BE
Magnetic
MOTOS ACUATICAS
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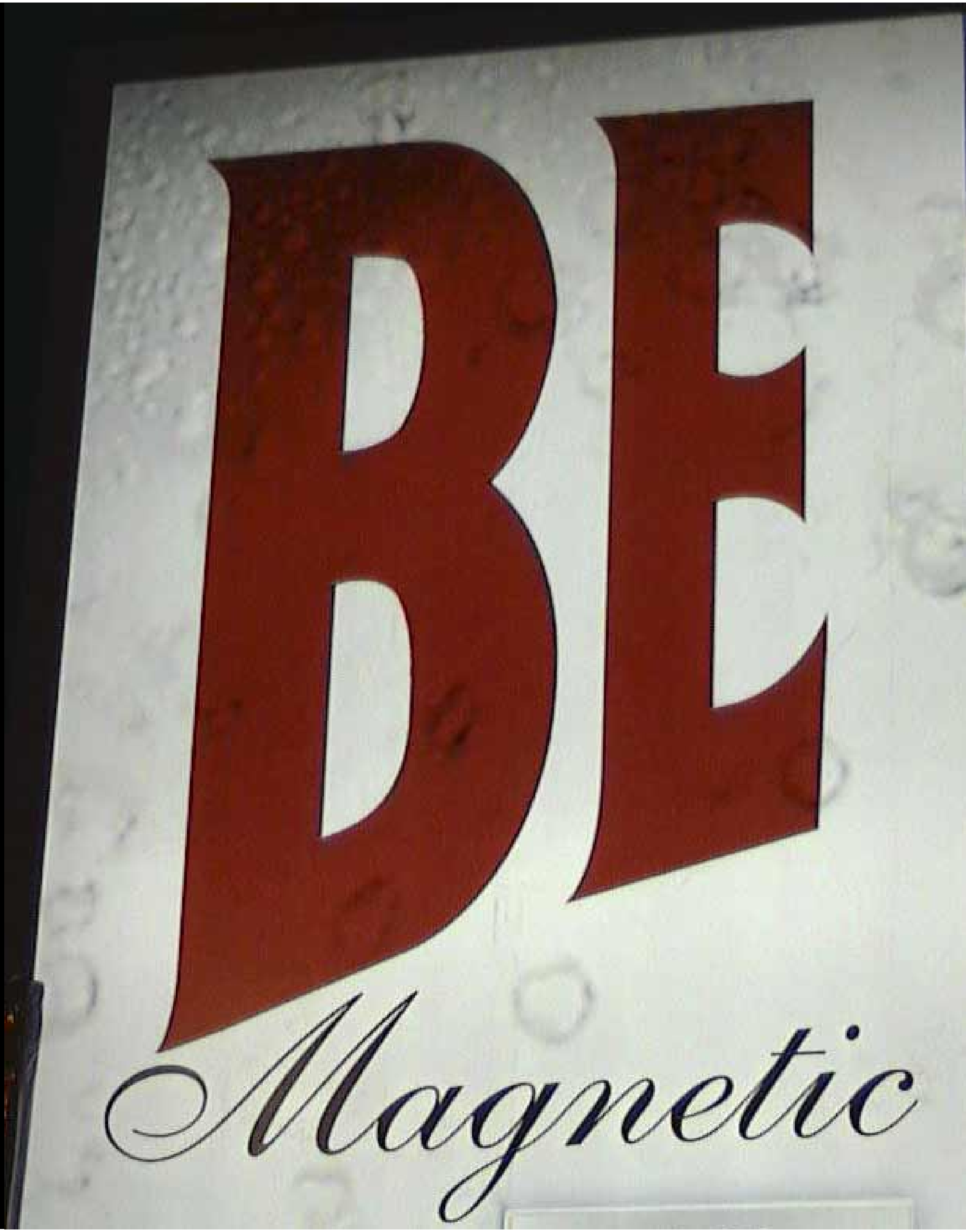


This is NOT

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} 10^{-9}
mole …	**molecule …**
10^{+23}	**1**

macroscopic world	atomic or molecular world	« wonder » world

Lewis Carroll, Through the looking-glass, Penguin Books, London, 1998 Illustrations by John Tenniel macroscopic world

atomic or molecular world

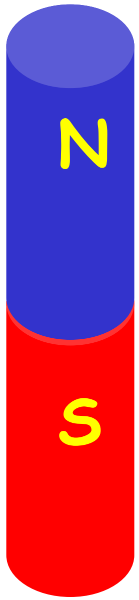
« wonder » world

macro

quantum

macroscopic world

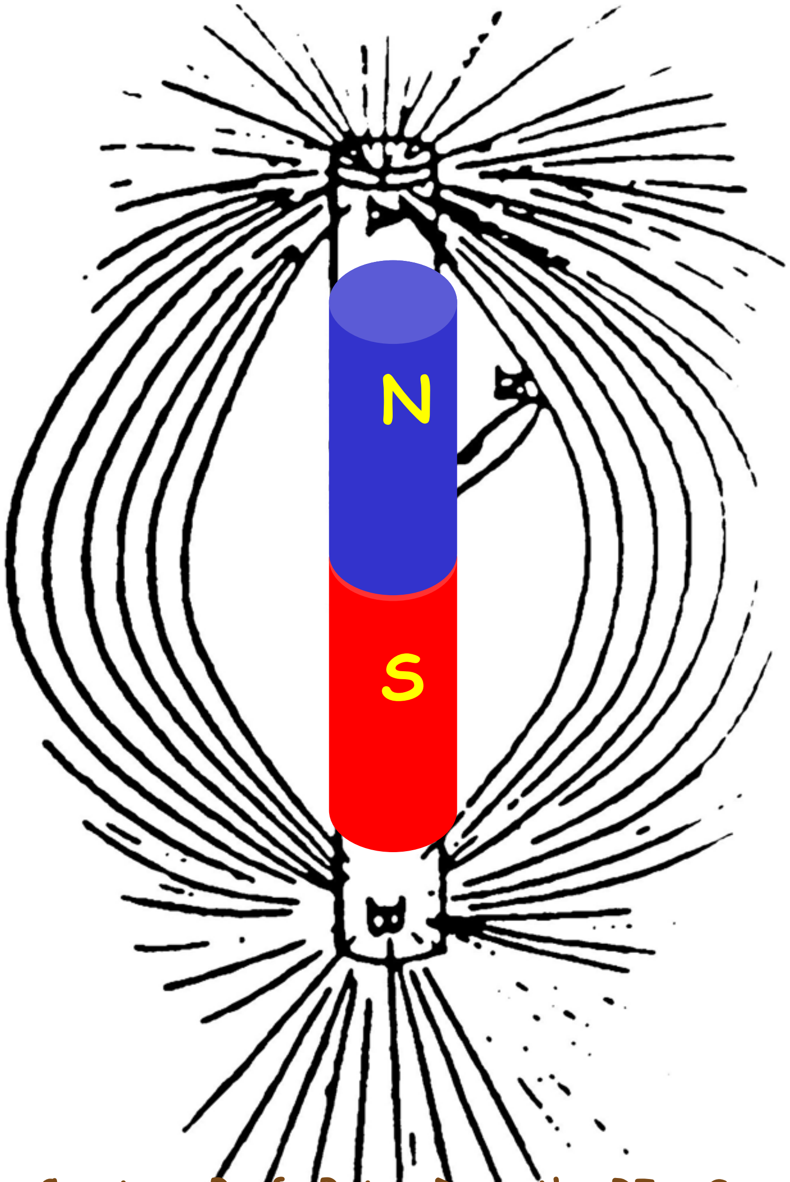
« traditional, classical » magnets



macro

macroscopic world

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



macro

Courtesy Prof. Peter Day, the RI ; See also :
The Philosopher's Tree, The Institute of Physics Publishing, Bristol, 1999)

Courtesy Prof. Frank James, the RI

M. Faraday's magnetic laboratory

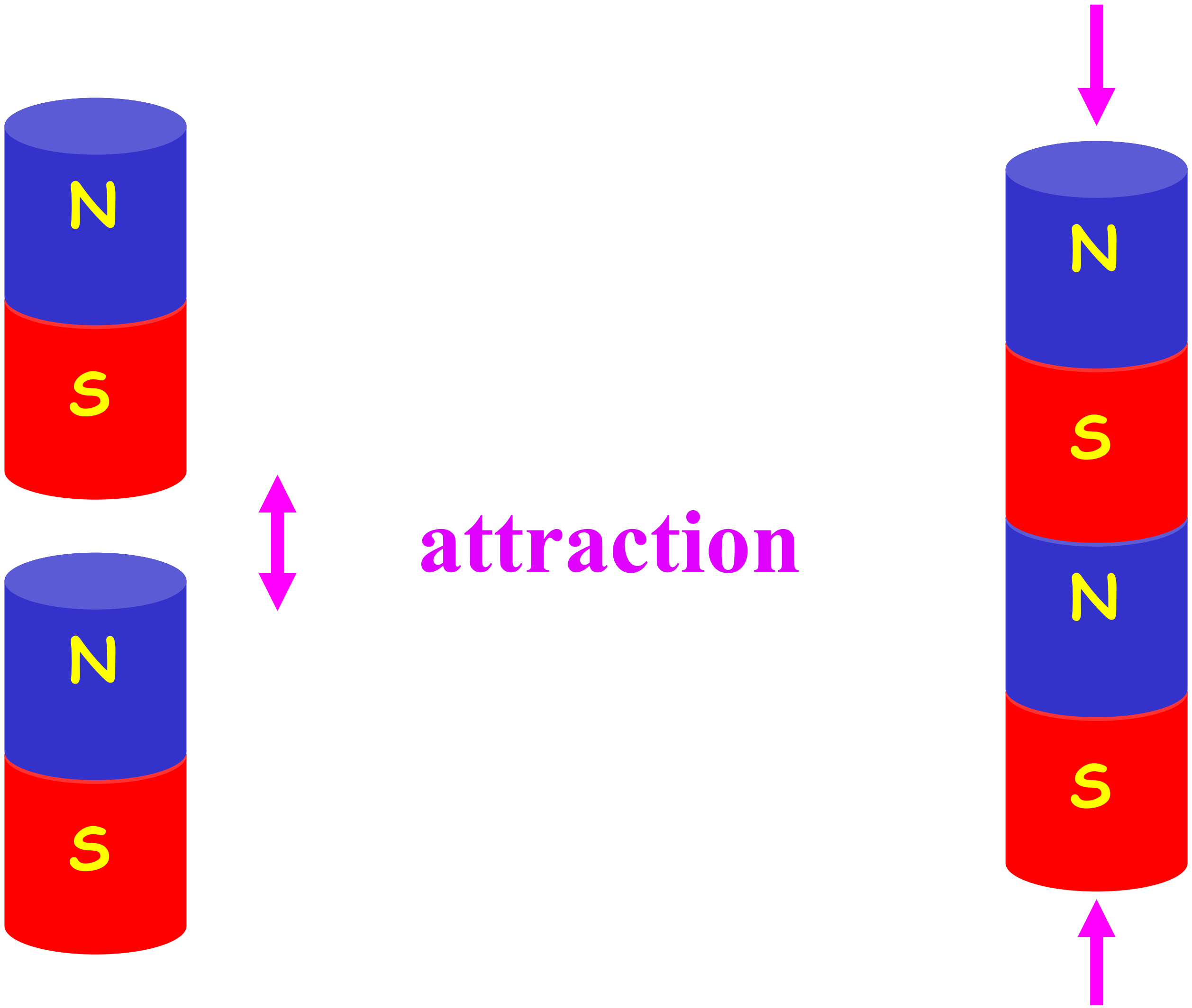
Courtesy Prof. Frank James, the RI

M. Faraday in his laboratory

Courtesy Prof. Frank James, the RI

macroscopic world

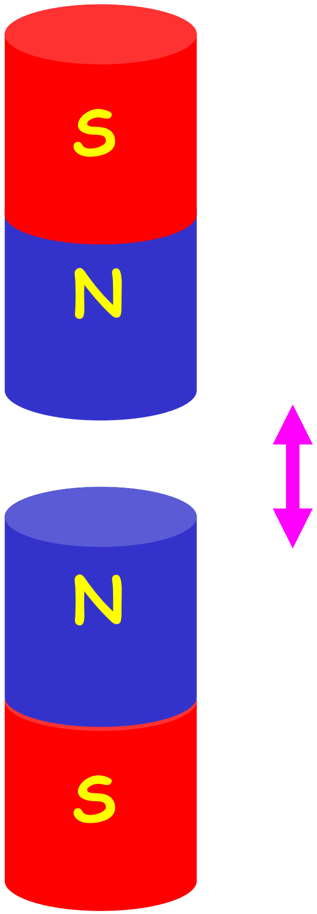
« traditional » magnets



macro

macroscopic world

« traditional » magnets

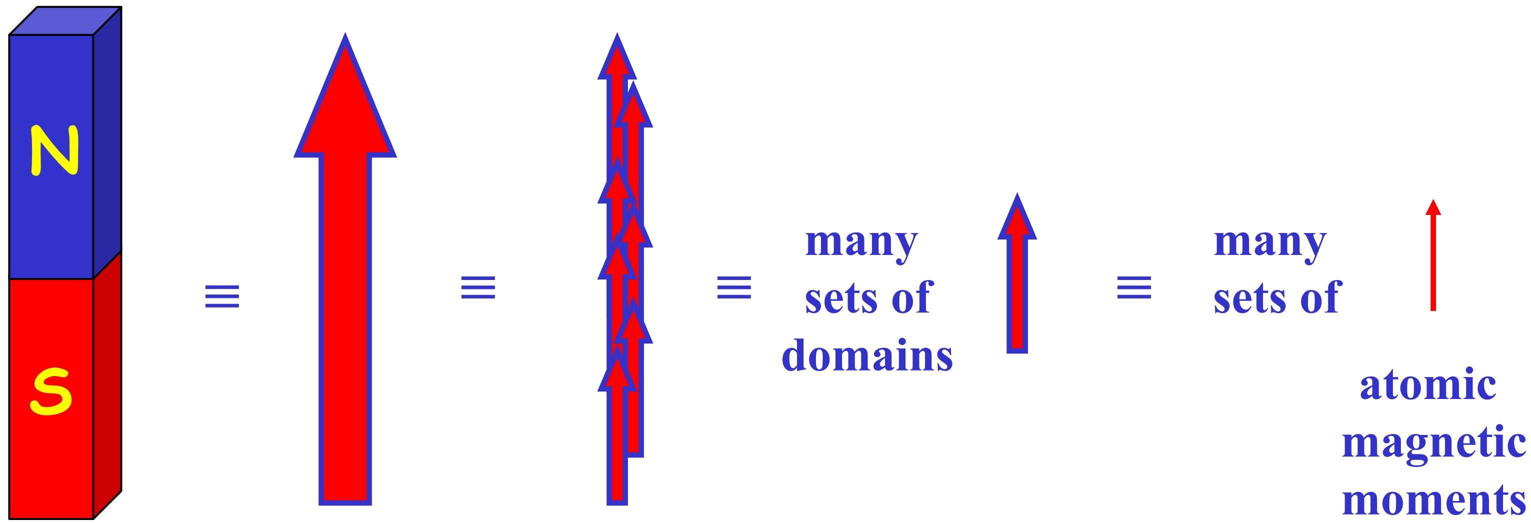


repulsion

macro

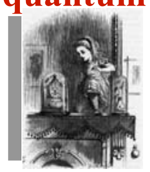
macroscopic world

looking closer to the magnetic domains



macro

quantum



Physics : Macroscopic *Mesoscopic* *Nanoscopic*

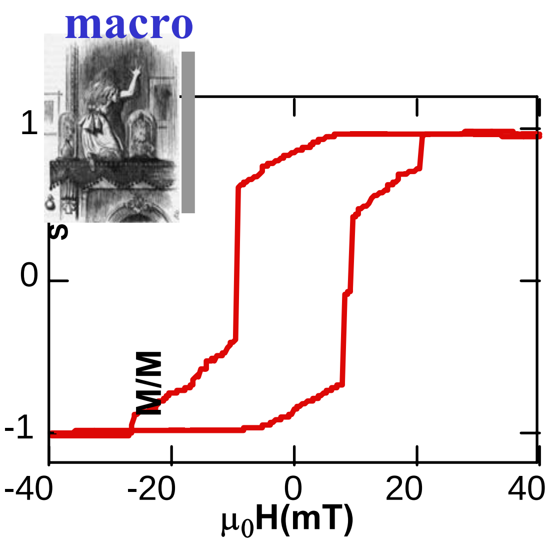
permanent magnets	micron particles	nanoparticles	clusters	molecular clusters	individual spins

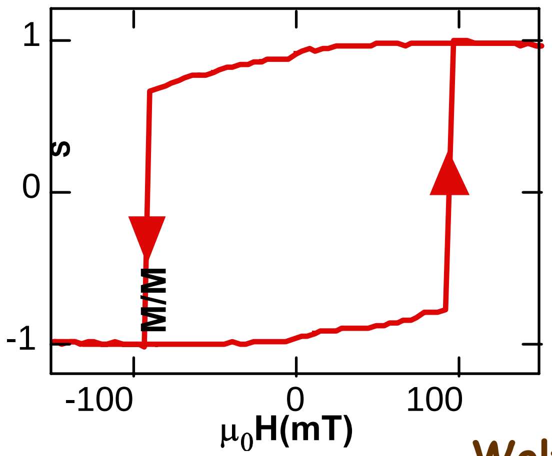
S = 10^{20} 10^{10} 10^{8} 10^{6} 10^{5} 10^{4} 10^{3} 10^{2} 10 1

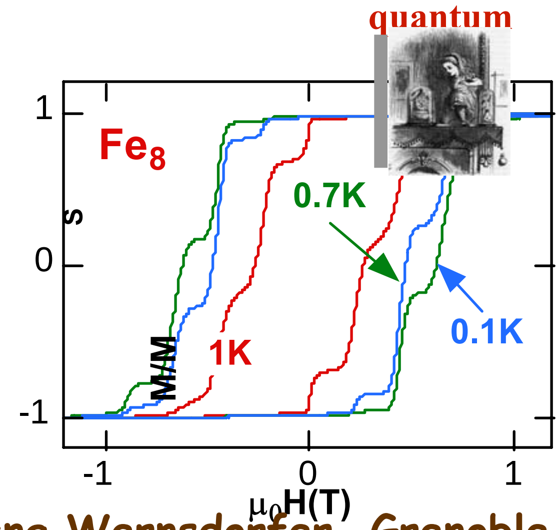
multi - domain
nucleation, propagation and annihilation of domain walls

single - domain
uniform rotation
curling

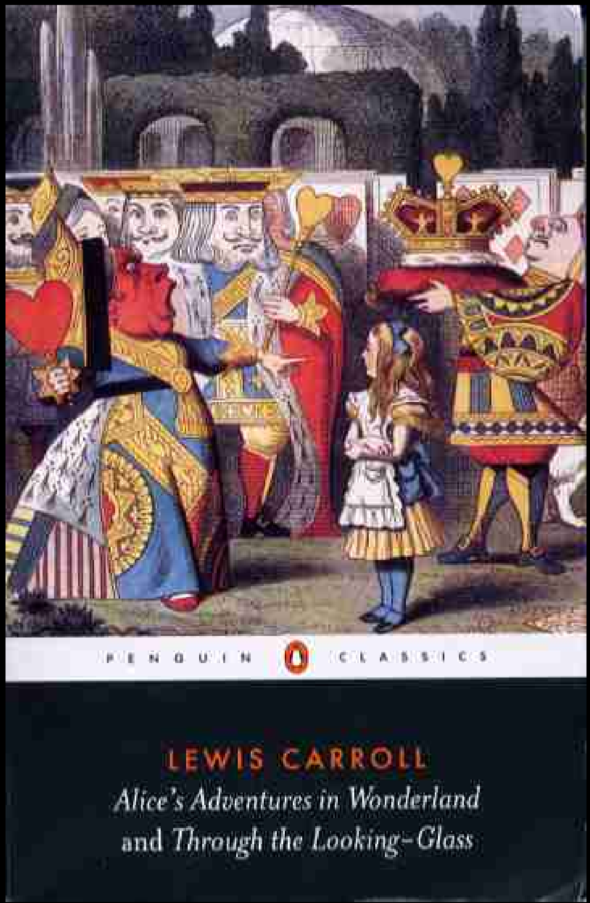
magnetic moment
quantum tunneling,
quantization
quantum interference







Wolfgang Wernsdorfer, Grenoble



"No ! no ! The adventures first" said the Gryphon in an impatient tone : "explanations take such a dreadful time."

Lewis Carroll, Alice's Adventures in Wonderland, Penguin Books, London, 1998 Illustrations by John Tenniel

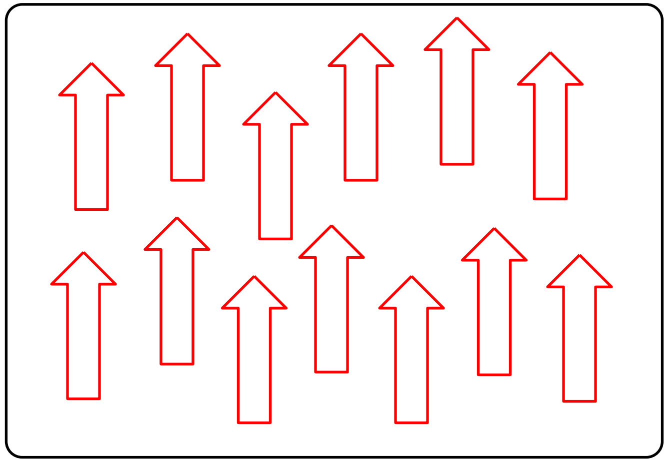
Everyday life
is full of useful *magnets*
which traditionally take the form
of three-dimensional solids,
oxides, metals and alloys

macro

Magnets
Domains
Curie Temperature

The magnetic moments order at Curie temperature

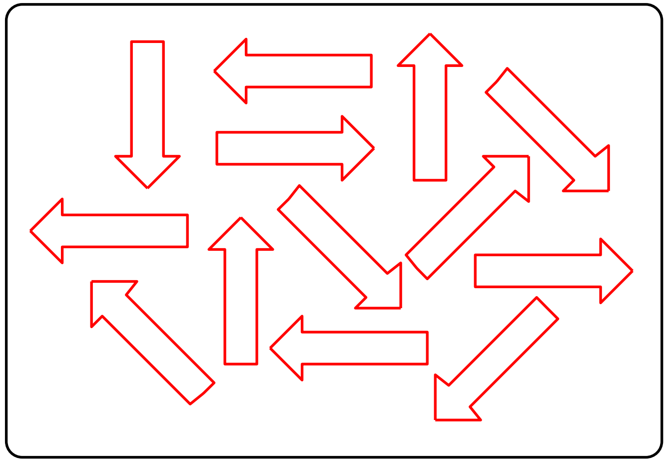
A set of molecules / atoms :



T_C

$kT \approx J$

Magnetic Order Temperature or Curie Temperature



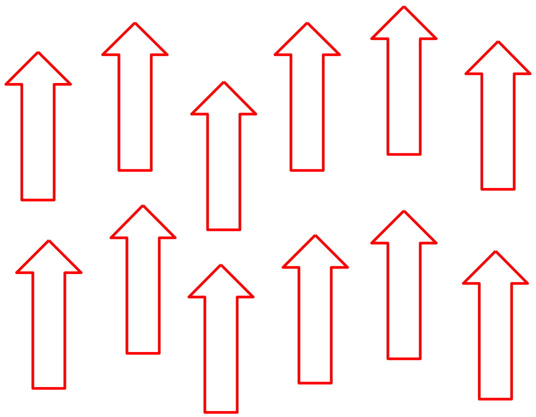
Solid, Magnetically Ordered thermal agitation (kT) weaker than the interaction (J) between molecules

$kT << J$

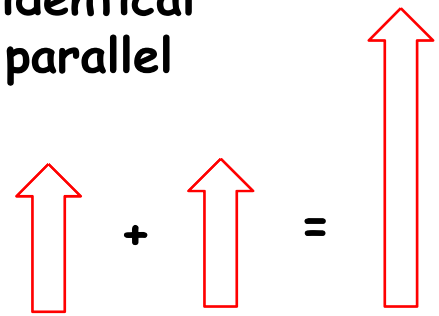
… **Paramagnetic solid** : thermal agitation (kT) larger than the interaction (J) between molecules

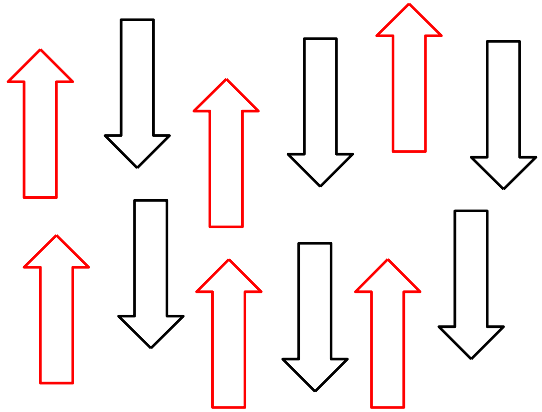
$kT >> J$

Magnetic Order :
ferro-, antiferro- and ferri-magnetism

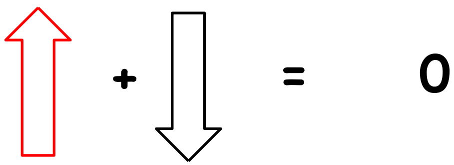


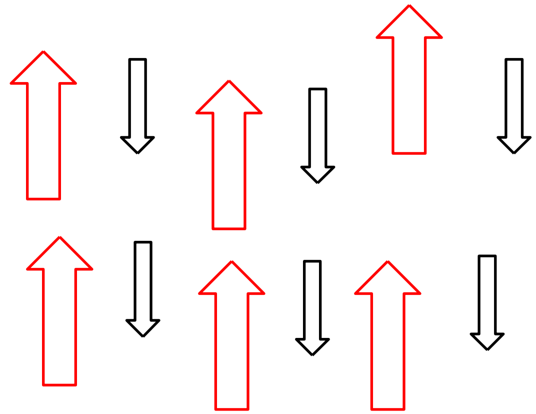
Ferromagnetism :
Magnetic moments
are identical
and parallel



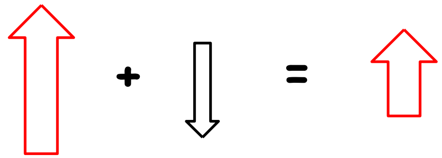


Antiferromagnetism :
Magnetic moments
are identical
and anti parallel



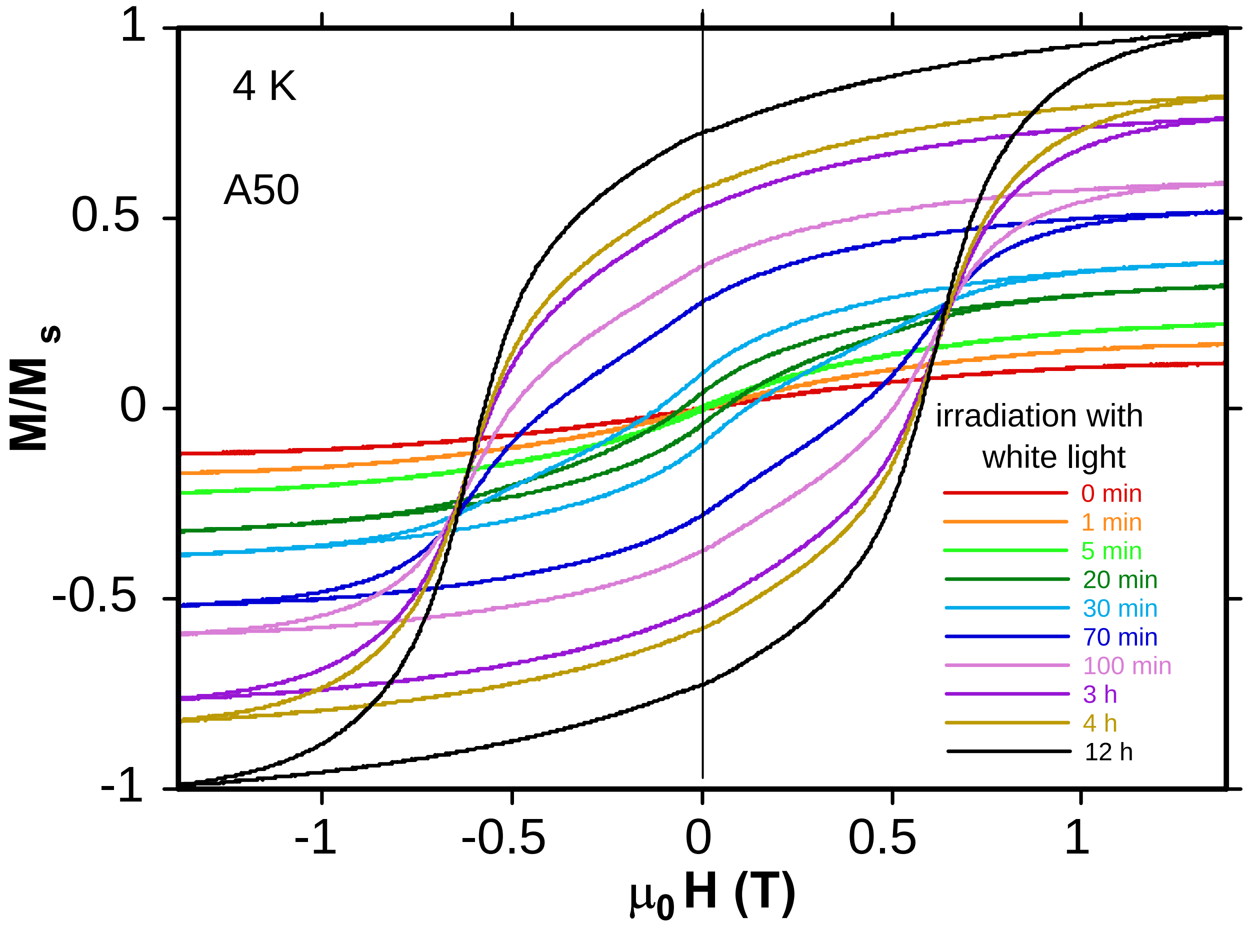


Ferrimagnetism (Néel) :
Magnetic moments
are different
and anti parallel



Magnetization of nanoparticles of Prussian Blue analogues,

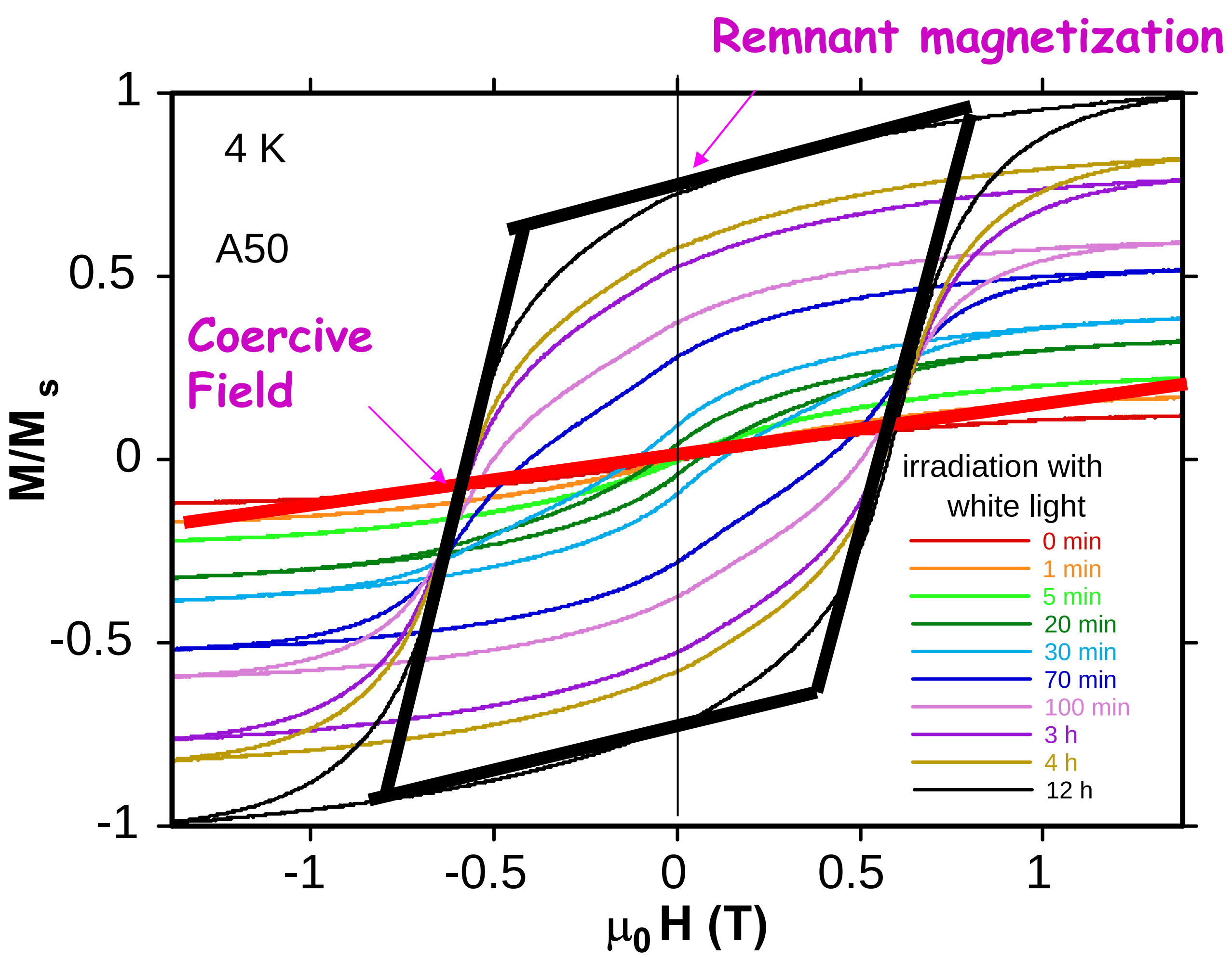
MicroSQUID, 4 K



(A. Bleuzen, W. Wernsdorfer)

Magnetization of nanoparticles of Prussian Blue analogues,

MicroSQUID, 4 K

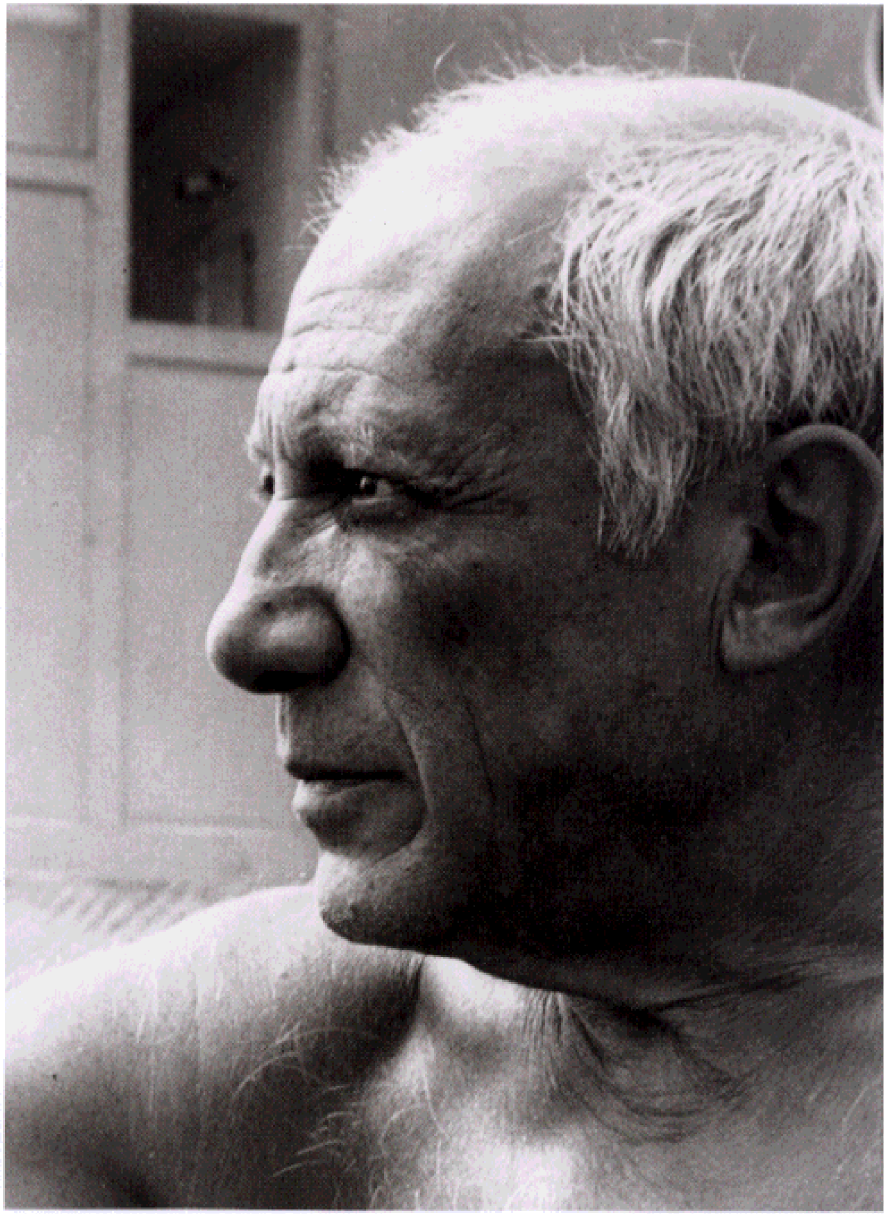


(A. Bleuzen, W. Werndorfer)

« He seemed to give off a radiance,

an inner fire,

and I couln't resist this magnetism



Fernande Olivier, Loving Picasso, H.N. Abrams Publishers, New York, 2001, p.139

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 μ_B

quantum

everything, tiny, elementary

* but do not forget nuclear magnetism !

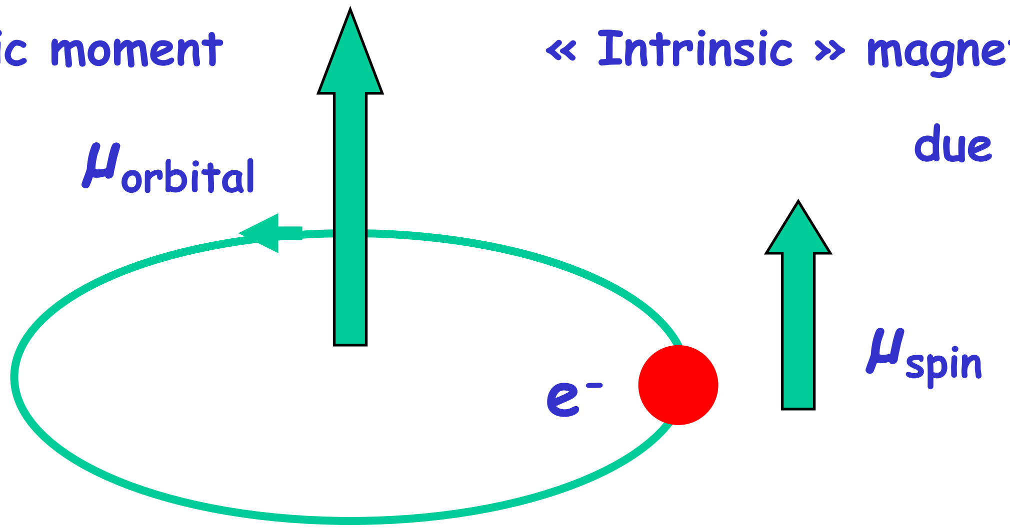
Origin of *Magnetism*

« Orbital » magnetic moment

« Intrinsic » magnetic moment

due to the spin

$s = \pm 1/2$



$\mu_{orbital} = g_l \times \mu_B \times \ell$

$\mu_{spin} = g_s \times \mu_B \times s \approx \mu_B$

quantum

$$\mu_{total} = \mu_{orbital} + \mu_{spin}$$

Origin of *Magnetism*

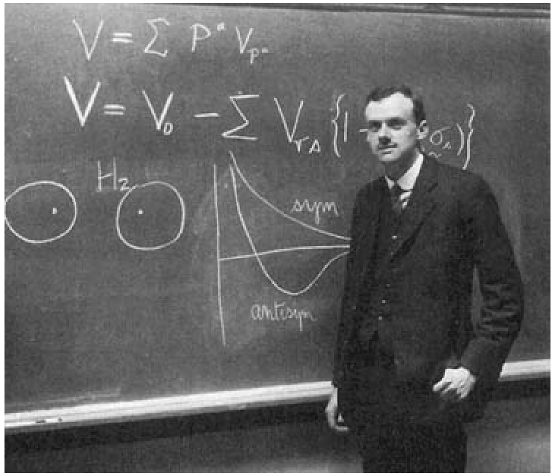
… in molecules

electrons *
in atoms
in molecules

quantum

* forgetting the nuclear magnetism

Dirac Equation



The Principles of Quantum Mechanics, 1930

Nobel Prize 1933

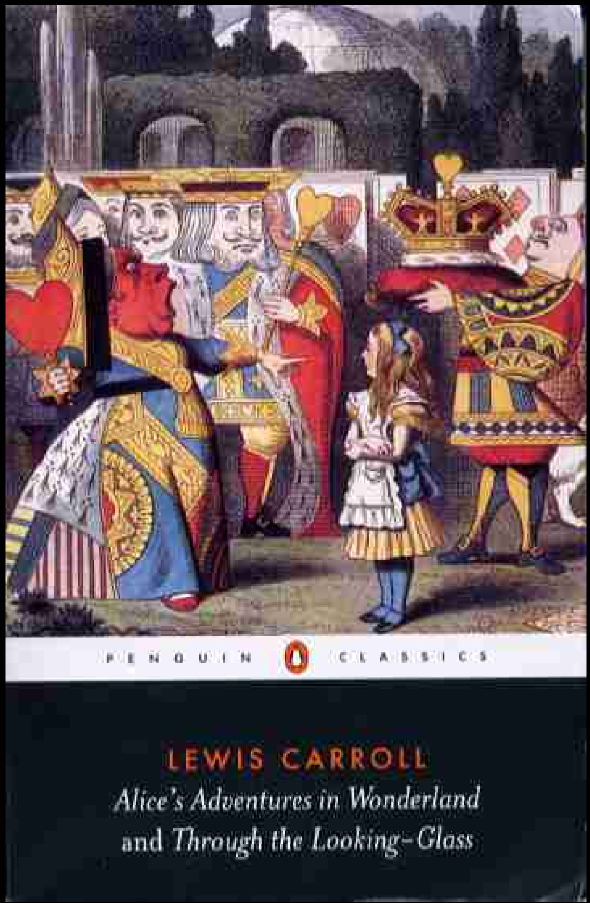
$$(E'+e\varphi)\psi = [\frac{1}{2m}(\mathbf{p} + \frac{e}{c}\mathbf{A})^2 + \frac{eh}{2mc}\sigma \bullet \nabla \times \mathbf{A} - \frac{p^4}{8m^3c^2} - \frac{eh^2}{8m^2c^2}\nabla \bullet \nabla\varphi - \frac{eh}{4m^2c^2}\sigma \bullet \nabla\varphi \times \mathbf{p}\ ]\psi$$

1905

1928

http://www-history.mcs.st-and.ac.uk/history/PictDisplay/Dirac.html

Representations, Models, Analogies …



"When I use a word", Humpty Dumpty said, … "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"

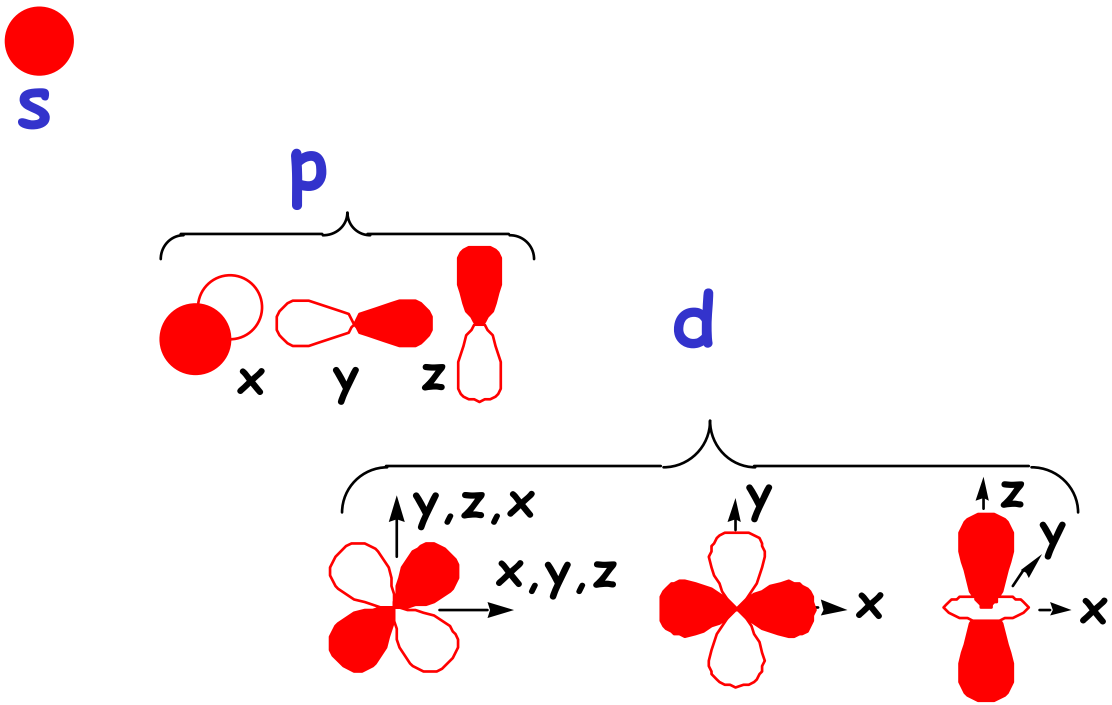
"The question is", said Humpty Dumpty, "which is to be master – that's all."

Lewis Carroll, Through the Looking-Glass, Penguin Books, London, 1998 Illustrations by John Tenniel

Electron : corpuscle and wave

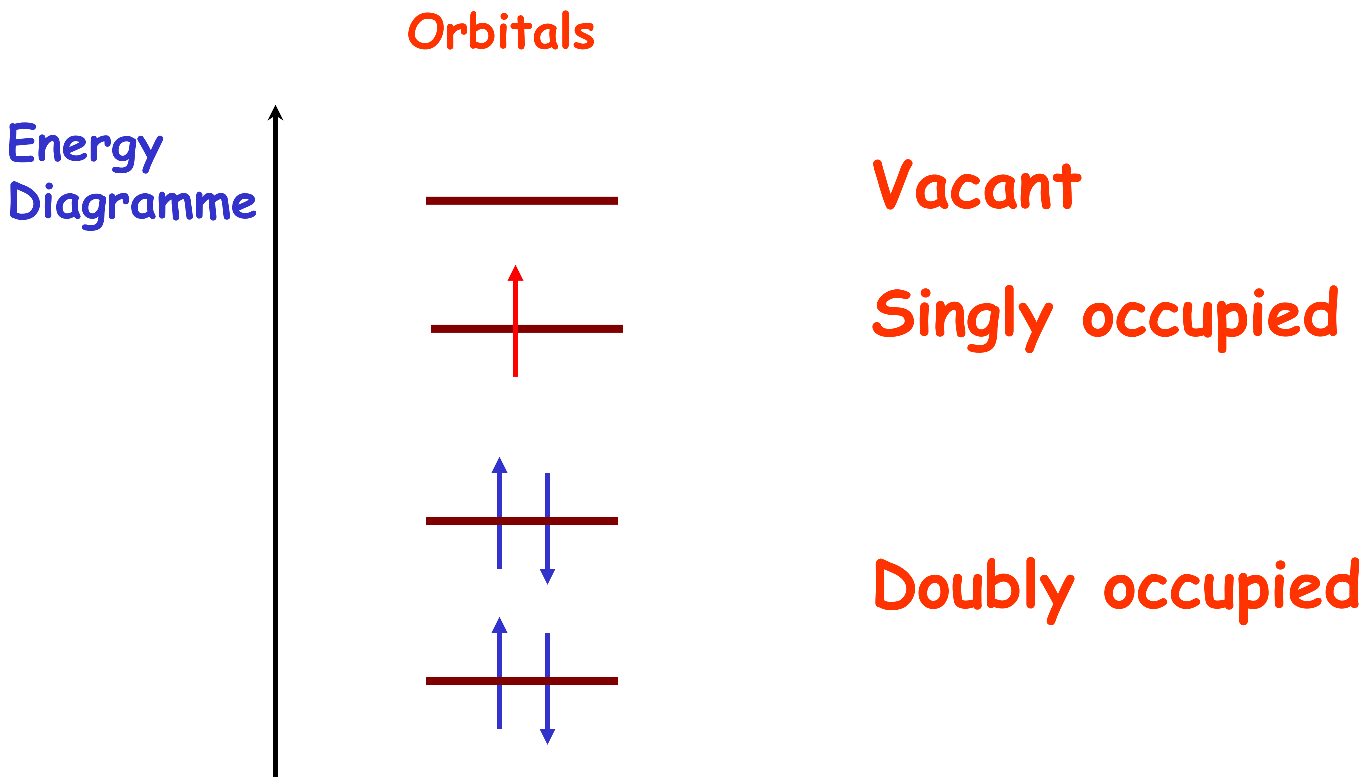
Wave function or « orbital » $\Psi_{n,\ l,\ m_l}$ ...

l = 0 1 2 3



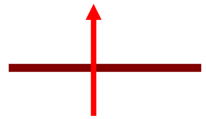
angular representation

Electron : also an energy level



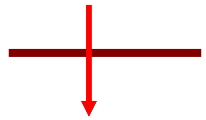
Electron : also a spin !

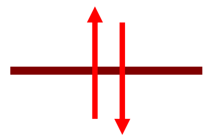
Up



Singly occupied

Down





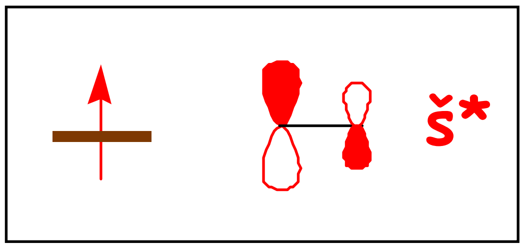
Doubly occupied

« Paramagnetic »

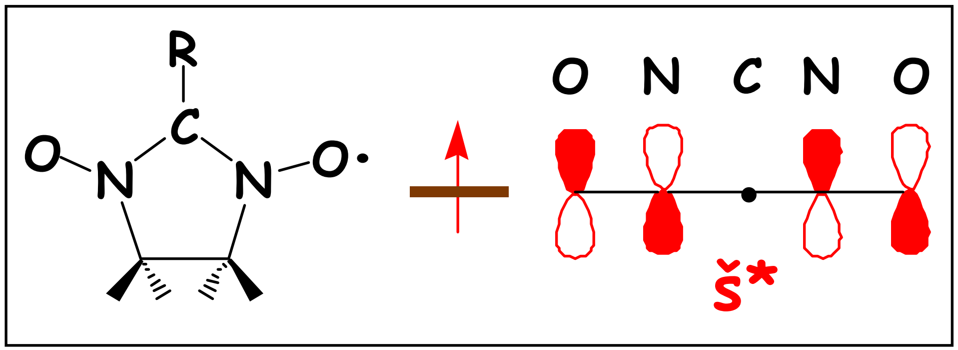
$S = \pm 1/2$

« Diamagnetic »

$S = 0$

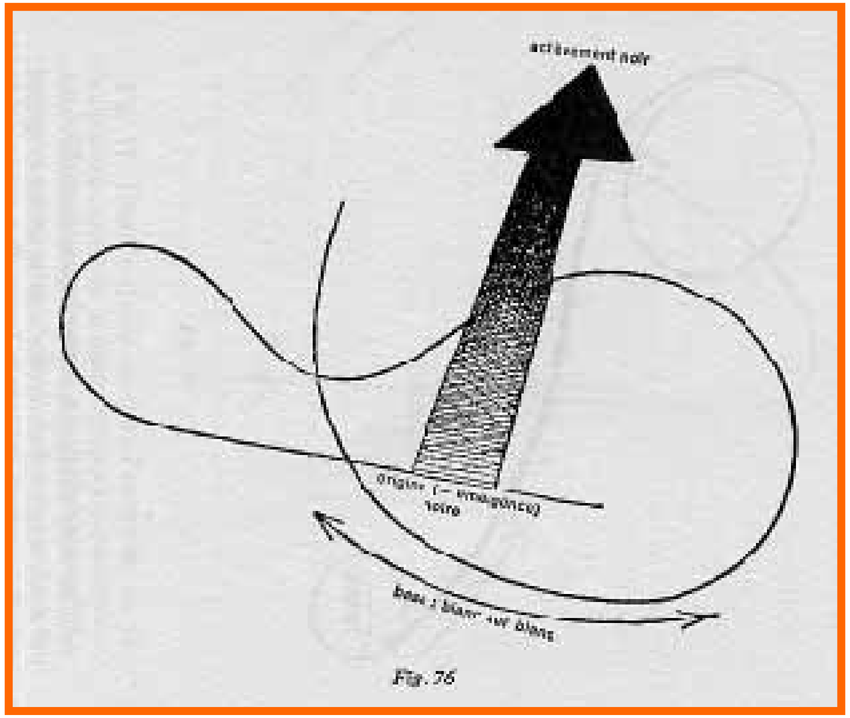


Nitrogen Monoxyde $NO^{\cdot}$

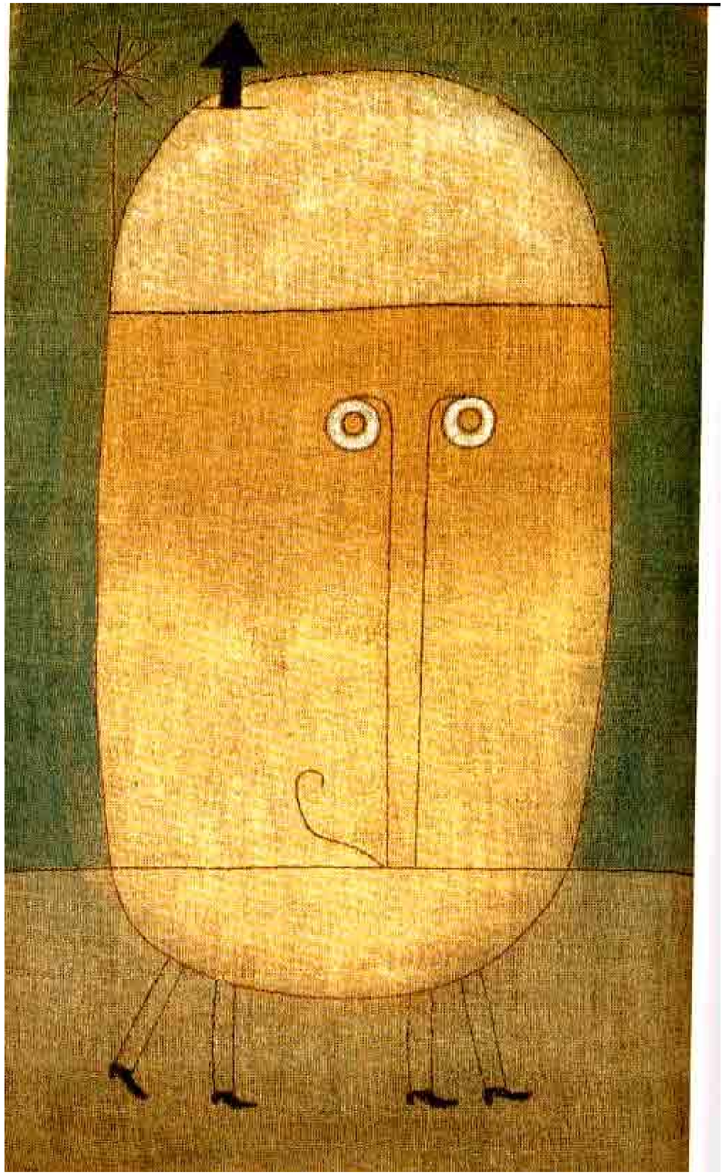


Nitronylnitroxyde

Analogy : Spin and Arrow

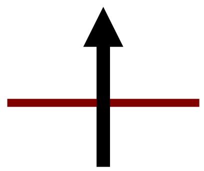


Paul Klee, Théorie de l'art, Denoël, Paris



An Isolated Spin

Spin in Maya World ?

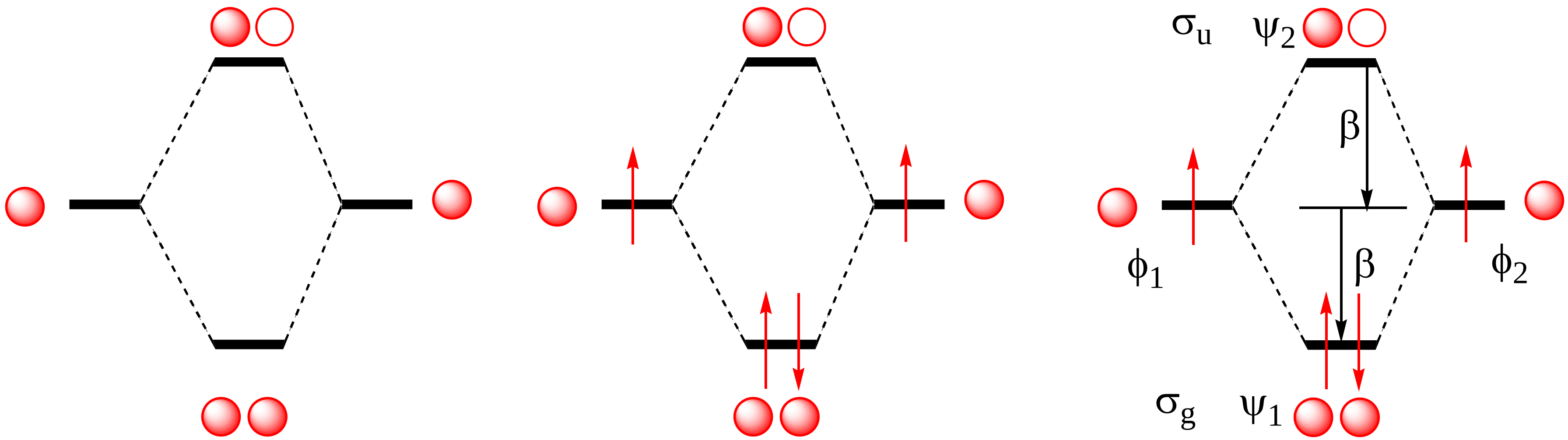


Uxmal, Palacio del Gobernador, Mayab, Yucatan, July 2004

Molecules

are most often regarded
as isolated, non magnetic, creatures

Dihydrogen

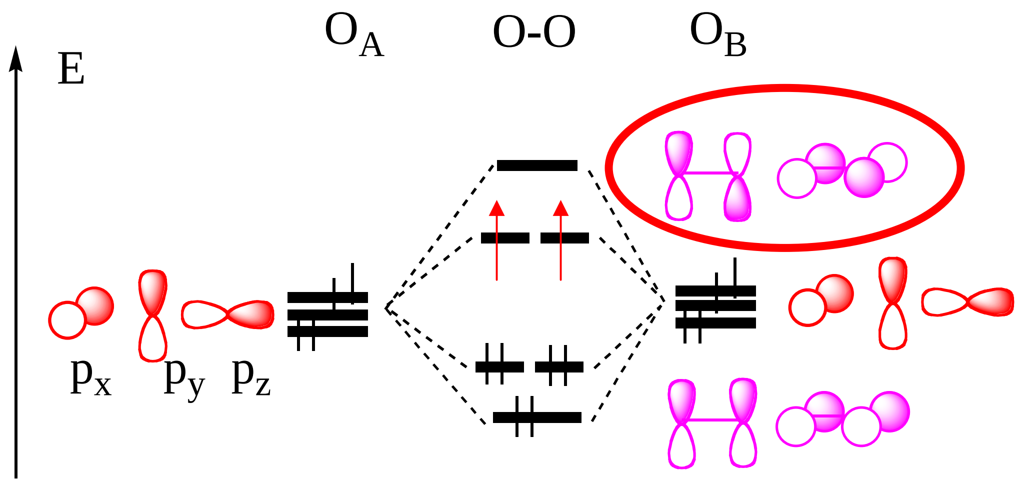


diamagnetic
Spin S = 0

the *dioxygen*

that we continuously breathe

is a *magnetic molecule*



orthogonal π molecular orbitals

paramagnetic, spin S =1

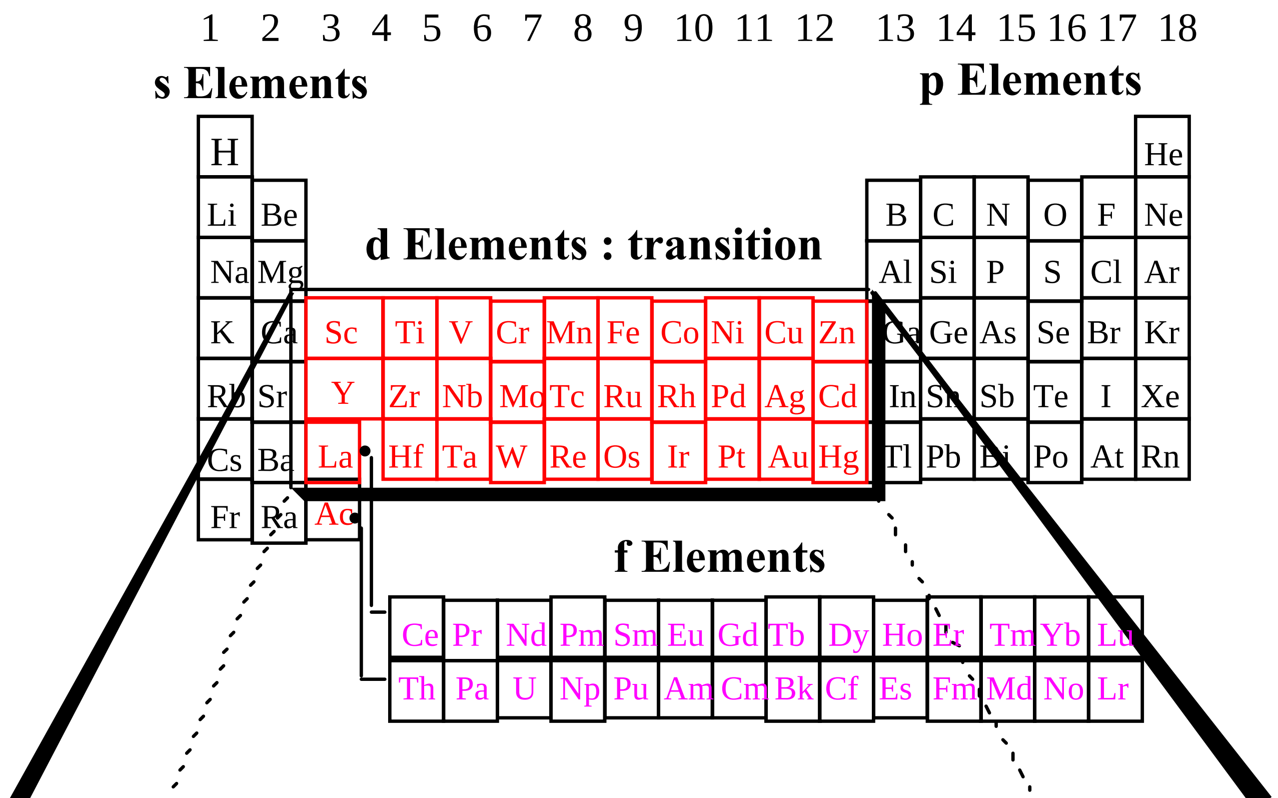
Two of its electrons have parallel magnetic moments that shapes aerobic life and allows our existence as human beings

when dioxygen is in an excited state
it can becomes a singlet (spin S=0)
and strange reactivity appears
sometines useful (glow-worm …)

macro

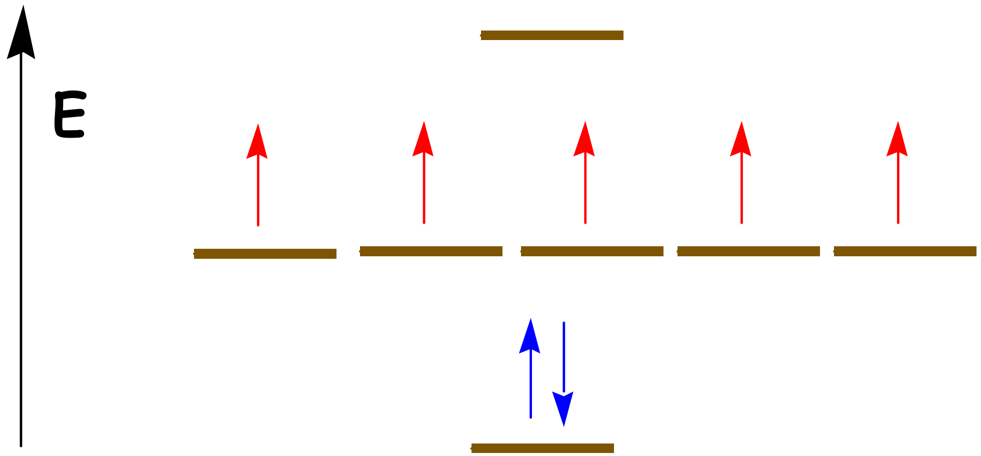
Paramagnetic O_2
Luminol Light

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)



44,956 **Sc** 21	47,867 **Ti** 22	50,942 **V** 23	51,996 **Cr** 24	54,938 **Mn** 25	55,845 **Fe** 26	58,933 **Co** 27	58,693 **Ni** 28	63,546 **Cu** 29	65,39 **Zn** 30
88,906 **Y** 39	91,224 **Zr** 40	92,906 **Nb** 41	95,94 **Mo** 42	98,906 **Tc** 43	101,07 **Ru** 44	102,91 **Rh** 45	106,42 **Pd** 46	107,87 **Ag** 47	112,41 **Cd** 48
138,91 **La** 57	178,49 **Hf** 72	180,95 **Ta** 73	183,84 **W** 74	186,21 **Re** 75	190,23 **Os** 76	192,22 **Ir** 77	195,08 **Pt** 78	196,97 **Au** 79	200,59 **Hg** 80

Transition Elements



5 d orbitals

⇩

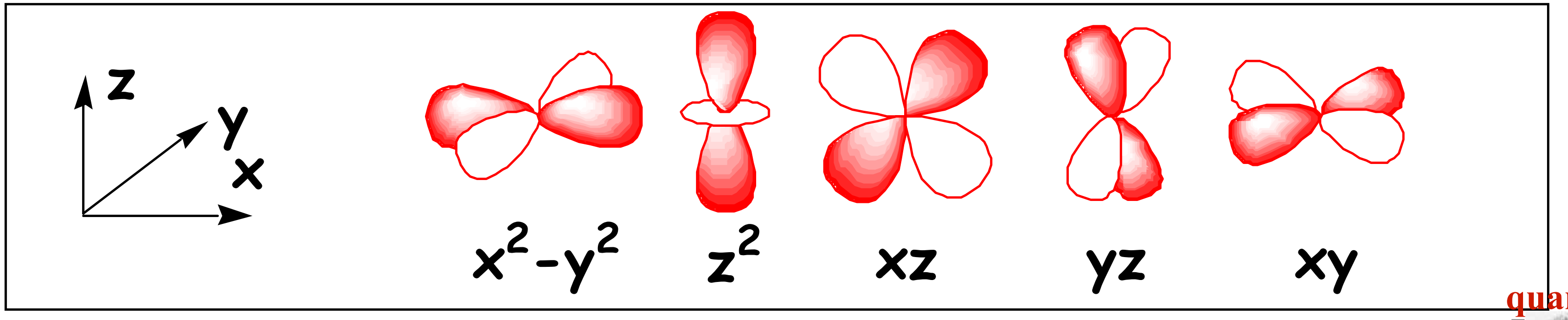
Unpaired Electrons

⇩

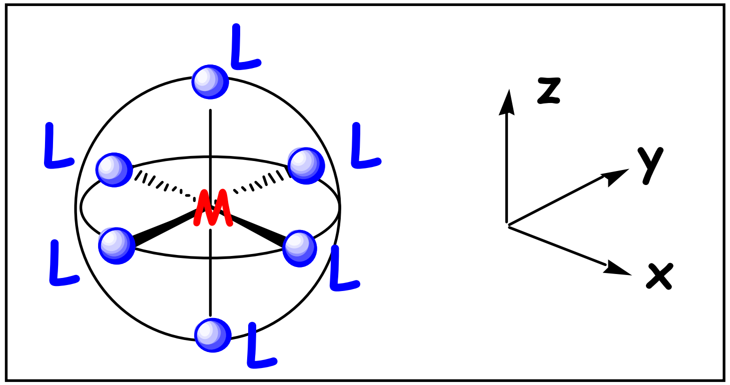
Partial Ocupancy

Paramagnetism

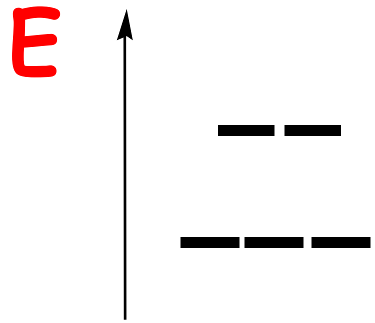
Conductivity



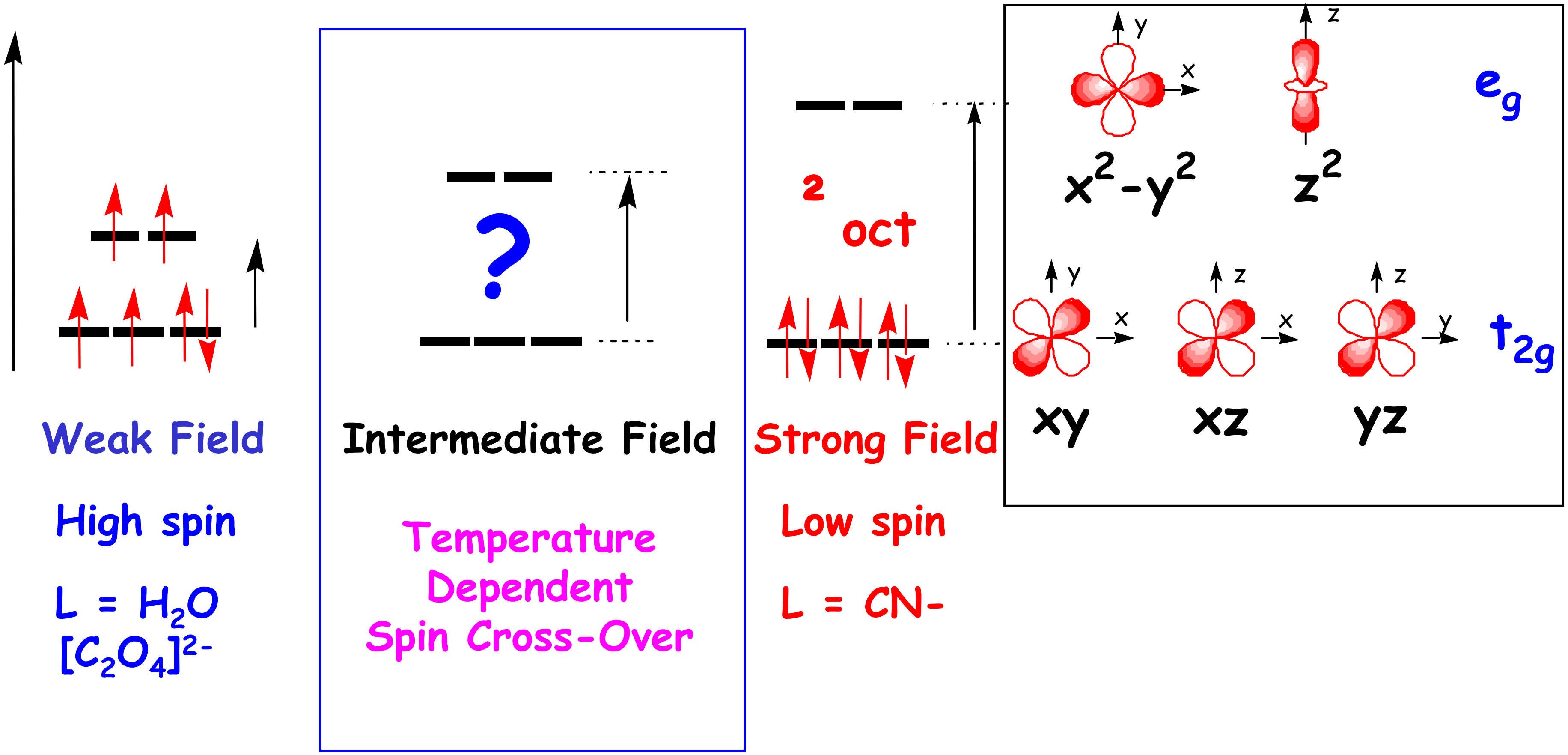
Mononuclear complex ML_6



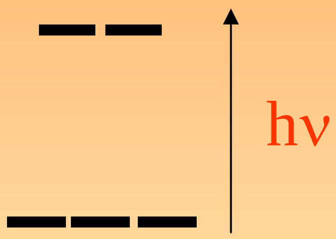
Splitting of the energy levels



How large is the splitting ?



The complexes of transition metal
present often delicate and beautiful colours
depending mostly on the splitting of the d orbitals

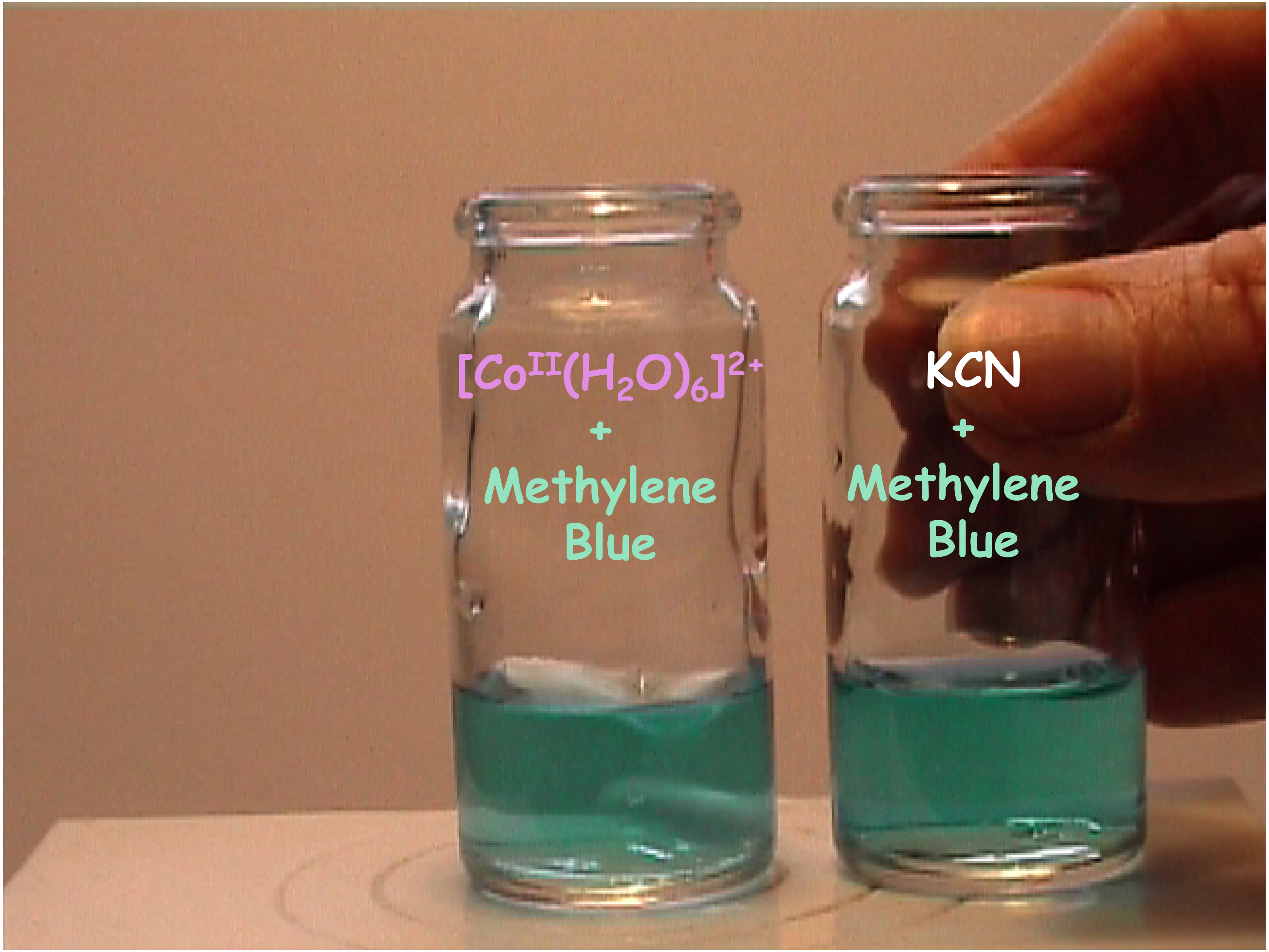


macro

Colours in water
Geometry changes
Spin changes

story of
jumping electrons
and moving spins …

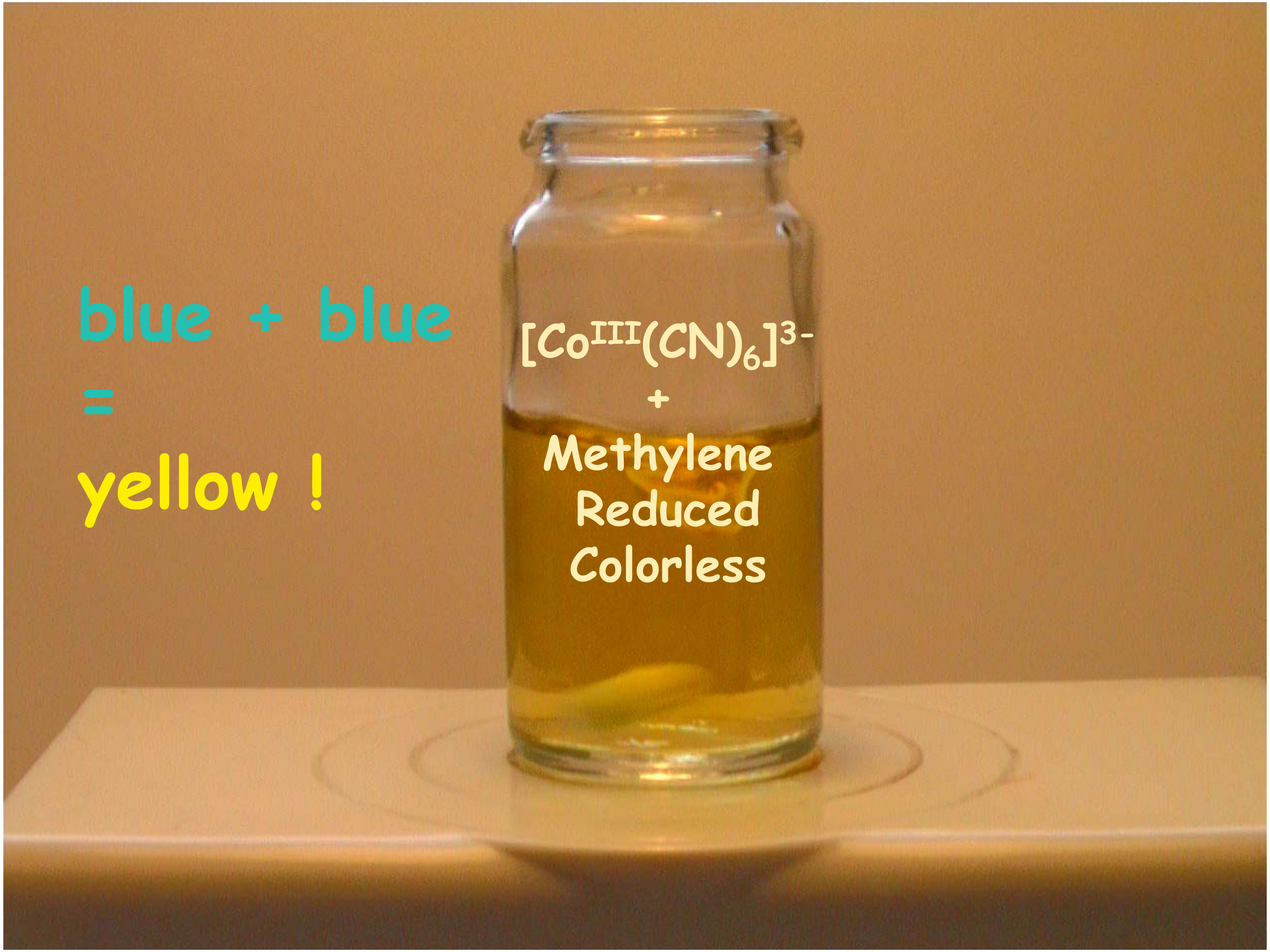

two
blue
solutions

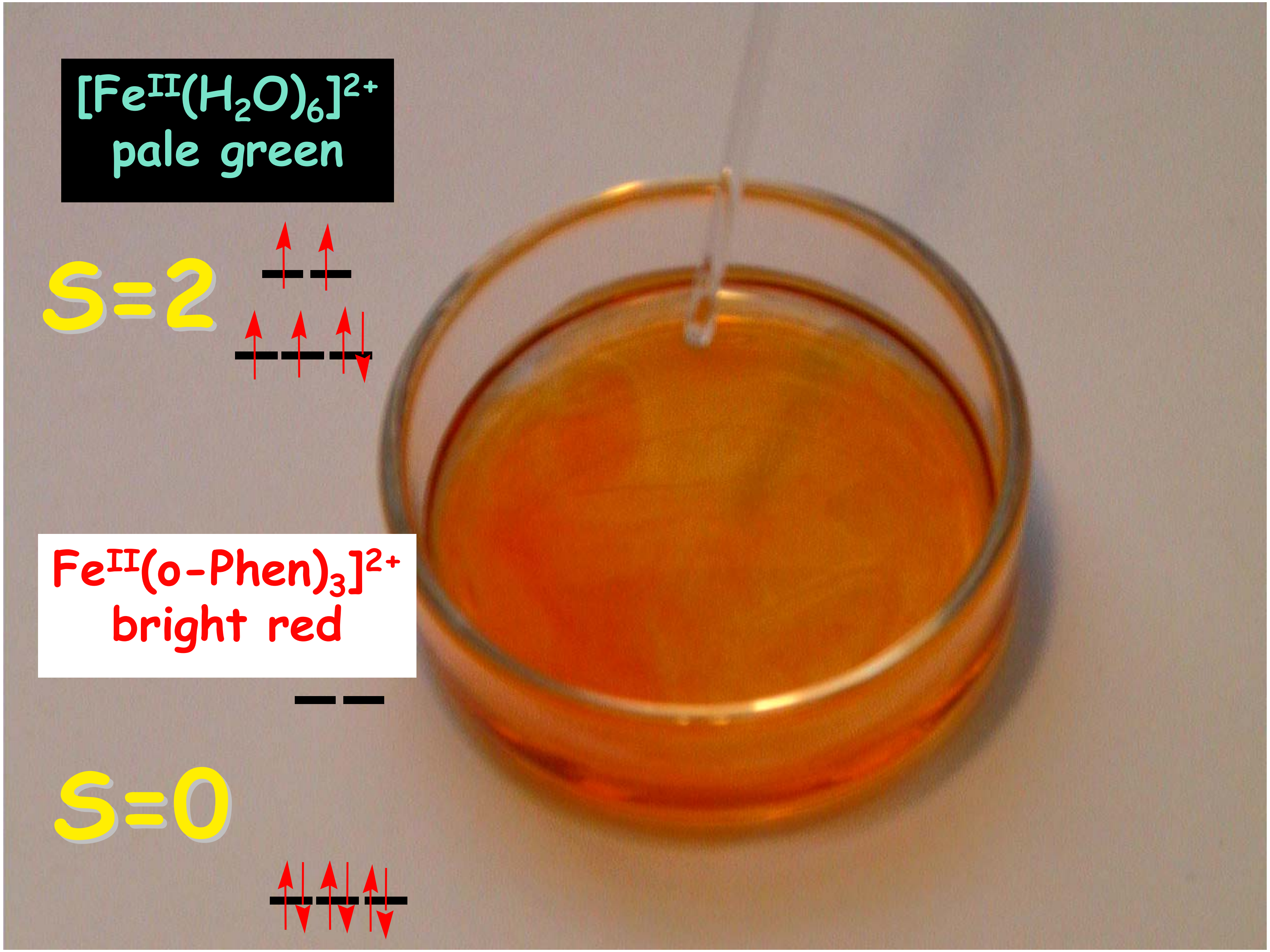


[Co^II(H2O)6]2+
+
Methylene
Blue
KCN
+
Methylene
Blue

QuickTime™ et un
décompresseur DV - PAL
sont requis pour visionner cette image.

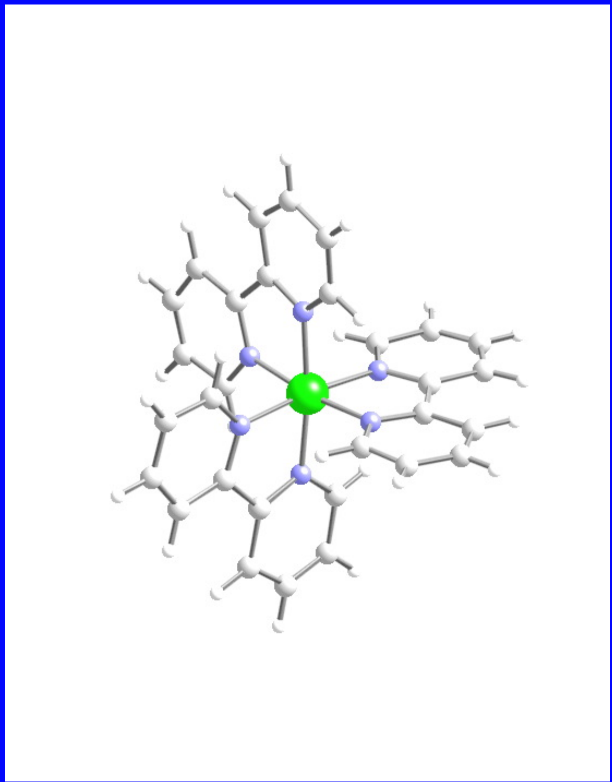

one
yellow
solution


blue + blue
=
yellow !
[Co^III(CN)6]3-
+
Methylene
Reduced
Colorless

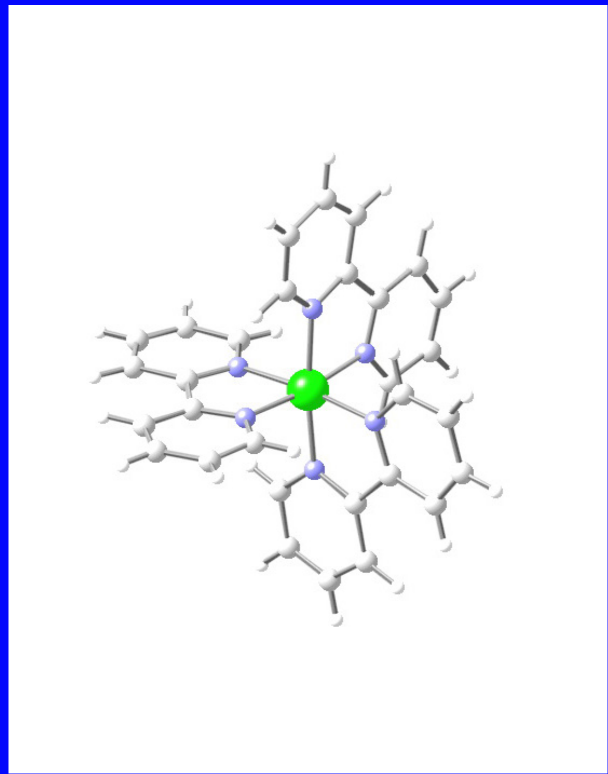


[Fe^II(H2O)6]2+
pale green
S=2
Fe^II(o-Phen)3]2+
bright red
S=0

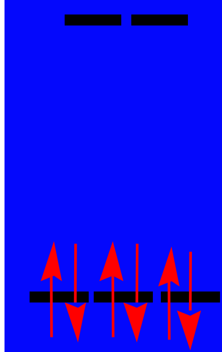
Low spin, chiral, $Fe^{II}(bipyridine)_3]^{2+}$



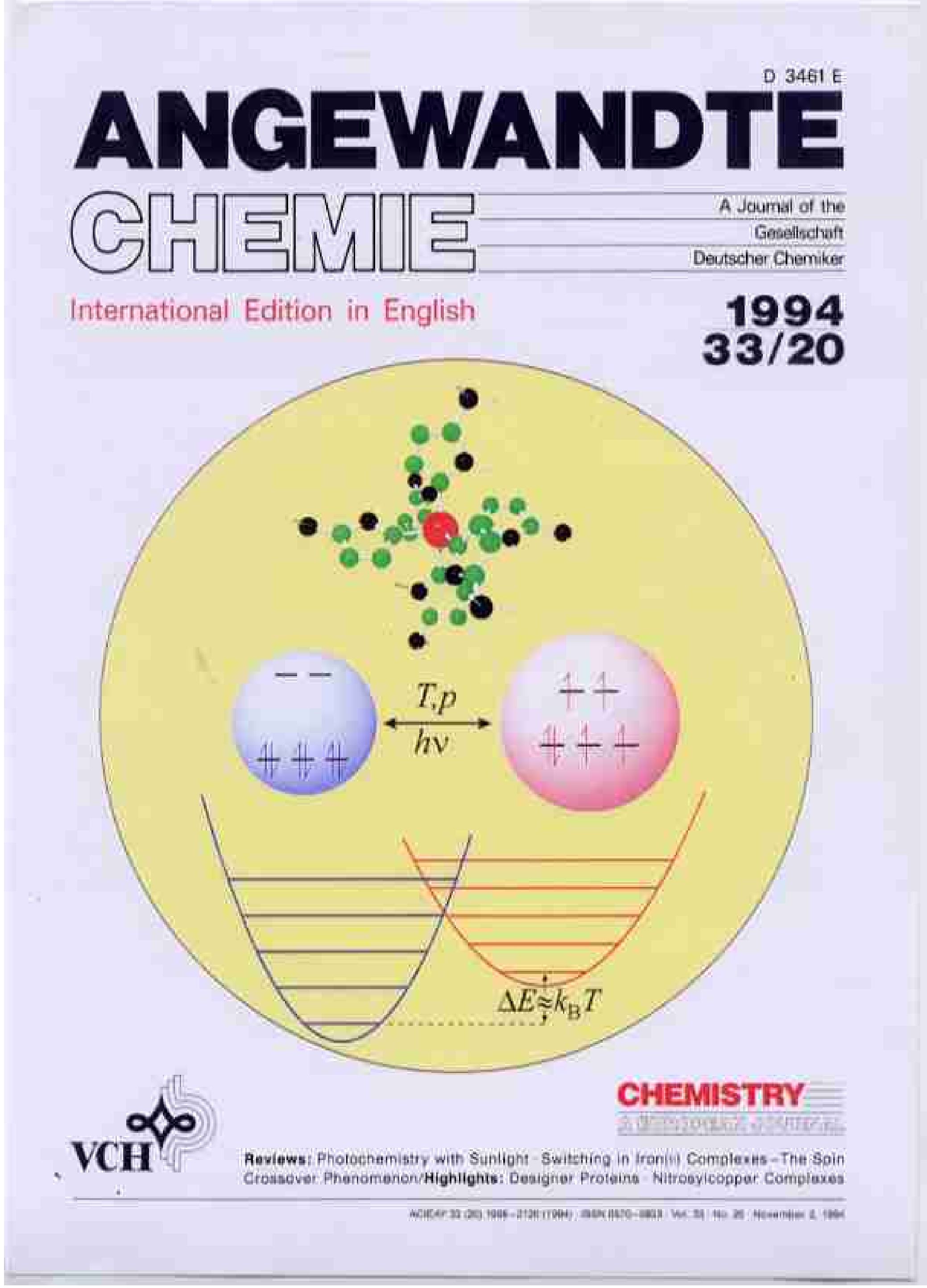
Λ



Δ



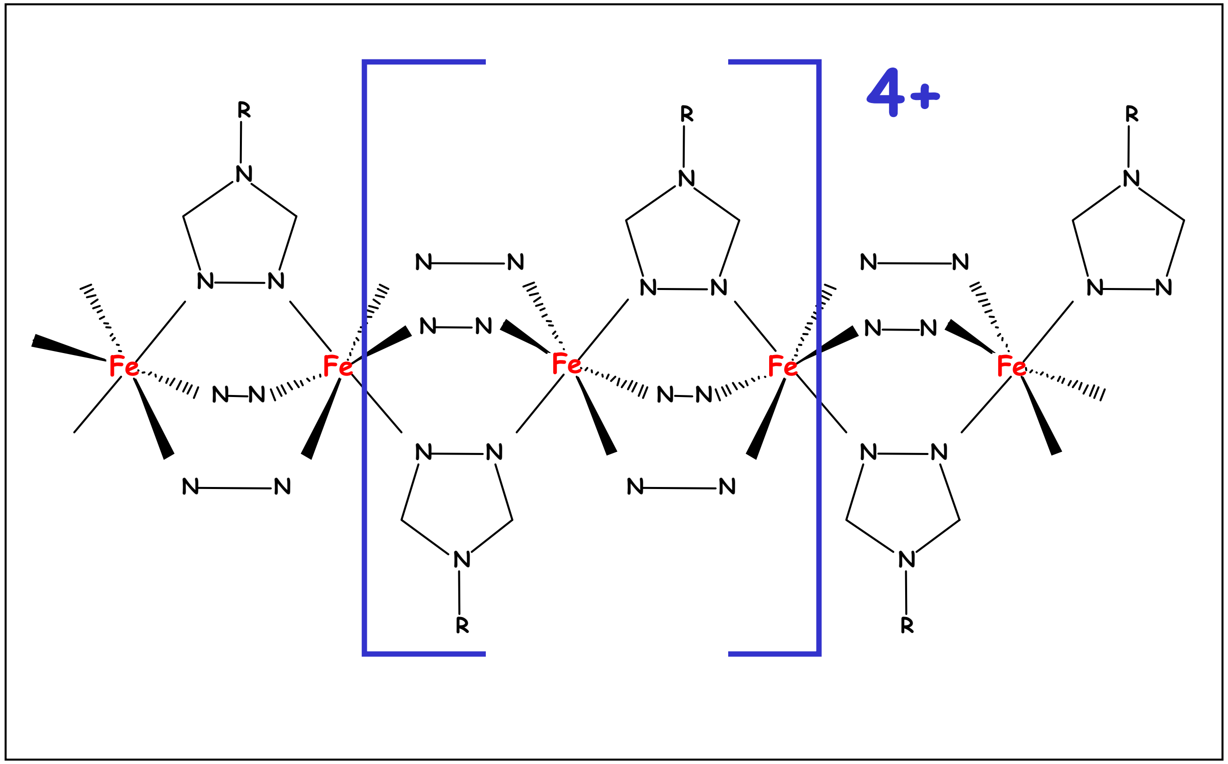
Playing with ligands,
the chemist is able
to control
the spin state



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

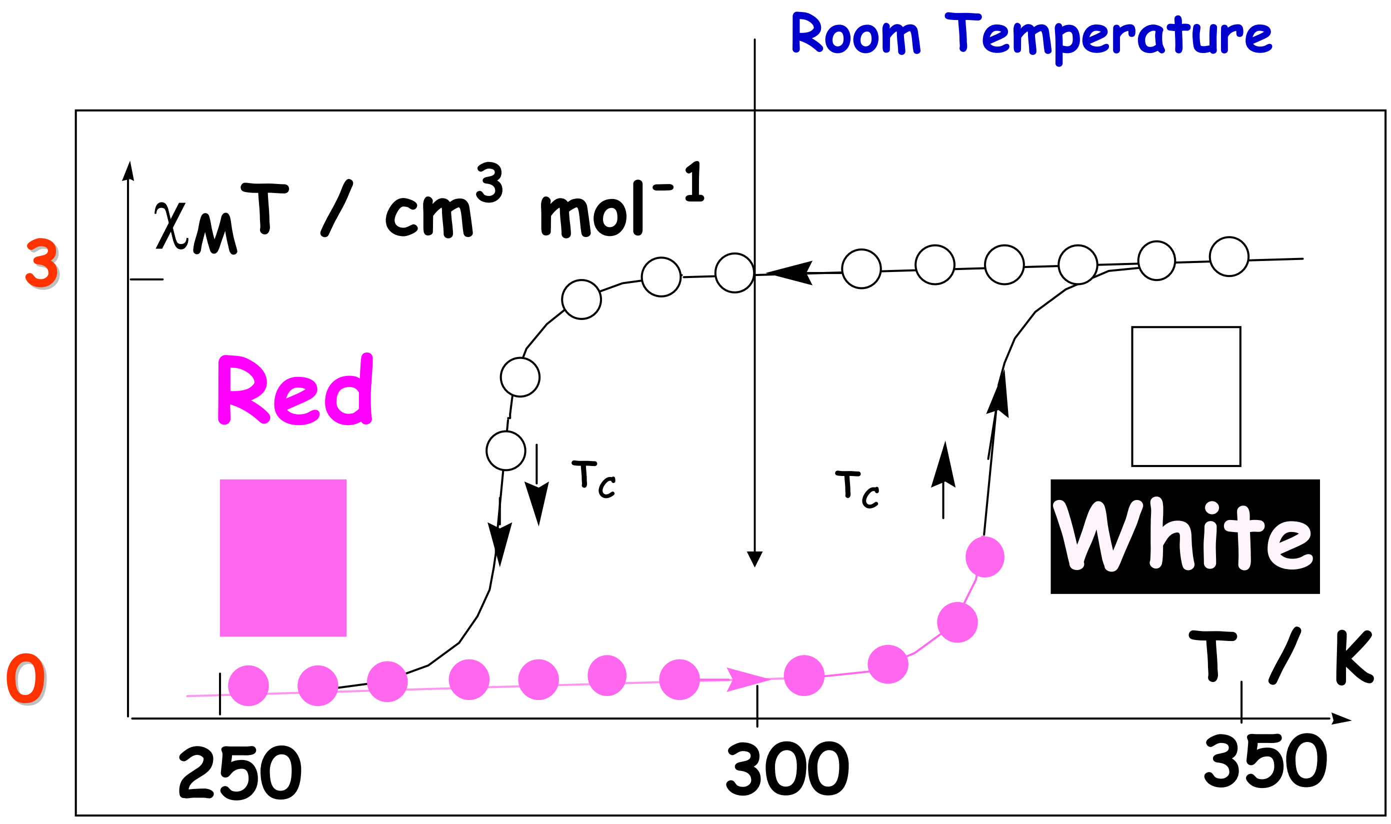
$\chi_M T$ = Constant

$\chi_M T \approx n\ (n+2)\ /8$ ...

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

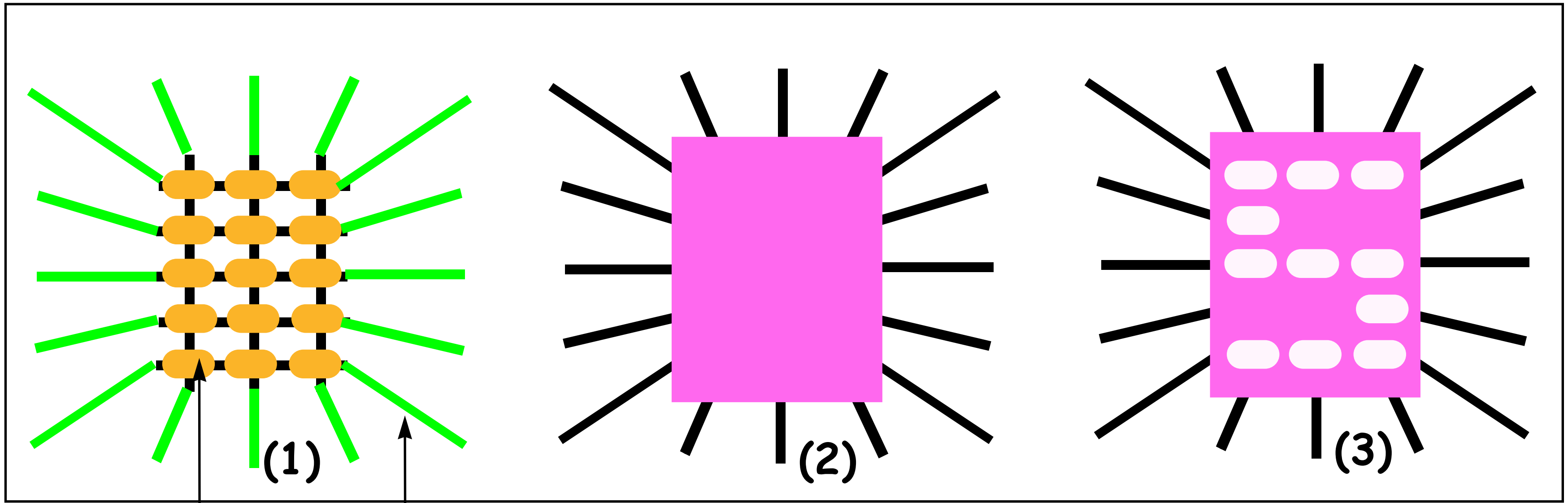
and use in display, memories …

macro

Spin and colour changes

Spin Cross-over

Display Device



Joule and Peltier Elements

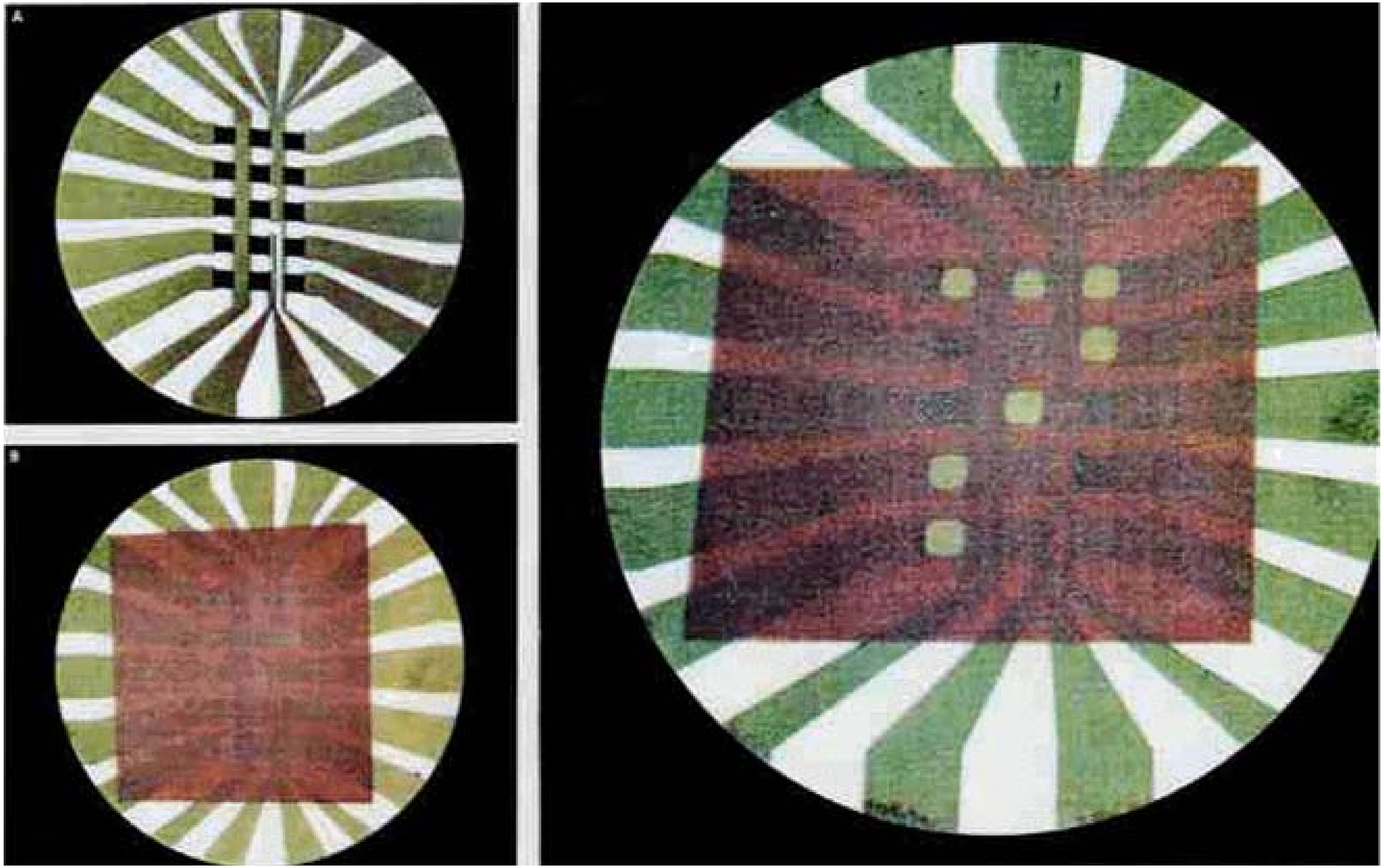
Connections

Compound in Low spin state (Thin Layer)

Display

O. Kahn, J. Kröber, C. Jay *Adv. Mater.* 1992, 718
Kahn O., *La Recherche*, 1994, 163

From the molecule to the material and to the device …



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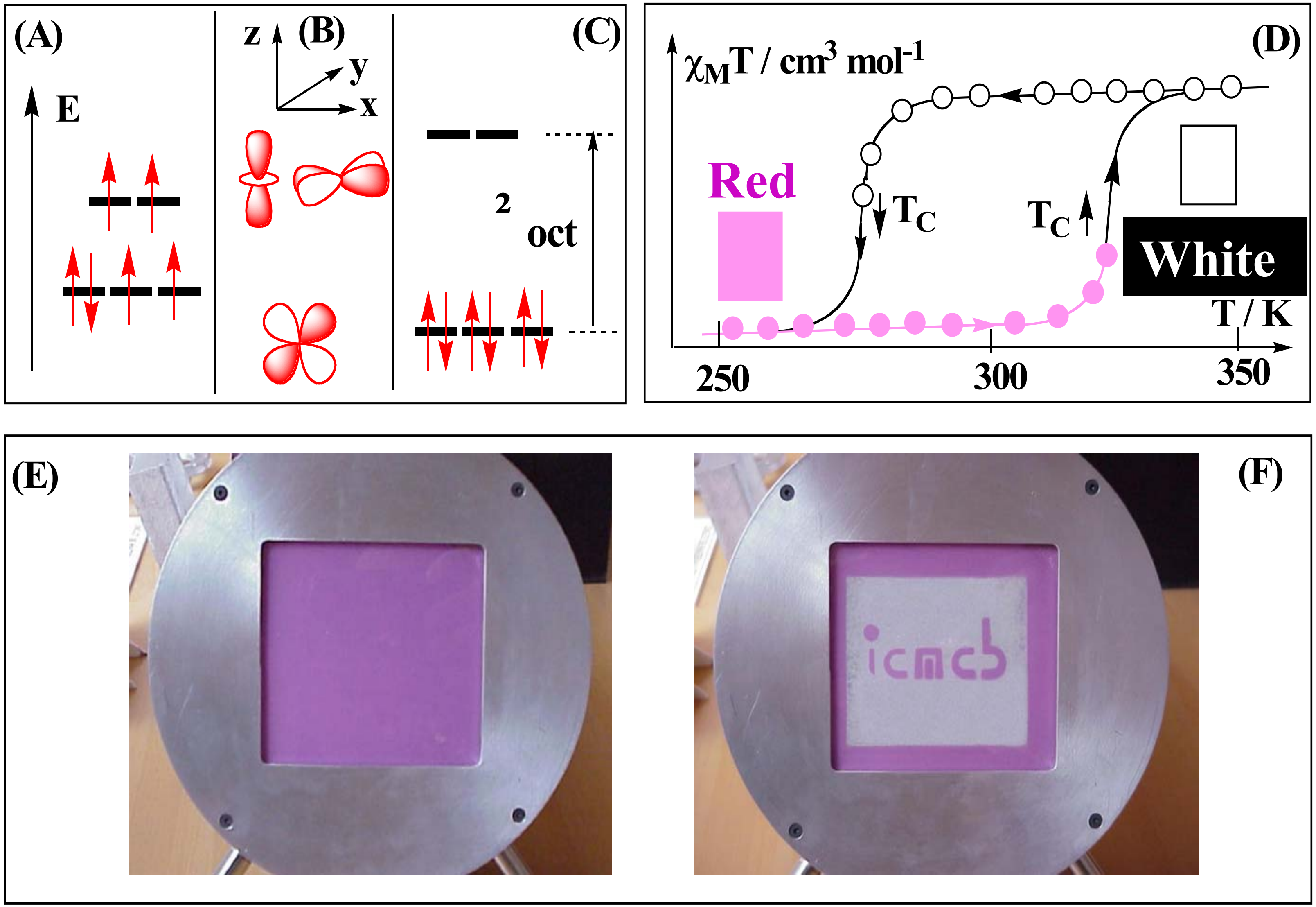
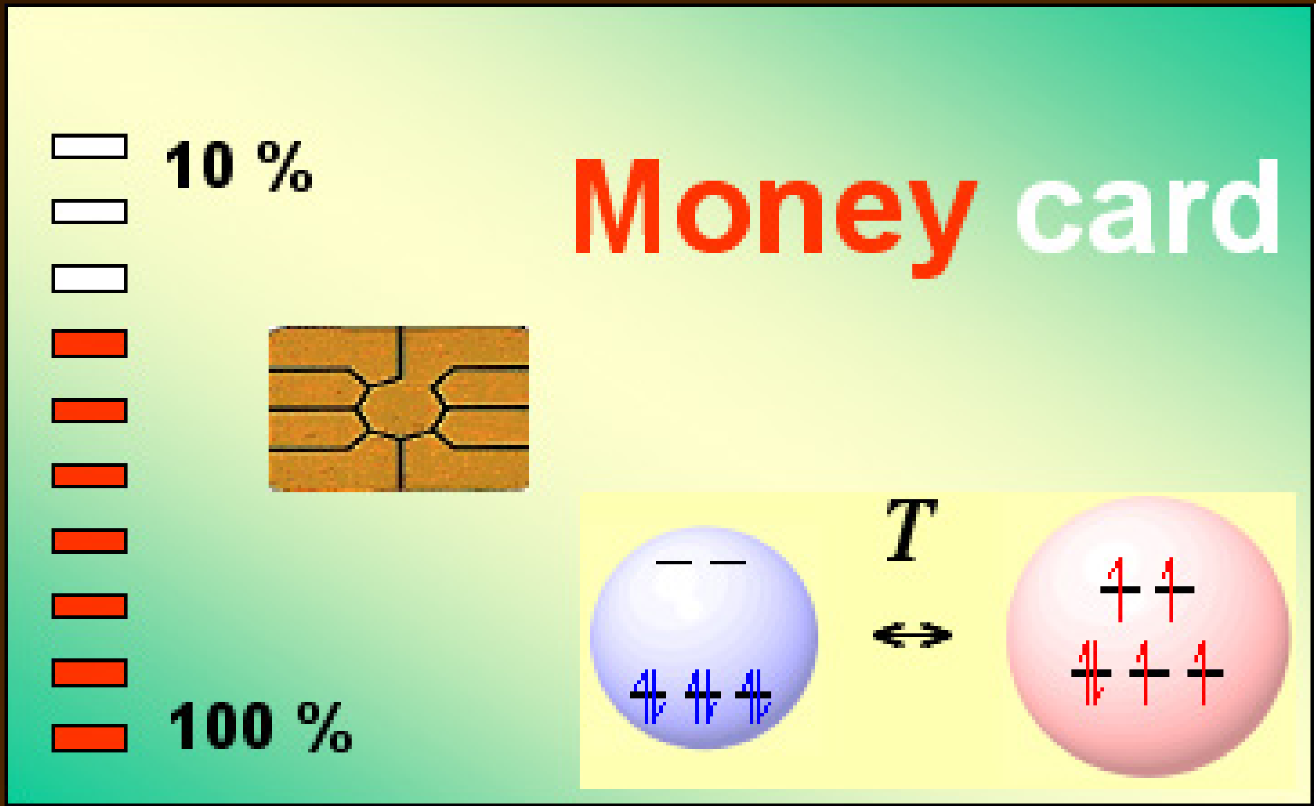


From J.F. Letard, ICMC Bordeaux



O. Kahn, Y. Garcia, Patent

May we go further

and dream of *molecular magnets*

i.e. low density,

biocompatible

transparent

or colourful magnets ?