How molecules become magnetic … and the resulting wonderland

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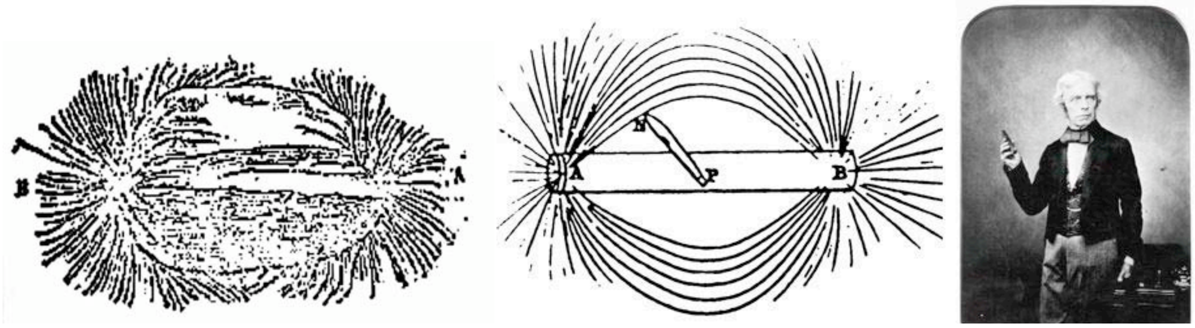
In everyday life, the word “magnetism” most often refers to solid materials, metals, alloys, oxides. As for molecules, they are considered to be isolated, non-magnetic objects. Nevertheless, *to be or not to be* (magnetic) is not the appropriate question: everything is magnetic; the true problem lies in determining how. The purpose of this lecture is to illustrate the magnetism of molecules through some experiments.

Magnetism: from magnets to molecules

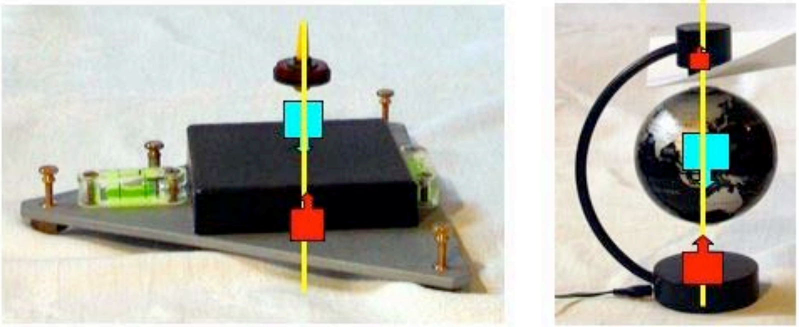
In everyday life, the substances called magnets can be classified in two categories: “hard” magnets and “soft” magnets. “Hard” magnets remain magnetized permanently; they are magnetic even when there is no applied magnetic field. That is, they have an important remnant magnetization in a zero applied magnetic field. Magnetite, whose chemical formula is written Fe_3O_4, is a hard magnet known for a long time. “Soft” magnets are not permanent magnets; they are attracted to hard magnets but lose their magnetization rapidly when the hard magnet is removed (their remnant magnetization is weak or zero). Metallic iron is a soft magnet. Hard magnets (neodymium-iron-boron alloy, for example) create around them a magnetic field, which can be visualized by soft magnets (iron powder for example). Figure 1 represents pioneering experiments, one of them by Michael Faraday, illustrating the magnetic “lines of force”. On the right, Michel Faraday can be seen at Royal Institution of Great Britain (London), bearing a magnet, not a cigar.



(a) (b) (c)

Figure 1: First experimental illustration of magnetic field lines around a permanent magnet, revealed by iron powder : (a) from N. Cabeo [Philisophia magnetica in qua natura penitus explicatur, Coloniae 1629, p.18]; (b) from M. Faraday (1832) ; (c) Michel Faraday bearing a permanent magnet (private communication, P. Day and F. James, Royal Institution, London). [See also: P. Day, The Philosopher’s Tree, The Institute of Physics Publishing, Bristol, 1999].

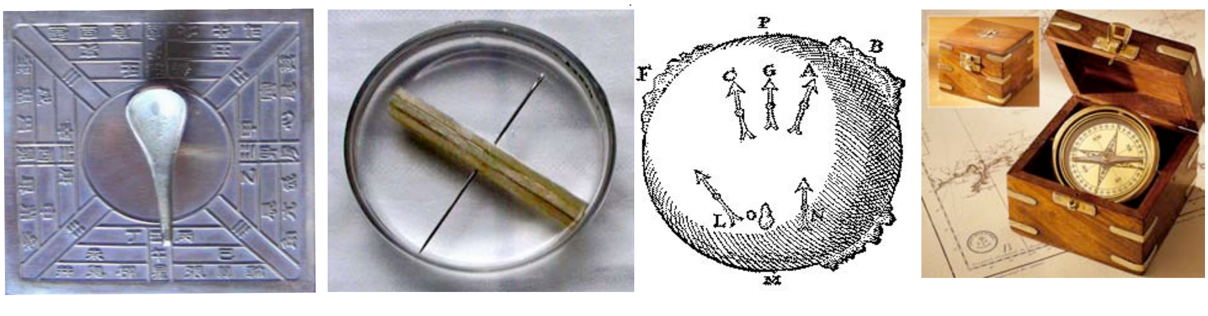
The magnetic field is not visible and magnetic interactions manifest themselves at a distance, without direct contact, as shown by the popular experiments on levitation (Figure 2). This has resulted in charlatans using magnets and magnetism in a mercantile and abusive manner. One such swindler was Messmer, a famous doctor from Vienna who commissioned Mozart to write *Bastien and Bastienne*, and was later celebrated, with a smile, by the same Mozart in *Cosi Fan Tutte* (Scene IV, Despina, “pietra mesmerica”, mesmerising stone). Messmer deceived many people with his theory of "animal magnetism" before being thrown in gaol for fraud. Even today there are websites popularizing such "theories" and rewarding practices. In common language also, the charm and charisma of some people, of their eyes in particular, are often qualified as "magnetic". For example, Fernande Olivier, one of the first mistresses of Picasso, confessed in her book *Loving Picasso*, that on August 4th, 1904, "This radiance, this internal fire that one felt in him, released some kind of magnetism to which I was unable to resist." Examples are numerous - how many tourism flyers celebrate the magnetism of a place or hotel, how many perfume companies use the same arguments (like the present *sensuel et magnétique, sensual and magnetic* publicity campaign of Yves Saint-Laurent).



(a) (b)

Figure 2: Levitating objects: (a) levitating top ; (b) levitating earth. The weight is exactly opposite to the magnetic force created by the magnets on the magnetized substances contained in the top and in the globe. The interaction needs no contact and gives some strange and "magical" character to a perfectly normal and well understood phenomenon.

One of the oldest, best known and most useful applications of magnetism is the compass. It was an important navigation tool, enabling the great discoveries of the XV-XVIth centuries, from C. Columbus, Vasco de Gama, J. Cartier or Zhong He in Spain, Portugal, France and China. The needle orients in the earth magnetic field, due to the huge metallic masses of the earth nucleus. It was invented in China (Han Dynasty, 250-50 before Christ), placed in a box by the Italian navigators of Amalfitan Coast (hence its name in Italian, French and Latino languages (bussola, small box).



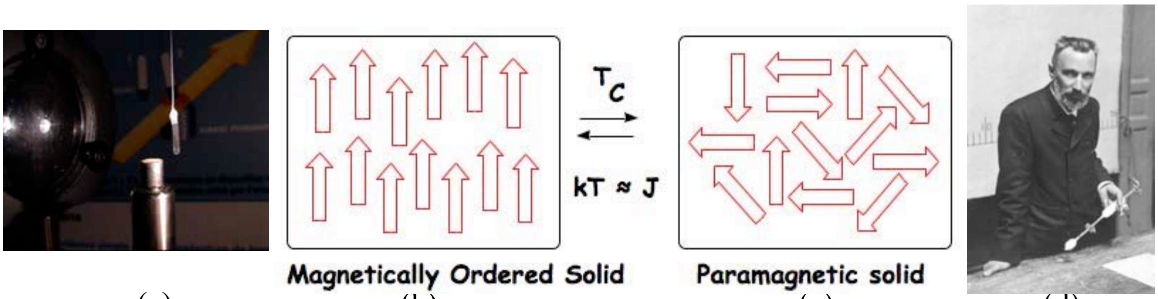
(a) (b) (c) (d)

Figure 3: A well known application of magnetism: the compass. (a) Si Nan model – Museum of chinese history, Beijing; (b) simple chinese compass ; (c) *terrella* used by William Gilbert in de Magnete, 1600 ; (c) (d) compass in a box (bussula, boussole …)

Magnets and magnetism also provide a source of inspiration and excitement for young children (Figure 4) (warning : do not swallow magnets !). The statement by A. Einstein is revealing : « 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.* » [in J.D. Livingston, *« Driving force : the natural magic of magnets »* Harvard University Press, Cambridge MA, 1997] . "Magnets" adorn fridge doors and display boards … More seriously, in a world often dominated by the market, hard and soft magnets play crucial roles in motors, transformers, etc … and magnet industry is a very important one.

Figure 4: enthusiastic children playing with magnets
[Courtesy Sacha Delannoy, Mathis and Robin Héraud and their mothers, Marion and Laura].

A peculiarly important physical quantity for our purpose is the Curie temperature (T_C), discovered by Pierre Curie (Figure 5d). It indicates the temperature when an ordered magnetic state tends to a disordered state (or the reverse) (Figure 5b). The "nail experiment" consists of heating a nail suspended on a pendulum. At room temperature, a permanent magnet strongly attracts the nail and displaces it from its original vertical position (the iron has an ordered magnetic state). When the temperature of the nail reaches 770ºC, the Curie temperature of iron, the magnetic state of iron becomes disordered. This causes the nail to become less attracted to the magnet and its weight pushes it away. The experiment can be illustrated much more easily using the device shown in Figure 5a. The nail is replaced by a molecule-based magnet with T_C of 42ºC and the heating source is a light beam (instead of a Meker burner). Depending on the exact experimental conditions, it is possible to obtain a regular oscillating movement. When the sample is out of the light beam its temperature decreases below the T_C, which makes it attracted to the magnet once again, and a new cycle begins. This is a thermodynamic machine using the absorption of light (free when coming from the sun) to heat the sample (heat source) and the atmosphere (also free ...) to cool it again (heat sink). This can be viewed as an easy and inexpensive way to transform solar energy into mechanical energy (Figure 5a).



(a) (b) (c) (d)

Figure 5: Curie Temperature: (a) "nail experiment" using a molecule-based magnet at room temperature ; centre, model of the transition from a magnetically ordered solid (b) to a disordered magnetic solid (c) when the interaction between magnetic moments become of the

same order of magnitude as the thermal quantum of energy kT ; (d) Pierre Curie presenting experiments in the theatre of Physics to the students of Faculté des Sciences of Paris University in 1900 (Picture, courtesy of:musée Curie, Paris).

Remembering that magnets have a direction and one end seeks north, they can be represented by an arrow. When looking more closely at a magnet, one can observe that it is made of smaller magnetic areas or "domains". Each domain is made up of many aligned magnetic moments, and each magnetic moment is ultimately borne by one atom or one molecule (Figure 6).

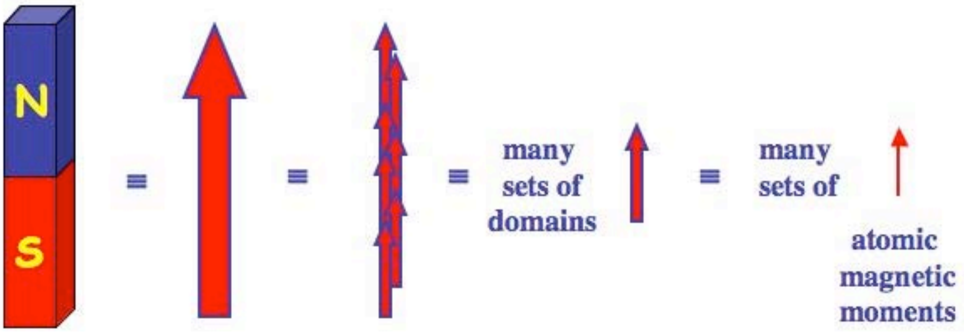


Figure 6: Division of a magnet into domains and magnetic moments.

Let us define the magnetization (abbreviation M) as the way a substance can be magnetized in an external applied magnetic field. By applying a magnetic field to a magnet, one can change the magnetization direction. If the magnetization of a magnet is plotted as a function of the applied magnetic field and the field is swept from zero to high positive values, to symmetrical negative values and back again, the resulting graph often gives a "hysteresis" cycle or loop (Figure 7). Hysteresis is defined as the retardation of an effect when forces acting upon a body are changed. The hysteresis loop depends enormously on the system, as shown in Figure 7.

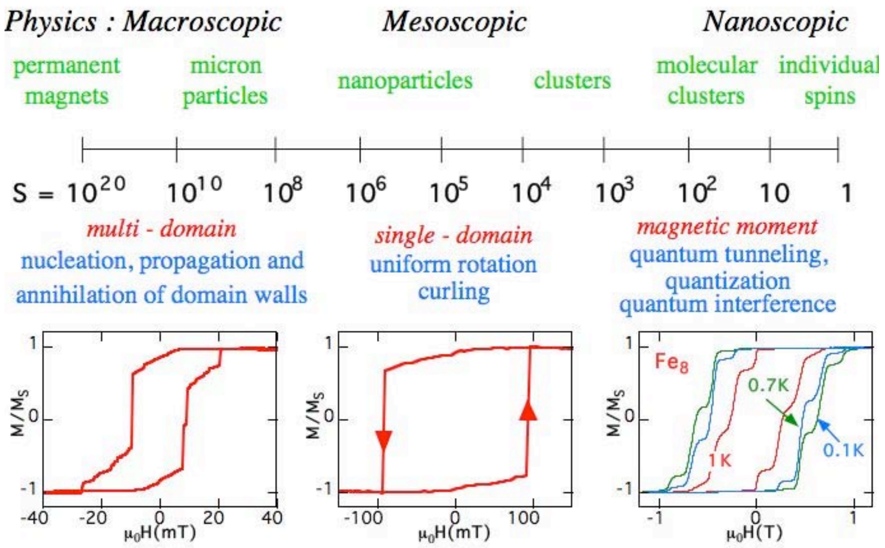


Figure 7: From macroscopic to nanoscopic physics, from domains to quantum physics (adapted from W. Wernsdorfer, I.L. Néel, Grenoble): the magnetization as a function of applied magnetic field presents an hysteresis loop whose nature is completely different with

the size of magnetic moments. Molecular magnetism (right) is dominated by quantum phenomena.

It is possible to demonstrate the existence of domains through experiments. Figure 8 displays an experiment proposed by J. Tejada (University of Barcelona) where the domains of a magnetic thin layer located between crossed polarisers (a) and in magnetic field (b) are revealed by the Faraday effect (c).


(a) (b) (c)

Figure 8: The domains of a magnetic thin layer located between crossed polarisers (a) revealed by the Faraday effect (c). When a magnetic field is applied (b), the reorientation in each magnetic domain changes in a different way. The light's polarization and transmission reveals domains and domains walls (c) [courtesy: J. Tejada, Université de Barcelona].

Everything above concerns the "classical", macroscopic, magnetism, at our scale, with innumerable useful applications. For most people, molecules are not included in this "magnetic" category. Nevertheless, the air that we breathe all the day long, consists essentially of a mixture of molecules of nitrogen, N_2 and oxygen, O_2 (each molecule is made of two atoms of nitrogen N or oxygen, O). The two molecules are "magnetic", each of its kind. The molecules of nitrogen are diamagnetic: placed in an intense magnetic field they are very weakly repelled. The molecules of oxygen are paramagnetic: placed in an intense magnetic field they are weakly attracted. We shall explain these properties in a while but the following experiments illustrate them simply: a powerful U magnet is first plunged in liquid nitrogen (T_{eb} = 77K) (Figure 9a) and it is not attracted between the two poles of the magnet. The magnet is then plunged in liquid oxygen (T_{eb} = 90K) which sticks between the poles of the magnet (Figure 9b, c)).

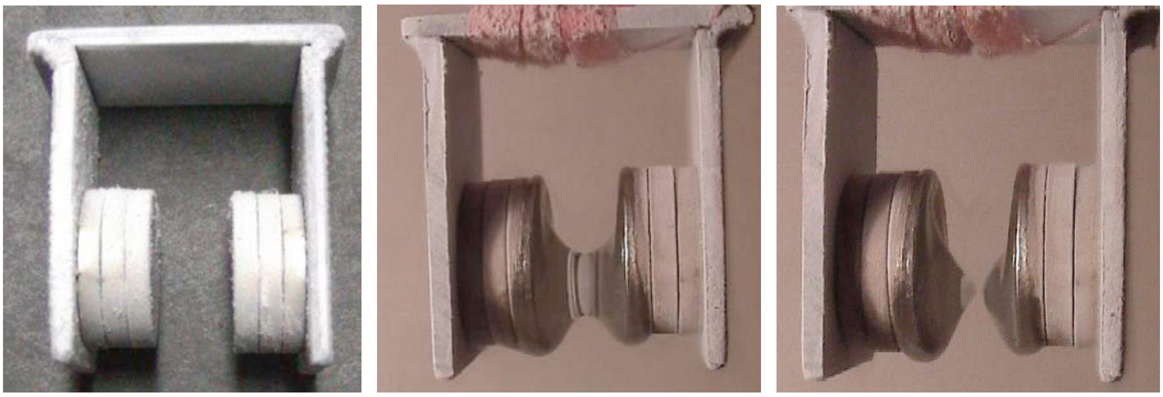

(a) (b) (c)

Figure 9: Magnetic properties of the air's molecules: a) liquid nitrogen, diamagnetic, is not fixed on the poles of the permanent magnet ; b) liquid oxygen, paramagnetic, is attracted as a liquid cylinder between the two poles of the permanent magnet ; c) at room temperature,

liquid oxygen evaporates and the remaining liquid is attracted by one or the other pole [device by Prof. S. Gao, Peking University].

The quantum world

In all the cases, solid, liquid or gas, magnetism finds its origin in the magnetic properties of the electron. Here we enter a new, very peculiar world, discovered at the end of the XIXth century and the beginning of the XXth and recently celebrated in 2005 - the year of physics. This world is quantified; discontinuity substitutes the continuity of macroscopic world. It is a world with well established rules, governed by quantum numbers and mathematical functions. It is a world where dimensions become very small, where nanometer (= 10^{-9} meter = 1 meter / 1000 000 000) replaces the meter, where the quantity of matter becomes extremely small, a world where the molecule replaces the mole (a mole of molecules is made of $6{,}023\times10^{+23}$ molecules, i.e. the Avogadro constant, a figure difficult to imagine, obtained by multiplying 10 by itself twenty three times …). It is also a world whose concepts are difficult to grasp in a simple way but that can be approximated by analogies, models, representations… It is a world that can be considered as wonderful, even more wonderful than the one that Alice discovers in her Wonderland. We shall rely on the illustrations of John Tenniel: Alice on one side of the mirror to illustrate the world at our scale, macroscopic, classical and Alice on the other side of the mirror entering in Lewis Caroll's wonderland, which will be for us, the quantum world.

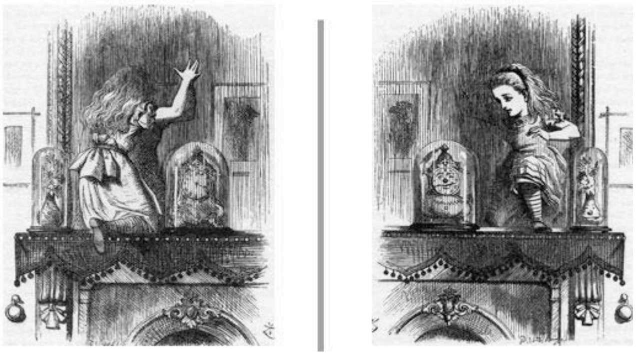
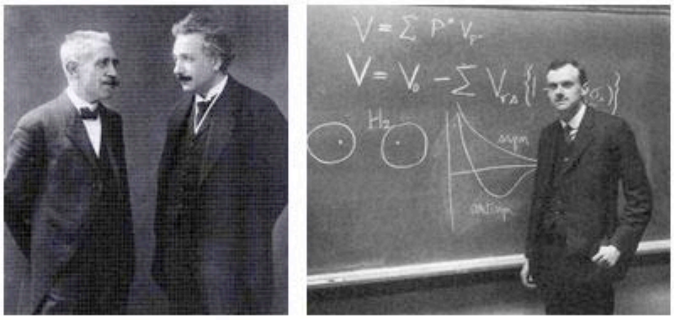


Figure 10: Alice through the looking-glass or how to proceed from the macroscopic world to a marvellous world which will be for us, with the complicity of the reader, the quantum world [Lewis Carroll, Through the looking-glass, Penguin Books, London, 1998. Illustrations by John Tenniel].

The electron and its magnetic properties in the atom

The electron has many faces: it is first a particle, with an elementary mass, an elementary, negative charge, an elementary magnetic moment, the Bohr magneton; it is also a wave, described by a mathematical function called a wave function. This function is a solution of Schrödinger's equation, an equation proposed by the Austrian physicist Erwin Schrödinger. In an atom, where the electrons with their negative charge are turning around a positively charged nucleus, each wave function is associated with an energy corresponding to some stationary state of the atom. It is precisely one of the marvels of the quantum world which allows two charges of opposite sign to coexist in a stable manner rather than to precipitate one against the other as in our classical world… The existence of the stable atom is based on this marvellous property. The wave function of one unique electron has been fully described by Paul Dirac, including its relativistic aspects implying that the atomic magnetic moment is directly related to the "spin". The pioneering work of Paul Dirac was celebrated by the Nobel Prize for Physics in 1933. The equation can be found in the book of P.A.M. Dirac, *The Principles of Quantum Mechanics*, 1930 (Cambridge). We give this equation to satisfy the curiosity of the reader, without defining all the terms introduced therein which would lead us too far from a simple, experimental, treatment of our subject. Figure 11 depicts the designer of the equation at the blackboard, Albert Einstein father of the theory of relativity in discussion with Paul Langevin, a French physicist having contributed strongly to clarify concepts in magnetism at the beginning of the XXth century.



(a) (b)

Figure 11: a) Paul Langevin and Albert Einstein [ESPCI photographic archives] ; b) Paul Dirac. [Website, http://www-history.mcs.st-and.ac.uk/history/PictDisplay/Dirac.html]

The atomic wave functions ϕ are defined by three quantum numbers, $\phi_{n,\ell,m}$: the principal quantum number, n, which determines the energy; the secondary quantum number, ℓ; and the magnetic quantum number, m_ℓ.. n is an integer which can take any value from one to infinity; ℓ can take all integer values between 0 and n-1; m_ℓ can take all values between $-\ell$ and $+\ell$. It is useful at this stage to "visualize" the corresponding wave functions and see the zones in space where it is the most probable to find the electron around a atomic nucleus (Figure 12). The symmetry of the orbitals is important: when we go from one point with coordinates x, y, z to the point of opposite coordinates -x, -y , -z (the operation is called an inversion around an inversion centre), the wave function can either keep its value and its sign $\phi_{n,\ell,m}(+x, +y, +z) = \phi_{n,\ell,m}(-x, -y, -z)$ in which cases it is said to be even (or *gerade* in German, abbreviated to *g*), or it can change its sign $\phi_{n,\ell,m}(+x, +y, +z) = -\phi_{n,\ell,m}(-x, -y, -z)$ in which case it is said to be odd (or *ungerade* in German, abbreviated to *u*).

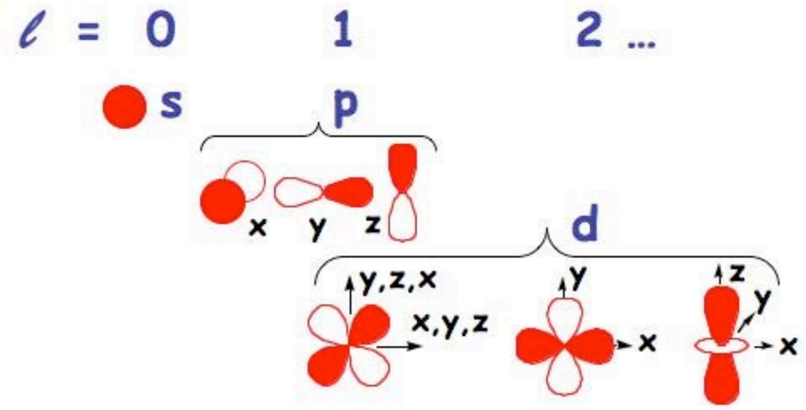


Figure 12: Schematic angular representation of atomic orbitals for different values of the secondary quantum number ℓ. There are $2\ell+1$ orbitals. The orbitals are named s as *sharp*, for $\ell = 0$ (one s orbital), p as *principal*, for $\ell = 1$ (three p orbitals), d for $\ell = 2$ (five d orbitals) , etc… The coloured part represents by convention the part of space where the wave function is positive. The white zones circled with a coloured line indicate the places where the wave

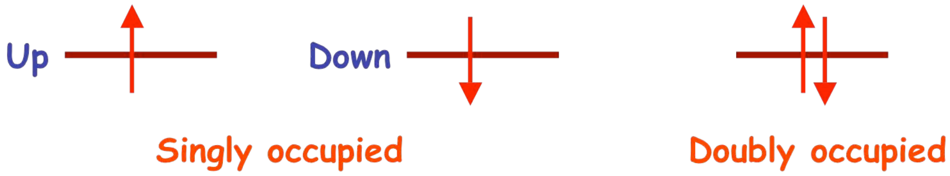
function is negative. The limit of the volumes represented corresponds to a surface where the value of $\phi_{n,\ell,m}$ is constant. Note the symmetry properties of the orbitals (even, *g* or odd, *u*): s and d orbitals are *g*, p orbitals are *u*.

The different orbitals correspond to different energies that the chemists gather in an energy diagram of the orbitals (1s, 2s, 2p, 3s, etc ..). To complete our description of the electron in the atom, and specifically the magnetic properties, it is convenient to introduce a fourth quantum number - the spin quantum number, equal to s = ½. This number has a corresponding magnetic moment and since spin means to turn on oneself, it is appropriate to associate a rotational direction to the magnetic moment. Spin direction can be directed upwards (*up*) for $m_s = +½$ or in an opposite direction, downwards (*down*), $m_s = -½$. This can be expressed by:

$$\mu_{spin} = g_s \times \mu_B \times s \approx \mu_B \qquad [1]$$

where g_s is a factor close to 2 and μ_B is the Bohr magneton. As a simple approximation, the magnetic moment can be considered equal to the Bohr magneton, μ_B.

The occupation of the orbitals by electrons is ordered by a very strict principle which bears the name of Wolgang Pauli. The principle can be formulated in a variety of ways, but the simplest is undoubtedly the following: two electrons from the same atom cannot be described by the four same quantum numbers. As the orbital is defined by three quantum numbers n, ℓ and m_l, a maximum of two electrons of opposite spins (one spin up, $m_s = + ½$, and the other spin down, $m_s = - ½$.) can exist in each orbital. If an orbital has only one electron, it gives rise to an elementary magnetic moment and a paramagnetic state. If the orbital contains two electrons, this results in overall zero spin (S = ½ - ½) and a diamagnetic state. In this case, the electrons are said to be paired or that they form a pair of electrons (a faithful pair, evoked by L. Salem, in his book “*The marvelous molecule*”).



(a) (b) (c)

Figure 13: Occupation of an atomic orbital by electrons: (a-b) singly occupied level, (a) *up* for $m_s = + ½$, (b) *down* for $m_s = - ½$ and (c) doubly occupied level.

Two more words on the “filling” of an orbital by electrons – the process follows a very simple principle (known as Aufbau or “of construction”): the lower energy levels must be filled before those of higher energy (like building a wall, one starts at the bottom). The first level (n = 1) consists of only one *s* orbital (1s), the second level (n = 2) is comprised of one *s* orbital (2s) and three *p* orbitals (2p), the third level consists of an *s* orbital (3s), three *p* orbitals (3p) and five *d* orbitals (3d) etc…. When an atom has an odd number of electrons, like boron, B, with 5 electrons, it has at least one lone electron and the atom is paramagnetic. However, although carbon has six electrons, it is not diamagnetic - it has a spin of 1. This property is due to a third rule, the Hund’s rule after the name of Friedrich Hermann Hund, a german physicist: the three *p* orbitals have the same energy (it is said that they are *degenerate*) which means electrons will initially occupy one p orbital each before being paired in same orbital. The higher spin state, spin of 1, is most stable. A simple example of this principle will be presented later in the text, when J will be defined as the energy difference between the zero spin state (S=0, called a *singlet* state) and the spin state of ½ + ½ (S= 1, called a *triplet* state). There is no mystery in these appellations since they correspond to the spin multiplicity, 2S+1 (=1 for S=0, singlet and =3 for S=1, triplet). This phenomenon is due to the orthogonal nature of the p orbitals. The p orbitals do not overlap; the mathematical integral that defines the overlap is strictly zero.

Figure 14: How do two electrons occupy two orthogonal orbitals (which do not overlap) with the same energy ? Hund's rule says that the more stable state is the one with the highest spin multiplicity, the triplet, S=1.

The last thing to be said about magnetism due to the electrons is that the movement of the electron around the atom creates a magnetic moment known as the orbital magnetic moment. This is a quantum phenomenon which can be represented in the classical world by the magnetic field created perpendicular to a coil in an electric circuit. In the atom, the orbital magnetic moment is proportional to the quantum number:

$$\mu_{orbital} = g_l \ \mu_B \ \ell \qquad [2]$$

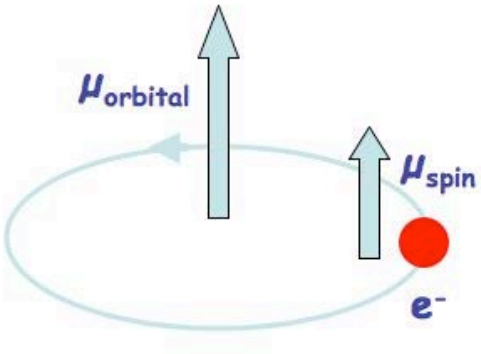


Figure 15: Orbital magnetic moment $\mu_{orbital}$ and spin magnetic moment μ_{spin} for an electron.

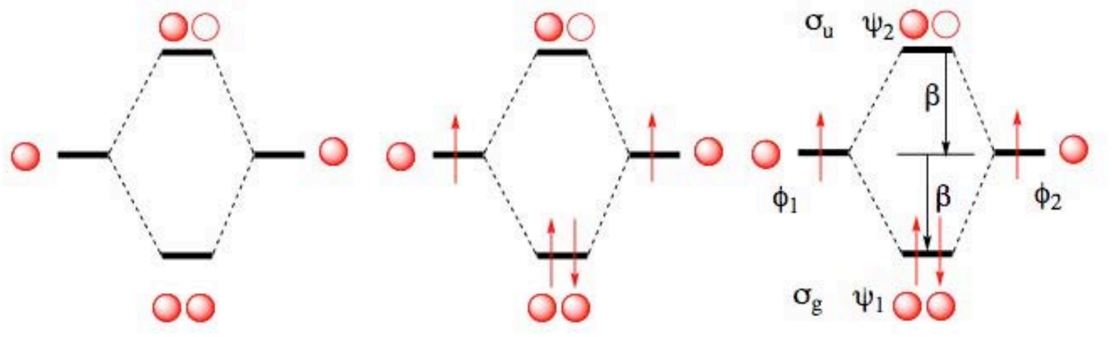
In many cases, this orbital magnetic moment can be ignored. Sometimes, there is a coupling between the moments of spin and orbit, which one calls the spin-orbit coupling. We neglect these aspects at first approximation. There is also a contribution to magnetism by the core of the atoms and their *nuclear spin*. Although nuclear spin is extremely important for many applications, in imagery for example, we will not consider it here.

Electrons in molecules

A molecule is the assembly of several atoms. The wave functions describing the electrons in molecules can be represented as linear combinations of the atomic orbitals mentioned above. The resulting wave functions are molecular orbitals (OM). The rules of occupation by electrons are the same as for atomic orbitals.

The dihydrogen molecule

Figure 16 shows how two atomic 1s orbitals of two close hydrogen atoms (ϕ_1 and ϕ_2) overlap, and combine, in phase and out of phase, along the axis (σ), to give the molecular orbitals (Ψ_1 and Ψ_2) of the dihydrogen molecule (it is a rule: the total number of molecular orbitals must be the same as the number of initial atomic orbitals). When the orbitals are combined in phase, Ψ_1 (+ +), they are more stable than the atomic orbitals alone (there is an energy of stabilisation, β) and this is the origin of the chemical bond. The resulting molecular orbital connects the two atoms and is known as a bonding orbital. The two electrons can be placed using the same rules as for the atom: with two electrons of opposite spins, one up and one down, the orbital is occupied and the pair of electrons is diamagnetic. Combination of orbitals in opposition of phase Ψ_2 (+ -) is less stable than the atomic orbitals alone. In this case, the molecular orbital is regarded as an antibonding orbital and it remains empty.



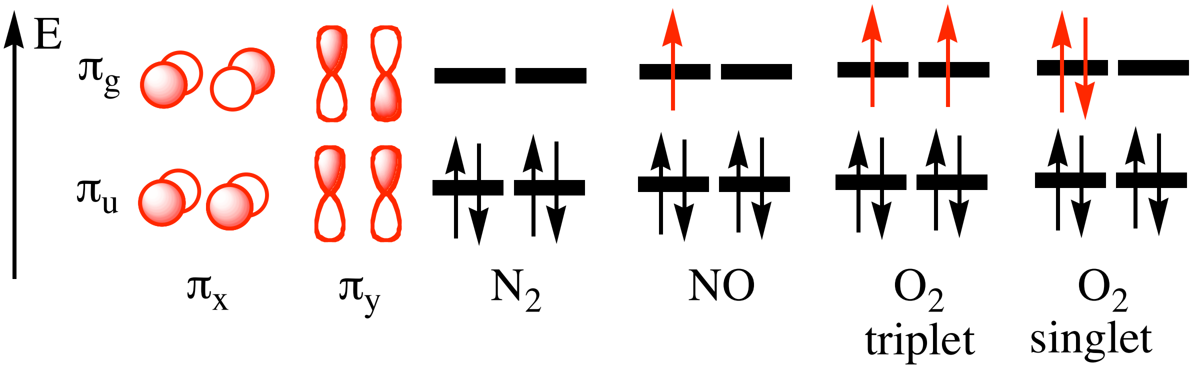
(a) (b) (c)

Figure 16: Formation of a dihydrogen molecule: (a) combination of atomic orbitals ; (b) pairing of the spins in the bonding molecular orbital ; (c) name and numbering of atomic orbitals ϕ and molecular orbitals (OM) Ψ, stabilization energy β, axial symmetry labels σ_g and σ_u for Ψ_1 and Ψ_2 OMs

Molecules of dinitrogen (diamagnetic) and dioxygen (paramagnetic)

The dihydrogen molecule is very simple because each hydrogen atom has only one electron. When the atoms that make up the molecule are made up of several electrons, things become more interesting – and more difficult … -. Atomic orbitals combine according to symmetry rules, and orbitals that have an axis of symmetry about the molecular axis (overlap axially), like that of the hydrogen molecule, are defined as sigma (σ) orbitals. The orbitals that lay along the sides of the molecule give rise to the molecular orbitals of pi (π) symmetry, etc. Figure 17a shows how the p(x,y) orbitals of two nitrogen atoms overlap to form the π symmetry molecular orbitals, even or odd (*g* or *u*). These orbitals are degenerate because the axes x and y are equivalent. The σ orbitals have been omitted for clarity. The next step is to distribute the electrons of the two atoms of nitrogen into the molecular orbitals of the molecule, remembering the principle of construction (the lowest energy orbital is populated first). In a dinitrogen molecule, there are three pairs of electrons which lead to three bonds (a σ–bond, not represented here, and two π-bonds). All of the electrons are paired, so the nitrogen molecule is diamagnetic.

Figure 17 also shows the occupation of the four molecular π orbitals of similar molecules nitrogen monoxide, NO, and oxygen, O_2 (Figures 17c-d). Simply, the only difference between the molecules is that the oxygen atom comprises one more electron than the nitrogen atom (8 instead of 7). In nitrogen monoxide there are 15 electrons, which is one more electron than the dinitrogen molecule (14 electrons). The additional electron is placed in one of the antibonding molecular orbitals of symmetry p. The nitrogen monoxide molecule is paramagnetic (17c) (spin = ½). Dioxygen has 16 electrons, which is two more electrons than the dinitrogen molecule. For these two electrons, one is faced with the same problem as seen above with the carbon atom and Hund’s rule leads us to the same solution: one electron is placed in each of the degenerate antibonding molecular orbitals (x and y). These orbitals are orthogonal to each other (fig. 17d). This results in a triplet state (spin S=1)! The singlet state (S=0), where two electrons are paired in same orbital, is an excited state for dioxygen (Figure 17e). These simple molecular orbital diagrams can be used to explain the magnetic properties of dinitrogen and dioxygen (shown in the experiments of Figure 8).



(a) (b) (c) (d) (e)

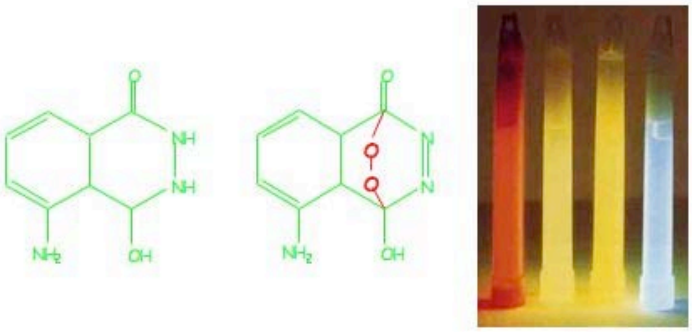
Figure 17: Occupation of the so-called π orbitals (a) of dinitrogen; (b) of nitrogen monoxide ; (c) of triplet dioxygen (d) ; of singlet dioxygen (e).

This situation leads us to an observation of interest general. The air that we breathe primarily consists of dinitrogen and dioxygen. Dinitrogen is a particularly stable molecule; it is diamagnetic and does not readily react with anything. Dioxygen, on the other hand, reacts with practically all other chemical elements. It reacts with dihydrogen to form water, H_2O; it reacts with carbon, hydrocarbons or sugars to form water and carbon dioxide, H_2O and CO_2; and it reacts with metals to form oxides. However, the living, both vegetable and animal, bathe in an atmosphere of dioxygen without reacting violently (which is fortunate because otherwise we would be reduced to some metallic oxides and phosphates, water, and carbon dioxide - the thermodynamically stable state of the components of the human body). On the contrary, in the lungs, dioxygen is fixed on haemoglobin. This is a slow combustive oxidation reaction on the level of the muscles and fibres. We owe this situation with the fact that dioxygen is paramagnetic and that its reactions with diamagnetic compounds is slow. These reactions occur only while heating in a flame or thanks to complex molecular machines like haemoglobin. We thus only exist as something other than the thermodynamically stable state of a human thanks to the magnetic properties of dioxygen…

What happens when the two oxygen electrons are placed in same orbital (Figure 17e)? The dioxygen singlet is an excited species. It is produced in particular by the chemical reaction of hydrogen peroxide, H_2O_2, with oxidants such as hypochlorite which one finds in bleach, in basic medium. Once produced, the dioxygen singlet can be de-energized to give again the dioxygen triplet, either by emission of a beautiful red light or by reaction with other molecules which can in their turn emit light. This is what occurs in the case of luminol and other luminescent molecules, as shown in the Figure 18. The light emitted by the glow-worm, found in footpaths during summer at night, is also produced by this reaction. More commonly, camping shops sell luminous sticks of various colours and various light intensities as sources of emergency light. The luminous collars used during summer dances are based on the same phenomenon. The reactivity of dioxygen singlet is thus completely different from that of the dioxygen triplet.

$$O_2 \text{ singlet (excited)} \rightarrow O_2 \text{ triplet (stable)} + \text{luminescent energy (red)}$$

$$O_2 \text{ singlet} + \text{luminol} \rightarrow \text{Excited species of luminol} \rightarrow \text{light}$$

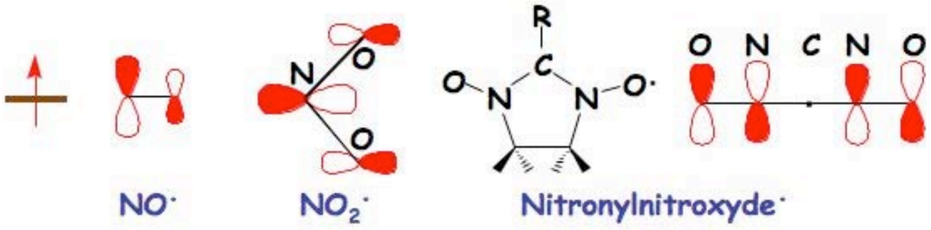


(a) (b) (c)

Figure 18: Reactivity of an oxygen singlet: produced during a chemiluminescent reaction, it can react with molecules like luminol (a) whose excited states (b) return to an unexcited state by light emission (c).

Radical molecules

The nitrogen monoxide molecule, NO (Figure 17c) is one example of a stable molecular radical: the molecule carries a spin S=1/2 (Figure 19a-b). It is very important in biological processes. There are many other examples. NO can react with oxygen to give nitrogen dioxide, NO_2, which is also paramagnetic (Figure 19c). Many organic molecules also belong to this category, for example the radical nitronylnitroxides (Figure 19d). In all the cases, the lone electron is located in the "frontier" orbital, high in energy, bonding or antibonding: *the "magnetic" electrons do not take part in the bonds and the stability of the molecule.*



(a) (b) (c) (d)

Figure 19: Some stable paramagnetic radical molecules, and singly occupied molecular orbitals: (a) simply occupied level ; (b) $NO^{\bullet}$; (c) $NO_2^{\bullet}$; (d) nitronylnitroxide$^{\bullet}$.

Now we come to the main point of this discussion: how chemists, knowing the rules which govern the interaction between electrons, can tune the spins of the molecules to obtain the magnetic materials that they wish? One understands that it is not easy to synthesise magnetic material because one must obtain stable molecules (that is, strong bonds which are diamagnetic pairs) and at the same time, keep lone "magnetic" electrons and control the very weak interactions between them (Figure 20)!

If one uses the lone electrons to form bonds, one obtains diamagnetic compounds! It is what occurs when one reacts two molecules of nitrogen dioxide, NO_2. Each NO_2 molecule has one lone electron, and the molecule that is formed, N_2O_4, is diamagnetic. One can easily visualize this reaction because nitrogen dioxide is brown and the dimer molecule is colourless. The reaction, which releases heat, is easily carried out by lowering the temperature (Figure 21). It is a reversible reaction: when it is reheated, the red-brown gas of nitrogen dioxide occurs again.

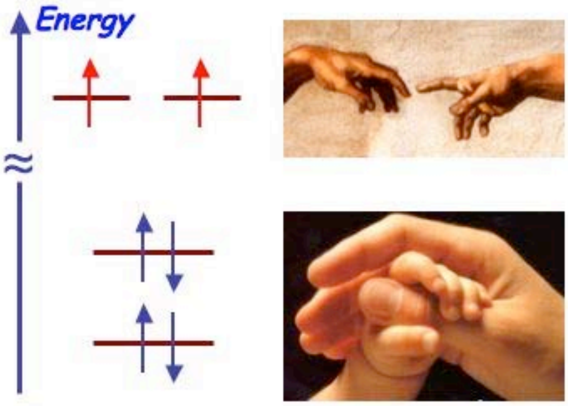
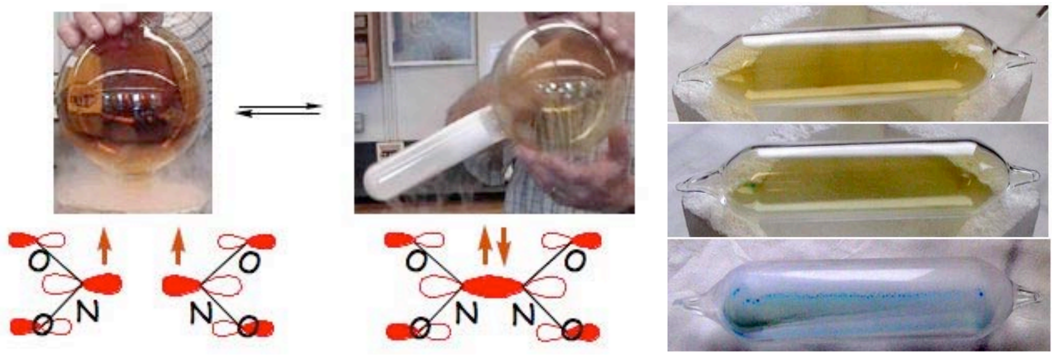


Figure 20: The dilemma: build strong chemical bonds with electrons organized in diamagnetic pairs (bottom), keep the unpaired electrons (top) and control the very weak interaction between them (with images of a strong family link and of the Michelangelo's ceiling of Sixtine Chapel in Rome).

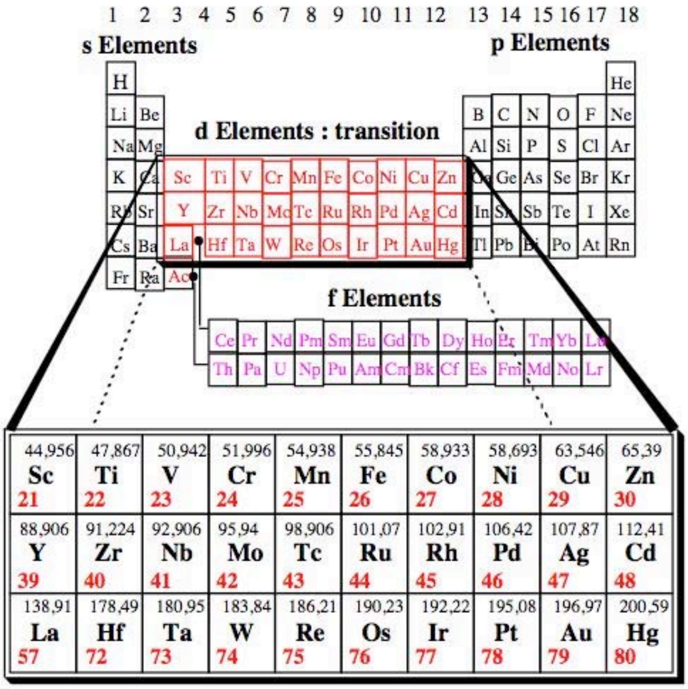


(a) (b)

Figure 21: (a) Paramagnetic nitrogen dioxide NO_2 (brown) and the corresponding singly occupied molecular orbital. The dimerisation reaction is favoured at low temperature; (b) It gives a diamagnetic colourless molecule, N_2O_4 with the formation of an N-N bond; (c) decreasing the temperature in a sealed tube filled with NO_2 : top, room temperature, NO_2; middle, mixture of NO_2 and colorless $N_2 O_4$; bottom, close to liquid nitrogen temperature : colorless N_2O_4 but, in presence of residual NO in the tube, also appears N_2O_3, a light blue liquid.

Complexes of the transition metals

The transition metals are the elements of periodic table (Figure 22) which have a d orbital partially occupied by electrons.



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

Figure 22: Periodic table of the elements emphasizing the columns 1 to 18, the elements s, the elements p and the transition elements d.

There are five d orbitals (characterized by the quantum number ℓ=2), which makes it possible to obtain spins of S=0 to S=5/2: the manganese(II) ion, Mn^{2+} or Mn(II), and the ferric ion, Fe^{3+} or Fe(III) have a S=5/2 spin (Figure 23). Other elements, like lanthanides, have seven f orbitals (ℓ =3) which can be partially filled, giving a possible spin of S=7/2 for the gadolinium(III) ion, Gd^{3+} or Gd(III). If an isolated transition metal ion has orbitals with the same energy, it is said that they are degenerate.

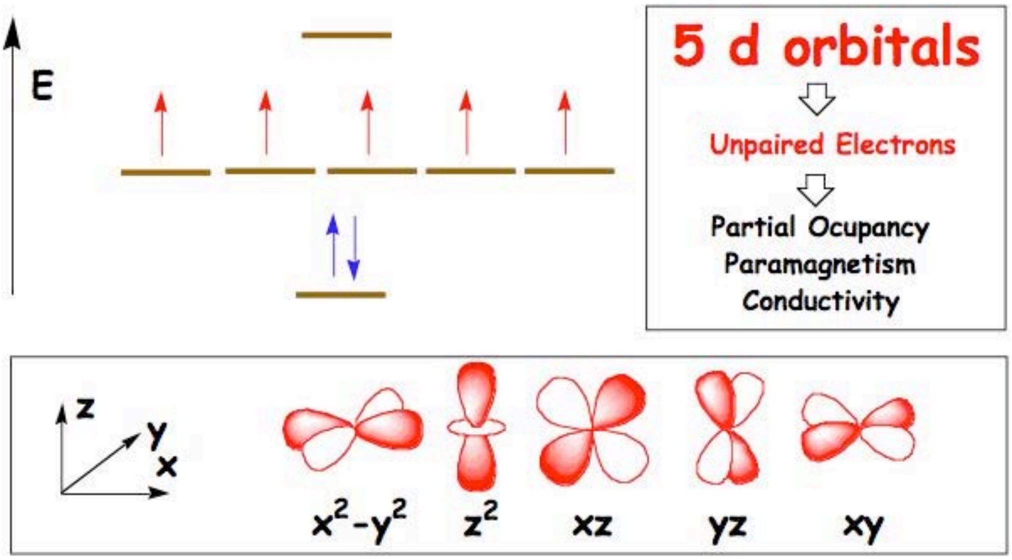


Figure 23: The d orbitals of transition elements at the origin of the magnetic, conducting and optical properties of those elements and of their derivatives. They present an even symmetry

(*g*). The example corresponds to a d^5 electronic configuration, either a Mn(II) or a Fe(III) ion, spin S= 5/2.

The transition metal ions can be surrounded by molecules which we call ligands (meaning "which binds", from Latin *ligare*) to form larger molecules, called metal *complexes*. The electrostatic interaction due to the creation of bonds between the ion and the ligands is called the "ligand field". Ligand field theory is an extremely rich and useful application of quantum mechanics and of the theory of symmetry for the study of these complexes. For our purpose, it is enough to know that the approach of the ligands modifies the energy of the metal orbital in a particular way and that new molecular orbitals are formed by the combination of the metal orbital and those of the ligands… the lone electrons are then distributed in these new energy levels. For an octahedral complex ML_6 where the ligands, L form an octahedron around the metal ion, M, the orbitals are divided into two groups called t_{2g} and e_g according to group theory (Figures 24 and 25).

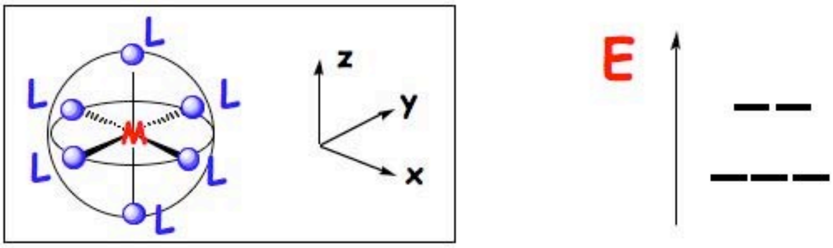
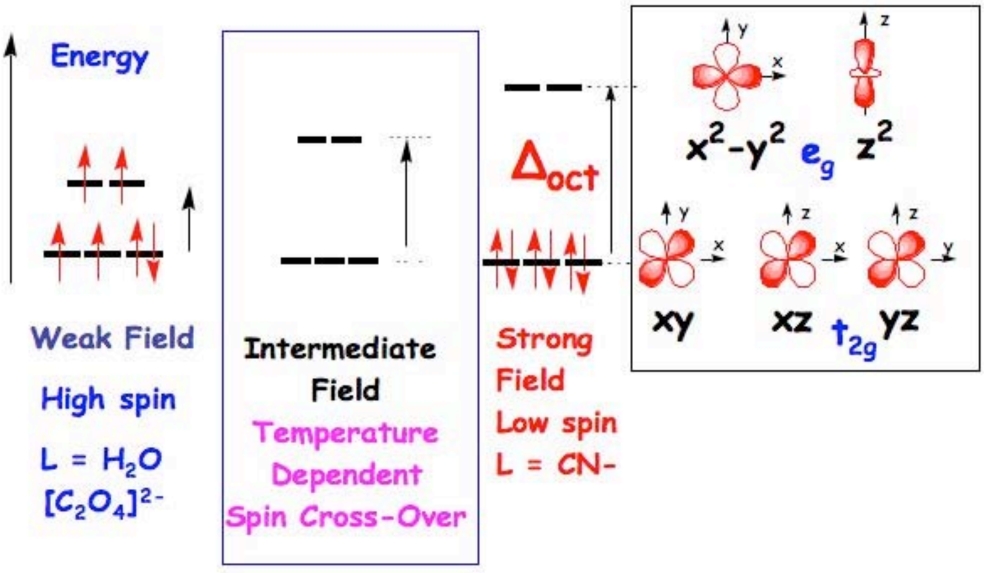


Figure 24: Change in the energy of the levels in an octahedral field.



(a) (b) (c) (d)

Figure 25: (a-c) Ligand field, role of the ligands and influence on the magnetic properties; (a) weak field and high spin electronic configuration with molecular ligands as water; (c) strong field and low spin electronic configuration with molecular ligands as cyanide; (b) intermediate situation where depending on some parameter (T, P, light, …) a spin cross-over can show up ; (d) angular representation of the t_{2g} and e_g d orbitals.

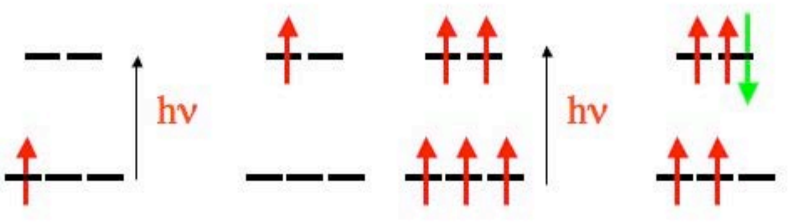
The variation in energy between the levels t_{2g} and e_g, called Δ_{oct}, the ligand field splitting, depends on the nature of the ligands. The distribution of the electrons in the levels is called the *electronic configuration*. The occupation of orbital depends on the nature of the ligands and the importance of the ligand field. Figure 25 shows the two manners of distributing the electrons in the orbitals of octahedral complexes of the iron(II) ion, with six electrons in the d orbital, d^6. In a ligand field where Δ_{oct} is small, for example in the hexaaqua iron (II) ion, $[Fe(II)(H_2O)_6]^{2+}$ (Figure 25a), the first five electrons occupy all of the levels available and the sixth electron is paired in one of the t_{2g} orbitals. One obtains a spin S=2 (strong spin or high spin). If one replaces water by the cyanide ion CN^-, bound by carbon, one obtains a complex hexacyanoferrate(II), $[Fe(II)(CN)_6]^{4-}$, where the ligand field is very strong, Δ_{oct} is very large and from the fourth electron, the electrons are paired in the orbital lowest in energy (Fig 25c). All of the electrons are paired and the spin of the complex is S=0 (weak spin or low spin). By removing an electron, one would obtain a trivalent iron(III) ion, with five electrons in the d orbital, d^5. In weak field, in $[Fe(III)(H_2O)_6]^{3+}$ for example, the spin is 5/2 and in strong field, like $[Fe(III)(CN)_6]^{3-}$, the spin is ½. When the ligand field is intermediate, an extremely interesting situation occurs, where the population of the orbitals can vary according to the temperature or from the pressure… this is what gives rise to the phenomenon of *spin transition or spin cross-over.*

The colours of the transition metal complexes

The colour of the complexes in water (Figure 26) is one of the manifestations of the presence of the ligand field, which varies with the metal ions. The colour of the solutions reflect the variation in energy between the t_{2g} and e_g orbitals and, very exactly, the difference in energy between the two configurations a) and b) of the figure (Figure 27): a) fundamental state; b) excited state caused by the absorption of a photon hν. The colours are not very intense because the transitions are "forbidden" for symmetry reasons. The transitions which require a spin inversion (as in the case of Mn(II)) are also spin forbidden and become extremely weak, as the very pale colour of a Mn(II) solution indicates. Moreover, a solution of zinc(II) ions is colourless because all d orbitals are occupied (electronic configuration d^{10}).

Figure 26: Change in colour of aqueous solutions of divalent ions of the first line of the transition elements of the periodic table, from vanadium(II) to zinc(II) (from R. Thompson, University of British Columbia, Vancouver). The colour changes with the number of electrons in the

d orbitals and the energy gap between the t_{2g} and e_g d orbitals. The colours are weakly intense since the transitions between d orbitals are "forbidden" for symmetry reasons. It some cases, they are also forbidden due to compulsory changes in spin during the transition. The solution of Mn(II), very weakly pink, appears colourless.

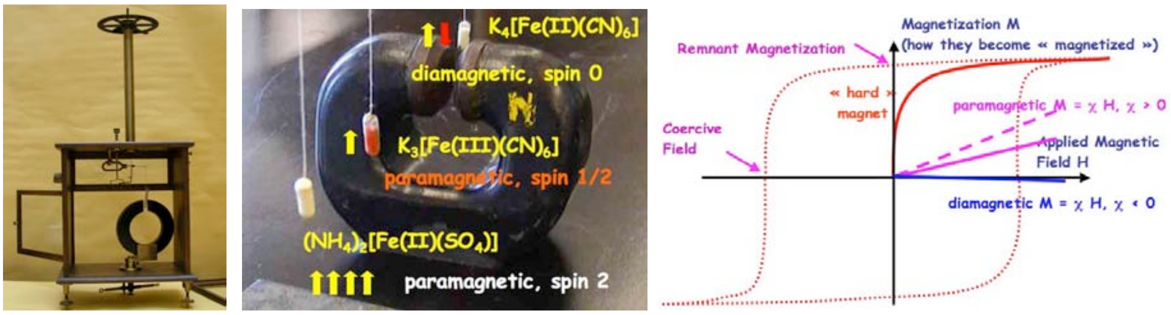


(a) (b) (c) (d)

Figure 27: Schemes of electronic transitions between the d orbitals of transition metal complexes: (a) ground state of a d^1 complex; (b) d^1 excited state after photon absorption, without spin change ; (c) ground state of a d^5 complex; (d) d^5 excited state after a photon absorption: it is necessary to reverse one spin and this transition is spin-forbidden. Observe the very pale pink colour of the solution of the manganese(II) ion in Figure 26. The slightly more intense pink, observable at the top of the liquid in the Mn(II) tube, corresponds to a longer length gone across by the light along the tube compared to the perpendicular directions.

The magnetic properties of transition metal complexes

It is possible to measure the magnetism of a substance using complex balances or instruments such as Gaussmeters or magnetometers. Figure 28a shows the magnetic balance designed and used by Pierre Curie. However, it is possible to use simpler devices to get an idea of the number of lone electrons in a metal complex (Figure 28b). One approaches a magnet with a container containing the sample: the more strongly the sample is attracted, the larger the number of lone electrons.



(a) (b) (c)

Figure 28: a) Pierre Curie's magnetic balance (collection de physique, Université Pierre et Marie Curie) ; (b) permanent magnet and samples to show that the magnetization depends on the number of electrons per mole in para- or dia-magnetic complexes (R. Thompson, University of British Columbia, Vancouver) ; (c) schematic magnetization curves for diamagnetic and paramagnetic samples and a hard magnet.

The way in which bodies magnetize is called magnetization, M. In simple cases, magnetization is proportional to the applied magnetic field, H. The proportionality constant, for a mole of matter, is called the magnetic susceptibility and is represented as χ_M.

$$M = \chi_M H \qquad [3]$$

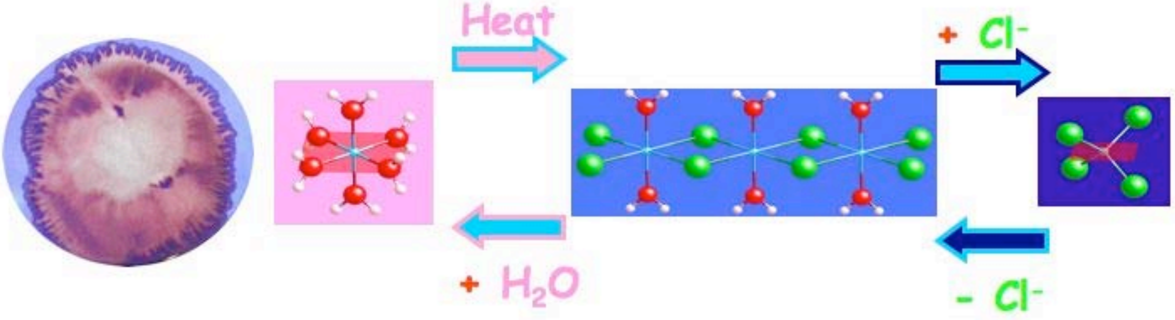
Diamagnetic substances have a very small negative magnetic susceptibility, which is due to the paired electrons. In very simple cases of paramagnetic compounds, magnetic susceptibility χ_M depends on the number, n, of lone electrons in the molecule and is given by the law established by Pierre Curie (and known as the Curie Law) which can be written:

$$\chi_M \, T = C \approx n(n+2)/8 \qquad [4]$$

With the system of units used here (known as emu-cgs), susceptibility is expressed in $cm^3 \, mol^{-1}$. Thus, in Figure 28b, a container of a low spin iron(II) sample $[Fe(II)(CN)_6]^{4-}$, S=0, where all the electrons are paired, is slightly pushed away from the magnet (Figure 28c, blue curve, slope $\chi_M < 0$). A container of an iron(III) sample with only one lone electron, $[Fe(III)(CN)_6]^{3-}$, S=1/2, is less attracted than a container of a high spin iron(II) sample $[Fe(II)(H_2O)_6]^{2+}$, S =2, with 4 lone electrons (Figure 28c, curved purple lines of different slopes, $\chi_M > 0$). One also observes that the behaviour of a “hard” magnet (red curve) does not obey the Curie law. The first magnetization curve has a very steep slope and then, when the field is varied around a zero value, one obtains a hysteresis loop (from the Greek *husterein*, being late). We find a strong remnant magnetization (at zero magnetic field) and a large coercive force (the amount of magnetic field that must be applied to obtain zero magnetization). In zero field, one can observe that the system is bistable, the magnetization can be positive or negative. The result of this is that the system has some kind of a “memory”. It “remembers” what state it was last in, positive or negative, in a similar way a light switch “remembers” if it was on or off. This means that hard magnets can be used to store information … Nevertheless, one should be very careful in using such words. “Memory” is a word widely spread in electronic industry for storage information elementary elements. Nevertheless, human memory and brain are much more complex that those elementary elements. Once, Paul Langevin said, that “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. » …

How can chemists vary the magnetic properties?

One can change the magnetic properties of transition metal complexes by simply varying the ligands around the metal ion. A simple experiment illustrating the flexibility of this chemistry is shown in Figure 29: it is possible to easily change the ligands, the geometry and the colour.



(a) (b) (c) (d)

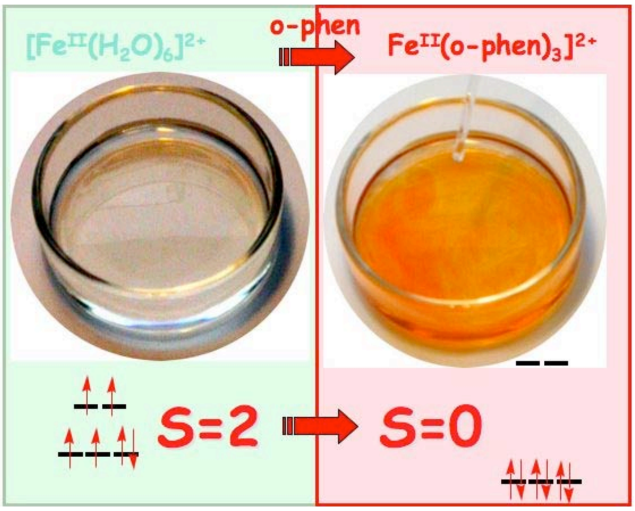
Figure 29: Flexibility of the surrounding (coordination sphere) of transition metal ions. Case of cobalt(II) chloride: (a) Experiment ; (b-c) changes in the surroundings of cobalt(II) observed in the experiment : (b) hexaaqua cobalt(II) light pink;(c) (bis μ-chloro)cobalt(II) chain, blue; (d) tetrachlorocobaltate(II), intense purple-blue.

Changes of ligands and geometry

When a filter paper is impregnated with a concentrated solution of cobalt chloride, $CoCl_2$, $6H_2O$, the paper becomes pink pale due to the formation of $[Co(II)(H_2O)_6]^{2+}$ (Figure 29b). If the paper is then heated using a warm air heater (or a hair drier…), the dry paper becomes light blue. This is due to the formation of the chain illustrated in Figure 29c where two cobalt ions are connected by two chloride ions, Cl^-. The chlorides act as bridges between neighbouring cobalt(II). Two water molecules remain above and below the ribbon of the chain on each cobalt(II). This chemical reaction is sometimes used to give a summary indication of the relative humidity of an atmosphere. The phenomenon is indeed reversible: the addition of some water drops (or a wet atmosphere) causes the pink colour to return. However, one also observes the formation of another species, one with an intense purple-blue colour. This occurs on the parts of the paper where chloride ions have accumulated and is the formation of the tetrahedral complex $[Co(II)(Cl)_4]^{2-}$. The colour is more intense because the tetrahedron does not have a centre of inversion and the electronic transitions become permitted by symmetry (Figure 29d). So on the filter paper it is possible to observe areas of each of the three colours, pink where it is wet, light blue where it is dry and dark blue where the chloride ions accumulate. However, throughout the cycle of these reactions, the spin of the complexes remains the same. How to change the spin ?

Changes of spin

This is shwon in experiment of Figure 30. In a transparent glass Petri dish (to be able to project on an overhead projector), one places diluted solution of Mohr salt which contains the octahedral species $[Fe(II)(H_2O)_6]^{2+}$, S=2 spin (Figure 30a). One then adds a drop or two of an alcoholic solution of orthophenanthroline (o-phen), an organic molecule with two nitrogen atoms likely to bind to the iron (II) ion. One immediately observes an intense red colouring due to the formation of the complex $[Fe(II)(o\text{-phen})_3]^{2+}$, illustrated in Figure 30b. The ligand field of the three molecules of orthophenanthroline is strong and the new complex has a low spin, S=0. It is worth noting that the three molecules of orthophenanthroline form a propeller (Figure 30c), which can turn on the right or the left: the two propellers cannot be superimposed upon each other in the same way that our two hands, right and left, cannot be: these complexes are chiral. Part d) of the figure shows another rare example of non superimposable objects, two mexican sea-shells

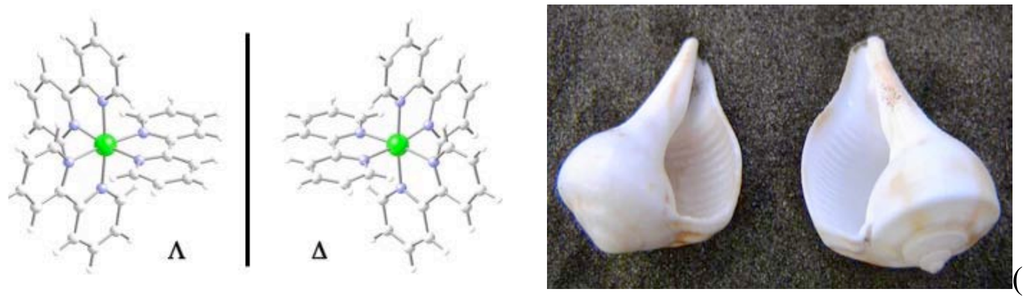


(a)

Paul LANGEVIN
la pensée et l'action

Textes recueillis et présentés par Paul Labérenne
Préfaces de Frédéric Joliot-Curie et Georges Cogniot
Editions sociales

(b)



(c) (d)

Figure 30: (a) Control of the magnetism (spin state) of a iron(II) metallic complex using ligands: from high spin in the pale green hexaaquairon(II) complex, $[Fe(II)(H_2O)_6]^{2+}$, to low spin in the brilliant red $[Fe(II)(o\text{-}phen)_3]^{2+}$, by simply substituting the six water molecules with three orthophenanthroline molecules ; (b) Paul Langevin recommends to scientists to join thought and action: having understood the nature of the ligand field, the chemist is able to work on modifying the properties in a predictable way. [Paul Langevin, La pensée et l'action, Editions Sociales, Paris] ; (c) the complexes formed are a 50:50 mixture of the chiral species (look at the way the helix is turning right or left); d) "enantiomeric" sea-shells, a rare phenomenon rather common in Mexico Gulf.

Complexes with spin crossover: from the quantum world to the bench

It is possible to get a ligand field of medium strength, due to the wide range of ligands available from organic chemistry. This is an intermediate case, where some complexes are high spin at high temperature and become low spin at low temperature, changing their colour with the ligand field! Figure 31a illustrates the diagrammatic structure of a chain of iron(II) ions bound by three neutral molecules of triazole, substituted by an organic group, R. The basic unit of the chain carries the two positive charges of the iron(II) ion. Negative ions (anions) are placed between the chains and ensure the electroneutrality of the compound. At high temperature, the compound is white and high spin (S=2); at low temperature, the complex is the red of Bordeaux wine and low spin (S=0). When the chemist varies the conditions of synthesis, the substituents R and the anions, it is possible to obtain the curve of susceptibility of the Figure 31b [one can check the values of $\chi_M T$ for n = 0 ($\chi_M T=0$) and n=2 ($\chi_M T=3$) using formula [4]…]. What is important here is not only the transition from the high spin (HS) to low spin (LS) (LS ← HS) when the temperature is reduced below the ambient (300K) and the opposite transition (BS → HS) when the temperature is raised, but also the fact that the temperature of transition is different with the descent T ↓ and with the rise T ↑ (T ↓ ≠ T ↑). This phenomenon is called "hysteresis" and it is due to the interaction between the chains in the structure. It is the source of an important property of the system which one calls the bistability: at a temperature ranging between T ↓ and T ↑, the system can be high spin or low spin, white when it comes from high temperatures or red when it comes from low temperatures: it "remembers" its thermal past, it has a "memory". This property can be used in the demonstrations of the display device shown in Figure 26b. Heaters (by Joule effect) or cooling elements (by Peltier effect) allow the display of dots of different colours used in a display (display panels, telephone card…). This example links of the use of quantum mechanics and thermodynamics with the physical properties and applications.

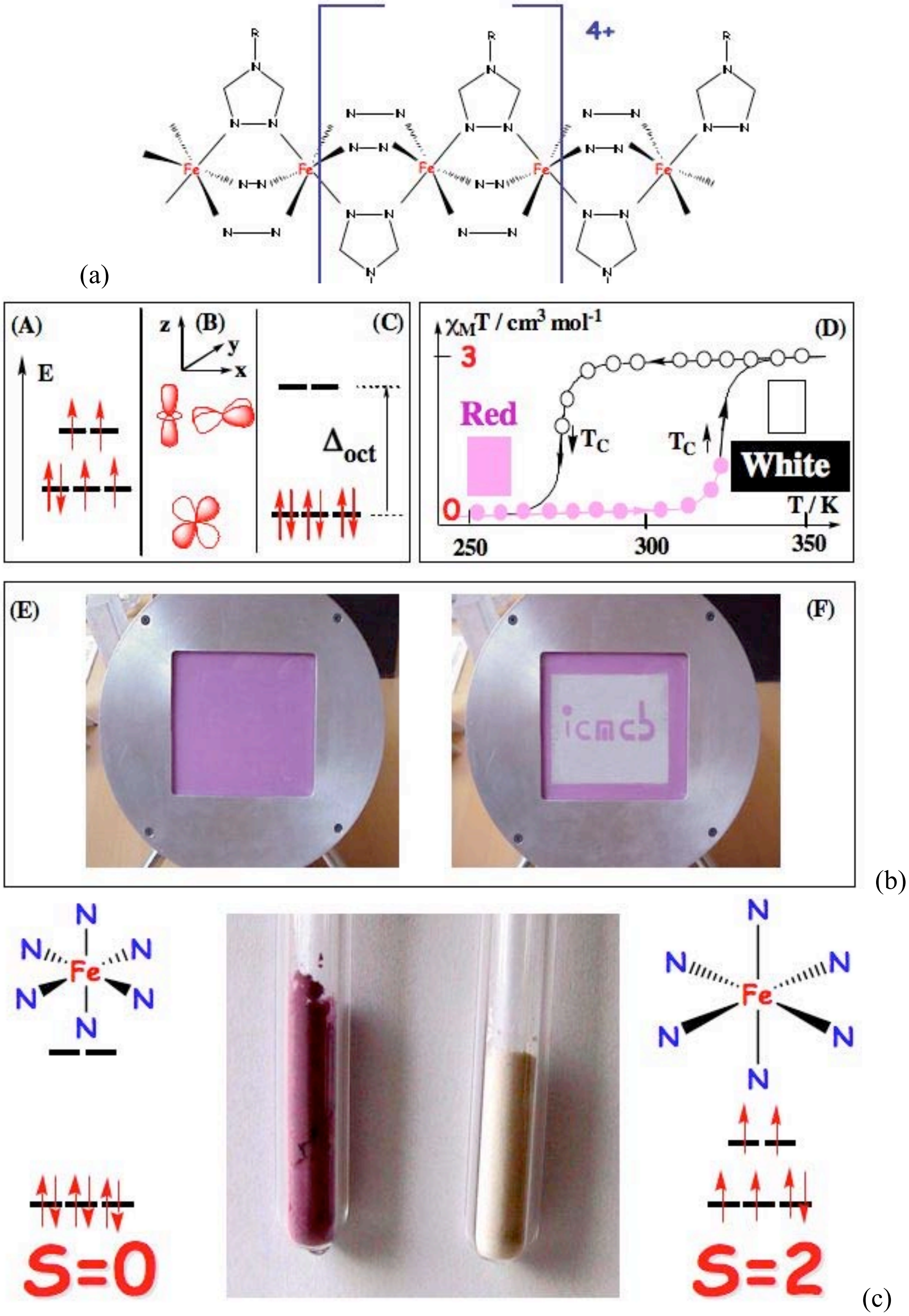


Figure 31: (a) Schematic structure of the iron(II) chain with triazole bridges, presenting a spin cross-over ; (b) from ligand field and quantum chemistry schematic to the demonstration: (A-C) orbitals and iron(II) spin states ; (D) magnetic susceptibility and bistability of the system ; (E-F) display demonstration [courtesy J.F. Letard, ICMC Bordeaux] ; (c) Experiment presenting samples synthesized during students practical works in UPMC Paris [Courtesy Prof. C. Roux, C. Train, A. Proust]. The transition from low to high spin corresponds to a huge increase of the Fe-N distances (20 pm).

Interaction between electrons on nearby atoms: from molecule to magnet

Parallel spins or antiparallel: how?

Until now, we have only examined examples where the properties rely only on isolated transition metal ions. Even in the chains mentioned previously, interactions between neighbouring metal ions were not fully responsible for the magnetic properties.

We thus cross a new step in complexity by introducing the exchange interaction, which is a quantum electrostatic interaction between two electrons on nearby sites. Once again, we must greatly simplify the situation. We need to find the means of controlling the interaction so that two electrons on nearby centers have their spins parallel ↑↑ (resulting in a triplet state, S=1) or antiparallel ↓↑ (resulting in a singlet state, S=0)! When the electrons are localised, they do not tend to jump from one center to another, and the situation can be summarized by Figure 32. The difference between energy of the singlet E_S and that of the triplet E_T is the spin coupling constant. It is called J (=E_S - E_T). If the triplet state is the ground state, J must be positive and the coupling is said to be *ferromagnetic*. If the singlet is the ground state, J must be negative, and the coupling is antiferromagnetic. This “spin strategy” corresponds to the “orbital strategy” we have already seen: combining two wave functions leads to the formation of a pair of electrons (antiferromagnetic coupling, dihydrogen), if the two wave functions are orthogonal, this leads to ferromagnetic coupling (dioxygen). It is enough to generalize as the orbital diagrams in Figure 32 indicate. There are, of course, quantum formulas and models to make the demonstration quantitative, but the qualitative approach is sufficient here. The orbital strategy can then lead to the choice of structure and electronic structure of the components, *i.e.* a “chemical strategy”.

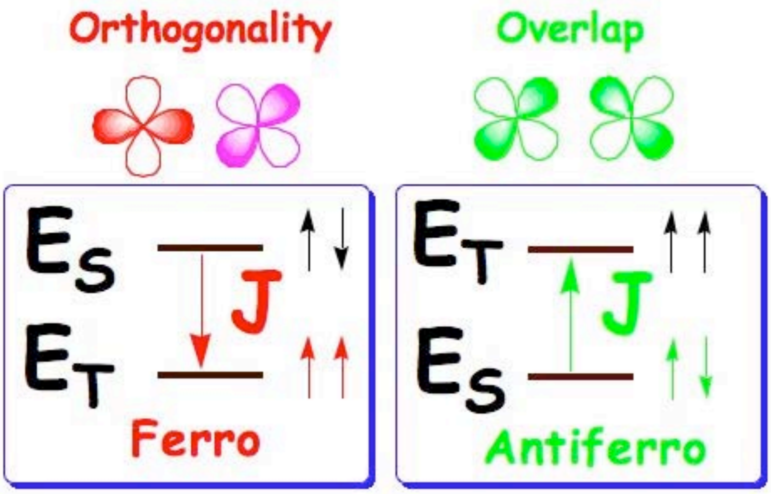
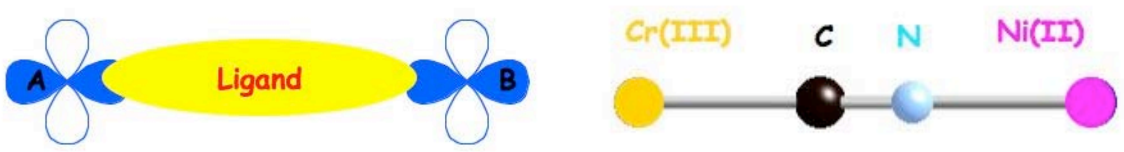


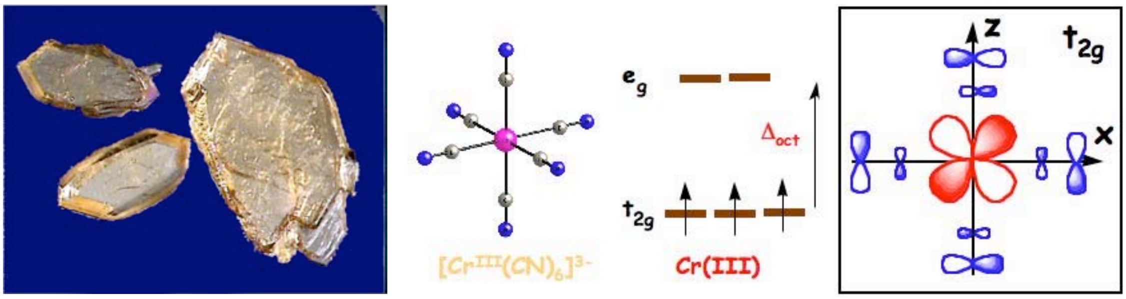
Figure 32: Spin strategy and orbital strategy: ferromagnetism is born from orbital orthogonality and antiferromagnetism comes from coupling.

It is also important to control the value of the spin coupling constant, J: coupling between free metal ions without any bridging ligands would be very weak and the wave functions would decrease very quickly. The bridging ligands thus play a very great part. Figure 33a shows coupling between two d orbitals facilitated by a ligand and Figure 33b shows an unsymmetrical bridging cyanide ion, CN^-, between two different metal ions. Figure 34 shows beautiful single crystals of $K_3[Cr(CN)_6]$, the structure of the octahedral complex hexacyanochromate(III) and its electronic structure; hexacyanochromate a very useful and very stable precursor for building molecular magnetic materials. Caution: cyanide ions can be dangerous because of ingestion or because they can give the very poisonous hydrogen cyanide gas, HCN. They should be handled with precaution.



(a) (b)

Figure 33: (a) The role of the ligand in the interaction of two metallic orbitals ; (b) a linear and unsymmetrical example of a bridge, the cyanide ion.

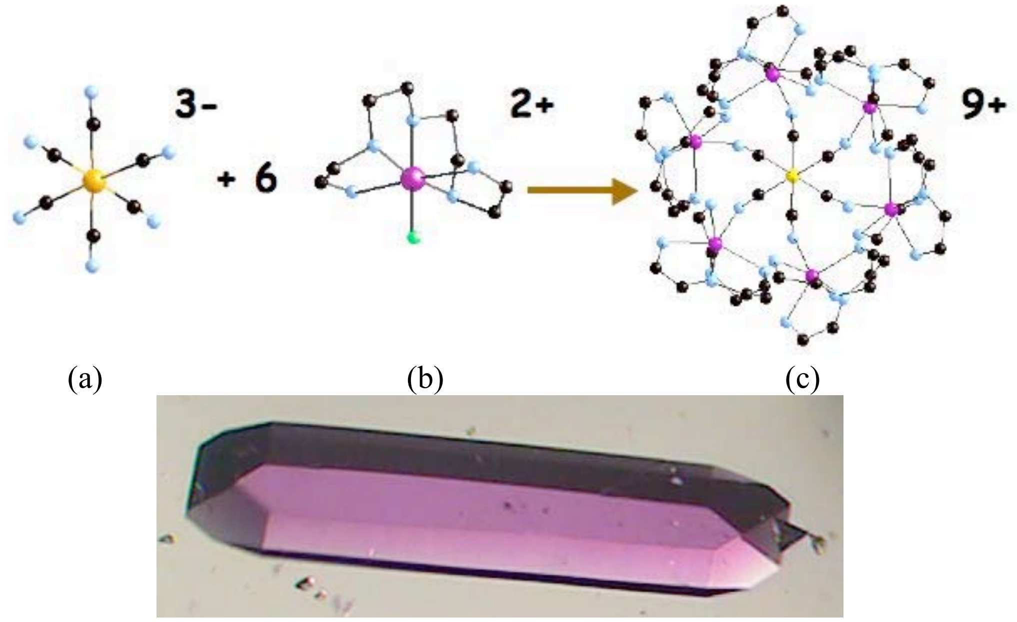


(a) (b) (c) (d)

Figure 34: (a) Crystals of $K_3[Cr(III)(CN)_6]$; (b-d) Electronic structure of the octahedral complex $[Cr(III)(CN)_6]^{3-}$: (b) ball and stick representation; (c) electronic configuration, spin S=3/2; (d) the d singly occupied orbital around the Cr(III) ion is very delocalized to the cyanide ions.

How to obtain molecules with high spin?

We have to combine the chemical strategy (complexes comprising of many metals, or polynuclear: Figure 35), spin strategy (how to combine the spins *a priori*? Figure 36), and orbital strategy (to carry out the desired interactions).



(a) (b) (c)

(d)

Figure 35: Chemical strategy: using acid-base reactions to build complex molecules from simple precursors $[Cr(III)(CN)_6]^{3-}$, spin 3/2 (a) and ML^{2+} (variable spin) (b) to give a spherical molecule $[Cr(III)(CN\text{-}ML)_6]^{9+}$, in summary CrM_6 (c) and the beautiful single crystal in shown in (d) [Courtesy V. Marvaud, C. Guyard-Duhayon].

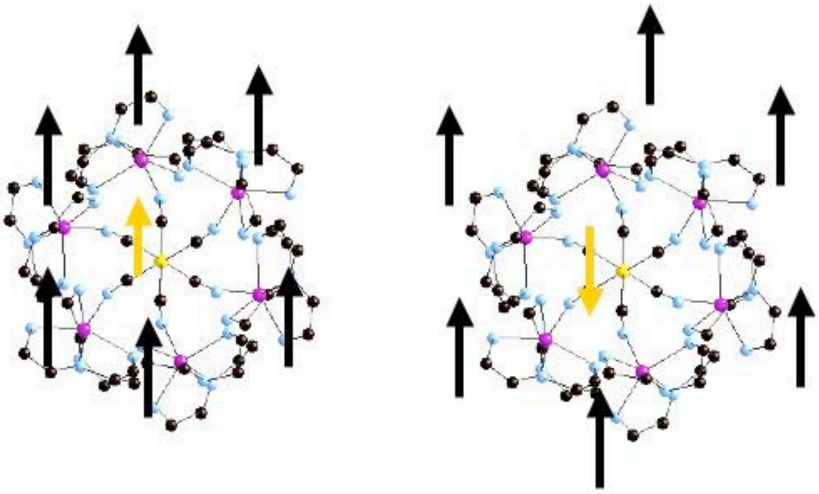


Figure 36: Spin strategy: the interaction can be ferromagnetic and all the spins are added (S_A+S_B) or antiferromagnetic and the spins are subtracted (S_A-S_B). In this last case, when ($S_A \neq S_B$), the total spin is non-zero, the system is known as *ferrimagnetic* according to the expression suggested by Louis Néel.

The chemical and spin strategies are supplemented by the orbital strategy: orthogonality creates ferromagnetism; overlapping gives rise to antiferromagnetism. Without going into detail, if the M(II) ion in a CrM_6 complex is nickel(II) (spin 1), the chromium and nickel orbitals are orthogonal and the spin of the complex becomes S= 15/2 = 6x1 + 3/2. If the metal is manganese(II) (spin 5/2), three chromium and manganese orbitals overlap causing the metals to interact antiferromagnetically. The complex is *ferrimagnetic* and the spin of the complex, at low temperature, becomes S= 27/2 = 6x5/2 - 3/2. S=15/2 or 27/2 are values which do not exist in the periodic classification… where the maximum is 7/2 for the gadolinium(III) ion…

Towards ferro- and ferri-magnets based on molecular precursors

Extending the strategy used for the molecule, it should be possible to obtain solids showing magnetic order at a temperature as high as possible (highest Curie temperature). Louis Néel, French physicist and Nobel laureate, proposed that the Curie temperature, T_C defined previously was proportional to the number of magnetic neighbours, z and the constant absolute value of coupling $|J|$, $T_C \propto z\,|J|$.

Prussian blue, highlighted for the first time as a pigment in 1704 by a draper from Berlin by the name Diesbach, is often regarded as the first known compound of coordination chemistry. It has a cubic structure, it comprises iron(II) and iron (III) ions, *i.e.* two different oxidation states. It is an intense blue compound with “mixed valence”. It is prepared today as shown in the Figure 37.

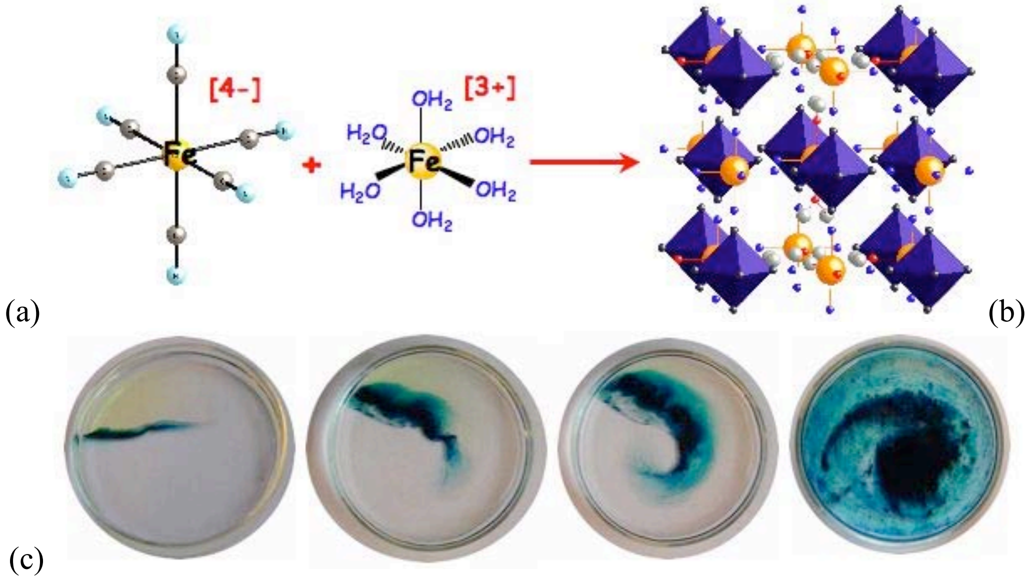
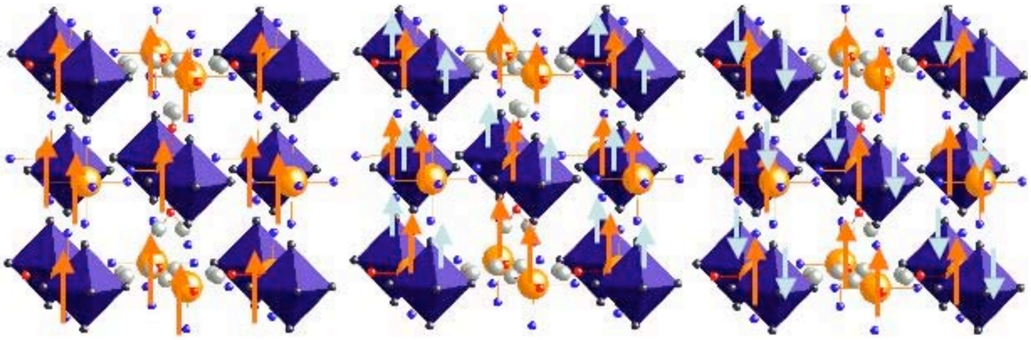


Figure 37: Formation of Prussian blue: (a) chemical reaction; (b) Structure; the blue octahedrons are the $[Fe(II)(CN)_6]^{4-}$ ions and the yellow spheres are the iron(III) ions; (c) progressive precipitation in a Petri dish, crystals of potassium ferrocyanide and iron(III) chloride placed on opposite sides of the dish, water is then added. The precipitate is formed where the solutions come into contact by convection.

Prussian blue is the neutral compound $[Fe(III)_4[Fe(II)(CN)_6]_3]$ containing three ferrocyanide, $[Fe(II)(CN)_6]^{4-}$, and four iron(III) ions. As can be seen in Figure 37, it is a cubic structure with ferrocyanide located on the corners and the centre of the faces and iron(III) ions in the middle of each edge. However, some of the sites corresponding to the ferrocyanide are vacant and are filled by water molecules which bond to the iron(III) ions. These vacancies are very important for the properties. Since 1704, Prussian blue has had beautiful career as a pigment in paint and elsewhere. One can illustrate this aspect of the chemistry by carrying out an experiment on cyanotypes. A photographic paper impregnated with ferric oxalate, $[Fe(III)(C_2O_4)_3]^{3-}$, is covered with a negative of the image to reproduce and is irradiated with white light. At the irradiated places, an internal redox (reduction-oxidation) reaction occurs which transforms iron(III) into iron(II) and oxalate into carbon dioxide. By reacting potassium ferricyanide, $K_3[Fe(III)(CN)_6]$, with the iron(II) formed during the irradiation, one reveals the latent image (Figure 38). Prussian blue is formed only at the places exposed to light.

Figure 38: Preparation of a cyanotype reproducing a photograph of Pierre and Marie Curie on their wedding day (original provided by Curie museum, Paris): irradiation of the photographic paper, development baths, and production of the image.

The magnetic properties of this compound are less exciting, it is a ferromagnet at the very low temperature of 5.6 Kelvin. One of the interesting things about Prussian blue is that it has a simple, cubic structure. Beyond its rigid appearance, it is, in fact, very flexible chemically: one can replace the iron(II) and iron(III) ions almost at will to obtain a great family of analogues with very diverse properties. It is this flexibility which enabled us to choose appropriate pairs of transition metals to create increasingly stronger ferromagnetic and antiferromagnetic interactions between metal neighbours (Figure 39). During this process we obtained an analogue - a vanadium(II) chromicyanide(III) complex whose Curie temperature is higher than the ambient temperature (Figure 40).



(a) (b) (c)

Figure 39: Orientation of the spins in Prussian blue analogues in the magnetically ordered phase: (a) Prussian blue itself below 5.6K; (b) ferromagnetic analogue: all the spins are parallel; (c) ferrimagnetic analogue: the spins of the closest neighbors are antiparallel. If these spins are different, the total spin is non zero.

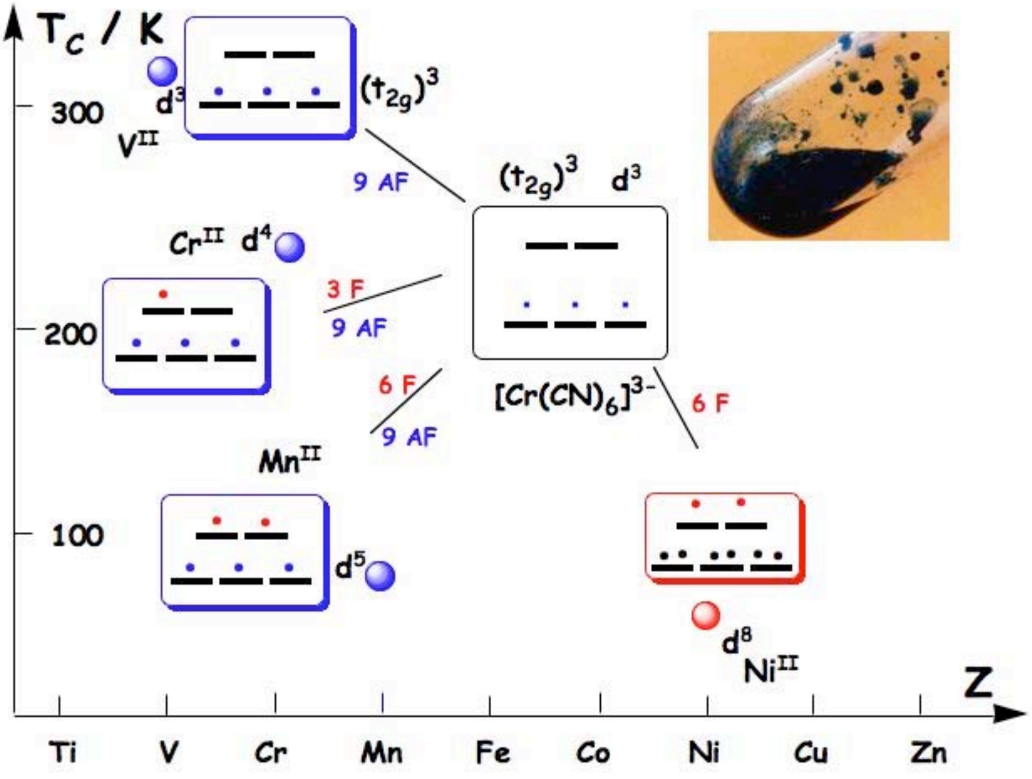
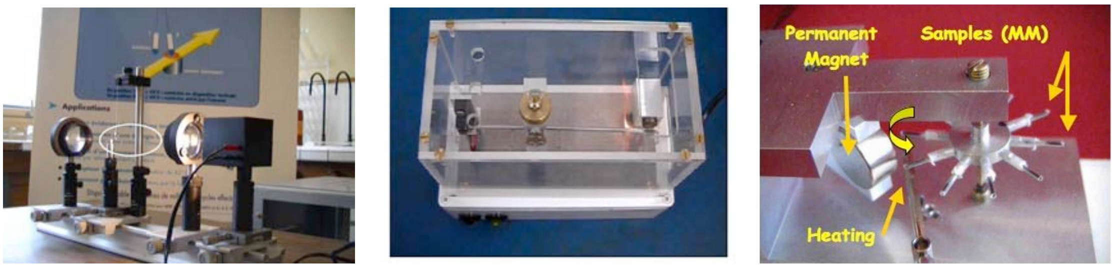


Figure 40: Diagram showing magnetic analogues of Prussian blue of the type $[\mathrm{A(II)}_4[\mathrm{Cr(III)(CN)}_6]_{8/3}$ (where A(II) is a paramagnetic metal ion) as a function of the atomic number Z of A(II) and the Curie temperature T_C, along with a diagrammatic analysis of the competing magnetic interactions (F, ferromagnetic, AF, antiferromagnetic). The derivative $[\mathrm{V(II)}_4[\mathrm{Cr(III)(CN)}_6]_{8/3}]\bullet n\mathrm{H_2O}$ (VCr), is ferrimagnetic at room temperature and is a transparent deep blue of low density (as shown in insert).

As seen previously with the complexes exhibiting spin crossover, one can use the new Prussian blue analogues for a range of applications. Three demonstrations of applications can be seen Figure 41, conceived and carried out in collaboration with Gerard Keller (UFR of pharmacy, Université Paris-Sud, Chatenay-Malabry) and F. Tournilhac (ESPCI). In the three cases, the system moves from an ordered ferrimagnetic phase to the disordered paramagnetic phase at a temperature close to ambient (42ºC). In the cases of (a) and (c), the source of energy is light (free with the sun) and the heat sink is the atmosphere. In the case (b), it is the atmosphere which is probed through opening and closing of an electric circuit.

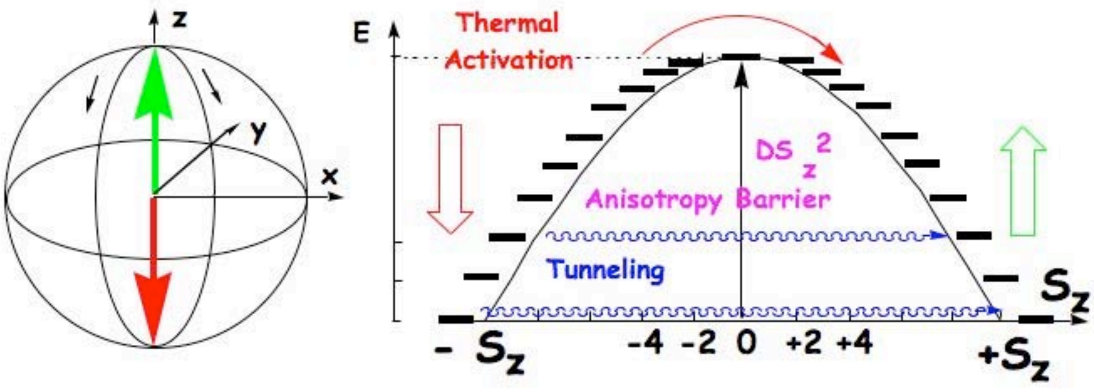


(a) (b) (c)

Figure 41: Three devices using the properties of molecular magnets with precursor VCr, with Curie temperature close to ambient: (a) an oscillating, thermodynamic machine which tranforms light energy into mechanical energy; (b) magnetic switch and thermal probe; (c) revolving magnet.

Let's go back to the isolated molecule and welcome the single molecule magnet

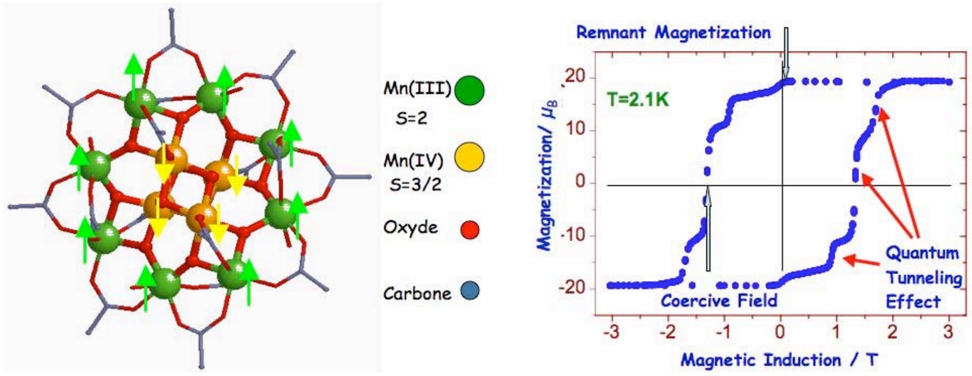
Another field that has received a lot of attention recently is that of *single molecule magnets*. The question here is how to obtain a solid that is magnetically ordered at long distances WITHOUT interaction between the molecules. Figure 42 summarizes how this is possible. The anisotropic (directionally dependent) barrier, which enables the magnetic moment of a molecule to remain in a given direction (for example, for keeping information) is of purely molecular origin. Once directed in a direction, the magnetization of the molecular solid relaxes very slowly either by thermal action, above the barrier, or by "tunnelling effect" through the anisotropic barrier. This is another of the wonders of quantum mechanics, to be able to cross obstacles without having to jump them.



(a) (b)

Figure 42: (a) inversion of magnetization in a system of axial anisotropy; only the orientations along the z axis are favoured, straight up (green) or down (red); (b) a quantum system of high spin, S, with a negative constant of anisotropy, D results in an anisotropic barrier of value DS^2: the inversion of magnetization can be achieved either by heating (most common) or by the tunnel effect (see Figure 43b).

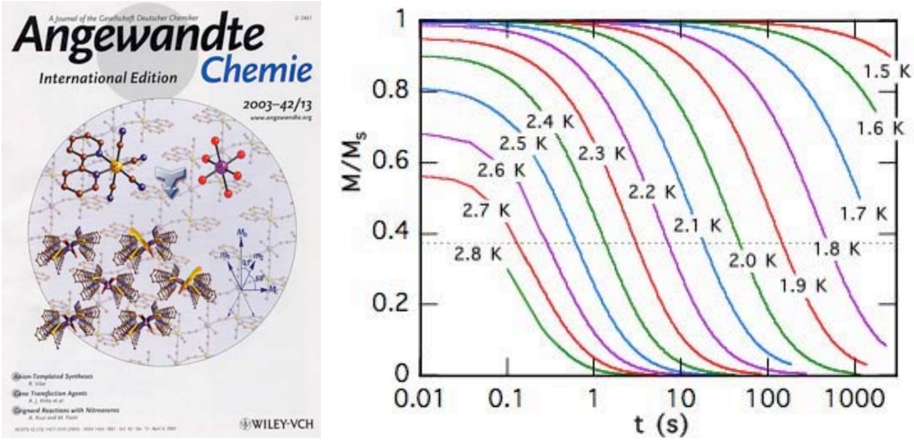
The first molecule in which the quantum tunnelling phenomenon was observed was synthesized in Wroclaw (Poland) by a chemist named Lis. It is illustrated in Figure 43a. The physicists gave it the nickname “Mn12”. The molecule indeed consists of 12 manganese ions, eight Mn(III) ions and four Mn(IV) ions, bound by oxide and acetate ions, which interact to form a S=10 spin ground state with a large anisotropic barrier (approximately 70K). The curve of magnetization according to the field, recorded at a temperature of 2 Kelvin is very remarkable (Figure 43b): it shows that the molecular crystal of Mn12 behaves like a traditional hard magnet, with strong remnant magnetism and a strong coercive field, and at same time the crystal behaves like a quantum system. At certain values of the magnetic field, the curve shows regularly spaced staircase formations which are the signature of the magnetic quantum tunnelling effect. This effect was first observed in 1993 by several teams of researchers, including that of Dante Gatteschi (University of Florence) who provided the next figure.



(a) (b)

Figure 43: (a) Structure of the molecule “Mn12” and a diagram of its spin structure (. (b) Hysteresis loop of “Mn12” showing both traditional and quantum character (communication from D. Gatteschi and R. Sessoli).

Since this date, many systems have been obtained which present the properties of slow relaxation of magnetization. The curve in Figure 44b (obtained on a very sensitive magnetometer, a microSQUID, by W. Wernsdorfer of the Institute Louis Néel in Grenoble) shows the slow relaxation that varies with temperature of a chain-magnet synthesized by R. Lescouëzec (Universitad of Valencia and Université Pierre and Marie Curie).



(a) (b)

Figure 44: The cover of a European scientific journal announcing the appearance of a new "chain-magnet". (b) Slow relaxation of the magnetization of this "chain-magnet" according to temperature (R.Lescouëzec, Mr. Julve, W. Wernsdorfer).

These systems open a new way towards high density magnetic information storage: it indeed becomes possible to dream of anisotropic molecular systems with high spin, assembled from the bottom or "bottom up" from small molecular precursors, on which it would be possible to store information on a SINGLE molecule, as the diagram in Figure 45 illustrates. The challenge is formidable but provides a remarkable field for synthetic chemists, quantum physicists and engineers to work together in synergy.

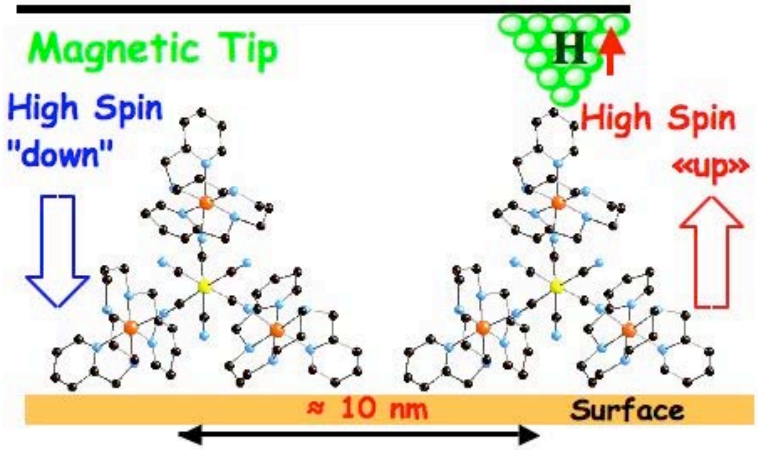


Figure 45: A marvellous dream: the storage of magnetic information on a molecule, the ultimate density of information possible. A layer of anisotropic molecules with high spin cooled within a magnetic field align their magnetic moments along the direction of the field (to the bottom, in blue). A magnetic point approaches one of the molecules and, using a very weak applied field, reverses the magnetization of only one molecule: a challenge for chemists, physicists and engineers, illustrated with a diagram of a real molecule "CrNi3"… (synthesized by Valerie Marvaud, Université Pierre and Marie Curie).

The marvellous future

Here we arrive at the end of this short incursion into the world of molecular spins, we have passed from the quantum world to the macroscopic one, seen the application of the theory, and taken the rigorous formula to the dream. It is a field continually under development which is interested not only in small, with "nano" but also with the complex. At a time when a Japanese Nobel laureate in Chemistry affirms that the synthesis of any molecule is now within reach of the chemist, the challenge is to conceive and synthesise increasingly complex systems, to meet new needs. These systems are not required to have only one property or function, but several functions: it is the world of multipurpose materials. These functions can exist alongside each other (magnetism and transparency) or they can interact with each other to create and highlight new properties. This is what occurs in the chiral magnets seen in Figure 46. These magnets are built around one of the chiral molecules we examined in Figure 25, with metal ions chosen similarly to the analogues of the Prussian blue. Here, the bridge between the ions is the oxalate, the simplest of organic dicarboxylic acids $[C_2O_4]^{2-}$. As for the chirality, there are right magnets and left magnets, as controlled by the chemist…

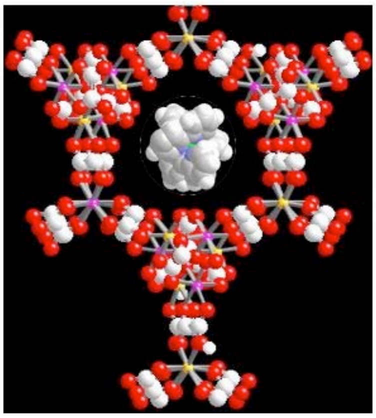
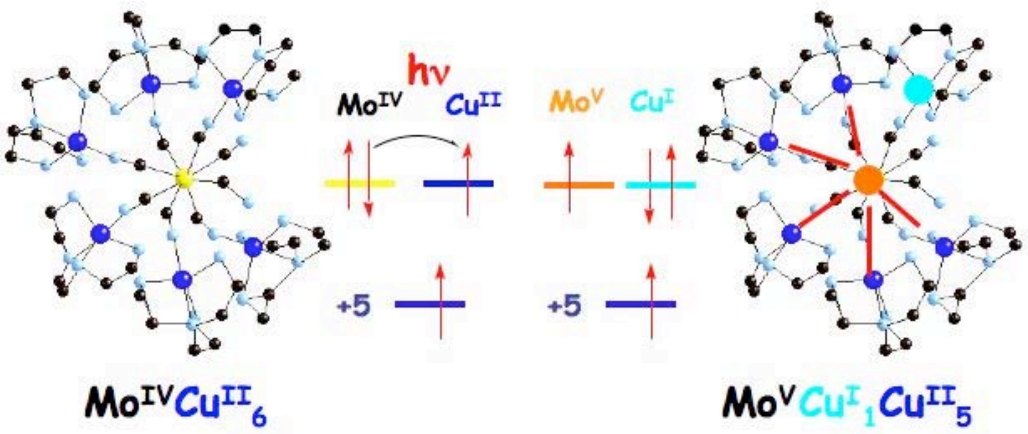


Figure 46: Chiral magnet (optically active): a three-dimensional bimetallic network with bridging oxalate rolled up around a chiral precursor (F. Pointillart, C. Train, Mr. Gruselle). The simultaneous presence of the magnetic properties and chirality and the interaction between the two creates a third property.

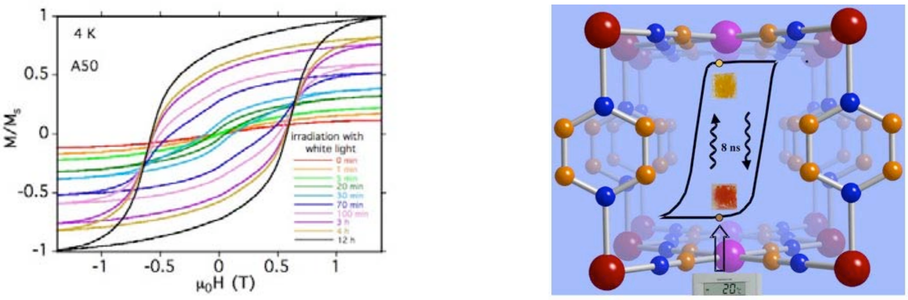
Amongst the many fields of application for molecular magnets, we finish (unfortunately without experiments for the while …) by showing how irradiation by light can change or even create magnetic properties: molecular switching leading to a high spin state (Figure 46), formation of a magnet (Figure 47a) and fast switching in a spin crossover system at room temperature (Figure 47b).



(a) Six spins S=1/2 isolated

(b) Creation of spin S=3

Figure 47: (a) An electronic transition transfers an electron from one metal atom to another in a $MoCu_6$ complex and (b) “turns on” exchange interactions (in red) resulting in an S=3 spin state (J.M. Herrera, V. Marvaud).



(a) (b)

Figure 48: Two recent photomagnetic systems: (a) a paramagnetic cobalt- and iron-based Prussian blue analogue is transformed into a magnet by light (A. Bleuzen, W. Wernsdorfer); (b) light allows a very fast exchange between two magnetic states at ambient temperature (A. Bousseksou).

We hope we have shown that the world of magnetic molecules provides some good examples for better understanding, and even demystifying, magnetism and its applications. We would like to have also convinced you that the world of molecular magnetism holds considerable potential for the production of new magnetic objects. These new objects, with foreseeable and flexible properties - beautiful, light, soluble, and easy to shape - will some day take a place amongst the vast amount of useful materials in our everyday life.

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