Nanomagnetismo molecolare: dalla fisica classica alla meccanica quantistica

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Outline

• Few words on magnetic field and magnetic systems
• Nanosystems. The case of molecular nanomagnets
• “Classical” effects
• Quantum effects and applications
Magnetism &
magnetic field
Magnetism and magnetic field

Natural examples: rock magnetism and earth's field

Earth's magnetic field changes over time because it is generated by a geodynamo (in Earth's case, the motion of molten iron alloys in its outer core).

The North and South magnetic poles wander widely over geological time scales, but sufficiently slowly for ordinary compasses to remain useful for navigation. However, at irregular intervals averaging several hundred thousand years, the Earth's field reverses and the North and South Magnetic Poles relatively abruptly switch places. These reversals of the geomagnetic poles leave a record in rocks that are of value to paleomagnetists in calculating geomagnetic fields in the past. Such information in turn is helpful in studying the motions of continents and ocean floors in the process of plate tectonics.

\[ B_{\text{Earth}} = 0.25 - 0.65 \text{ Gauss} \]
**Il campo magnetico**

- Esiste sempre **UNA “sorgente” di campo magnetico**. Tipico esempio: la calamita
- **Sorgenti** di campo magnetico **di interesse**: elettromagneti, magneti superconduttori, magneti in genere
- **E’ all’origine della forza magnetica (e/o viceversa)** fra due o più oggetti
- Ad oggi esistono **molto esempi quotidiani** di utilizzo del campo magnetico

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Levitazione diamagnetica della rana in alti campi magnetici (10 Tesla; il campo terrestre è 0.00005 Tesla)

Il “più grande” magnete del mondo (CERN)

Treno a levitazione magnetica

Levitazione dovuta a superconduttori ad alta temperatura critica
Il campo magnetico dovuto a cariche elettriche circolanti

Filo elettrico percorso da corrente: legge di Biot-Savart

Fra due fili percorsi da corrente: forza magnetica

La limatura di ferro fornisce la direzione del campo magnetico generato dalla corrente che percorre il filo (vista dall'alto)
Il campo magnetico dovuto a cariche elettriche che ruotano su se stesse

**Origine del campo magnetico**: particelle aventi carica elettrica in moto

**Altro tipo di moto di carica** che genera un campo magnetico:
rotazione di una carica elettrica intorno a un asse

Rotazione (spinning) dell'elettrone su se stesso: piccola calamita!!

Rotazione dell'elettrone e del nucleo su se stessi

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*Formation of the 21-cm Line of Neutral Hydrogen*

*Higher energy state: Proton and electron spins aligned*

*Emission of 21-cm photon*

*Lower energy state: Proton and electron have opposite spins*
Magnetism in materials has atomic origin!!

- **Orbital** magnetic moment
- **Intrinsic** magnetic moment due to the spin $s = \pm 1/2$

\[
\mu_{\text{orbital}} = g_\ell \times \mu_B \times \ell
\]
\[
\mu_{\text{spin}} = g_s \times \mu_B \times s = \mu_B
\]
\[
\mu_{\text{total}} = \mu_{\text{orbital}} + \mu_{\text{spin}}
\]

\[
\mathcal{M} = (1/V) \sum_i m_i = (1/V) \sum_i \mu_{\text{orb}} + \mu_{\text{spin}} 
\]

**Magnetization**

In MM, often $\mu_{\text{orb}} \sim 0 \implies$ magnetism given by $\mu_{\text{spin}}$
“Std” magnetic systems: hysteresis and domain walls

Bulk ferromagnet

When driving magnetic field drops to zero, the ferromagnetic material retains a considerable degree of magnetization. This is useful as a magnetic memory device.

The driving magnetic field must be reversed and increased to a large value to drive the magnetization to zero again.

The hysteretic loop shows the "history dependent" nature of magnetization of a ferromagnetic material. Once the material has been driven to saturation, the magnetizing field can then be dropped to zero and the material will retain most of its magnetization (it remembers its history).

Material magnetized to saturation by alignment of domains.

Toward saturation in the opposite direction.

Material magnetized to alignment of domains.
….. toward….
“Nano” - physics
i.e.
reducing the size of the systems to nm scale
Few examples of “nano” Magnetism applications

Information Technology

- Data storage
- Quantum computing

Energy

- Transportation
- Energy storage

Biomedicine

- Magnetic Resonance Imaging (diagnosis)
- Magnetic Fluid Hyperthermia (tumour therapy)
- Magnetic (drug) delivery
Magnetic structures

macroscopic

atomic

permanent magnets
micron particles
nanoparticles
clusters
molecular clusters
atoms

multi-domains
single-domains
spins

$S = 10^{20} 10^8 10^6 10^5 10^4 10^3 10^2 10^1$

1 mm
20 nm
3 nm
1 nm
MESOSCOPIC MAGNETISM

Classical  Quantum

permanent magnets  micron particles  nanoparticles  clusters  molecular clusters

size

$S = 10^{23}$  $10^{10}$  $10^{8}$  $10^{6}$  $10^{5}$  $10^{4}$  $10^{3}$  $10^{2}$  $10$  $1$

multi-domain nucleation, propagation and annihilation of domain walls

single-domain uniform rotation

Ferritin  Single molecule quantum tunneling, quantum interference

Mn$_{12}$-ac

Fe$_8$
Basic dates in history of Molecular magnets or "single-molecule magnets"

- 1993 early magnetic studies on Mn12
- 1996 QTM in Mn12
- 1997 QTM in Fe8
- 2000 Mn12 on surface
- 2002 Agilent Technology Award to Sessoli, Gatteschi, Barbara, Wernsdorfer, Friedman
- 2004 TbPc2 (phtalocyanines)
- 2007 Mn6
- 2009 Fe4 on surface
- 2015 Zavoisky award to Prof. D. Gatteschi
Related research activities

- QTM & other quantum effects
- Magneto-thermal effects
- SMM on surfaces
- SMM for spintronics
- Increase anisotropy barrier
- Molecular Magnetics (Mol. Magn.)
- Mechanisms for M retention
Some applications

- Memory storage
- Magneto-thermal effects
- Molecules on surfaces (read and write)
- Information Storage & Processing:
  - Molecular spintronics
  - Quantum computation
  - Hybrid cavities
Typical Magnetic Molecule

1 nm

magnetic core

ligand

A “total” molecular spin

Pavia, 07/06/16
A single crystal is a collection of identical nanomagnets well separated one another and perfectly oriented.
Another example of nanomagnet: crystal of Fe8

Few magnetic ions per molecule

Unit repeated over all the crystal

Negligible magnetic interactions among molecules i.e.
Molecular nanomagnets or single molecule magnets

Studying the bulk ⇒ Investigating the single molecule
**Molecular Nanomagnets (MNM)**

Wide variety: rings (Fe10, Fe6, Cu8, Cu6, Cr8, ...

“clusters”, Single Molecule Magnets (Mn12, Fe8, Ni10, Cr4, Fe4, ...

chains, Single Chain Magnets (CoPhOMe, Dy-Ph, Gd-R, ...

- Crystals made up of very weakly interacting molecules

⇒ magnetic properties determined by single molecule

- Clusters and rings can be designed at will:
  - number of interacting magnetic ions (spins) ÷ geometric spatial arrangement of the ions
  - single ion spin dimension (s=1/2, ..., s=5/2)
  - exchange interaction J (AF, FM)
Example: High-spin Molecular magnets
Some high spin nanomagnets

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

Fe$_8$ $S = 10$

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

Fe$_{19}$ $S = 33/2$

Lis, 1980

Wieghardt, 1984

Winpenny, 1999

Powell, 2000
Example:
Low-spin
Molecular magnets
Some AF ring-like $S_T=0$ nanomagnets

Cr(III) $s = 3/2$
AF ground state
(total spin $S_T = 0$)

$J \approx 17.2$ K
$\Delta_{0 \rightarrow 1} \approx 9.4$ K

Fe(III) $s = 5/2$
AF ground state
(total spin $S_T = 0$)

$J \approx 13.8$ K
$\Delta_{0 \rightarrow 1} \approx 5.5$ K

Cr8
$S_T=1$
$9.4$ K
$S_T=0$

Fe10
$S_T=1$
$5.5$ K
$S_T=0$

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Other nanomagnets.....

Fe30

Dy6

“toroidal” moment

Mn 3x3 grid

Phtalocyanines-based (double deckers)

Single-chain magnets (1D magnetic nanowires)
Example: Molecular chains
Examples of molecular chains

single chain magnets

(a) CoPhOMe  
(b) MnPhOMe

Gd-R chain. Villain’s conjecture

\[ d_{\text{local}} = 0.51 \, D \]
\[ \theta_{el} = 62^\circ \]
\[ d_{\text{local}} = 1.22 \, D \]
\[ \theta_{el} = 81^\circ \]
Why Physics of Molecular magnets is so interesting?
Classical Physics involved

- Physics of low-dimensional systems (how magnetism depends on crystal and spin dimensionality)
- Spin dynamics: how spins move when T and H are varied
- System’s dynamics, e.g., Brownian motion (due to temperature effect)

Quantum Physics involved

Due to finite number of magnetic ions ⇒ discrete energy levels
- Gapped ground state: level crossing effects
- “Macroscopic” quantum tunneling and/or tunneling of the Neel vector (after D. Loss et al.)
- Spin dynamics in zero dimension
- Measurement of the decoherence time (quantum computation)
- Quantum entanglement
The switch from classical (physics) to quantum mechanical depends often on temperature region of operation.
“Classical” (not trivial !!) physics:

Nanoparticles

Molecular nanomagnets at “high” temperature
Nanomagnetism for “classical” NPs

Below a critical temperature, $T_C$, some materials exhibit spontaneous magnetization (ferro- and ferrimagnetism). Demagnetizing field induces domain formation (i.e. uniformly magnetized regions of different shape and size are formed).

\[
E = E_{ex} + E_k + E_\lambda + E_D
\]

$E_{ex}$ exchange energy, $E_k$ magnetocrystalline anisotropy energy, $E_\lambda$ magnetoelastic energy, $E_D$ magneto-static energy

Typical values of domain wall width are in the 10-100 nm range.

The width of the domain wall depends on the anisotropy and exchange coupling and

\[
\delta = \pi \sqrt{A/K}
\]

$A$ = exchange energy density ($J/m^2$)
$K$ = magnetic anisotropy energy density ($J/m^2$)
Single Domain Nanoparticles

Total wall energy per area unit: \[ E_\sigma = 2(AK)^{1/2} \]

Reducing the dimensions of the crystal: competition among \( E_\sigma \) and the magnetostatic energy, \( E_\lambda \). But \( E_\lambda \) scales with the volume, \( E_\sigma \) with the surfaces.

There exists a lower limit in size, \( D \), corresponding to the single domain state.

\[ D = \frac{18}{\mu_0 M_S^2} E_\sigma \]

When \( D < \delta \) all the spins are coupled (Exchange Energy is constant). The inversion of \( M \) occurs through a coherent movement of all the spins of the particle.

Typical \( D \) values:
- Fe 15 nm
- Co 70 nm
- Ni 55 nm
- NdFeB 100 nm
- Fe\(_3\)O\(_4\) 128 nm
- \( \gamma \)-Fe\(_2\)O\(_3\) 166 nm
Energy barrier \( \Delta E = k_A V \)

- \( k_A \) = anisotropy constant, \( V \) = particle volume

- The inversion of \( M \) occurs through a coherent movement of all the spins of the particle

- Stoner-Wolhfarth model:
  - \( \Delta E \)
  - \( z \) = easy-axis of \( M \), \( \theta \) = angle (\( z, M \))

- Neel correlation time:
  - \( \tau_N = \tau_0 \exp(\Delta E/k_B T) \)

- The Neel correlation time increases exponentially with the energy barrier.

If NPs interact: Vogel-Fulcher model,

\[ \tau_N = \tau_0 \exp[\Delta E/k_B(T-T_0)] \]
Also in MM for studying the fundamental physical processes and for the applications we need to follow the typical times of the systems.

For example some MM are superparamagnetic.
How to detect the dynamics typical of systems?

The (extended) “resonance” concept
Il fenomeno della risonanza

- Consiste in una risposta "aumentata" dei sistemi (molla, chitarra/microfono, ponti, nuclei, elettroni, molecole,...) sollecitati da una azione esterna agente a frequenze proprie dei sistemi stessi.

Quando si ha risonanza c'è un picco nella risposta del sistema.
Il fenomeno della risonanza

Se la molla viene “forzata” dall’esterno alla sua frequenza, aumenta l’ampiezza della sua oscillazione.

AMPIEZZA DELLA MOLLA (MAX ALLUNGAMENTO)

AMPRIEZZA DELL’OSCILLATORE FORZATO
Il fenomeno della risonanza

RISONANZA SONORA: effetto Larsen in chitarre amplificate

20 Hz – 500 Hz

Time 2.00 & 3.15
Il fenomeno della risonanza

RISONANZA MECCANICA:
Ponti di Tacoma che oscillano e poi crollano causa vento a circa 67 km/h

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Conditions for observing a resonance typical of motions inside the investigated system:

stimulate the system with a frequency $\omega_{\text{meas}}$ near a typical system frequency $\nu_c = 1/\tau_c$:

$$\omega_{\text{meas}} \tau_c \approx 1$$

Possible motions: spin motion, Brownian motion, molecular motion
FOR THIS PURPOSE
ONE CAN USE DIFFERENT
TECHNIQUES ABLE TO
DETECT MAGNETIC PROPERTIES

Concept of response function
(e.g. specific heat, magnetic susceptibility)
Typical times/frequencies: how to observe the dynamics

SPM particle blocking is noticeable when $\tau_m = \tau_N$ at a given temperature.
Some response functions

(to the external stimuli)
Molecular magnets

DC susceptibility: Curie law for $T > 100K$

RINGS

Just one atom makes the difference!!

Cr$_3$Zn “Open Ring”
Cr$_3$ “Closed Ring”

![Graph showing DC susceptibility vs. temperature for Cr$_3$ and Cr$_3$Zn with different magnetic fields.](image)
The first single molecule magnet: Mn$_{12}$-acetate

Lis, 1980

\[ [\text{Mn}_{12}\text{O}_{12}(\text{CH}_3\text{COO})_{16}(\text{H}_2\text{O})_{4}] \cdot 2\text{CH}_3\text{COOH} \cdot 4\text{H}_2\text{O} \]

R. Sessoli et al. JACS 115, 1804 (1993)
AC susceptibility typical data: varying the frequency

Spin block: “Blocking” temperature

Maximum (response) for
\[ \omega_{AC} \tau = 1 \]
\( \tau = \) correlation time of spins
i.e. Neel time!

Mn12
Another “source” for understanding the response function.

An historical technique for Pavia:

Nuclear Magnetic Resonance
An historical technique for Pavia: Nuclear Magnetic Resonance

1944

Isidor Isaac Rabi

The Nobel Prize in Physics 1944 was awarded to Isidor Isaac Rabi "for his resonance method for recording the magnetic properties of atomic nuclei".

1945/46: Bloch - Purcell

1948/50

Esperimenti RMN di Luigi Giulotto (Università di Pavia)
\[ H = H_Z + H_D + H_{CS} + H_Q + H_{hyp} + H_J + H_{ce} \]

- **\( H_Z \)** = Zeeman interaction, path 1 \((\propto B_0 \sim 10^9)\)
- **\( H_D \)** = Dipolar interactions among nuclear spins, path 2,3 \((\propto I \cdot S \cdot r^{-3} \sim 10^{3-5})\)
- **\( H_{CS} \)** = Chemical shielding interaction, path 6 and 3 \((-1 \sim 10^5)\)
- **\( H_Q \)** = Quadrupolar interaction (nuclei \(I > 1/2\)) with surrounding \(\nabla E\), path 3 \((10^3 \sim 10^7)\)
- **\( H_{hyp} \)** (paramagnetic shift) = hyperfine e-n dipolar (pseudocontact) and contact interactions, path 3 (influenced by 5)
- **\( H_J \)** = J-coupling, path 2 via path 3
- **\( H_{ce} \)** = interaction of nuclei with conduction electrons (e.g. nuclei, Knight shift), path 3
NMR

- Absorption spectra (almost static response)
- Nuclear time to reach equilibrium $1/T_1$:
  - nuclear dynamical response
- Also $T_2$
EXAMPLE AT ROOM TEMPERATURE

1D spin diffusion
Molecular chains

No spin diffusion
Molecular rings

\[ 1/T_1 = A \left(1 + \left(H/H_c\right)^2\right) + C \quad \text{(ms}^{-1}) \]

\[ 1/T_1 = PH^{1/2} + Q. \]
AGAIN “CLASSICAL” BEHAVIOUR
DETECTING SPIN MOTION

Vs temperature behaviour

Peaks $\rightarrow$ max resp. function at

$$\frac{1}{T_\chi T} = A \left[ \frac{\lambda_{\chi g}(T)}{\omega_c^2(T) + \omega_e^2} + \frac{\lambda_{\chi a}(T)}{\omega_c^2(T) + \omega_e^2} \right]$$

\begin{align*}
(a) & \quad \text{Cr}_8 \text{Zn} \\
(b) & \quad \text{Cr}_8
\end{align*}
"Quasi-classical" effect: Muon Spin Resonance, a local technique similar to NMR.

Peaks at $\omega_{\text{meas}}\tau \approx 1$

$\text{Mn}12_{\text{max}}$ when $\omega_{\text{meas}}\tau_c \approx 1$

In this case a bit more complicate due to quantum structure of energy levels.
… going to quantum world
Struttura atomica e nucleare

Organi → tessuti → molecole
→ Atomi → nuclei
Particelle atomiche e subatomiche
Struttura atomica e nucleare

Quantizzazione dei Livelli energetici

Esempio: atomo di idrogeno

Un sistema quantistico non può assumere (in modo continuo) tutti i valori di energia
Quantum Physics of Mn12

Few N spins : \((2s+1)^N\) levels

The first single molecule magnet: Mn$_{12}$-acetate

Lis, 1980

\[
\text{Mn(III)} \quad \text{Green} \quad S = 2 \\
\text{Mn(IV)} \quad \text{Orange} \quad S = 3/2 \\
\text{Oxygen} \quad \text{Red} \\
\text{Carbon} \quad \text{Blue}
\]

\[
[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4 \cdot 2CH_3COOH \cdot 4H_2O]
\]

R. Sessoli et al. JACS 115, 1804 (1993)
Discrete levels. Superparamagnetic behaviour

**Quantum effects at the nanoscale** ($S = 10$)

**Simplest case:** axial (cylindrical) crystal field

\[
\hat{H} = D\hat{S}_z^2 \quad (D < 0)
\]

Eigenvalues given by:

\[
E(m_s) = -|D|m_s^2
\]

- Small barrier - $DS^2$
- Superparamagnet at ordinary temperatures

\[\Delta E \sim DS^2 \quad 10-100 \text{ K}\]

"up"

Thermal activation

\[|D| \sim 0.1 - 1 \text{ K}\]

for a typical single molecule magnet
Quantum effects at the nanoscale ($S = 10$)

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Quantum computing in molecular magnets

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Shor and Grover demonstrated that a quantum computer can outperform any classical computer in factoring numbers and in searching a database by exploiting the parallelism of quantum mechanics. Whereas Shor’s algorithm requires both superposition and entanglement of a many-particle system, the superposition of single-particle quantum states is sufficient for Grover’s algorithm. Recently, the latter has been successfully implemented using Rydberg atoms. Here we propose an implementation of Grover’s algorithm that uses molecular magnets, which are solid-state systems with a large spin; their spin eigenstates make them natural candidates for single-particle systems. We show theoretically that molecular magnets can be used to build dense and efficient memory devices based on the Grover algorithm. In particular, one single crystal can serve as a storage unit of a dynamic random access memory device. Fast electron spin resonance pulses can be used to decode and read out stored numbers of up to $10^5$, with access times as short as $10^{-10}$ seconds. We show that our proposal should be feasible using the molecular magnets Fe$_8$ and Mn$_{12}$. 

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Tunnel splitting
Thermally assisted Quantum Tunneling

Quantum effects at the nanoscale ($S = 10$)

Break axial symmetry:

$$\hat{H} = D\hat{S}_z^2 + \hat{H}_T$$

$\hat{H}_T \Rightarrow$ interactions which do not commute with $\hat{S}_z$

- $m_s$ not good quantum #
- Mixing of $m_s$ states
  $\Rightarrow$ resonant tunneling (of $m_s$) through barrier
- Lower effective barrier

\[ \Delta E_{eff} < \Delta E \]
Applying a field: levels change (Zeeman effect)

Application of a magnetic field

Spin projection - $m_s$

$\hat{H} = D\hat{S}_z^2 + \hat{H}_T + g\mu_B\vec{B} \cdot \hat{S}$

$\vec{B} \cdot \hat{S} = B_x\hat{S}_x + B_y\hat{S}_y + B_z\hat{S}_z$

Several important points to note:

- Applied field represents another source of transverse anisotropy
- Zeeman interaction contains odd powers of $\hat{S}_x$ and $\hat{S}_y$

For now, consider only $B//z$:
(also neglect transverse interactions)

$E(m_s) = -|D|m_s^2 + g\mu_B Bm_s$

- Magnetic quantum tunneling is suppressed
- Metastable magnetization is blocked ("down" spins)
Applying a field: levels change (Zeeman effect)

Application of a magnetic field

\[ \hat{H} = D \hat{S}_z^2 + \hat{H}_I + g \mu_B \vec{B} \cdot \hat{S} \]

\[ \vec{B} \cdot \hat{S} = B_x \hat{S}_x + B_y \hat{S}_y + (B_z \hat{S}_z) \]

Several important points to note:
- Applied field represents another source of transverse anisotropy.
- Zeeman interaction contains odd powers of \( \hat{S}_x \) and \( \hat{S}_y \).

For now, consider only \( \vec{B} \parallel z \):
(also neglect transverse interactions)

\[ E(m_s) = -D m_s^2 + g \mu_B B m_s \]

- Resonant magnetic quantum tunneling resumes
- Metastable magnetization can relax from "down" to "up"
the relaxation time becomes $T$-independent

appearance of step-like hysteresis loop of $M$


drop of the relaxation time in proximity of LA

vertical steps for $H_z$ values corresponding to the LA
Quantum energy level crossing
The $S_T=0$ homometallic ring-like systems

**Fe(III) $s = 5/2$**
- AF ground state (total spin $S_T = 0$)
- $J \approx 13.8 \text{ K}$
- $\Delta_{0\rightarrow 1} \approx 5.5 \text{ K}$

**Cr(III) $s = 3/2$**
- AF ground state (total spin $S_T = 0$)
- $J \approx 17.2 \text{ K}$
- $\Delta_{0\rightarrow 1} \approx 9.4 \text{ K}$

**Fe(III) $s = 5/2$**
- AF ground state (total spin $S_T = 0$)
- $J \approx 21 \text{ K}$
- $\Delta_{0\rightarrow 1} \approx 15.6 \text{ K}$

**Cr8**
- $S_T = 1$
- $S_T = 0$
- $J \approx 17.2 \text{ K}$
- $\Delta_{0\rightarrow 1} \approx 9.4 \text{ K}$

**Fe10**
- $S_T = 1$
- $S_T = 0$
- $J \approx 13.8 \text{ K}$
- $\Delta_{0\rightarrow 1} \approx 5.5 \text{ K}$

**Fe6:Li**
- $S_T = 1$
- $S_T = 0$
- $J \approx 21 \text{ K}$
- $\Delta_{0\rightarrow 1} \approx 15.6 \text{ K}$

Pavia, 07/06/16
Hamiltonian for ring nanomagnets:

\[ \Sigma_i J \mathbf{s}_i \cdot \mathbf{s}_{i+1} + \Sigma_i U(\mathbf{s}_i) + \Sigma_{ij} U_{ij}(\mathbf{s}_i, \mathbf{s}_j) + g \mu_B \mathbf{B} \cdot \Sigma_i \mathbf{s}_i \]

- \( U(\mathbf{s}_i) = \) crystal field anisotropies
- \( U_{ij}(\mathbf{s}_i, \mathbf{s}_j) = \) intramolecular dipolar interactions, hyperfine couplings, D-M interaction, higher order exchange, etc.

Approximate energy levels (Landè rule):

\[ E(S_{\text{TOT}}) = \frac{P}{2} S_{\text{TOT}} (S_{\text{TOT}} + 1) \quad P = 4 \frac{J}{N} \]

- \( N = \) number of magnetic ions in the ring

- Level crossing fields depend on the angle \( \theta \) between field and molecular axis \( z \)
- **POSSIBLE LEVEL REPULSION AT CROSSING FIELDS (LEVEL ANTICROSSING)**
ANTICROSSING OR AVOIDED LEVEL CROSSING (ALC)

In some rings there is experimental evidence for level repulsion at crossing fields (ALC).

Questions (experimental) on fundamental structure of levels arise:

1) How can we distinguish LC from ALC?
2) What is the “value” of ALC, i.e. the “gap” at the crossing?
3) How (if) levels’ lifetime affects the degree of ALC?
4) Does any other quantum effect (e.g. QT of the Neel vector, QTNV in brief) occurs, especially near ALC or LC?

Macroscopic probes (magnetization, EPR, specific heat,....) help, but give not definitive answers.
Evidences for ground state spin change & LC/LAC: torque and specific heat on single x-tals

1) Peaks of $dM/dH$ at crossing fields; 2) Plateaus in $M(H)$ corresponding to $S=0, 1, 2, \ldots$ states

**Ferric wheel**

Fe$_{10}$

\[ \theta (H, \text{unique axis}) = 49.8^\circ \]

**Fe6:Li**

\[ \theta = (H, c) = 25^\circ \]

**Cr$_8$(Piv)$_{16}$**

\[ \text{[Cr}_8\text{F}_8\text{Piv}_{16}] \] single crystal

- **Angular dependence** of the crossing field

- **Specific heat**

  \[ \Delta C (\text{a.u.}) \]

  \[ \text{B (T)} \]

\[ \Rightarrow \text{Level anti-crossing (LAC)} \]

- **From specific heat**: very small LAC

- **Cr$_8$ single crystal**: $T = 0.4 \text{ K}$

- **Magnetic Field (T)**

- **Torque**

  \[ \text{Magnetic Field (T)} \]

  \[ \theta = 45^\circ \] (angle between unique axis and B)
Fit parameters:

$\Delta_1 = 0.10 (5) \text{ K}$, $A^2 = 9 (1) \cdot 10^{13} \text{ rad}^2 \text{ Hz}^2$, $B^2 = 7 (1) \cdot 10^{13} \text{ rad}^2 \text{ Hz}^2$, $\Gamma_1 = 4.0(3) \cdot 10^4 \text{ H T} \text{ rad Hz}$, $\Gamma_2 = 4.0(6) \cdot 10^6 \text{ T rad Hz}$

The $H$ and $T$ dependences are due to direct, Raman or Orbach processes? Between nuclei and phonons or electrons and phonons? Does QTNV play any role?
Looking for high anisotropy barrier
For having e.g. room temperature
Storage memories
High anisotropy Single ion Magnets: Tb-double deckers of phtalocyanines

$\text{Tb}^{3+} (J=6) = U_{\text{eff}}/k_B = 80K$

**AC susceptibility hysteresis**

*Pavia, 07/06/16*
Other quantum effects
Quantum phase interference (Berry phase)

\[ P = 1 - \exp \left( -\frac{\pi \Delta^2}{4 \hbar g \mu_B S dH/dt} \right) \]
Glauber dynamics of spin chain

(a) CoPhOMe

\[ d_{\text{local}} = 0.51 \, D \]

\[ \theta_{el} = 62^\circ \]

Single chain magnets

*Angew. Chem. Int. Ed.* **2001**, *40*, No. 9

AC susceptibility

NMR
Phonon trapping in Ni10

[Ni10(O)(dbm)4(thme)4(BzO)2(ttOH)6]

Nonequilibrium Dynamics in Ni10 powders

From SQUID: slowing down of $M$, i.e. non equilibrium situation

From NMR: narrow line (FWHM \(\sim\) 100 KHz) i.e. no local field due to “giant” S

For comparison: Fe8
Phonons are no more a heat bath but the joint dynamics of spin+phonons dominates (phonons populations $n_{ph}$ are not fixed solely by thermostat temperature).

\[ \Delta \nu^2_{tot} = \Delta \nu^2_d + \Delta \nu^2_m \]

\[ \Delta \nu^2_m = \sum_{\mathbf{R}} \sum_{i \in \mathbf{R}} \left( \langle \nu_{R,i} - \nu_0 \rangle_{\Delta t} \right)^2 / N \]

\[ \sum_{i \in \mathbf{R}} \left( \langle \nu_{R,i} - \nu_0 \rangle_{\Delta t} \right)^2 \approx \gamma^2 \sum_{i \in \mathbf{R}} \left[ \sum_{j \in \mathbf{R}} \frac{A(\theta_{i,j})}{r_{i,j}^3} \langle m_{z,j} \rangle_{\Delta t} \right]^2 \]

(i) The dependence of $\langle m_{z,j} \rangle_{\Delta t}$ on $j$ is weak and can be neglected.

(ii) The average molecular magnetization over $\Delta t$ is nearly homogeneous.

\[ \Delta \nu^2_m = \gamma^2 \sum_{\mathbf{R}} [\langle \mu_z \rangle_{\Delta t}]^2 A / N = BM^2 \]
Magnetocaloric effect: entropy of a magnetic system

The Magnetocaloric Effect (MCE) is the adiabatic temperature change of a material upon application of a magnetic field.
Entropy and MCE for Magnetic nanoparticles

classical case

\[ Z = \left[ 4\pi \frac{kT}{mH} \sinh \left( \frac{mH}{kT} \right) \right]^N, \]

\[ S_C = -\frac{\partial (kT \ln Z)}{\partial T} \]

\[ = Nk \left[ \ln(4\pi) + \ln \left( \sinh \left( \frac{mH}{kT} \right) / \left( \frac{mH}{kT} \right) \right) + 1 - \frac{mH}{kT} \coth \left( \frac{mH}{kT} \right) \right]. \tag{5} \]

\[ \Delta S_C \approx -\frac{Nm^2H^2}{6kT^2} = -\frac{-mM_BH^2}{6kT^2}. \]

quantum case:

\[ Z = \sum_{\nu} \text{exp} \left( -\frac{\mu_B H}{kT} \nu \right) \]

\[ S = k_B \ln(2J + 1) \]

\[ \Delta S_Q = -\frac{N\mu_B^2 J(J+1)H^2}{6kT^2}. \]

McMichael et al.

*Journal of Magnetism and Magnetic Materials* 111 (1992) 29–33

Determination of MCE from experiments

\[ \Delta S = \frac{Q_{rev}}{T} \]

\[ \int_A^B \left( \frac{\delta Q}{T} \right)_{rev} \]

from specific heat data:

\[ S(T)_H = \int_0^T \frac{C(T)_H}{T} \, dT. \]

from magnetization data:

\[ \Delta S_m(T)_{\Delta H} = \int_{H}^{H_f} \left( \frac{\partial M(T, H)}{\partial T} \right)_H \, dH. \]
# MCE - a comparison

<table>
<thead>
<tr>
<th>Inter-metallic</th>
<th>$\sum (\gamma/K\gamma K)$</th>
<th>T(K)</th>
<th>$\Delta H (T)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>inter-metallic</td>
<td>$\sim 3$</td>
<td>$&lt;10K$</td>
<td>$3T \rightarrow 0$</td>
</tr>
<tr>
<td>Mn12</td>
<td>$\sim 3$</td>
<td>$\sim 3K$</td>
<td>$7T \rightarrow 0$</td>
</tr>
<tr>
<td>Mn10</td>
<td>12</td>
<td>2K</td>
<td>$3T \rightarrow 0$</td>
</tr>
<tr>
<td>Fe14</td>
<td>4</td>
<td>6K</td>
<td>$7T \rightarrow 0$</td>
</tr>
<tr>
<td>PBA</td>
<td>1</td>
<td>200K</td>
<td>$3T \rightarrow 0$</td>
</tr>
<tr>
<td>Mn32</td>
<td>15</td>
<td>18</td>
<td>$3T \rightarrow 0$</td>
</tr>
<tr>
<td>Gd2</td>
<td>40</td>
<td>2K</td>
<td>$7T \rightarrow 0$</td>
</tr>
</tbody>
</table>
Recent theoretical study (2013) on MCE

- By explicitly considering Carnot refrigeration cycles, we theoretically show that the best molecules for magnetic refrigeration between $T = 10\text{K}$ and the sub-Kelvin region are **those made of strongly ferromagnetically coupled magnetic ions**, contrarily to the established belief. (E. Garlatti et al, APPLIED PHYSICS LETTERS 103, 202410 (2013))

![Graphs showing S/R vs Temperature for different cases of magnetic ions and fields](image)
Magnetic Molecules on surfaces
Single molecule read and write

review by N. Domingo et al., Chem. Soc. Rev. 2011
A. Cornia, D. Tahlam, M. Affronte (2016)
Sunset of Mn12 & sunrise of Fe4

doi:10.1038/nmat2374
Methods of deposition

- air
- high vacuum
- ultra-high vacuum

- liquid phase
- electro-spray
- sublimation

molecules and nanoparticles:
- functionalized surfaces and buffer layers
- pre-patterned surfaces
- dip-pen
- graphene

self assembly
Integrity checks (also magnetic properties)

STM: lateral size as expected

XPS: stoichiometric elemental ratios are respected

<table>
<thead>
<tr>
<th>Derivative</th>
<th>Cr-2p/Ni-2p</th>
<th>F-1s/Cr-2p</th>
<th>N-1s/7Cr-2p</th>
<th>S-2p/7Cr-2p</th>
<th>O-1s/7Cr2p</th>
<th>C-1s/7Cr-2p</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr7Ni-<em>bu</em></td>
<td>7.2 ± 0.5</td>
<td>1.17 ± 0.05</td>
<td>1.10 ± 0.15</td>
<td>-</td>
<td>29 ± 5</td>
<td>90 ± 15 [88]</td>
</tr>
</tbody>
</table>
Self-assembly!

Cr$_7$Ni-bu

Cr$_7$Ni-thiobu

monolayer
Recently addressing Fe4 molecules

Here, we probe electrical transport through individual Fe4 SMMs using a scanning tunnelling microscope at 0.5 K. Correlation of topographic and spectroscopic information permits identification of the spin excitation fingerprint of intact Fe4 molecules. Building from this, we find that the exchange coupling strength within the molecule’s magnetic core is significantly enhanced.

Figure 1 | Fe₄ molecule adsorbed on the Cu₂N surface. (a) [Fe₄(L)₂(dpm)₆] resting on the Cu₂N surface.
Molecular spintronics and quantum computation

SPINTRONICS

- Classical bit $\uparrow \downarrow$
  - Monolithic (only spin)
  - Hybrid (spin & charges)

QUANTUM COMPUTATION

- Quantum bit (superposition of states)
  - coherance + entanglement

MOLECULAR SPINTRONICS

- Passive (ex: spin valve)
- Active (ex: spin transistor)

MOLECULAR ELECTRONICS

Pavia, 07/06/16
Quantum bits

\[ \Psi = \alpha \uparrow + \beta \downarrow \]
Cr7Ni

Quantum coherence in antiferromagnetic rings

Glued Cr7Ni in which fluoride groups are replaced by alkoxides
G. Timco et al. Angew. Chem. 2008, 47, 9681

F. Troiani, V. Bellini, and M. Affronte

Ardavan et al. PRL 98, 057201 (2007)

M. Pavia, 07/06/16
Entanglement as a genuine quantum phenomenon

- separate objects with well defined states.
- weak (initial) coupling.
- the states of each subsystem can no longer be described independently from one to another!
- the state of the global system cannot be factorized

**Example of separable state:**

\[ |\Psi\rangle = |\uparrow_A\rangle |\downarrow_B\rangle \]

**Example of entangled state:**

Bell (or Einstein, Podolsky, Rosen) state

\[ |\Psi\rangle = \frac{|\downarrow_A\downarrow_B\rangle + |\uparrow_A\uparrow_B\rangle}{\sqrt{2}} \]

A measurement of the second qubit always gives result depending on the state of the first.

REVIEWS OF MODERN PHYSICS, VOLUME 81, p.865 APRIL–JUNE 2009, Horodecki et al.
Rules of “this” game

To entangle the spins of different molecular units

Nanotechnology 21, 274009 (2010)
<table>
<thead>
<tr>
<th>molecule</th>
<th>references</th>
<th>Identification of qubit &amp; scalability</th>
<th>Reliable state preparation</th>
<th>Decoherence time</th>
<th>Control of coupling</th>
<th>Read out coupling</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr₂Ni</td>
<td>PRL. 2007, 98 047201</td>
<td>S-1:2 Crystals &amp; assembly on surface</td>
<td>by cooling in magnetic field</td>
<td>1.5 μs @ 1K</td>
<td>yes</td>
<td>ESR</td>
</tr>
<tr>
<td>V₁₈</td>
<td>Nature, 2008 453, 263</td>
<td>S-3:2 in solution</td>
<td>by cooling in magnetic field</td>
<td>0.4 μs @ 4K</td>
<td></td>
<td>ESR</td>
</tr>
<tr>
<td>Cu₃</td>
<td>unpublished</td>
<td>S-1:2</td>
<td>by cooling in magnetic field</td>
<td>~1 μs @ 1K</td>
<td></td>
<td>ESR</td>
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<tr>
<td>Nit-Radicals</td>
<td>unpublished</td>
<td>S-1:2 on surface</td>
<td>Pseudo-pure state</td>
<td>3 μs @ 70K</td>
<td></td>
<td>ESR</td>
</tr>
<tr>
<td>(malonyl) radicals</td>
<td>Nature Chem. 2009, 29, 4793-4796</td>
<td>S-1:2 - nuclear I</td>
<td></td>
<td></td>
<td>yes</td>
<td>ENDOR</td>
</tr>
<tr>
<td>POM polyoxometallate</td>
<td>unpublished</td>
<td>S2:1-2 Crystals</td>
<td>by cooling in magnetic field</td>
<td>0.64 μs @ 1K</td>
<td></td>
<td>ESR</td>
</tr>
<tr>
<td>Fe₄</td>
<td>Phys. Rev. Lett. 2003, 91, 147201</td>
<td>S-5 multiplet</td>
<td>by cooling in magnetic field</td>
<td>0.7 μs @ 1K</td>
<td>yes</td>
<td>ESR</td>
</tr>
<tr>
<td>Fe₈</td>
<td>PRL. 2009, 102, 067203</td>
<td>S-10 multiplet</td>
<td>by cooling in magnetic field</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Mn₁₂</td>
<td>Nature 2001, 410, 881</td>
<td>S-10 multiplet</td>
<td>by cooling in magnetic field</td>
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<tr>
<td>Er³⁺ ions</td>
<td>Nature Nanotechnol. 2009, 2, 39</td>
<td>J-15:2 Impurities in crystalline matrix CaWO4</td>
<td>by cooling in magnetic field</td>
<td>μs @ 2K</td>
<td></td>
<td>ESR</td>
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<tr>
<td>Tb₂</td>
<td>PRL. 2012, 107, 247201</td>
<td>2x J-6</td>
<td></td>
<td></td>
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<td>ESR</td>
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<tr>
<td>SMM linked by diketonates</td>
<td>Chem. - Eur. J. 2006, 12, 11788</td>
<td></td>
<td></td>
<td></td>
<td>yes</td>
<td></td>
</tr>
</tbody>
</table>

*Note: ESR, ENDOR, and FSR stand for Electron Spin Resonance, Electron Nuclear Double Resonance, and Field-Driven Spin Relaxation, respectively.*
Cavity-assisted Quantum Information Processing

superconducting resonators with Molecular Nanomagnets

In progress.
YBCO resonator already realized
The end

Any questions ??