A lecture proposed by

SPP Molekular Magnetismus (DFG)

How molecules go magnetic ...

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Why experiments?

because ...

- experiment arises curiosity
- experiment is speaking ...
- experiment is demonstrating ...
- experiment can be beautiful!
Why experiments in magnetism?

because ...

- it is an important phenomenon ...
- it arises curiosity ...
- it needs to be demystified and explained ...
- and experiments are beautiful!
Why experiments in molecular magnetism?

because ...

- our live relies on it and nobody knows ...
- it is badly known or unknown ...
- it can be explained simply ...
- and experiments are beautiful!
Goals?

1) Citizen awareness
2) Attract good students to our discipline
3) Here: convincing you that such experiments are possible to realize during Science Festivals.
Comments about a possible ...

LECTURE

(abridged ...)
This is NOT the question or not?
Everything is magnetic

... How?
Everything is magnetic ...

... How?

Pierre Curie
Lectures Notes
Fonds documentaire ESPCI
Everything is magnetic ...

... How?

Pierre Curie
Annales de Chimie
7ème série, V, 1895, 289
(Thèse de P. Curie)
Fonds documentaire ESPCI
Everyday life is full of useful magnets which traditionally take the form of three-dimensional solids, oxides, metals and alloys.

Magnets in our world

We are in a real world, at our size
A pioneering experiment
by M. Faraday
« Faraday lines of forces »
about magnetic flux

macroscopic world

Courtesy Prof. Peter Day, the RI; See also:
The Philosopher’s Tree, The Institute of Physics Publishing, Bristol, 19999
A *magnet* creates a magnetic field

« Lines of field »
What is a magnet?
What is NOT a magnet?

Magnetization
Magnetization:
How behave objects in a magnetic field?

- Remnant Magnetization
- Coercive Field
- Magnet « hard »
- Applied magnetic Field $H$
- Magnetization $M$ (how do they become « magnetized »?)
Tout est magnétique

... Comment?

Pierre Curie
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INTRODUCTION.

Les corps se divisent, au point de vue de leurs propriétés magnétiques, en trois groupes distincts :

1° Les corps d’imagnétiques, qui comprennent le plus grand nombre des corps simples et composés;

2° Les corps faiblement magnétiques, parmi lesquels se trouvent l’oxygène, le baryte d’ammoniac, le palladium, le platine, le manganèse, enfin les sols de manganèse, de fer, de nickel, de cobalt, de cuivre, de didymus;

3° Les corps ferro-magnétiques, qui comprennent le fer, le nickel, le cobalt, la magnétite (Fe₃O₄) et encore l’acier, la fonte et divers alliages.

À première vue, ces trois groupes sont absolument tranchés; cette séparation supporte-t-elle un examen plus approfondi? Existe-t-il des transitions entre ces groupes? S’agit-il de phénomènes entièrement différents, ou avons-nous affaire seulement à un phénomène unique plus ou moins déformé? Ces questions préoccupaient beaucoup Faraday qui y revient souvent dans ses Mémoires. Il avait eu une expérience importante: On savait depuis fort longtemps que le fer perd à la chaleur rouge ses propriétés magnétiques. Faraday a montré qu’aux températures élevées le fer reste encore magnétique, bien que faiblement. Un même corps peut...
Everyday life is full of useful magnets which traditionally take the form of three-dimensional solids, oxides, metals and alloys.

**Curie Temperature**
The magnetic moments order at Curie temperature

A set of molecules / atoms:

- Solid, Magnetically Ordered
  - thermal agitation \((kT)\) weaker than the interaction \((J)\) between molecules
  - \(kT \ll J\)

- Magnetic Order Temperature or Curie Temperature

- Paramagnetic solid:
  - thermal agitation \((kT)\) larger than the interaction \((J)\) between molecules
  - \(kT \gg J\)
Magnetic ordering: Curie Temperature ...

... a demonstrator
from macroscopic to atomic world

looking closer to smaller and smaller magnets

= = =

many sets of «domains»

= many sets of atomic magnetic moments
How \textit{magnets} behave?

Domains
Domains
**Physics: Macroscopic**

- Permanent magnets

**Mesoscopic**

- Micron particles
  - Nanoparticles
  - Clusters

**Nanoscopic**

- Molecular clusters
  - Individual spins

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

**Multi-domain**
- Nucleation, propagation and annihilation of domain walls

**Single-domain**
- Uniform rotation
- Curling

**Magnetic moment**
- Quantum tunneling
- Quantization
- Quantum interference

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**Graphs**

- **Macro:** Magnetic moment vs. magnetic field ($H$) for macroscopic materials.
  - Fe
  - $T = 0.1K, 0.7K, 1K$

- **Mesoscopic:** Magnetic moment vs. magnetic field ($H$) for mesoscopic materials.
  - $0.1K, 1K$

- **Nanoscopic:** Magnetic moment vs. magnetic field ($H$) for nanoscopic materials.
  - $0.1K, 0.7K, 1K$

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*Wolfgang Wernsdorfer, Grenoble*
Everyday life is full of useful magnets

Compasses

Magnetic Earth

1600
William Gilbert
De Magnete
Jan van den Straet (Giovanni Stradanus), Bruges, 1523 ; Florence, 1605
Nova Reperta, vers 1620-1630, 14 planches gravées par Jérôme Wierix et Adriaen Collaert, éditées par Philippe Galle

Calcul de la longitude. Burin 22 x 28 cm around 1600 Inv. n° 11786
Compasses, Jiangomen station, Beijing
The fascination of magnets on children

« A wonder of such nature I experience as a child of 4 or 5 years, when my father showed me a compass. That this needle behaved in such a determined way did not at all fit into the nature of events which could find a place in the unconscious world of concepts (effects connected with direct « touch »). I can still remember – or at least believe I can remember – that this experience made a deep and lasting impression upon me. Something deeply hidden had to be behind things. »

A. Einstein

Everyday life is full of useful magnets.
Everything is magnetic

... thanks to electrons ...
Origin of *Magnetism*

... the electron *

I am an electron
- rest mass $m_e$,
- charge $e^-$,
- magnetic moment $\mu_B$

everything, tiny, elementary

* but do not forget nuclear magnetism!
Origin of Magnetism

« Orbital » magnetic moment

\[ \mu_{\text{orbital}} = g_l \times \mu_B \times \ell \]

« Intrinsic » magnetic moment due to the spin

\[ s = \pm \frac{1}{2} \]

\[ \mu_{\text{spin}} = g_s \times \mu_B \times s \approx \mu_B \]

\[ \mu_{\text{total}} = \mu_{\text{orbital}} + \mu_{\text{spin}} \]
Dirac Equation

\[ (E' + e\phi)\psi = \left[ \frac{1}{2m} (p + eA)^2 + \frac{e\hbar}{2mc} \mathbf{\sigma} \cdot \nabla \times A - \frac{p^4}{8m^3c^2} - \frac{e\hbar^2}{8m^2c^2} \nabla \cdot \nabla \phi - \frac{e\hbar}{4m^2c^2} \mathbf{\sigma} \cdot \nabla \phi \times p \right] \psi \]

The Principles of Quantum Mechanics, 1930

Nobel Prize 1933

http://www-history.mcs.st-and.ac.uk/history/PictDisplay/Dirac.html
About what are we speaking?

Representations, Models, Analogies ...
Analogy: spin and arrow

Paul Klee, Théorie de l’art, Denoël, Paris

An isolated spin...
Electron: corpuscle and wave

Ψ⁺  Ψ⁻

Ψ

Wave function

Hokusai, the great wave in Kanagawa
Electron: corpuscle and wave

Wave function or « orbital » \( \Psi_{n, l, m, ...} \)

\[
\begin{array}{cccc}
l = & 0 & 1 & 2 & 3 \\
\end{array}
\]

\( s \)

\( p \)

\( d \)

angular representation
Electron: also an energy level

Energy Diagramme (« ladder »)

Principle 1: fill from the bottom (aufbau)
Electron: orbital and spin!

Nitrogen oxide NO⁻:

Nitronylnitroxyde

Up

Down

Singly occupied

« Paramagnetic »

mₛ = ± 1/2

Quantum
Electron: orbital and spin!

Doubly occupied

$S = \frac{1}{2} - \frac{1}{2} = 0$

« Diamagnetic »

Principle 2: no more than TWO electrons per level (orbital) with different spins!

(Pauli's exclusion principle)
Molecules are most often regarded as isolated, non-magnetic, creatures.

Dihydrogen

Diamagnetic
Spin $S = 0$
$\text{N}_2 \text{ Diamagnetic}$
Pouring liquid dinitrogen

liquid dinitrogen does NOT stick

diamagnetic
the *dinitrogen* is a *diamagnetic molecule*

diamagnetic, spin $S = 0$

All electrons are paired in bonds, very stable molecule
when dioxygen is in its ground state
it is a triplet (spin $S=1$)
and its reactivity is weak

\textbf{Paramagnetic $O_2$}
liquid dioxygen does stick

$O_2$ is paramagnetic
the dioxygen that we continuously breathe is a magnetic molecule

paramagnetic, spin $S = 1$

Two of its electrons have parallel magnetic moments that shapes aerobic life and allows our existence as human beings
when dioxygen is in an excited state
it can becomes a singlet (spin S=0)
and strange reactivity appears
sometimes useful (glow-worm ...)

Singlet dioxygen

Luminol Light
dioxygen singlet (spin $S=0$)

luminol

macro

glow-worm ...

Documents from Nassau and Alvarez
More complex molecular frameworks called metal complexes built from transition metal and molecules are able to bear up to five or seven electrons with aligned magnetic moments (spins)
Il sistema periodico ... (Primo Levi)

È bello raccontare i guai passati ...
Transition Elements

5 d orbitals

Unpaired Electrons
Partial Occupancy
Paramagnetism
Conductivity

\[ x^2 - y^2 \quad z^2 \quad xz \quad yz \quad xy \]
Mononuclear complex $ML_6$

Splitting of the energy levels
An indirect manifestation of the presence of unpaired electrons: the colour
Aqueous solutions of the first row 3d elements: Cr⁶⁺, Mn⁷⁺, Fe²⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺.
Complexes of transition metal ions often display beautiful colours essentially to d levels splitting.

Colours in water
Geometrical Changes
Spin Changes
The complexes of transition metal present often delicate and beautiful colours depending mostly on the splitting of the d orbitals.
Complexes of transition metal ions often display beautiful colours essentially to d levels splitting.
A direct manifestation of the presence of unpaired electrons: the magnetism or interaction with a magnetic field.
How large is the splitting?

Energy

Weak Field
High spin
L = H₂O
[C₂O₄]²⁻

Intermediate Field

Temperature Dependent
Spin Cross-Over

⚠️

Strong Field
Low spin
L = CN⁻

Δₐₒᶜᵗ

x²-y²
z²

xy
xz
yz
t₂g

e₉
Curie Law

\[ \chi_m T = \text{Constant} \]

Pierre Curie, 1900 Paris

Curie Balance
$K_4[\text{Fe(II)(CN)}_6]$ Diamagnetic, spin 0

$K_3[\text{Fe(III)(CN)}_6]$ Paramagnetic, spin 1/2

$(\text{NH}_4)_2\text{Fe(II)(SO}_4)_2$ Paramagnetic, spin 2
Magnetization: how objects behave in a magnetic field?

Magnetization $M$ (how they become « magnetized »)

- Paramagnetic $M = \chi H, \chi > 0$
- Diamagnetic $M = \chi H, \chi < 0$

Applied magnetic field $H$
Playing with ligands, the chemist is able to control the geometry and symmetry of complexes (colour, magnetism)
Co(II)Cl₂, 6H₂O: from octahedral to tetrahedral

Heat

Co²⁺ → 2 Cl⁻ + H₂O

+ Cl⁻

- Cl⁻
Playing with ligands, the chemist is able to control the spin state
Hysteresis allows bistability of the system and use in display, memories ...

Spin and colour changes
$[\text{Fe}^{II}(\text{H}_2\text{O})_6]^{2+}$

pale green

Fe$^{II}(\text{o-phen})_3]^{2+}$

bright red

$S=2$

$S=0$
Low spin, chiral, Fe$^{II}$(bipyridine)$_3$]$^{2+}$
Playing with ligands, the chemist is able to control the spin state.
Spin Cross-Over

A Fe(II) « Chain » with spin cross-over

Triazole substituted Ligand (R) ; insulated by counter-anions

Many groups : Leiden, Mainz, Kojima, O. Kahn, C. Jay, Y. Garcia, ICMC Bordeaux
Transition Cross-over Demonstrator by Jean-François Letard
The very samples presented were synthesized by students in Paris during practical works
Courtesy Prof. C. Roux, C. Train, A. Proust
Spin Cross-Over

Bistability Domain

The system « remembers » its thermal past!

O. Kahn, C. Jay and ICMC Bordeaux
Then, memory?

« It is an essential character of living being that the sensation leaves traces. There is nothing comparable in material world. It is a real joke to name « memory » the hysteresis phenomenon. » …

Paul Langevin, *Discussion sur la matière vivante*, 10ème semaine internationale de synthèse, 1938, PUF, 1943, 219-223
From the molecule to the material and to the device ...
Money card

O. Kahn, Y. Garcia, Patent
May we go further
and dream of *molecular magnets*
  i.e. low density,
  biocompatible
  transparent
  or colourful magnets?
Do the chemists know how to align the spins of electrons in molecules, parallel or antiparallel?
Understanding ...

why the spins of two neighbouring electrons 
\((S = 1/2)\) become:

antiparallel ? or parallel ?

\[ S=0 \]

Singlet

\[ S=1 \]

Triplet
\[
J = 2k + 4\beta S
\]

if \( S = 0 \)

Orthogonality

if \( S \neq 0; |\beta S| >> k \)

Overlap

\( O_2 \) Hund

\( H_2 \) Aufbau

\( E_S \) \( E_T \) Ferro

\( E_T \) \( E_S \) Antiferro
Tell it with flowers (find the orbital)

Overlap (σ) isolated

Overlap (π)

Orthogonality

Flowers from the garden of the Gulbenkian’s Foundation, Lisbon
Exchange interactions can be very weak ...

Exchange interactions

order of magnitude: \( \text{cm}^{-1} \) or Kelvins ...

« Chemical » bonds

Robust!

order of magnitude: \( \gg 150 \text{ kJ mol}^{-1} \) ...

Michelangelo, Sixtin Chapel, Rome
Please, avoid pairing electrons into bonds ...
Avoid ...

\[ \text{NO}_2 \text{ Dimerisation} \]

... to pair the « magnetic » électrons
Interpretation(s)

Thermodynamics (Le Chatelier ...)

Equilibrium: \[ 2 \text{NO}_2 \rightleftharpoons \frac{1}{2} \text{N}_2\text{O}_4 + \text{Heat} \]

Orbital

Pairing of electrons, bonding

DIA-magnetic!
A beautiful artefact

When some residual NO is present in the vessel:

Reaction: \( \text{NO}_2 + \text{NO} \xleftrightarrow{\frac{1}{2}} \text{N}_2\text{O}_3 \)

Brown \( \rightarrow \) colorless \( \xrightarrow{\frac{1}{2}} \) Blue green
≈ 5 Å
Orbital Interaction ...
Which ligand? Why not …

- Cyanide, CN^-?
Cyanide Ligand

Friendly ligand: small, dissymmetric, forms stable complexes

Warning: dangerous, in acid medium gives HCN, lethal
Dinuclear \( \mu \)-cyano heterometallic complexes

NB: A dissymmetric ligand helps to get stable heterometallic complexes...

« Birds of the same feathers flock together » ...
Polynuclear complex, synthetic strategy

Hexacyanometalate “Heart” Lewis Base + Mononuclear Complex Lewis Acid → Polynuclear Complex

3− + 6
2+ → 9+
Ferromagnetic ...

Ferrimagnetic ...

Eros

Nocturnal separation, 1922

Paul KLEE
... High Spin Heptanuclear Complexes

\[
\begin{align*}
\text{CrCu}_6 & : S = 9/2 \\
\text{CrNi}_6 & : S = 15/2 \\
\text{CrMn}_6 & : S = 27/2
\end{align*}
\]

Hexagonal \ R -3

\[
\begin{align*}
a = b &= 15.27 \, \text{Å}; \\
c &= 78.56 \, \text{Å} \\
a = b &= 90°; \\
g &= 120°; \\
V &= 4831 \, \text{Å}^3
\end{align*}
\]

Marvaud et al., Chemistry, 2003, 9, 1677 and 1692
How to manipulate electrons *between* molecules?

Towards magnets

The saga of high $T_C$ Prussian Blues Analogues
Diesbach, draper in Berlin ...

... prepares a blue pigment « Prussian blue »

... said to be the first coordination compound
Classical Coordination Chemistry...

$3[\text{Fe(CN)}_6]^{4-}_{\text{aq}} + 4\text{Fe}^{3+}_{\text{aq}} \rightarrow \{\text{Fe}_4[\text{Fe(CN)}_6]_3\}^0 \cdot 15\text{H}_2\text{O}$
Cyanotypes

Einstein a portrait, Cyanotypes by F. Villain, CIM2, UPMC
Magnetic Properties of Prussian Blue

\[ T_C \propto z |J| \]

\( z \) : number of magnetic neighbours
\( |J| \) : coupling constant between nearest neighbours

\[ T_C = 5.6 \text{ K} \]

Néel, 1948
Ferromagnetic Prussian blue analogues...

\[ T_C \propto z |J| \]

\[ J_{\text{Ferro}} > 0 \]

Orthogonality

\[ T_C \gg 5.6 \text{ K} \]
Ferrimagnetic Prussian blue analogues ...

\[ T_C \propto z |J| \]

\[ J_{\text{Antiferro}} < 0 \]

Overlap ...

\[ T_C >> 5.6 \text{ K} \]
$V_4[Cr(CN)_6]_{8/3}.nH_2O$

Room Temperature $T_C$

On a rational basis!

Ferlay et al., *Nature*, 1995

Mallah et al., *Science*, 1993

2[Cr$^{III}$ (CN)$_6$]$^{3-}$ + 3V$_{aq}$$^{2+}$ → [V$_3$[Cr$^{III}$ (CN$_6$)]$_2$]$^0$

A blue, transparent, low density magnet at room temperature
Devices

Based on Room temperature Magnets
Prussian blue analogues
Other device
Magnetic Switch...
Or thermal probe ...

Permanent Magnet
Hot
Sample (MM)
Couple
Up to 2004 ... magnetic analogues used as ... devices and demonstrators
... another demonstrator

- Permanent Magnet
- Sample (MM)
- Heater
... another demonstrator
Chemists have managed to transform isolated single molecules into magnets

Single Molecule Magnets
What is named Single Molecule Magnet?

High Spin Anisotropic
High Spin Paramagnetic Molecule
Single Molecule Magnet
Single Molecule Magnet

Towards information storage at the molecular level?

\[ T < T_{\text{Blocking}} \]
Single molecule magnets
\[
[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4].2CH_3COOH.4H_2O
\]

or \( Mn_{12} \)

\[
\begin{align*}
S &= 8 \times 2 - 4 \times 3/2 = 10 \\
Mn(III) &\quad S=2 \\
Mn(IV) &\quad S=3/2 \\
Ion Oxyde &\quad S=2 \\
Carbone &\quad S=3/2
\end{align*}
\]

From D. Gatteschi and R. Sessoli
Mn12 is a hard magnet

Bistability: in zero field the magnetisation can be positive or negative depending on the story of the sample.
The dream...

High Spin "down"

Magnetic Tip

Surface

≈ 10 nm

quantum

macro
Surface Magnetic Tip

≈ 10 nm

High Spin "down"

High Spin "down"

Surface

quantum

macro
The dream …

Magnetic Tip

High Spin "down"

HSM «up»

Surface

≈ 10 nm

information storage at the molecular level!
Nanosciences ...  

High Spin "down"  

≈ 10 nm  

Surface  

... a challenge for chemists and friends ...
The possibilities are endless ...
Another popular non scientific use of the word «magnetism» as attractive but less recommended...
An interaction through space invisible, incomprehensible ...

Magnetism = Magic!

To be demystified ...
Levitating top
« This flask is equipped with magnets and induces in its centre an intense magnetic field which magnetizes the whole liquid.

Keep in the magnetic flask, tap or mineral water or any other drink, from 15mns to several hours, for an optimum magnetization.

Drink daily Magnetized Water: in preference, 1 cup when getting up, 1 or 2 in the morning and the afternoon and 1 cup at bedtime.

As a matter of fact, the body and the blood are composed at 70 and 80% of water, hence magnetized water, more lively, more energetizing due to its magnetic properties, carries its energy into the whole organism.

Active research in hospitals, worldwide and mainly in China, have demonstrated the beneficent effects of magnetized water.

Some specialists foresee that ..

Magnetism will play an important rôle in the world of tomorrow.
M. Noyori, Hanoi, October 2003

Today the chemist is able to synthesize any molecule at will.
NEW MAGNETIC OBJECTS

High spin Molecules

High $T_C$ Magnets
Photo-Magnets

Single Chain Magnets

Chiral Magnets
BEAUTIFUL OBJECTS

High spin Molecules

High $T_C$ Magnets
Photo-Magnets

Single Chain Magnets

Chiral Magnets
**NEW PROPERTIES**

**High spin Molecules**

**High T<sub>C</sub> Magnets**

**Photo-Magnets**

**Single Chain Magnets**

**Chiral Magnets**

Unpolarised light

\[ \gamma^d(w)k \cdot M \]

\[ I_d^+ \neq I_d^- \]
Earth needs care ....

Science for peace ... (Vincenzo Balzani)
Pablo Picasso

Child with a dove, 1901
oil on canvas, 73x54 cm
Private collection
on loan to National Gallery