BE Magnetic

VII CAMPEONATO DE ESPAÑA BEEFEATER RAIDS

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This is NOT the question or not?
Everything is magnetic

... How?
macroscopic world
atomic or molecular world

« wonder » world

meter ... nano meter ...

$1 / 1\ 000\ 000\ 000 = 10^{-9}$

mole ... molecule ...

$10^{+23}$

1
macroscopic world  atomic or molecular world  "wonder" world

macroscopic world  atomic or molecular world  « wonder » world
macroscopic world
« traditional, classical » magnets
macroscopic world

A pioneering experiment by M. Faraday «Farady lines of forces» about magnetic flux

Courtesy Prof. Peter Day, the RI ; See also : The Philosopher’s Tree, The Institute of Physics Publishing, Bristol, 1999)
M. Faraday’s magnetic laboratory

Courtesy Prof. Frank James, the RI
M. Faraday in his laboratory

Courtesy Prof. Frank James, the RI
macroscopic world
« traditional » magnets

attraction
macroscopic world
« traditional » magnets

repulsion

macro
macroscopic world
looking closer to the magnetic domains

≡ ≡≡

many sets of domains

≡

many sets of atomic magnetic moments
Physics: Macroscopic  Mesoscopic  Nanoscopic

- permanent magnets
- micron particles
- nanoparticles  clusters
- 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

- Fe₈
- 0.7K
- 0.1K

Wolfgang Wernsdorfer, Grenoble
"No! no! The adventures first" said the Gryphon in an impatient tone: "explanations take such a dreadful time."
Everyday life is full of useful *magnets* which traditionally take the form of three-dimensional solids, oxides, metals and alloys.
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

\[ T_c \]

\[ kT \approx J \]

... Paramagnetic solid: thermal agitation \((kT)\) larger than the interaction \((J)\) between molecules

\[ kT \gg J \]
Magnetic Order:

Ferromagnetism: Magnetic moments are identical and parallel

\[ + \uparrow + \uparrow = \uparrow \]

Antiferromagnetism: Magnetic moments are identical and anti parallel

\[ + \uparrow + \downarrow = 0 \]

Ferrimagnetism (Néel): Magnetic moments are different and anti parallel

\[ + \uparrow + \downarrow = \uparrow \]
Magnetization of nanoparticles of Prussian Blue analogues, MicroSQUID, 4 K

(A. Bleuzen, W. Werndorfer)
Magnetization of nanoparticles of Prussian Blue analogues, MicroSQUID, 4 K

Remnant magnetization

irradiation with white light

(A. Bleuzen, W. Werndorfer)
"He seemed to give off a radiance,
an inner fire,
and I couldn't resist this magnetism
How magnetism comes to molecules?

... the different faces of the electron
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

\[ s = \pm 1/2 \]

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

\[ \mu_{\text{total}} = \mu_{\text{orbital}} + \mu_{\text{spin}} \]
Origin of **Magnetism**

... in molecules

electrons *

in atoms

in molecules

* forgetting the nuclear magnetism
Dirac Equation

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

The Principles of Quantum Mechanics, 1930

Nobel Prize 1933

http://www-history.mcs.st-and.ac.uk/history/PictDisplay/Dirac.html
"When I use a word”, said Humpty Dumpty, “it just means what I choose it to mean – neither more nor less “

“The question is”, said Alice, whether you can make words mean so different things”

“The question is”, said Humpty Dumpty, “which is to be master – that’s all.”
Electron: corpuscle and wave

Wave function or «orbital» $\Psi_{n, l, m, \ldots}$

\[ l = 0 \quad 1 \quad 2 \quad 3 \]

s

p

\[ x, y, z \]

angular representation
Electron: also an energy level

Energy Diagramme

Orbitals

- Vacant
- Singly occupied
- Doubly occupied
Electron: also a spin!

- **Up**
- **Down**

Singly occupied

- «Paramagnetic»
  - $S = \pm 1/2$

Doubly occupied

- «Diamagnetic»
  - $S = 0$

Nitrogen Monoxyde NO$^-$

Nitronylnitroxyde
Analogy: Spin and Arrow

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

An Isolated Spin
Spin in Maya World?

Uxmal, Palacio del Gobernador, Mayab, Yucatan, July 2004
Molecules are most often regarded as isolated, non magnetic, creatures.

Dihydrogen is diamagnetic with Spin $S = 0$. The arrow diagram illustrates the spin configurations of the dihydrogen molecule.
the **dioxygen** that we continuously breathe is a **magnetic molecule**

Two of its electrons have parallel magnetic moments that shapes aerobic life and allows our existence as human beings.

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 ...)

Paramagnetic $O_2$
Luminol Light
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)
<table>
<thead>
<tr>
<th></th>
<th>s Elements</th>
<th></th>
<th></th>
<th>p Elements</th>
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</thead>
</table>
| 1 | H          | 2 | Li | B          | 15| O
| 2 | Be         | 3 | Na | Mg         | 16| F
| 3 | Al          | 4 | Si | P          | 17| Cl
| 4 | Si          | 5 | S  | Ar         | 18| K
| 5 | S           | 6 | Cl | Br         | 19| Rb
| 6 | Ar          | 7 | K  | Rb         | 20| Sr
| 7 | K           | 8 | Ca | Sr         | 21| Ba
| 8 | Sr          | 9 | Ba | Ba         | 22| Ra
| 9 | Ra          | 10| Al | Al         | 23| Ce
| 10 | Ce        | 11| Ti | Ti         | 24| Mn
| 11 | Mn         | 12| Zr | Zr         | 25| Fe
| 12 | Zr         | 13| Hf | Hf         | 26| Co
| 13 | Hf         | 14| Ta | Ta         | 27| Ni
| 14 | Ta         | 15| W  | W          | 28| Cu
| 15 | W          | 16| Re | Re         | 29| Zn
|   |            |   |   |            |   |   |
| 17| Y           | 18| Sc | Sc         | 30| Au
| 18| Sc         | 19| Ti | Ti         | 31| Hg
| 19| Ti         | 20| V  | V          | 32| U
| 20| V          | 21| Mn | Mn         | 33| Th
| 21| Mn         | 22| Cr | Cr         | 34| Pa
| 22| Cr         | 23| Fe | Fe         | 35| U
| 23| Fe         | 24| Co | Co         | 36| Np
| 24| Co         | 25| Ni | Ni         | 37| Am
| 25| Ni         | 26| Cu | Cu         | 38| Cm
| 26| Cu         | 27| Zn | Zn         | 39| Bk
| 27| Zn         | 28| Nb | Nb         | 40| Fl
| 28| Nb         | 29| Mo | Mo         | 41| Cf
| 29| Mo         | 30| Tc | Tc         | 42| Es
| 30| Tc         | 31| Ru | Ru         | 43| Fm
| 31| Ru         | 32| Rh | Rh         | 44| Md
| 32| Rh         | 33| Pd | Pd         | 45| No
| 33| Pd         | 34| Ag | Ag         | 46| Lr
| 34| Ag         | 35| Cd | Cd         | 47| Rf
| 35| Cd         | 36| Au | Au         | 48| Db
| 36| Au         | 37| Hg | Hg         | 49| Yb
| 37| Hg         | 38| Tm | Tm         | 50| Dy
| 38| Tm         | 39| Er | Er         | 51| Ho
| 39| Er         | 40| Tc | Tc         | 52| Dy
| 40| Tc         | 41| Re | Re         | 53| Ho
| 41| Re         | 42| Os | Os         | 54| Er
| 42| Os         | 43| Ir | Ir         | 55| Tm
| 43| Ir         | 44| Pt | Pt         | 56| Yb
| 44| Pt         | 45| Au | Au         | 57| Dy
| 45| Au         | 46| Hg | Hg         | 58| Ho
| 46| Hg         | 47| Tm | Tm         | 59| Er
| 47| Tm         | 48| Dy | Dy         | 60| Tc
| 48| Dy         | 49| Ho | Ho         | 61| Re
| 49| Ho         | 50| Er | Er         | 62| Os
| 50| Er         | 51| Tm | Tm         | 63| Ir
| 51| Tm         | 52| Dy | Dy         | 64| Pt
| 52| Dy         | 53| Ho | Ho         | 65| Au
| 53| Ho         | 54| Er | Er         | 66| Hg
| 54| Er         | 55| Tm | Tm         | 67| Tc
| 55| Tm         | 56| Dy | Dy         | 68| Re
| 56| Dy         | 57| Ho | Ho         | 69| Os
| 57| Ho         | 58| Er | Er         | 70| Ir
| 58| Er         | 59| Tm | Tm         | 71| Pt
| 59| Tm         | 60| Dy | Dy         | 72| Au
| 60| Dy         | 61| Ho | Ho         | 73| Hg
| 61| Ho         | 62| Er | Er         | 74| Re
| 62| Er         | 63| Tm | Tm         | 75| Os
| 63| Tm         | 64| Dy | Dy         | 76| Ir
| 64| Dy         | 65| Ho | Ho         | 77| Pt
| 65| Ho         | 66| Er | Er         | 78| Au
| 66| Er         | 67| Tm | Tm         | 79| Hg
| 67| Tm         | 68| Dy | Dy         | 80| Re
| 68| Dy         | 69| Ho | Ho         |
Transition Elements

5 d orbitals

Unpaired Electrons
Partial Occupancy
Paramagnetism
Conductivity

Quantum
Mononuclear complex $ML_6$

Splitting of the energy levels

\[ E \]
How large is the splitting?

Weak Field
High spin
$L = \text{H}_2\text{O} \quad [\text{C}_2\text{O}_4]^{2-}$

Intermediate Field
Low spin
$L = \text{CN}^-$

Strong Field
Spin Cross-Over

Temperature Dependent

$\text{t}_{2g}$

$\text{e}_g$

$\Delta^2 \text{oct}$

$z^2 - y^2$

$xy, xz, yz$
The complexes of transition metal present often delicate and beautiful colours depending mostly on the splitting of the d orbitals.
story of jumping electrons and moving spins ...
two blue solutions
\[ \text{[Co}^{II}\text{(H}_2\text{O})_6]\text{]}^{2+} + \text{Methylene Blue} \]

\[ \text{KCN} + \text{Methylene Blue} \]
QuickTime™ et un décompresseur DV - PAL sont requis pour visionner cette image.
one yellow solution
blue + blue = yellow!

$[\text{Co}^{III}(\text{CN})_6]^{3-}$

Methylene Reduced Colorless
\([\text{Fe}^{II}(\text{H}_2\text{O})_6]^{2+}\) pale green

\(S=2\)

\([\text{Fe}^{II}(\text{o-Phen})_3]^{2+}\) bright red

\(S=0\)
Low spin, chiral, Fe$^{II}$\((\text{bipyridine})_3\)^{2+}
Playing with ligands, the chemist is able to control the spin state.
Review by Philipp Gütlich et al. Mainz University Angewandte Chemie 1994
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
Curie Law

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

\[ \chi_M T \approx n \frac{(n+2)}{8} \ldots \]

if \( n = 4 \), \( \chi_M T \approx 3! \)
Spin Cross-Over Bistability Domain

The system « remembers » its thermal past!

O. Kahn, C. Jay and ICMC Bordeaux
Hysteresis allows bistability of the system and use in display, memories ...

Spin and colour changes
Spin Cross-over Display Device

Kahn O., La Recherche, 1994, 163

Joule and Peltier Connections
Compound in Low spin state (Thin Layer)
Display
From the molecule to the material and to the device ...

O. Kahn, C. Jay and ICMC Bordeaux
From J.F. Letard, ICMC Bordeaux
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?