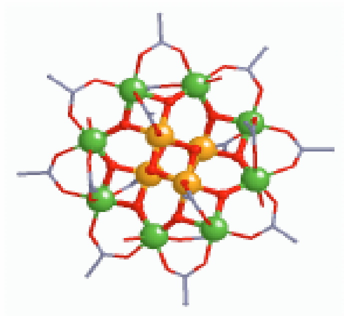


2nm

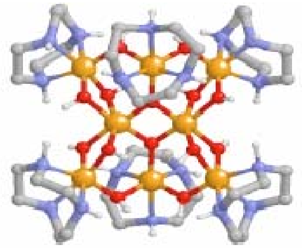


1nm

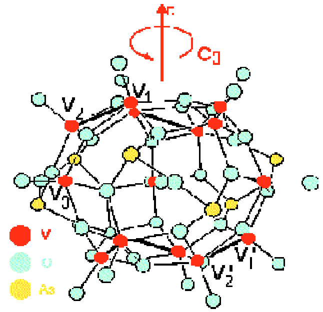
Single Molecules



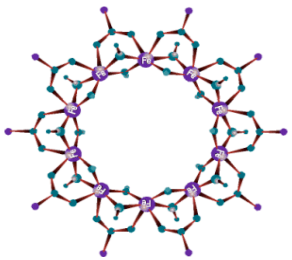
Mn12 (S=10)



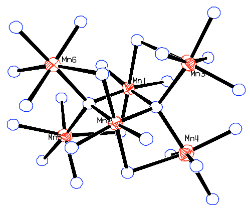
Fe8 (S=10)



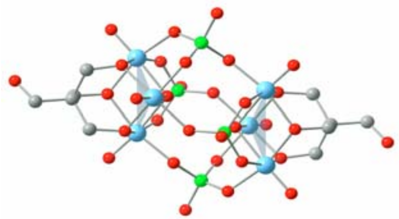
V15 (S=1/2)



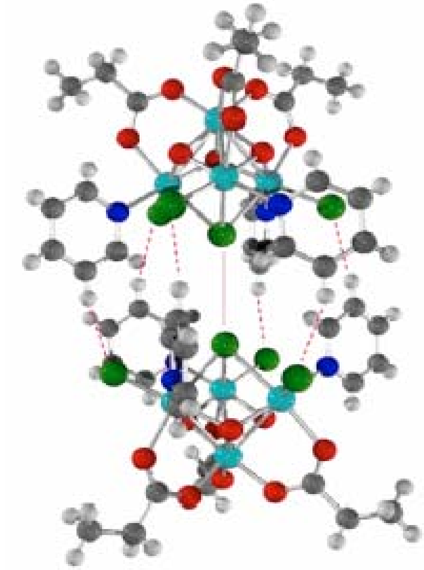
Fe10 (S=0)



Mn6
(S=4+4)

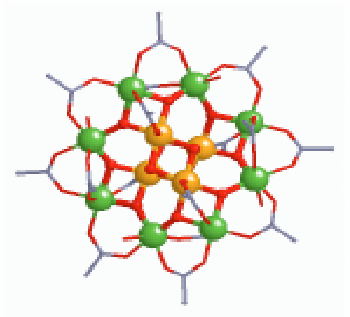


V6
(S=1/2,3/2)

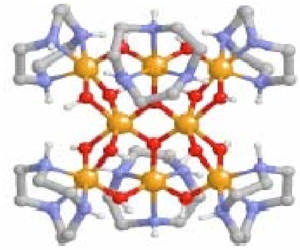


$[Mn4]_2$
(S=9/2+9/2)

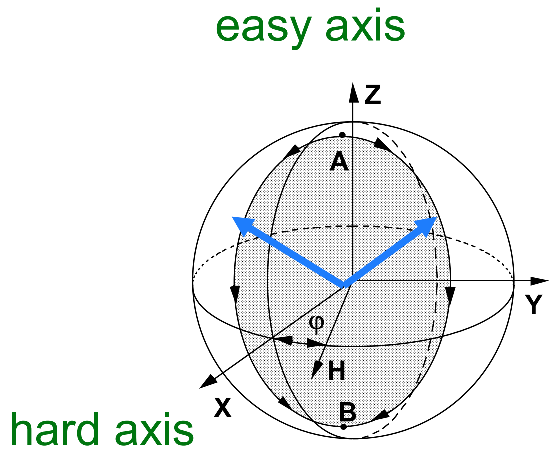
Quantum spin tunneling and phase interference(Mn12 and Fe8)

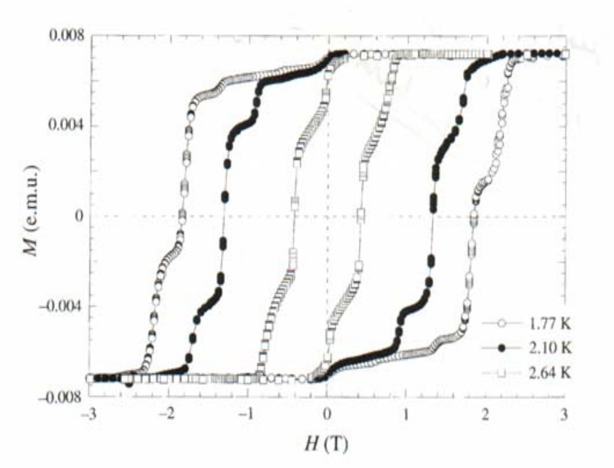


Mn12 (S=10)



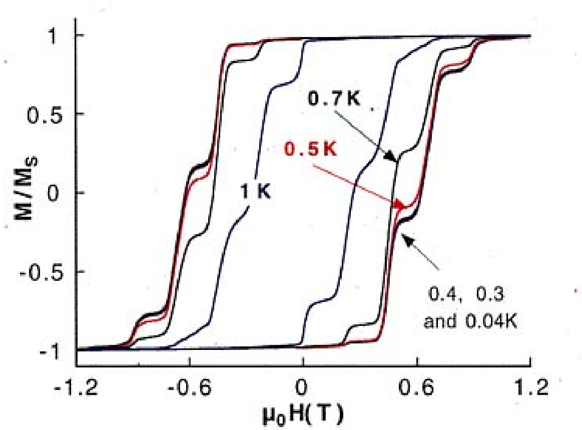
Fe8 (S=10)





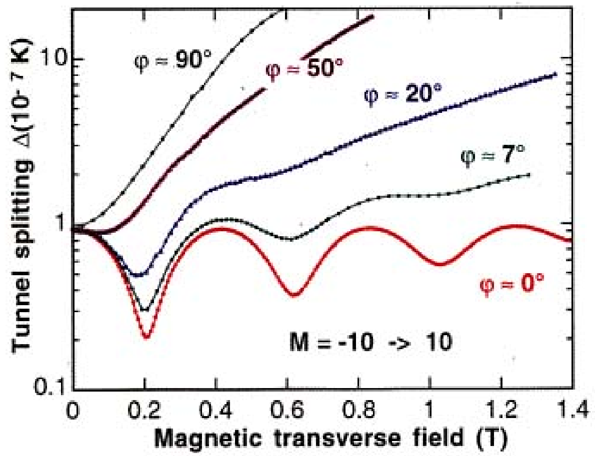
[Friedman et al, PRL (1996)

Thomas et al, Nature (1996)]



[C. Sangregorio, et. al.

PRL 1997]

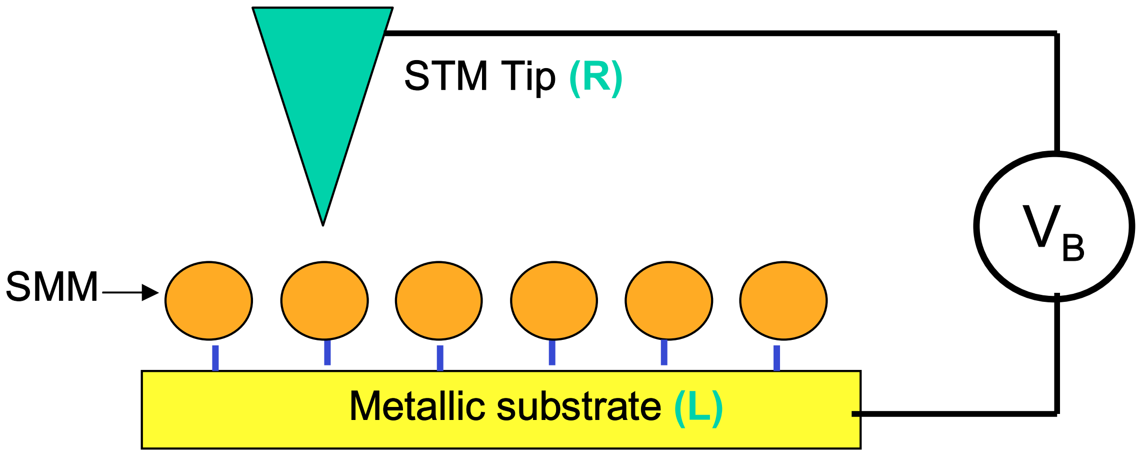


[A. Garg, EPL 1993;
Wernsdorfer and Sessoli,
Science, 1999]

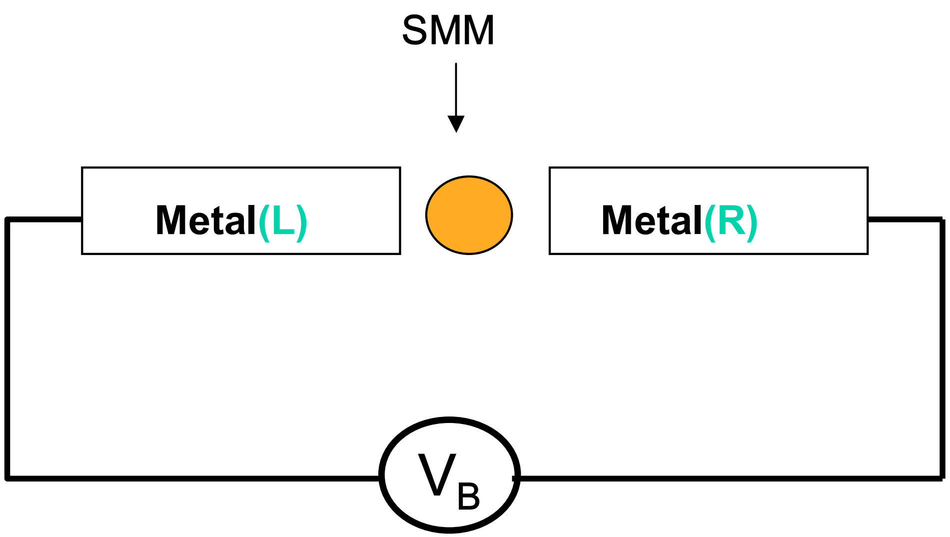
Electronic Transport in SMM

To study the electronic and magnetic properties of a SMM and eventually to develop electronic devices

STM-SMM-Metal



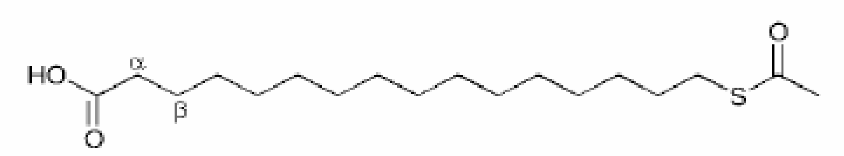
bridge junction geometry



Previous Work

[A. Cornia et al, Angew. Chem. (2003)]

$Mn_{12}O_{12}$(16-sulfanylhexadecanoate)$_{16}$(H_2O)$_4$: **long hydrocarbon chain**



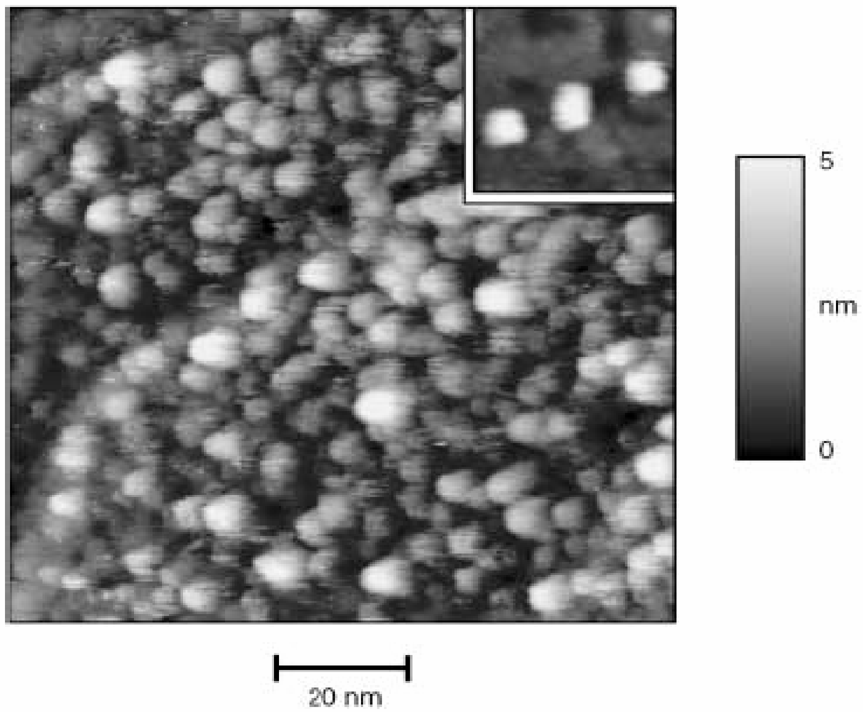


Figure 3. Constant-current STM image of Au-bound Mn_{12} clusters (set-point = 5 pA, bias = 1.3 V, scan size = 100 nm, scan rate = 3 Hz). The inset shows three isolated molecules (setpoint = 10 pA, bias = 0.8 V, scan size = 30 nm, scan rate = 3 Hz).

film

ADVANCED MATERIALS

Isolated Single-Molecule Magnets on the Surface of a Polymeric Thin Film**

By *Daniel Ruiz-Molina*, *Marta Mas-Torrent*, *Jordi Gómez*, *Ana I. Balana*, *Neus Domingo*, *Javier Tejada*, *María T. Martínez*, *Concepció Rovira*, and *Jaume Veciana**

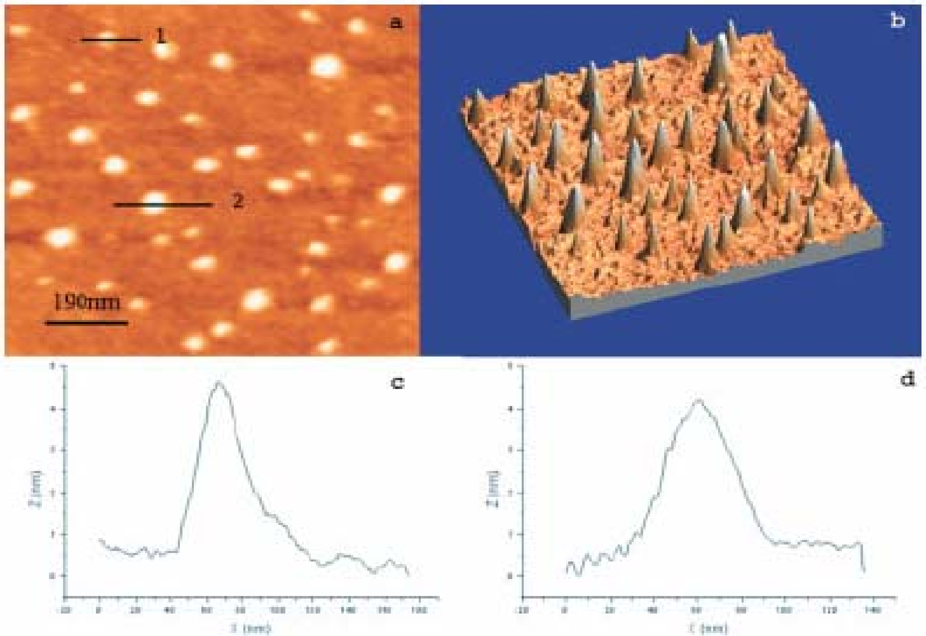


Fig. 2. AFM images of a thin nanocomposite film, made from a polycarbonate polymeric matrix and the Mn_{12} complex, which has been treated with pure CH_2Cl_2. a) Topographical top-view image. b) The corresponding 3D image of the same area. c) Height profile at location marked 1 in (a). d) Height profile at location marked 2 in (a).

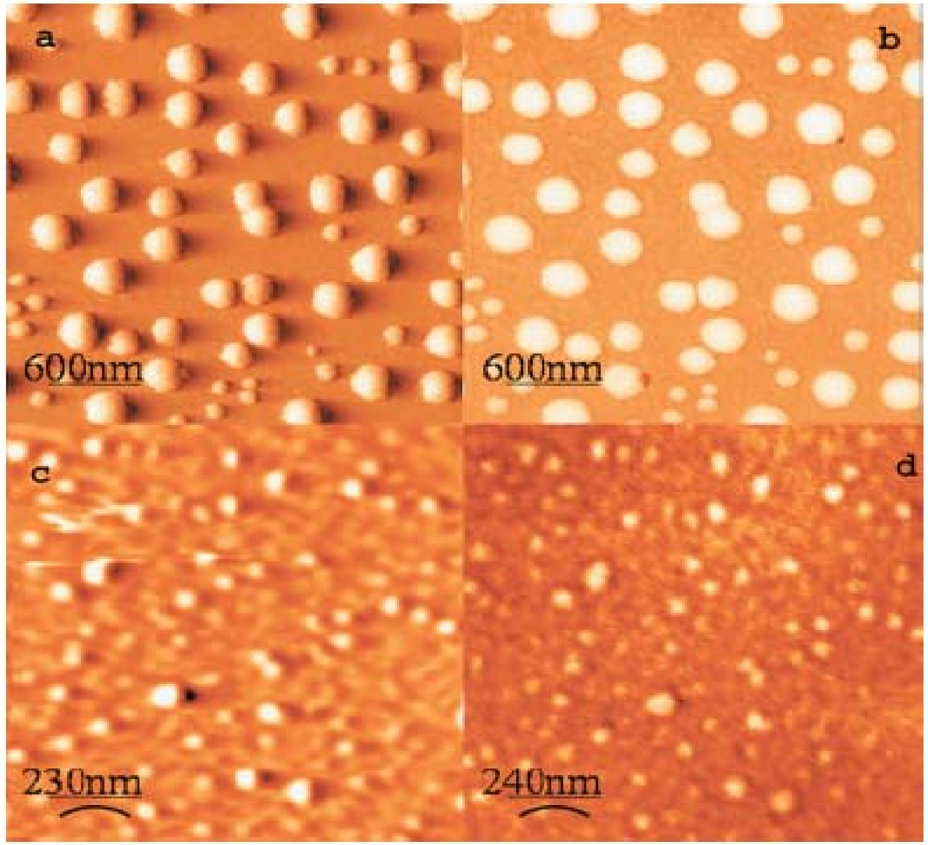
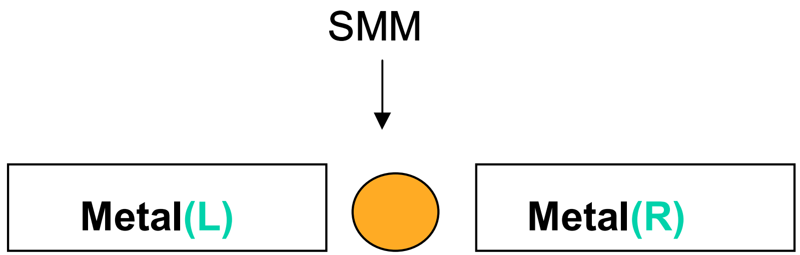


Fig. 3. MFM images of nanocomposite thin films treated with CH_2Cl_2/hexane (1:1) (a,b) and with CH_2Cl_2 (c,d). a,c) Topographical images taken with the magnetic tip. b,d) Magnetic images of the same area after retracting the tip by 30 nm.

What do we expect in the electronic devices?



$$H = H_L + H_R + H_{SMM} + H_1$$

$$H_p = \sum_{k\alpha} \varepsilon_{pk} c^{+}_{pk\alpha} c_{pk\alpha} \qquad (p = L, R)$$

H_{SMM} :Hamiltonian of SMM

$$H_1 = \sum_{kk'\alpha} \left(T_{LR} c^{+}_{Lk\alpha} c_{Rk'\alpha} + \text{H.c.} \right) + \sum_{k\alpha} \sum_{k'\beta} \left(J_{LR} c^{+}_{Lk\alpha} \vec{\sigma}_{\alpha\beta} c_{Rk'\beta} \cdot \vec{S} + \text{H.c.} \right)$$

[J.A. Appelbaum, PRL, 1966; P.W. Anderson, PRL 1966]

Direct tunneling between two electrodes

Tunneling of electrons scattered by the spin of SMM

➡ Electric current I_{LR} ?

Electric current from L to R?

- The electric current can be computed using the Fermi golden rule.
- Study the very weak coupling limit so that the higher order process such as the Kondo effect may be safely neglected.
- In this case, it is enough to compute the electric current up to the leading order.

$$I_{LR} = e\sum_{m} P_m \sum_{k\alpha}\sum_{k'\beta} W_{Lk\alpha m\to Rk'\beta m'} f(\varepsilon_{Lk})[1-f(\varepsilon_{Rk'})] - (Lk\alpha m \leftrightarrow Rk'\beta m')$$

[J.A. Appelbaum, PRB 1967]

$W_{i\to j}$:Transition rate from the state i to j

$f(\varepsilon)$:Fermi-Dirac distribution function

P_m :Probability for the SMM to be in the state $S_z = m$

Leading contribution to the transition rate:

$$W_{i\to j} = \frac{2\pi}{\hbar}\left|\langle j|H_1|i\rangle\right|^2 \delta(E_i - E_j) \qquad [i, j = \{Lk\alpha m\}, \{Rk'\beta m'\}]$$

$$E_{pk\alpha m} = \varepsilon_{pk} + \mu_p + E_m$$

μ_p : Chemical potential shift in the electrode p

E_m :Energy of the state $S_z = m$ in the SMM

$eV = \mu_L - \mu_R$:Source-drain bias voltage

Electric current from L to R?(cont'd)

Up to the second order in $T_{LR}(J_{LR})$

$$I_{LR} = \frac{2e^2}{h}\left[\gamma_T + \langle S_z^2\rangle \gamma_J\right]V + \frac{e}{h}\gamma_J \sum_m P_m\left[S(S+1) - m(m\pm 1)\right]$$
$$\times\left[\zeta(E_m - E_{m\pm1} + eV) - \zeta(E_m - E_{m\pm1} - eV)\right]$$

$\gamma_T(\gamma_J) = 4\pi^2 N_L N_R |T_{LR}|^2 (|J_{LR}|^2)$:direct (spin-scattered) tunneling rate

$\langle S_z^2\rangle = \sum_m m^2 P_m$ $\quad\quad \varsigma(\varepsilon) = \varepsilon / [1 - \exp(-\beta\varepsilon)]$ $\quad\quad \beta = 1/k_B T$

Linear response conductance $(eV << |E_m - E_{m\pm1}|)$ [G-H Kim and TS Kim, PRL, 2004]

⇨ $$G = \frac{2e^2}{h}\left[\gamma_T + \gamma_J g_s(T)\right]$$ $\quad\quad \eta(\varepsilon) = d\varsigma(\varepsilon)d\varepsilon$

$$g_s = \sum_m P_m\left\{m^2 + \left[S(S+1) - m(m\pm1)\right]\eta(E_m - E_{m\pm1})\right\}$$

Spin exchange tunneling reflects the dynamics of the QTM inside the SMM

Probability for the SMM to be in the state $S_z = m$?

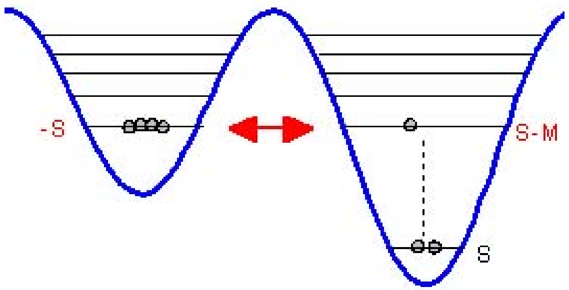
The effective Hamiltonian for the SMM such as Fe8

$$H_{SMM} = -DS_z^2 - g\mu_B S_z H_z + E(S_x^2 - S_y^2) + C\left(S_+^4 + S_-^4\right) - g\mu_B S_x H_x$$

In the absence of transverse terms, the energy level of the state $S_z = m$

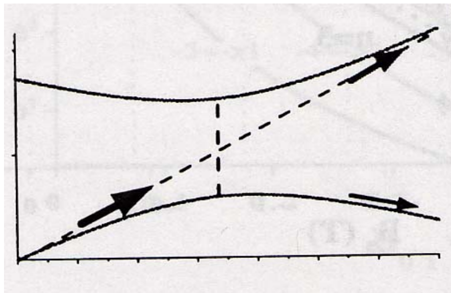
$$E_m = -Dm^2 - g\mu_B H_z m$$

Resonant fields: $H_z = H_M^{(0)} = MD / g\mu_B$



⇨ P_m ?

$$i\hbar \frac{\partial |\Psi(t)\rangle}{\partial t} = H_{SMM} |\Psi(t)\rangle$$



$$|\Psi(t)\rangle = \sum_{j=-S}^{S} a_j(t) |j\rangle \qquad P_m \equiv \lim_{t\to\infty} |a_m(t)|^2$$

The coupled 2S+1 differential eq. for $a_j(t)$

Probability for the SMM to be in the state $S_z = m$? (cont'd)

$$i\gamma_M \frac{da_M}{d\tau} = -\left[D_0 M^2 + \left(h_z^{(0)} + \tau\right)M\right]a_M + \frac{1}{2}E_0\left(q_{M-2}q_{M-1}a_{M-2} + q_{M+1}q_M a_{M+2}\right)$$
$$+\frac{1}{2}C_0\left(q_{M-1}q_{M-2}q_{M-3}q_{M-4}a_{M-4} + q_{M+3}q_{M+2}q_{M+1}q_M a_{M+4}\right)$$
$$+\frac{1}{2}h_{x0}\left(q_{M-1}a_{M-1} + q_M a_{M+1}\right)$$

where $-10 \le M \le 10$ for $S = 10$

$$\gamma_M = \hbar g \mu_B c / \Delta_M^2 \qquad \tau = g\mu_B ct / \Delta_M$$

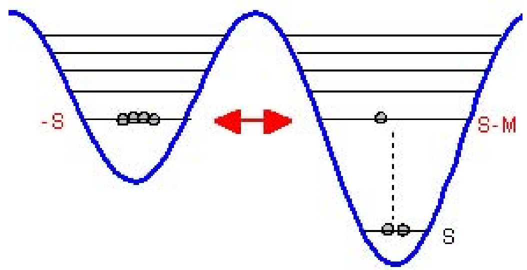
Field sweeping speed

$$q_M = \sqrt{(S-M)(S+M+1)}$$

$$D_0 = D/\Delta_M \qquad E_0 = E/\Delta_M \qquad C_0 = C/\Delta_M$$

$$h_z^{(0)} = g\mu_B H_M / \Delta_M \qquad h_x^{(0)} = g\mu_B H_x / \Delta_M$$

Δ_M :Level splitting between –S and S-M



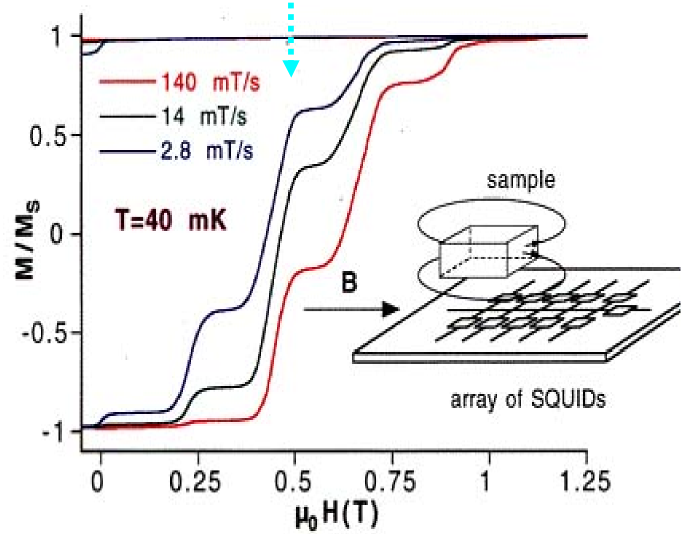
(ex) Fe8 $\left[Fe_8(tacn)_6O_2(OH)_{12}\right]^{8+}$

$D = 0.294\ K \qquad E = 0.047\ K$

$C = -3.2 \times 10^{-5}\ K$

$c = 0.14\ T/s$

$H_z = 0.429 + ct$



(i) $-10^{-5} < t < 3\times10^{-5} \Longleftrightarrow 0.429 - 1.4\times10^{-6} < H_z(T) < 0.429 + 4.2\times10^{-5}$

33 h (DEC AXP6000 5/266)

(ii) $-10\ \text{sec} < t < 10\ \text{sec} \Longleftrightarrow -1.4\ T < H_z < 1.4\ T$

$\mathbf{33 \times \left(5\times10^{5}\right)} \approx$ 1884 years !!

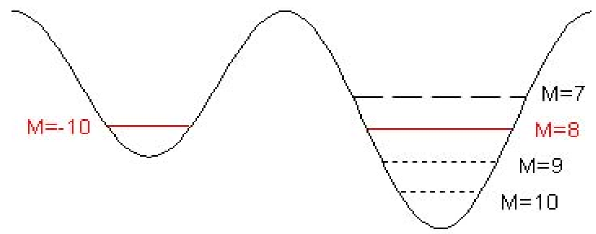
Two level approximation ?

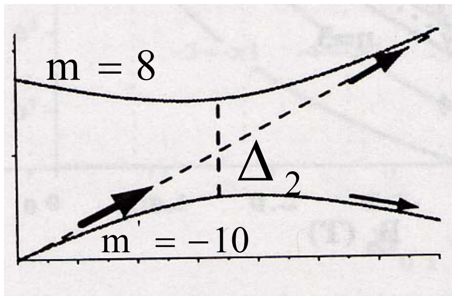
We introduce two-level model between –S and S-M

$$H_{eff} = \begin{pmatrix} -(10-M)g\mu_B ct & \Delta_M/2 \\ \Delta_M/2 & 10g\mu_B ct \end{pmatrix}$$

Δ_M :Level splitting between –S and S-M

(ex) tunneling between –10 and 8





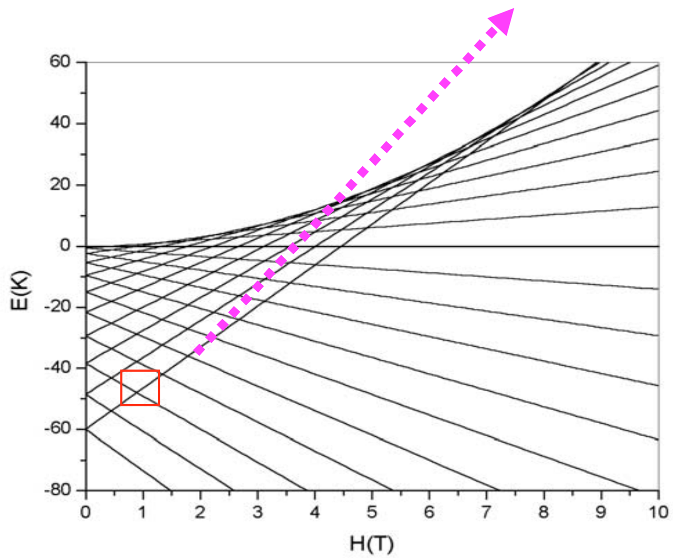
$$\left|\Psi_{eff}(t)\right\rangle = a_{-10}(t)\left|-10\right\rangle + a_{10-M}(t)\left|10-M\right\rangle$$

$$i\hbar\frac{\partial\left|\Psi_{eff}(t)\right\rangle}{\partial t} = H_{eff}\left|\Psi_{eff}(t)\right\rangle$$

$\Updownarrow$

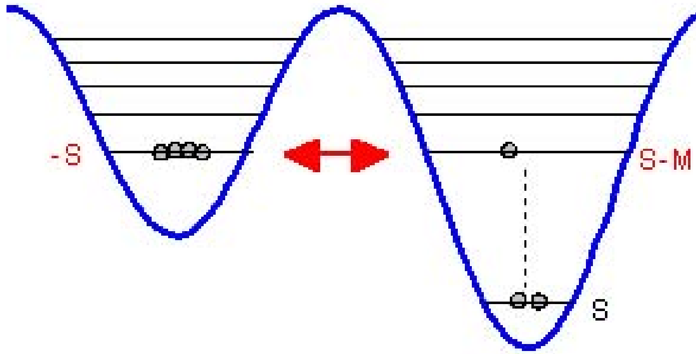
$$i\gamma_M\frac{\partial a_{10-M}}{\partial\tau} = -(10-M)\tau a_{10-M} + \frac{1}{2}a_{-10}$$

$$i\gamma_M\frac{\partial a_{-10}}{\partial\tau} = 10\tau a_{-10} + \frac{1}{2}a_{10-M}$$



Two level approximation(cont'd)

When we start with a ground state $S_z = -S$, the coefficient can be found analytically in the range of field $H_M \le H_z \le H_{M+1}$ by solving the differential equation.



$$a_{S-M}(\tau) = \sqrt{\lambda_M \prod_{j=1}^{M-1} F_j}\, \exp\left[-\frac{1}{4}\left(i\frac{M}{\gamma_M}\tau^2 + \pi\lambda_M\right)\right] D_{-i\lambda_M - 1}\left[-(1+i)\sqrt{\alpha_M}\,\tau\right]$$

D: parabolic cylinder function

$$\alpha_M = \frac{(2S-M)}{2\gamma_M}$$

$$\lambda_M = \frac{\Delta_M^2}{4(2S-M)\hbar g\mu_B c} \qquad F_j = \exp\left[-2\pi\lambda_j\right] \qquad H_M = \left(\frac{D}{g\mu_B}\right)M$$

$$\langle S_z \rangle = -10\left|a_{-10}\right|^2 + (10-M)\left|a_{10-M}\right|^2$$

Then, the corresponding probabilities are represented as

$$P_{-S} \equiv \lim_{t\to\infty}\left|a_{-S}(t)\right|^2 = \prod_{j=0}^{M} F_j$$

$$P_{S-M} \equiv \lim_{t\to\infty}\left|a_{S-M}(t)\right|^2 = (1-F_M)\prod_{j=0}^{M-1} F_j$$

Note that F_M and $1-F_M$ denote the probabilities for an SMM not to and to transfer from $S_z = -S$ to $S-M$ at the M-th resonant field.

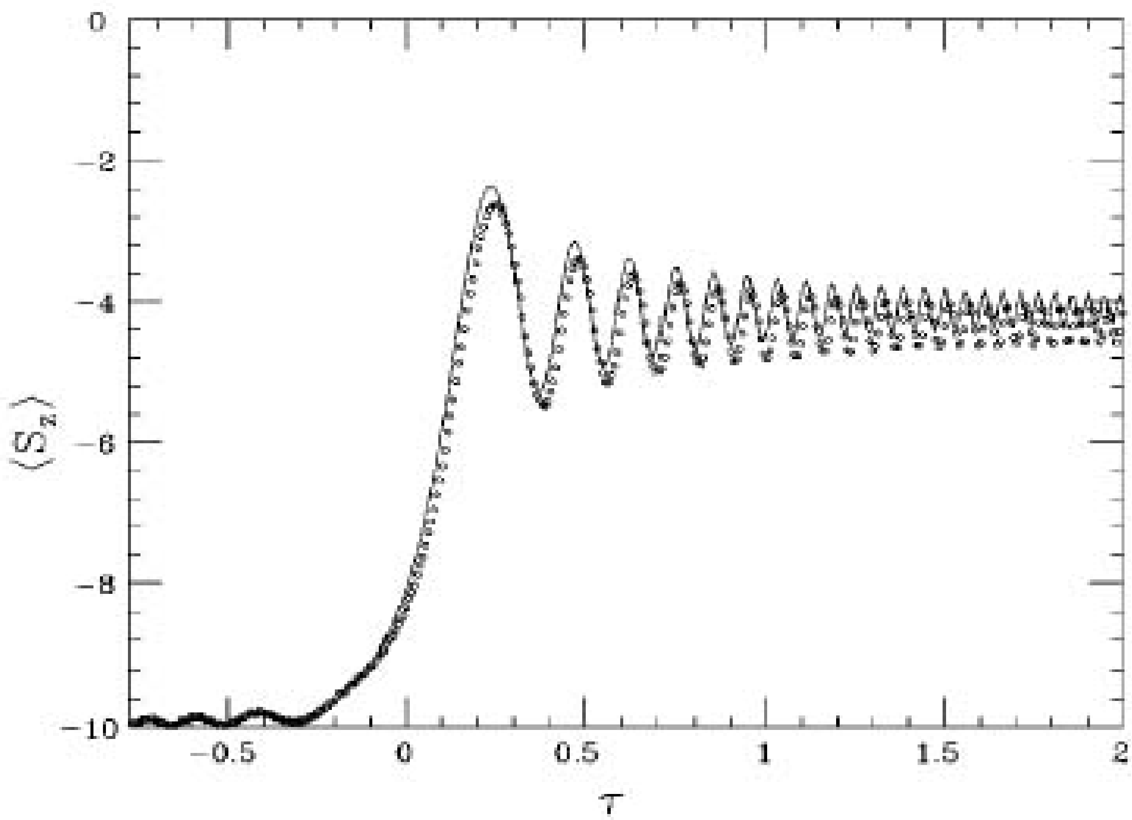


FIG. 2. Comparison between the average longitudinal spin value of the two-level model (continuous curve) and the exact 21-level Hamiltonian (open circles) around the anticrossing field $H_z = 0.429$ T. Crystal-field parameters are the same as in Fig. 1 except $C = -0.000\,058$ K.

[Rastelli and Tassi, PRB, 64, 064410 (2001)]

The two level approximation can reproduce quite well the results of the full diff. eq.

Electric conductance?

In the range of field $H_M \le H_z \le H_{M+1}$, we can find

- Electric conductance at zero temp.

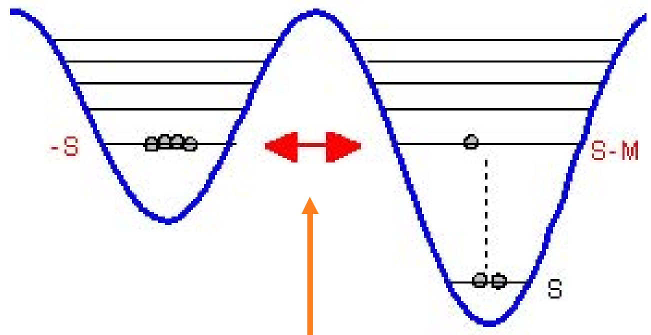
$$g_s(M) = \sum_m P_m \{m^2 + [S(S+1) - m(m \pm 1)]\theta(E_m - E_{m\pm1})\}$$

$$= S^2 + \sum_{n=0}^{M} nP_{S-n}$$

$\bar{g}_s$

two-level model

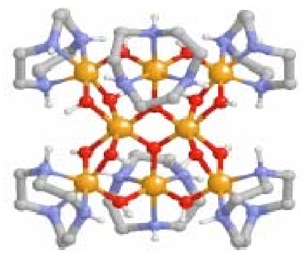
$$\bar{g}_s(M) = \sum_{i=1}^{M} \prod_{j=0}^{i-1} F_j - M \prod_{j=0}^{M} F_j$$



the probability for an SMM not to transfer from $S_z = -S$ to $S - M$ at the M-th resonant field.

$$F_M = \exp\left[-\frac{\pi \Delta_M^2}{2(2S - M)\hbar g \mu_B c} \right]$$

Example: Fe8

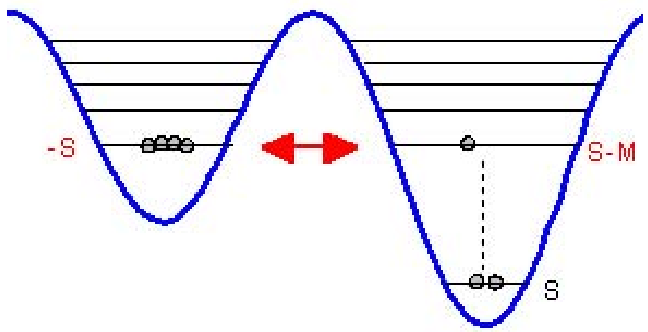


$$H_{SMM} = -DS_z^2 - g\mu_B S_z H_z + E(S_x^2 - S_y^2) + C\left(S_+^4 + S_-^4\right) - g\mu_B S_x H_x$$

$D = 0.294$ K $E = 0.047$ K $C = -3.2\times10^{-5}$ K $H_z = -H_s + ct$

The tunnel splitting Δ_M is calculated for $H_x = 0.1H_z$ at the resonant field by employing the numerical diagonalization.

M	H_M (T)	Δ_M (μK)
0	0	0.0589
1	0.215	0.0862
2	0.429	3.03
3	0.643	8.05
4	0.858	51.5



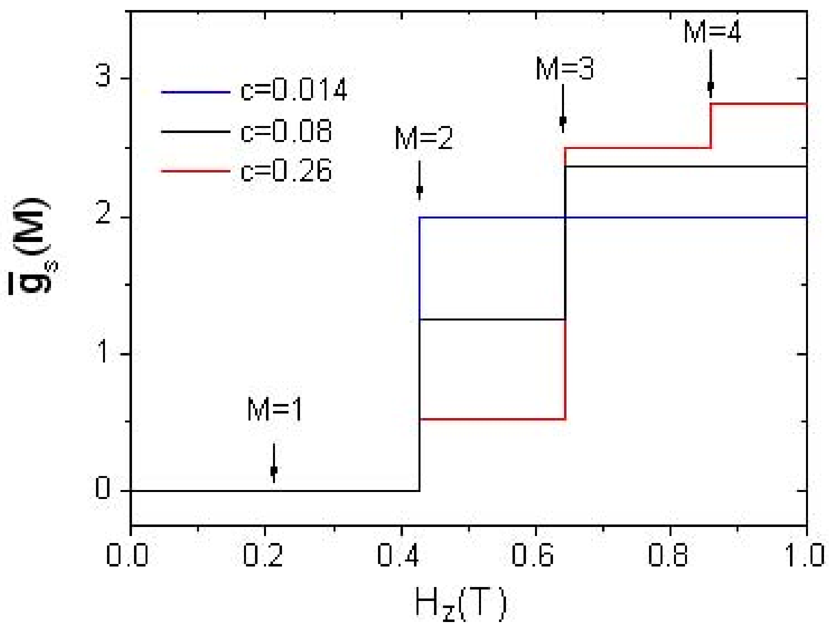
Example: Fe8(cont'd)

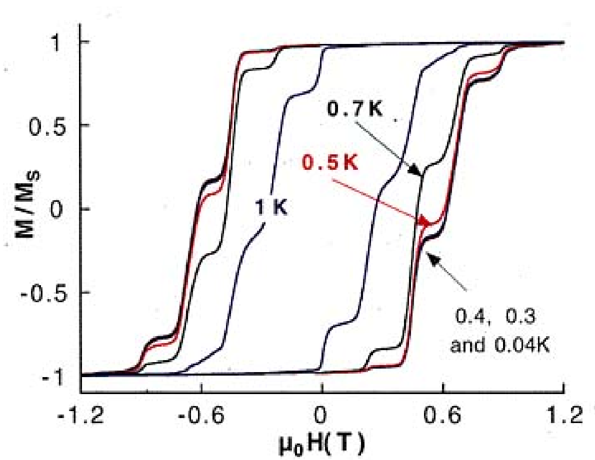
$$G = \frac{2e^2}{h}\left[\gamma_T + \gamma_J g_s(M)\right]$$

$$g_s(M) = S^2 + \bar{g}_s(M)$$

$$\bar{g}_s(M) = \sum_{i=1}^{M}\prod_{j=0}^{i-1} F_j - M\prod_{j=0}^{M} F_j$$

Conductance vs. longitudinal field.





- Similar to the magnetization curve, the conductance is featured with the stepwise increase as a function of magnetic field.

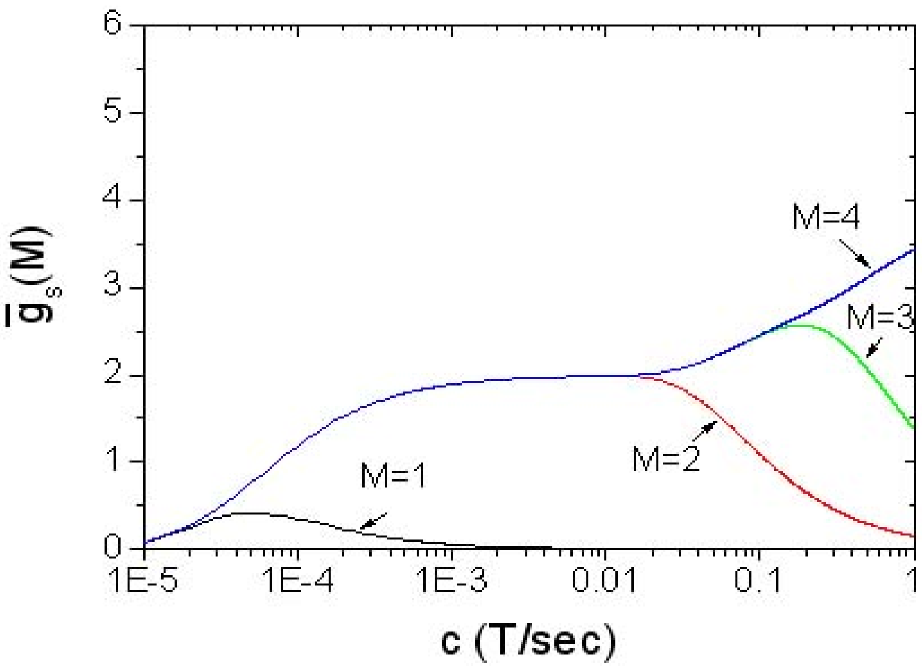
Example: Fe8(cont'd)

Conductance vs. the field sweeping speed

$$\bar{g}_s(M) = \sum_{n=0}^{M} n P_{S-n}$$

$$P_{S-M} \equiv \lim_{t\to\infty} \left|a_{S-M}(t)\right|^2 = (1 - F_M)\prod_{j=0}^{M-1} F_j \qquad F_M = \exp\left[-\frac{\pi \Delta_M^2}{2(2S - M)\hbar g \mu_B c} \right]$$

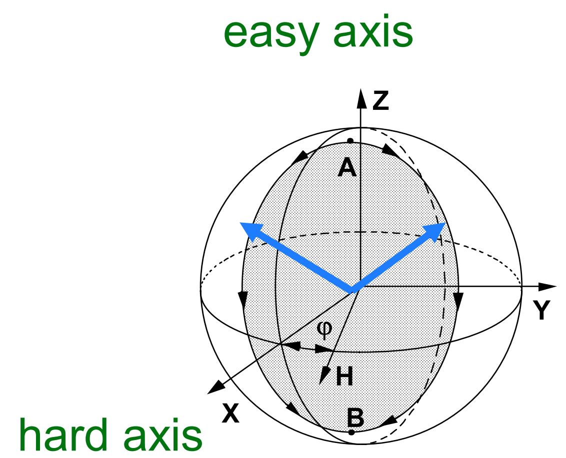
- The conductance $\bar{g}_s$ has the contribution $\delta\bar{g}_s = M P_{S-M}$ from the Mth resonance and is expected to have the maximum value at some value of c.

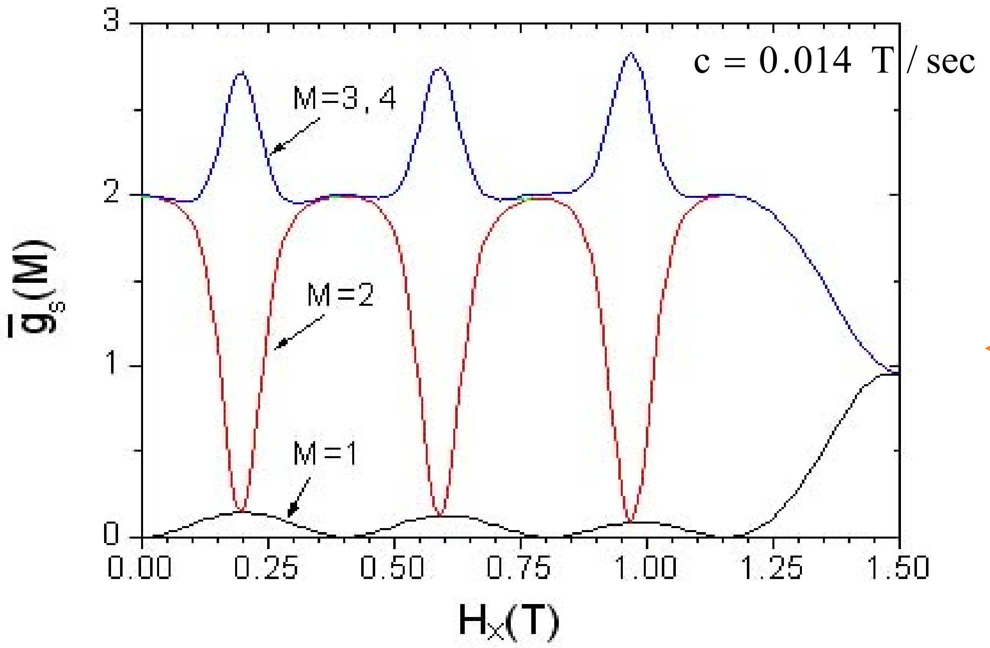


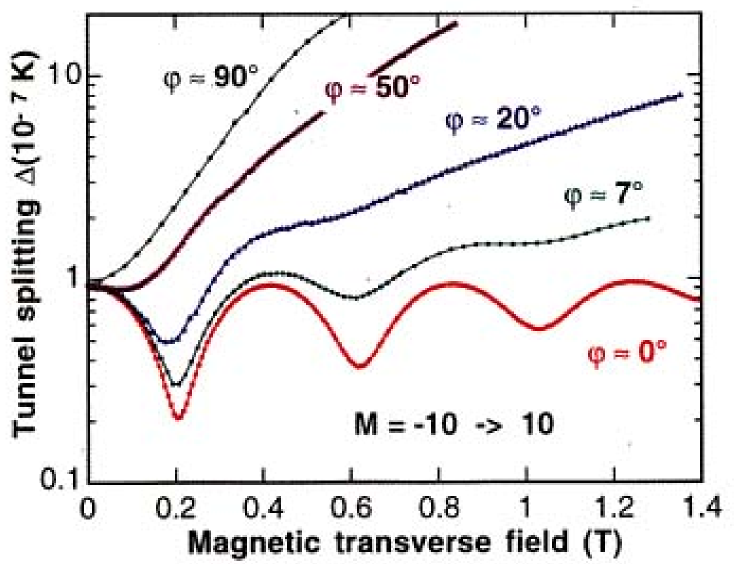
$$c_M^{max} \cong \left(\frac{\pi}{2\hbar g \mu_B}\right)\left(\frac{\Delta_M^2}{2S - M}\right)\left[\log\left(\frac{M\sum_{i=0}^{M} \nu_i}{1 + \sum_{j=1}^{M-1}\sum_{i=0}^{j} \nu_i}\right)\right]^{-1}$$

Example: Molecular magnet Fe8(cont'd)

- Conductance at the resonant field vs. transverse field







- Similar to the magnetization curve, the conductance at each resonant field oscillates with almost the same period of ~0.4 T.

- Such oscillatory conductance faithfully reflects the structure of Δ_M as a function of H_x

- The amplitude of oscillations depends sensitively on c

Summary

- Transport in SMM on metallic surface
- Two-level model and Fermi Golden Rule
- Conductance: stepwise behavior as a function of longitudinal field
- Oscillation in conductance as a function of transverse field
- The effect of relaxation process
  - Since all the transferred state $S_z = S - M \ (M = 1, 2, \ldots)$ lose the weight to the ground state, the value of $\bar{g}_s$ will rise stepwise with increasing field and might vanish in the end due to the relaxation process
  - Elapsed time between steps $(\leq O(10)s)$ << relaxation time of magnetization $(\sim O(10^4)s)$
- Possible exchange anisotropy in spin-scattered tunneling

$$g_s^{aniso} = g_s^{iso} + (a-1)\sum_{n=0}^{M} n(2S+1-n)P_{S-n} \qquad a = (J_\perp / J_z)^2$$

  - When a>1, the conductance steps are more enhanced.
  - For the case of a<1, the steps are reduced.
- Conductance at finite temperature