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BASIC INTERACTIONS IN CONDENSED MATTER MAGNETISM: QUALITATIVE ACCOUNT OF SELECTED TOPICS

Microscopic mechanisms of magnetic interactions

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A qualitative insight is given of some of the basic interactions at the origin of the magnetic behaviours observed in condensed matter, followed by brief discussions of ground states and excitations emerging from these interactions.

INTRODUCTION

A consistent account of the various aspects of the field of condensed matter magnetism is clearly illusory: the word " condensed matter magnetism" transposes to a wide spectrum of investigations that may range from those typical of applied material science to those concerned with quantum many body phenomena. What might be expected is at most an informal point of view on a few, necessarily incomplete and arbitrarily chosen themes. Catching a glimpse of the diversity of the field was however quite appealing. Attempt is therefore first made to enumerate in an eclectic way, a few aspects of applied magnetism as well as themes of fundamental interest. A qualitative insight of the most relevant microscopic interactions at the origin of the magnetic phenomena is then given. Emphasis is placed on the physical origin and not on the very detailed features of the different mechanism. Although now not surprising, a newcomer in the field will observe that the ultimate origin of these interactions refers essentially to the electric Coulomb interaction. A few outcomes of the described interactions are finally discussed, considering essentially the most familiar magnetic behaviours of ferromagnetism and antiferromagnetism. Since the variety of possible and observed magnetic phenomena is overwhelming, no exhaustive overview could be attempted. We conclude by pointing out the importance of the experimental means of investigation. A poor and very incomplete set of references, mainly reviews or monographs, will be mentioned. The original literature on the field is rather abstruse and so vast that it could not be reported here in a satisfactory way.

CONDENSED MATTER MAGNETISM: A FIELD OF A WIDE DIVERSITY

Although the power of a magnet to attract iron appears to be known in the old Egypt and Summer civilisations, no relevant applications had existed until this century, if we except the mariner's compass, most likely invented during the Zhou's dynasty in China. Applications emerged and developed when new discoveries and new insights were made possible by investigations at a more fundamental level. An understanding of the basic microscopic mechanisms at the origin of the different magnetic behaviours of the materials was in that respect of utmost importance. Consistent theoretical frameworks could be built up, that allowed to examine the different outcomes of given microscopic processes and to incorporate predictions.

Applied magnetism: the need for an understanding

A magnetic material may raise an interest for technical applications in a lot of ways according to its properties.

As a **hard magnet** (hard to magnetise or to demagnetise) [1] it may provide a constant induction field in a given volume of space, without the continuous expenditure of electric power or the generation of heat inherent to a field produced by a current in a conductor. A hard magnet is said be made into a permanent magnet when stability against the demagnetising action of stray fields, including its own, is achieved. It is then fundamentally an energy-storage device: once the magnet is magnetised, its energy is always available for use and is not drained away by a repeated use like the energy of a battery, because the magnet do not work and no net energy is transferred to the surrounding. The qualifying factors of intrinsic origin for a hard magnet are: a large spontaneous magnetisation and a large magnetocrystalline anisotropy in the widest range of temperature. As the prerequisites of any improvement, that calls for a deep understanding of the microscopic mechanism of the interactions from which these quantities will emerge, i.e. the **spin exchange** interactions and the **crystalline electric field** effects. A hard magnet is made a permanent magnet by another important property: the coercivity. It accounts for the fact that although a large magnetocrystalline anisotropy is existing to block up the rotation of the magnetisation, magnetic domains with reversed magnetisation direction are nucleated at the structural defects and a subsequent move of the domain walls may occur. As a result, a much lower inverse magnetic field than that expected to overcome the intrinsic magnetocrystalline anisotropy is sufficient for the reversal of the whole magnetisation. The coercivity is an extrinsic property associated with the microstructure of the material and involve additional interactions that become primordial at this scale: the long range **magnetic dipole-dipole** interaction.

As a **soft magnet** (easy to magnetise or to demagnetise) [2] a magnetic material may help to canalise an induction field in the required geometry of a magnetic device. It may as well help to detect an induction field in a given volume of space or else to screen parasitic induction fields, eventually at high frequency in the case of weakly dissipating materials. As for a hard magnet, the largest spontaneous magnetisation is once more requested in the widest range of temperature but now the magnetocrystalline anisotropy should be the lowest in order to canalise the highest induction flux in the material without losses. This calls again for a deep understanding of the **spin exchange** interactions and of the **crystalline electric field** effects. Used as a screen with respect to time dependent parasitic fields, a soft magnet should in addition not contains defects of the size of the characteristic width of the domain walls to avoid the pinning of these walls at the defects. It should moreover have a large resistivity to minimise the dissipating effects associated with the electric current induced by the move of the domain walls. Also highly relevant to consider are the **magnetoelastic interactions,** which should be the weakest to avoid the strain induced pinning of the domain walls.

The applications based on either of the basic features of hard and soft magnets form already a list so long, as to astonish the uninitiated if set into details. Hard magnets are used in a variety of electromechanical devices, e.g. in ac-current motors with electronic commutation, in electric devices as actuators for linear or turning movements e.g. in disk heads, in electroacoustic applications, in galvanometric instruments, ... as well as in all instances where magnetic forces at the macroscopic scale are involved, e.g. as with magnetic bugs, levitating vehicles, magnetic brakes,.... As components of micro-motors or micro-actuators, they find now more and more medical applications. We shall finally mention that they are basic building blocks of ondulars and wigglers in synchrotron radiation sources. The use of soft magnets is even more wide and not possible to enumerate in few sentences. We shall simply recall that they are basic building blocks of magnetic circuits, of electromagnets, of magnetic sensors and of electrotechnical devices such as transformers, rotating engines,... Soft magnets have also high frequency applications e.g. in microelectronics, cellular phones,... The word market of hard magnets was evaluated at 6 Giga Euro in 1995 and was found ever since to increase by more than 10% every year. That for soft magnets went up to about 10 Giga Euro in 1995. These estimates excluded the market of magnetic materials used in all audio/video and computed-related applications i.e. disk, dvd, magnetic tapes, heads for disk drives,... which by itself was found to reach 11 Giga Euro in 1995. A deep understanding of **Magnetooptic** effects [3] is here clearly of relevance concerning e.g. write in and read out processes in magnetic recording. Current trends in this field of applications are directed towards materials of reduced dimensionality, i.e. **thin films** [4], with the aim to promote novel applications such as magnetoresistive heads for disk drives, spin-switch or spin transistor, integration of magnetic and semi-conductor technology,.... All these possibilities emerged thanks to newly discovered phenomena such as giant magnetoresistance. Active investigations are currently directed towards getting a detailed insight of the effect, which involves a spin dependent scattering of electrons at the interfaces and/or in the bulk of the layers. Another behaviour, opening possibilities of spin electronics and new magnetic microscopy, is that of the half metals, defined as showing a gap in the band structure for a definite spin state.

The applications involving other magnetic properties of materials are as numerous. We may call to mind e.g. the **invar** alloys [5], useful for high precision mechanical devices in an environment of changing temperature e.g. telescope, supports of integrated circuits, nuclear reactors,...: the invar phenomenon accounts for a vanishingly small thermal expansion of a material over a wide range of temperature, which arises from a thermal contraction of magnetic origin compensating the usual phonon induced thermal expansion. A magnetic material may, more generally, transform a non magnetic signal e.g. mechanical, optical,... into that of an induction flux and conversely, enlarging considerably the field of applications in terms of sensors, actuators and more widely transducers. Among the applications using the **magneto-elastic** properties of materials [6] we find the sonars, the hydrophones, the sensors of position... New possibilities are continuously emerging as the increase of the performance of given magnetic properties proceeds. As an example, the magnetostriction of some compounds (Terfenol-D,...) allows now to conceive novel motors to displace heavy bodies at very low speed or novel magnetocardiographers where the probe, instead of an expensive SQUID detector, is a magnetostrictive film deposited on an optical fibber. A deep understanding of the **magneto-elastic interactions** is here of course necessary. Arising from the strain derivatives of the crystalline electric field, as a one-ion effect, eventually leading to a two-ions interaction, from a distance dependent exchange interaction or else from a local moment formation or change, these interactions may lead to isotropic as well as anisotropic macroscopic deformations. Among the different effects, it is often customary to distinguish more particularly the magnetovolume effects i.e. the spontaneous deformation at a magnetic ordering, the positive and negative Joule magnetostriction i.e. the field-induced parallel and perpendicular deformation of the material and the thermal expansion or contraction of magnetic origin [5, 6].

Although now widespread, the technical potentialities of applied magnetism are still far from being on the end. Exciting long-term perspectives exist, forming the basis of new incentives. As a matter of fact the diversity of the technical applications are answerable not only to given magnetic behaviours but also to the variety of the behaviours observed in the different magnetic materials and, often it is the improvement in the material synthesis that open new possibilities. A fascinating example is that of **molecular materials** showing the low spin to high spin transition [7]: a bistability that allow to materialise electronic functions (switching, amplification, information storage, signal processing,...) at the level of molecules or of a small assembly of molecules. We shall end here this rather sketchy overview of applied magnetism.

Magnetic Behaviours (the source of formal concepts)

A number of magnetic behaviours emerge from the basic magnetic interactions which a priori are not of any practical use but which are as important to investigate. A first reason is simply that these behaviours exist and we have to find out why they set up. Another reason is that by no means we may assume that nothing interesting could be learned from them. Of fundamental interest, the analysis of these behaviours are useful to check the internal consistency of given theoretical methods and may generate novel concepts that allow to build up unifying pictures of magnetism or to make a fruitful analogy with other fields of physics.

Accounting for all the different magnetic behaviours is of course not possible, except a few, simply because the set of all the possibilities is overwhelming. Among the most familiar and first discovered we have the **diamagnetism**, the **paramagnetism** the **ferromagnetism** and the **antiferromagnetism**. As other magnetic magnetic behaviours, we may quote the **ferrimagnetism**, the **helimagnetism**, the **non collinear**, **incommensurate**, **multi-propagating** or **multi-axial** magnetism,... Various transitions are associated to these different variants of magnetic orderings either on varying the temperature or on applying a magnetic field such as the spin-flip transition i.e. the field induced reversal of a sub-lattice of spins, the spin-flop transition i.e. the field induced reversal of the antiferromagnetic direction, the spin-slip transition i.e. the field-induced slippage of propagation vectors,... leading to an apparently unending list of possible magnetic behaviours and to phase diagram that to be explained requires to consider not only the **spin exchange** interactions but also the **crystalline electric field** effects [8], eventually with pair effects favouring quadrupolar orbital ordering, as well as the **magnetoelastic interactions** [9].

Among less familiar magnetic behaviours we could quote e.g. the **speromagnetism**, a state of frozen isotropic random distribution of local moments, observed in materials with a random-looking mixture of ferromagnetic and antiferromagnetic interactions and/or a random distribution of local magnetic anisotropy axes. Other variants of magnetism observed in these materials are the **asperomagnetism**, a state of frozen anisotropic random distribution of local moments, or the **sperimagnetism**, a state of frozen random distribution of local moments of different amplitude. When a sharp cusp in the ac magnetic susceptibility of these materials is observed at a given temperature, a **spin glass** state is empirically said to set up. Attempts at understanding the spin glasses [10] have led to intense experimental and theoretical investigations involving new concepts, e.g. magnetic frustration, replica symmetry and ergodicity breaking, ultra-metric state space,..., and developing towards models of neural networks. A deep insight is now achieved but open questions still remain, concerning e.g. the ground state, unique or not, or the spin dynamics at finite temperature, spin droplets flips or hierarchical spin flips.

At first invented for spin glasses, the concept of **frustration** was latter found to contain much wider physics. A frustration may come out without structural disorder in crystalline materials. A distinction is then made between the frustration associated with the spatial oscillation of the exchange interactions and the geometric frustration of antiferromagnetic interactions defined as the intrinsic impossibility to build a consistent spin configuration of opposite orientations, due to exchange loops involving odd numbers of spins. A geometrical frustration always leads to degenerate manifolds of spin configurations differing from each other by local spin transformations. A basic outcome is that short wavelength spin fluctuations are enhanced and the formation of local spin singlets is favoured. A fluctuation-induced ordering of spins may set up when there exist spin configurations of lowest zero-point fluctuation energy or, at finite temperature, of lowest fluctuation free energy. Otherwise an entropy of discrete ground state degeneracy, scaling with the number of spins, persist and novel magnetic phases may be induced, as a result of subtle microscopic processes. A wide number of possibilities are foreseen, in between different variants of dimmer and valence bond states corresponding to different linear combinations of spin singlet bond configurations on the lattice, flux phase states characterised by a non zero circulating spin current around closed loops, multi-spin orders associated with a breaking of solely space rotational invariance (nematic spin liquid) or with a breaking of solely time reversal and parity invariance (chiral spin liquid), states with a spin pairing non local in time,... All of these states describe a spin "rigidity" in the absence of a moment on a site and, as such are often indifferently termed as quantum **spin liquids** [11]. Another expected outcome of the geometrical frustration is that it might give birth to novel topological defects associated with a non-Abelian homotopy group, that should lead to new classes of transitions, generalising the Kosterlitz-Thouless vortices binding transition of spin rotators in 2D systems. Crossing and interaction of the topological defects are expected to generate a **topological glassy** phase but basically different from canonical spin glass.

We cannot at this point, not recall the long-standing problem of **phase transitions** and **critical phenomena** [12], the understanding of which could be considered as one of the so far best achievements of theoretical condensed matter physics. Conceptual approaches were formalised gradually, starting with the Landau theory of phase transitions where the vital importance of symmetry breaking was recognised, the concept of order parameter clearly defined and the non existence of transitions of order higher than two demonstrated. Of course not all the transitions are described within the same framework - examples are the liquid-gas transition, the percolation in random systems, etc. which involves specific approaches. A fascinating discovery was the universality of the behaviour of the thermodynamical variables in the vicinity of the ordering temperature, described by **critical exponents** depending upon only the space dimensionality and the number of degrees of freedom of the order parameter. A deeper insight of these critical exponents was made possible thanks to the concept of **scaling** and the idea of **renormalisation group** [13] borrowed from the field theory. All these steps in the understanding of the critical phenomena greatly benefited from the phase transitions observed in the magnetic systems, thanks to extremely pure and magnetically well-characterised samples which allowed accurate experimental investigations as well as to the insights provided by the theoretical analysis of various models. After all, the field of magnetism was essential in providing the exact solution of a many-body problem: the Onsager's solution of the 2D Ising model, which was certainly of great help in checking the numerical estimates of critical exponents. Initially strongly inspired by the models of magnetism, another example is the spin-1/2 quantum chain solved by the Bethe ansatz, the field of **exactly solvable models** [14] evolves at present as a quasi independent branch of mathematical physics with a high degree of sophistication, extending and developing variants of the Bethe ansatz method or finding out new methods such as the quantum inverse scattering method, methods based on the use of Witten's supersymmetric quantum mechanics,... to apply to other systems such as the Hubbard chain or the Kondo problem, or else discussing the existence or the non-existence a priori of an exact solution, formulated through relations such as the Yang-Baxter equations, the Zamolodchikov equations or through no-go theorems. Attempts are of course also made to map magnetic problems into problems of other fields of physics that could be fruitful for magnetism. It was thus proved that the 2D Ising model in the continuum limit, i.e. in the vicinity of the phase transition, can be mapped to the Dirac equation of a free fermion, by constructing a variable $\chi=\sigma\mu$, where σ is the order parameter and μ a disorder variable, dual to σ, defined at the end points of dislocation lines. As from an appropriate generalisation of the μ-variables, it was then proved that the 3D Ising model in the continuum limit can be reduced to an exactly solvable model, i.e. the Neveu-Schwarz-Ramond supersymmetric string, giving hope to find the critical exponents of the 3D Ising model. Unfortunately the problem awaits yet to be concretely solved.

We shall end this eclectic inventory of the fundamental aspects of condensed matter magnetism, far from being complete, by invoking the **quantum tunnelling** of magnetisation in mesoscopic systems[15], as an example of how a theme of fundamental interest naturally develops as soon as technical progresses, here in nano-technology and in the synthesis of new clustered materials, allow experimentally to investigate it. Although the idea of tunnelling between collective spin states separated by an energy barrier was around for a time, its adequate formulation taking account the effects of different **environments** (phonons, nuclear spins,...) is quite recent: the quantum resonance i.e. the oscillation across an energy barrier is found to be almost always destroyed, while the quantum tunnelling i.e. escape out of a metastable state and, above all, the quantum relaxation i.e. the incoherent tunnelling assisted by the environment can be observed in rather large magnetic clusters. An interesting outcome of the functional integral treatment of the problem was the discovery of a **topological term** in the magnetic action that forbids the tunnelling for half-integer mesoscopic spins, thus generalising the notion of Kramers degeneracy. A field of fundamental interest we could finally mention as an example of a so far poorly investigated one, at least experimentally, is **quantum chaos** in spin systems. A clear advantage of the spin systems is that unlike other chaotic systems, such as the Rydberg states of an atom, there is there the possibility to examine the whole spectrum of energy without the qualitative change due to an escape from a potential well, and also that, apparently, irregular behaviours might occur at low energy, including the vicinity of the ground state [16],

BASIC DYNAMIC VARIABLES AND INTERACTIONS

As to the question of what the magnetism of matter is, an answer in a few words could be: the field of (cooperative) effects of spin and orbital magnetic moments in the matter. An immediate observation is then in order: any electron has an intrinsic spin magnetic moment $\mathbf{M}_S=g\mu_B\mathbf{S}$, where g=2.0024... is the electron gyromagnetic ratio, $\mu_B=e\hbar/2m_e$ the Bohr magneton and **S** the electron spin. It may also possess an orbital magnetic moment $\mathbf{M}_L=\mu_B\mathbf{L}$, where **L** is the electron orbital angular momentum. $\mathbf{M}_L$ is associated with the stationary part of the current density generated by the electron motion in orbital space. A nucleus might similarly have a spin and/or an orbital magnetic moment but the corresponding amplitude is much weaker, being proportional to the nuclear magneton ($\mu_B/1836$). Consequently, the nuclear magnetism of a material can in general be neglected. An exception is the nuclear magnetism of He^3 [17].

Attention can be called here upon some misconceptions found in the literature, which are worthwhile to correct from a pure epistemological point of view. A spin is essentially a quantum mechanical variable and not a specific relativistic variable as often believed and inferred from the Dirac equation. As from general invariance principles using the Wigner theorem for transformations preserving the scalar product of an Hilbert space, self-adjoint operators can be built that transposes to dynamical variables. Assuming Galilean invariance the following operators are generated H (Hamiltonian), **X** (position), **P** (momentum) and **J** (angular momentum). An operator **L** (orbital angular momentum) can be buit as **X** x **P** which has the same properties as **J**, but there are no reasons to assume that the difference **S=J-L**, which is then no more a function of orbital variables should cancel. S, L, J can take integer values as dictated by invariance under the special orthogonal SO(3) group while only S and therefore J but not L can take half-odd integer values thanks to the special unitary SU(2) group universal covering of SO(3). The SU(2) group is not simply connexe and implies that the spinor i.e. the wavefunction of an half-odd integer spin is not invariant under a 2π rotation but a 4π rotation. At processing further and introducing an interaction with an electromagnetic field the surprising result is found that the intrinsic magnetic moment M of an elementary particle with mass μ and charge q is always $M=q/2\mu$ irrespective of its spin S, i.e. the gyromagnetic ratio is $g=1/S$. It is by the quantification of the field that radiative corrections arise correcting g as $2+f(\alpha)$ where $f(\alpha)$ is a function of the fine structure constant $\alpha=\hbar/m_e c$, leading e.g. to g=2.0024... for an electron. g for a proton is measured equal to 2.79275 and for a neutron, which has no net charge, equal to −1.91346, indicating that these are not elementary particles.

A final point of epistemological interest that we shall mention is that condensed mater magnetism is intrinsically quantum mechanical and that classical magnetism cannot exist, as stated by the **Van Leeuwen's theorem**. Its proof is quite simple: the Hamiltonian H of a system of particles of charge q_j and mass μ_j in a magnetic field $\mathbf{B} = \nabla \times \mathbf{A}$ is:

$$H = \sum_j \frac{1}{2\mu_j}\left\{p_j - q_j A(r_j)\right\}^2 + U(r_j)$$

to which will correspond the partition function $Z = \int \Pi d\mathbf{r}_j \int \Pi d\mathbf{p}_j \exp(-H/k_B T)$. At making the variable change $\mathbf{p}_j \longrightarrow \pi_j = \mathbf{p}_j - q_j\mathbf{A}(r_j)$ the volume element becomes $\Pi d\mathbf{r}_j\ \Pi d\pi_j$. As a result, the partition function Z and the free energy F become A-independent and thereby B-independent, so that the magnetic susceptibility always vanishes: $\chi = -\,\partial^2 F / \partial^2 F = 0$.

A magnetic behaviour of the system of electrons in a material is dictated by the way the magnetic moments of the electrons couple with each other or, with regard to the orbital part, are affected by the environments, which calls upon finding out which interactions are under the main concern. Among the most essential we have the exchange interaction, the effects of the electric field of the environment on the orbital motion of the electron and therefore on its orbital magnetic moment, the spin-orbit coupling and, as outcomes of the two formers, the magneto-elastic interactions. Other interactions exist but are in usual weaker. Among them, the interactions, within an atom or an ion, of the electrons with the scalar and vector potentials arising from the nuclear charge and current give rise to various couplings between the nuclear and electronic magnetic moments. Answerable to nuclear magnetism, these interactions are useful in probing the electron magnetism at the atomic scale [18]. Of course there are couplings with other degrees of freedom other than the magneto-elastic ones, which could also be fruitfully used to probe the magnetism, as e.g. the Faraday or Kerr effects in magnetooptics. Usually they are not relevant in fixing the magnetic states of a material. As the last but not the least, we may finally call to mind the magnetic dipole-dipole interactions. Of purely magnetic origin, these interactions are too weak and can never lead to a magnetic order at the ambient temperature. Being long ranged, decaying as r^{-3} where r stand for the distance between the magnetic moments, they become relevant at the mesoscopic level: the magnetic dipolar energy is as basic as the exchange or the magnetocrystalline anisotropy energy are for the coercivity mechanism in the magnets. We shall in the following essentially discuss the spin exchange interactions and crystalline electric field effects.

EXCHANGE INTERACTIONS

The exchange interactions are actually fictitious interactions that transposes to an effective coupling between spins arising from the electron-electron Coulomb repulsion, the electron's kinetic (delocalisation) energy and the Pauli exclusion (Fermi-Dirac statistics) associated with the indistinguishability of the electrons.

The concept of **indistinguishability** tells that, whenever, among all the possible paths contributing to the path-integral describing the dynamics of a given particle, some may intersect that describing the dynamics of another similar particle, the quantum uncertainties prohibit to keep track of the particle. Accordingly, the states of the system obtained from each other by merely interchanging the two particles must be physically equivalent. This equivalence means that the permutation operator associated with the interchange of the particles gives the same wavefunction as before the interchange, except for a possible phase change $\eta=\exp(i\theta)$. η may a priori depend on the paths used to perform an actual interchange. It turns out that it should be the same for all the paths that can be continuously deformed into one another, i.e. belonging to the same class of homotopy [19]. All paths in the three dimensional space can be deformed into one another, which implies that the initial wavefunction should be recovered after a double permutation, i.e. $\eta^2=1$. Apparently, there are then only two possibilities: the wavefunction is either symmetric with respect to the interchange ($\eta=1$), in which case the particles under concern are **bosons** or antisymmetric with respect to the interchange ($\eta=-1$), in which case the particles are **fermions** (the antisymmetry for fermions defines the **Pauli exclusion**). Any number of bosons may occupy a same quantum state while not more than one fermion can occupy a given quantum state. Consequently the statistical distribution describing the thermodynamical properties of a many-particle system will be different according to whether the particle are bosons (Bose-Einstein statistics) or fermions (fermi-Dirac statistics). If we consider now the spin of the elementary particles, we meet again a priori two possibilities: since the second quantised field associated with a particle should transform according to an irreducible representation of the proper Lorentz group

SO(3,1) in 3+1 dimensions, the spin can only be an integer or (by virtue of the SU(2) universal covering of SO(3)) an half-odd integer. A **spin-statistic theorem** has been formulated on general grounds in local quantum field theory [20], which states that the particles with an integer spin are bosons whereas the particles (such as electrons) with an half-odd integer spin are fermions and that the corresponding second quantised fields obey the equal-time commutation and anticommutation rules. At the root of this theorem is only the need to preserve causality in a theory with local interactions and the requirement of the existence of a lowest energy.

Actually other possibilities might exist. In one space dimension, the particles cannot experience their statistics since they cannot get past on each other: any statistics is then possible (an explicit way of getting fractional statistics is provided by a generalised version of the Jordan-Wigner transformation which from a fermion density on a one-dimensional lattice allows to built site operators obeying parafermion commutation rules). Exotic particles (anyons) characterised by complex exchange phase η may also exist in a two dimensional space since then the windings of paths cannot be disentangled by continuous deformation (i.e. an unambiguous (half-) winding number can be ascribed to any path) and paths with different winding numbers belong to different classes of homotopy. An interchange of anyons changes the phase η to its complex conjugate η^* and therefore, unlike the interchange of bosons or fermions, violates the parity and the time reversal symmetry. Such a possibility should not be viewed only as a mathematical curiosity, irrelevant to the real "word". A system of electrons moving on a plane, in the presence of a perpendicular magnetic field, does not have the time reversal symmetry and if the electron are polarised, in some sense the parity is also broken, leading to the fascinating properties of the quantum hall effect in its both integer and fractional aspects. A deep connection exist with the chiral spin liquids, in that the two are formalised within the Chern-Simons theory, which is the natural framework to describe the systems exhibiting fractional statistics [21, 22]. A generalisation including the three and even higher space dimension case has been anticipated assuming a non trivial topology of the configuration space of the multi-particle system (a "natural" example is the torus inherent to the periodic boundary conditions) and a topological spin-statistics theorem [23] has been formulated involving fractional spins. Fractional shifts of spin are compatible with the algebra of angular momentum if multi-valued wavefunctions, which are not representations of the permutation group but of the braid group, are allowed - this is actually not new: the SU(2) spinorial representations of SO(3) are double valued. Another approach not based on the phase change of the multi-particle wavefunction under a pair exchange but on the counting of independent multi-particle states [24] has also been proposed, generalising the Pauli exclusion and defining statistical distributions which interpolate between that of the bosons and of the fermions.

A physical interchange of electrons refers to an interchange of all its generic variables: the spin as well as the orbital variables. A multi-electronic wavefunction will then have a symmetric (resp. antisymmetric) spin component if its orbital component is antisymmetric (resp. symmetric). As a consequence, if there exist an interaction between the electrons involving solely the orbital variables and creating an unbalance in energy between the symmetric and the antisymmetric orbital wavefunctions, we shall get an energy difference in the relative orientation of the spins of the electrons, although no interactions involving these spins are taken into account: this is the origin of the exchange interactions.

Let us consider a system of two electrons. An antisymmetrical spin wavefunction may be compounded out of products of the spinors of each electron as $[\chi_\alpha(s_1)\chi_\beta(s_2)-\chi_\alpha(s_2)\chi_\beta(s_1)]/\sqrt{2}$ where s_1 and s_2 label the spin of the electrons and χ_α and χ_β are the spin up and spin down spinors. This wavefunction defines a singlet state of total spin S=0, to which a symmetric orbital wavefunction must be associated. On the other hand three symmetrical spin wavefunction may be obtained as $\chi_\alpha(s_1)\chi_\alpha(s_2)$, $[\chi_\alpha(s_1)\chi_\beta(s_2)+\chi_\alpha(s_2)\chi_\beta(s_1)]/\sqrt{2}$ and $\chi_\beta(s_1)\chi_\beta(s_2)$. They define a triplet state of total spin S=1, to which an antisymmetric orbital wavefunction must be associated. The orbital wavefunctions may be compounded out of single electron orbitals $\psi_u(\mathbf{r})$, u=a,b,.... It is then simpler to consider the case of two electrons localised about a same positive charge and take for $\psi_u(\mathbf{r})$ the complete set of orthogonal eigenfunctions associated with the sole interactions of one electron with the positive charge. In the orbital space, the singlet state will be described by a symmetrical wavefunction writing $[\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2)+\psi_a(\mathbf{r}_2)\psi_b(\mathbf{r}_1)]/\sqrt{2}$ and the triplet states will be described by an antisymmetrical wavefunction writing $[\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2)-\psi_a(\mathbf{r}_2)\psi_b(\mathbf{r}_1)]/\sqrt{2}$. The electrostatic interactions $e^2/|\mathbf{r}_1-\mathbf{r}_2|$ have different expectation values in these two states. The difference to first-order in perturbation:

$$2J_{12}(ab)=\langle V\rangle_{sing}-\langle V\rangle_{trip}=2e^2\int d\mathbf{r}_1\int d\mathbf{r}_2\ \psi^*{}_a(\mathbf{r}_1)\psi^*{}_b(\mathbf{r}_2)|\mathbf{r}_1-\mathbf{r}_2|^{-1}\psi_a(\mathbf{r}_2)\psi_b(\mathbf{r}_1),$$

may be reproduced by the imaginary interaction $-2J_{12}(ab)s_1.s_2$ acting solely in the spin space: this defines an exchange interaction. Since the electrons are assumed to be localised about a same positive charge, this **exchange interaction** is said to be **intra-atomic** and is characteristic of atoms, ions or even electrons temporarily localised about a nucleus in a metal.

Owing to the orthogonality of the single electron wavefunctions $\psi_u(\mathbf{r})$, u=a,b,..., the generalisation to a system of n>2 electrons localised about a same positive charge is performed straightaway: The exchange interactions write as the sum $-2\Sigma_{i,j<i}J_{ij}s_i.s_j$ of the bilinear coupling $J_{ij}s_i.s_j$ associated with each of the different n(n-1)/2 electron pairs (i,j) that can be formed. A second feature, associated with the orthogonality of the $\psi_u(\mathbf{r})$, u=a,b,... and the fact that the

Fourier transform of $V(\mathbf{r}_1-\mathbf{r}_2)$ is everywhere positive, is that J_{ij} is positive definite and may be interpreted as the self-energy of the charge distributions $\psi^*_a(\mathbf{r})\psi_b(\mathbf{r})$. Therefore, for any pair (a,b) of indices with $a \neq b$, the triplet state has always a lower energy than the singlet state. This is the origin of the **first Hund's rule**, which states that the ground state of an atom or an ion is a state of maximum multiplicity ($S=S\max$ where $\mathbf{S}=\Sigma_i \mathbf{s}_i$). If a=b, then the triplet state is impossible and only the singlet state exists, in which case the electrons are said to be paired. We would like finally to emphasise that there is no real justification of maintaining the electrons in definite single electron orbitals and that the electrostatic interactions induce various orbitals excitations leading to off-diagonal exchange interactions and couplings of single electron orbital moments. However the corresponding matrix elements write as integrals involving four different single electron orbitals and are then weaker than the exchange integrals J_{ij}. They give rise to the **second Hund's rule** which states that the ground state of an atom or ion is, among the states of maximum multiplicity , that with the maximum orbital moment ($L=L\max$ where $\mathbf{L}=\Sigma_i \mathbf{l}_i$).

Inter-atomic exchange interactions

If the electrons were to be distributed over different positive charges then single electron orbital wavefunctions $\psi_u(\mathbf{r})$, u=a,b,... centred on the respective positive charges should be used. One is then confronted with the non-orthogonality of these wavefunctions. In the case of the system of two electrons ranging over two positive charges, the non-orthogonality modifies the normalisation factor of the singlet and triplet orbital wavefunctions from $2^{-1/2}$ to $[2(1+R^2)]^{-1/2}$ and $[2(1-R^2)]^{-1/2}$ respectively, where $R=\int d\mathbf{r}\psi^*_a(\mathbf{r})\psi_b(\mathbf{r})$ is the overlap integral between the wavefunctions $\psi_a(\mathbf{r})$ and $\psi_b(\mathbf{r})$ centred, now, each on a different positive charge. The energy difference between the singlet and the triplet states is furthermore no longer as simple as above, since we have to take into account the additional interactions of each electron with the positive charge at which it is not localised about. The outcome is that the singlet state may turn out to be of lower energy than the triplet state, as in the hydrogen molecule. Anyway, the important point is that again a difference in energy exists between these states, which may be reproduced by an exchange interaction $-2J_{12}(ab)\mathbf{s}_1.\mathbf{s}_2$ acting solely in the spin space, where now $J_{12}(ab)$ depends on R^2 and may take a negative value. As the electrons are distributed over different positive charges the **exchange interaction** is said to be **inter-atomic** .

The non-orthogonality of the single electron wavefunctions $\psi_a(\mathbf{r})$ and $\psi_b(\mathbf{r})$ plays clearly a vital role for the inter-atomic exchange interactions. A generalisation to more complex molecules than hydrogen or solids is however delicate to perform when working with overlapping wavefunctions. Advantage could be taken of the translation symmetry of a crystal and use the Wannier functions. Unfortunately in so doing, we loose the intuitive meaning of the exchange integrals and the wrong conclusion would be made that the spin coupling is always bilinear ferromagnetic. A reason for this apparent paradox is that polar states, describing events where an electron hops on a site where another electron is already there, are incorporated in the Wannier functions by the orthogonalisation process. A rigorous approach shows that the lack of orthogonality may give rise not only to a bilinear coupling which might be antiferromagnetic but also to additional terms involving high-order rotationally invariant spin polynomials. A general formula for a crystal of hydrogenoid atoms (one electron in the open shell) is [25]:

$$-\Sigma_{i,j}J_{ij}\mathbf{P}_2(s_i,s_j) + \ldots + (-1)^{n-1}\Sigma_{i,j,\ldots,l}J_{ij\ldots l}\mathbf{P}_n(s_i,s_j,\ldots,s_l)$$

where the $J_{ij\ldots l}$ are generalised exchange integrals associated with compact permutations of the n i,j,...,l indices i.e. permutations that cannot be decomposed into permutations acting on disjoint subsets of indices and the $\mathbf{P}_n$ are projector operators acting in the spin space as:

$$P_n = \prod_{m = n/2-1,\ n/2-2,\ \ldots \geq 0} \frac{(s_1 + s_2 + \ldots + s_n)^2 - m(m+1)}{\frac{n}{2}\left(\frac{n}{2}+1\right) - m(m+1)}$$

With a crystal made of non-hydrogenoid atoms, the calculations are much more difficult. Assuming that the intra-atomic exchange interactions are always dominant over the inter-atomic ones, the bilinear exchange interactions $-\Sigma_{i(\mu)}\Sigma_{j(\nu)}J_{i(\mu)j(\nu)}s_i^{\mu}.s_j^{\nu}$ may be re-written, by virtue of the Wigner-Eckart theorem, as $-2\Sigma_{\mu,\nu<\mu}J_{\mu\nu}\mathbf{S}_{\mu}.\mathbf{S}_{\nu}$, where $\mathbf{S}_{\mu}$ stand for the sum $\Sigma_i s_i^{\mu}$ of the spin of all the electrons localised about a same positive charge μ and $J_{\mu\nu}$ is an appropriate linear combination of $J_{i(\mu)j(\nu)}$. Additional terms involving high-order rotationally invariant spin polynomials also exist: biquadratic exchange $-2\Sigma_{\mu,\nu<\mu}K_{\mu\nu}(\mathbf{S}_{\mu}.\mathbf{S}_{\nu})^2$, multi-site exchange $-\Sigma_{\mu,\nu,\lambda}A_{\mu\nu\lambda}(\mathbf{S}_{\mu}.\mathbf{S}_{\nu})(\mathbf{S}_{\mu}.\mathbf{S}_{\lambda})$, $-\Sigma_{\mu,\nu,\lambda,\delta}A_{\mu\nu\lambda\delta}(\mathbf{S}_{\mu}.\mathbf{S}_{\nu})(\mathbf{S}_{\lambda}.\mathbf{S}_{\delta})$, ... [26]

Apparently, the **bilinear exchange interaction** $-2\Sigma_{\mu,\nu<\mu}J_{\mu\nu}\mathbf{S}_{\mu}.\mathbf{S}_{\nu}$ is enough to describe, at least, the ground and low-lying excited states of most materials and there is no need to consider higher order terms. A few remarks can be made here: an overlapping of wavefunctions being distant dependant as well as over the symmetry of the wavefunctions involved, the exchange integral $J_{\mu\nu}$ may have different values according to the direction of the pair (μ,ν) in a crystal, leading to a possible anisotropy of the inter-atomic exchange interactions. Orbital excitations and orbital transfers are induced by the electrostatic interactions between electrons localised about different positive charges leading to off-diagonal inter-atomic exchange interactions and couplings of orbital moments. Also other interactions exist in a crystal (crystalline electric field, spin-orbit coupling) which may be strong and compete with the exchange interactions. All these features lead to the more general $-2\Sigma_{\mu,\nu<\mu}\mathbf{S}_{\mu}.\mathbf{J}_{\mu\nu}.\mathbf{S}_{\nu}$ form for the bilinear exchange interactions where $\mathbf{J}_{\mu\nu}$ is now an exchange dyadic. $\mathbf{J}_{\mu\nu}$ can be separated into a symmetric part defining the **anisotropic exchange** and an antisymmetric part corresponding to the **$\mathbf{D}.(\mathbf{S}_\mu \mathrm{x} \mathbf{S}_\nu)$ vectorial coupling**.

A qualitative insight can be given of the physics behind the sign of the exchange integral $J_{\mu\nu}$. With **orthogonal orbital** wavefunctions, we get a **ferromagnetic** exchange interaction between the spins, because therefore the electrons collective orbital state is antisymmetric and so forth vanishes at the points $\mathbf{r}_i$-$\mathbf{r}_j$ of intersection of the paths of the electrons, where the Coulomb potential is the largest. With **overlapping** (non orthogonal) **orbital** wavefunctions, we get an **antiferromagnetic** exchange interaction between the spins, because therefore an electron can take advantage of the mixing of the wavefunctions to reduce its kinetic energy by hopping to the second site while the other electron is there (polar state), parallel spins being of course restricted by the Pauli exclusion from this virtual process.

Exchange interactions involving mediators

Other more complex mechanisms exist, which also lead to an effective coupling of spins $\mathbf{S}_\mu$. A description of all of the different possibilities would however be too long and we shall only give a physical picture of four mechanism, involving the electrons of an intermediate medium: the superexchange in insulators such as the transition-metal oxides, sulphides, ..., the double-exchange in mixed-valency materials such as the manganates and, the indirect and mixing exchange in conducting materials such as the rare-earth transition-metal intermetallics.

Let us consider an ionic compound made of magnetic cations and diamagnetic anions. If the electron wavefunctions of the cations do not overlap with each other, then there are no direct inter-atomic exchange interactions. However, if the paired electrons of the anions are delocalised by chemical binding with the neighbouring cations, then there is a possibility for an electron of an anion to virtually hop on a neighbouring cation, through intermediate excited states. A simple example is provided by the copper-oxide antiferromagnet, made of Cu^{2+} magnetic cations of spin S=1/2 (one hole in the 3d atomic shell) and O^{2-} diamagnetic anions. As to remain qualitative, we shall restrict ourselves to one Cu-O-Cu triad: in the absence of the electron hops, the spin ground state of the triad is four-fold degenerate (two possible spin orientations on each copper). If we allow the diamagnetic electrons to hop, the electronic configurations of the triad will change to Cu^{1+}-O^{2-}-Cu^{3+} or Cu^{1+}-O-Cu^{1+}. Since the Cu^{2+} cations have only one free orbital state already occupied by an electron, the hops will be forbidden by the Pauli exclusion if the initial orientation of the two copper spins is parallel: the hop will depend on the spin state of the electron. As a consequence, the degeneracy in the relative spin orientation of the Cu^{2+} cations is lifted (the lowest-order correction to the ground state energy is fourth order in the copper-oxygen hopping energy): we get an effective coupling between the spins of the Cu^{2+} cations, defining the **superexchange interaction** [27] A generalisation to more complex systems can of course be worked out. A large number of intermediate excited states might then exist corresponding to as many exchange paths in the solid and the superexchange coupling is determined by those of the lowest energy. In most cases, the bilinear coupling $-2\Sigma_{\mu,\nu<\mu}J_{\mu\nu}S_{\mu}.S_{\nu}$ is dominant, nevertheless higher order coupling such as a biquadratic superexchange $-2\Sigma_{\mu,\nu<\mu}K_{\mu\nu}(S_{\mu}.S_{\nu})^2$ might not be always negligible. Whether the superexchange coupling is ferromagnetic or antiferromagnetic, strong or weak, will depend on the orbitals involved and on the ligand configuration. A few qualitative features of these orbitals might reveal themselves relevant for a prediction on the nature and strength of the exchange at least concerning the bilinear coupling. A simple rule is that if the cation-anion orbitals are orthogonal then a ferromagnetic coupling is likely, otherwise an antiferromagnetic coupling should be expected. Another simple rule is that the magnitude of the coupling gets smaller as the angle made by the triad M-A-M decreases from π (collinear M-A A-M bonds) to $\pi/2$ (perpendicular M-A A-M bonds).

As far as anions of the same valence are involved, the superexchange interactions is the sole spin coupling mechanism to be expected in the magnetic anions-diamagnetic cations materials if of course the anions orbitals do not overlap, otherwise the direct exhange interactions will also emerge. When however there is a mixed valency of the anions, an additional different exchange mechanism may exist, as in the perovskyte-type manganates $(A_{1-x}\ B_x)MnO_3$, where A is a trivalent rare-earth ion and B a divalent alkaline-earth ion. At the ends of the series (x=0 and x=1), these oxydes are insulators and show an antiferromagnetism associated with superexchange interactions. At intermediate compositions the electric conductivity increases by several order of magnitude and the material show a canted antiferromagnetism with a net ferromagnetic component. 1-X fraction of the Mn magnetic anions are then in the Mn^{3+} valence state, with three d electrons filling tightly bound corelike t_{2g} orbitals and one electron occupying an outer e_g orbital, giving rise to a collective spin $S = 2$. X fraction of the Mn magnetic anions are on the other hand in the Mn^{4+} valence state, with three d electrons filling the t_{2g} orbitals, giving rise to a collective spin $S_c = 3/2$. The outer electron e_g is able to hop forth and back between neighbouring Mn ions of different valency. However, the intra-atomic exchange interaction J_I, coupling the spin **s** of the e_g electron with the spin S_c of the core t_{2g} electrons is much larger than the corresponding hopping integrals V and the spin-orbit interaction. The spins of all the electrons on a given Mn ion can therefore not be coupled in any other way than ferromagnetically (first Hunds'rule), without an excessive cost in energy. As a result, the hopping of the e_g electron can occur if the collective spins of the core t_{2g} electrons of the neighbouring Mn ions are parallel but not if these spins are antiparallel. A quantitaive approach shows that the energy associated with a Mn_1-Mn_2 pair is $E = -J_I S_c \pm V\cos(\theta/2)$, where θ is the angle between the core spins $\mathbf{S}_{c1}$ and $\mathbf{S}_{c2}$ and has the quantum mechanical definition: $(2S_c+1)\cos(\theta/2) = |\mathbf{S}_{c1} + \mathbf{S}_{c2} + \mathbf{s}| + 1/2$. An effective ferromagnetic coupling of the core spins of the neighbouring Mn ions sets then in through the gain in kinetic energy associated with the therefore allowed hops of the e_g electron: this defines the **double exchange interactions** [28]. Another way to view them is in terms of a Kondo lattice model with ferromagnetic localised electron spin – itinerant electron spin exchange interactions.

Let us now consider a conducting material containing ionic spins with no direct exchange interaction between them. The itinerant electrons in the solid will come under the influence of a given ion where they will experience intra-atomic exchange interactions for a time. This temporarily coupling modifies the translation motion of the itinerant electrons by increasing around the ion the number of electrons of a given spin state and decreasing that of opposite spin. As the distance from the ion increases the corresponding excess or lack of electronic charge density decreases. The decrease occur in an oscillatory way, owing to the sharp wavevector cut-off at the Fermi level. Since the charge displacements are spin dependent, this gives rise to a static oscillatory spin polarisation density which will interact with the spin of a next ion. The mechanism can be considered as due to a spin dependent scattering event, which is carried to a second ion where the scattering will again depend upon the local spin configuration. As a consequence, the two ionic spins will interact cooperatively, giving rise to an effective **indirect exchange interaction** [29]. A bilinear coupling $-2\sum_{\mu,\nu<\mu} J_{\mu\nu} \mathbf{S}_\mu . \mathbf{S}_\nu$ is obtained to second order of perturbation in the itinerant electron spin - ionic spin exchange integral $\Gamma_{\mathbf{kk'}}$, where **k** and **k'** are the wavevectors of the itinerant electron before and after being scattered by the ionic spin. In usual the dependence of $\Gamma_{\mathbf{kk'}}$ on **k** and **k'** is neglected, which amounts at neglecting the spatial extent of the orbital component of the ionic wavefunction (contact interaction). Anisotropic bilinear, cross-term and multipole-multipole exchange interactions are again obtained when taking into account the ionic and itinerant electron orbital asphericity. An important feature of the indirect exchange interaction is that it is oscillatory and long-ranged, giving rise to a (non geometrical) magnetic frustration. The indirect exchange interaction is the origin of the coupling of the 4f electron spins in most rare earth metals and in a wide number of rare earth based alloys, where it leads to complex magnetic structures. Its materialisation is in principle not unlikely in systems as unexpected as *purely organic materials*. After all, molecules such as the benzene ring are nothing more than prototypes of metals made of a few atoms. Although we shall then have a discrete set of "itinerant electron" states instead of a continuum, there are no reasons for the mechanism not to work and mimic that in the rare earth metals. The spin polarisation oscillation should then be qualitatively understood as an outcome of the difference in the number of nodes of occupied and unoccupied "itinerant" wavefunctions. A priori, large exchange interactions can be foreseen which opens the fascinating perspective of ambient temperature organic magnets, all the more as the "itinerant electrons" in these materials might in fact themselves stabilise a high temperature ferromagnetism.

Another way an itinerant electron plays an intermediate role is through resonant scattering. A resonant scattering means that an incident itinerant electron arriving in an ion's vicinity in opportune circumstances can be temporarily captured in pseudo-atomic states around the ion. This occurs owing to a mixing (or hybridisation) of the orbital wavefunctions of the outer electrons of the ions with the delocalised orbital wavefunctions of the itinerant electrons. When the ion possesses a spin, the probability for an itinerant electron being captured by the ion and quantum tunnelled out again into an itinerant state becomes dependent upon the relative spin configurations of the ion and of the incident itinerant electron. We get a **mixing exchange interaction,** also termed symmetry exchange interaction since the wavefunctions that mix should share a same crystal point symmetry [30]. A spin information may be transferred from an ion to another so as again to allow the ionic spins to interact cooperatively. Unlike the indirect exchange interaction, where the itinerant electron spin - ionic spin exchange integral $\Gamma_{\mathbf{kk'}}$ is ferromagnetic and tend to polarise the localised spin moments, the mixing exhange couple the itinerant and localised electrons antiferromagnetically and tend rather to favour the formation of local singlets as in the **Kondo** state. According to the strength of the hybridisation on the other hand, the electrons of the localised spins can be partially delocalised. Different instances, requiring a proper formalism, can then be met in actual materials, from localised electrons but with interactions strongly renormalised by the itinerant electrons, through intermediate and fluctuating valency, up to full itinerancy. A mixing exchange interaction is found in the so-called anomalous rare earth metals such as the Ce, where the 4f electrons, owing to a larger spatial extent, hybridise strongly with the conducting electrons. A wealth of intermediate possibilities, where both the mechanism of indirect and mixing exchange interactions are operating with more or less equal relevance, are also materialised in the anomalous rare earth or actinide based alloys.

Itinerant electrons

A common feature of all the above exchange interactions is that at least one of the coupled spin is that of electrons localised about a same nucleus, so that the bilinear form $-2\sum_{\mu,\nu<\mu}J_{\mu\nu}\mathbf{S}_{\mu}.\mathbf{S}_{\nu}$, although valid only to some extent, makes sense. In the case of itinerant electrons, the formalism of second quantisation must be used to explicitly take into account the electronic hopping processes: it merely consists in introducing a field operator $\psi(\mathbf{r})$ which may be expanded in terms of a complete set of single-particle wavefunctions and writing the interactions in terms of this field operator.

A natural complete set of single electron wavefunctions describing the itinerant electrons in a metal is provided by the Bloch functions $\psi_{\alpha\mathbf{k}s}(\mathbf{r})$ (α: band index, $\mathbf{k}$: momentum index, s: spin index) that diagonalise the one-electron Hamiltonian H_0 defining the band structure $\varepsilon_{\mathbf{k}}{}^{\alpha}$ of the metal. Another set is that of the Wannier functions $\psi_{\alpha us}(\mathbf{r})$ (u: lattice site index) constructed from the $\psi_{\alpha\mathbf{k}s}(\mathbf{r})$ as $\psi_{\alpha us}(\mathbf{r})=(1/\sqrt{N})\Sigma_{\mathbf{k}(B.Z.)}\exp(-i\mathbf{k}.\mathbf{r}_u)\psi_{\alpha\mathbf{k}s}(\mathbf{r})$. A field operator may be defined as $\psi(\mathbf{r})=\Sigma_{\alpha us}\psi_{\alpha us}(\mathbf{r})c_{\alpha us}$ where $c_{\alpha us}$ ($c_{\alpha us}{}^{+}$) is the operator that annihilate (creates) an electron in the αus Wannier state. We may then write:

$$H_0 = -\Sigma_{\alpha uvs}\, t_{\alpha uv}\, c_{\alpha us}{}^{+}\, c_{\alpha vs}$$

where $t_{\alpha uv}=(1/N)\Sigma_{\mathbf{k}(B.Z.)}\exp(-i\mathbf{k}.(\mathbf{r}_v-\mathbf{r}_u))\varepsilon_{\mathbf{k}}{}^{\alpha}$ are the matrix elements describing the electron hops. $t_{\alpha uv}$ do not depend on the spin state s, if we forget the spin-orbit coupling - $t_{\alpha uv}=t_{\alpha vu}{}^{*}$ by hermiticity of H_0 - $t_{\alpha uv}$ can be taken real in the absence of an external gauge field. Much of the electron-electron interactions $e^2/|\mathbf{r}_i-\mathbf{r}_j|$ are incorporated self-consistently in H_0 but not entirely. The residual correlation leads to the additional quartic interaction Hamiltonian:

$$H_1 = \Sigma_{uvpq\alpha\beta\gamma\delta ss'}\, U_{uvpq}{}^{\alpha\beta\gamma\delta}\, c_{\alpha us}{}^{+}\, c_{\beta vs'}{}^{+}\, c_{\gamma ps'}\, c_{\delta qs}$$

where the $U_{uvpq}{}^{\alpha\beta\gamma\delta}$ are the matrix elements of the screened $e^2\exp(-\mu|\mathbf{r}_i-\mathbf{r}_j|)/|\mathbf{r}_i-\mathbf{r}_j|$ interaction. Screening is actually a dynamical process involving collective charge fluctuations characterised by a plasma frequency ω - It mostly comes out as an exponential decay within a Thomas-Fermi screening length because ω is high. Since the Wannier states are localised to within a unit cell, the main contributions to H_1 come from the terms with p=u and q=v or p=v and q=u. All the other terms are negligible. Assuming furthermore that the Fermi surface lies within a single conduction band, the matrix elements that couple states of different band index may be omitted. We loose in that way various orbital excitations and off-diagonal exchange. Among the terms that remain we have the two site interactions $\Sigma_{uv}U_{uvvu}n_u n_v$ ($n_u=\Sigma_s c_{us}{}^{+}c_{us}$) that couple the density fluctuations at different sites. We may neglect it, although we are not rigorously justified to do it, if we are not interested by the charge density instabilities. At the magnetic instabilities its contribution to the free energy can be expected to be not singular. Another term is the two site ferromagnetic exchange interactions $\Sigma_{uvss'}U_{uvuv}c_{us}{}^{+}c_{vs'}{}^{+}c_{us'}c_{vs}$, which we may also write as $-2\Sigma_{u,v<v}J_{uv}(\mathbf{S}_u.\mathbf{S}_v+n_u n_v/4)$, by defining $\mathbf{S}_u=(1/2)\Sigma_{ss'}c_{us}{}^{+}\sigma_{ss'}c_{us'}$ where $\sigma=(\sigma_x,\sigma_y,\sigma_z)$ are the Pauli matrices. When the Wannier functions are almost superposition of atomic orbitals, the two site ferromagnetic term gets weak. Omitting it, we finally obtain the **Hubbard Hamiltonian**:

$$H_{hub} = H_0 + H_1 = -\Sigma_{uvs}\, t_{uv}\, c_{us}{}^{+}\, c_{vs} + (U/2)\Sigma_{us}\, n_{us}\, n_{u-s}$$

with $U=2U_{uuuu}$. We get in this way the minimal model to describe a many fermion system with quartic interactions) [31].

Even though a number of oversimplifying approximations are made to deduce it, e.g. with regard to the orbital degeneracy of the itinerant electron states, the Hubbard Hamiltonian contains much of the physics of metallic magnetism and leads to a wide diversity of phenomena, perhaps still not all yet discovered [32]. We may also write it in a form that explicitly shows its invariance with respect to the local SU(2) symmetry, i.e. a local change of quantisation axis:

$$H_{hub} = -\Sigma_{uvs} t_{uv} c_{us}^{+} c_{vs} - (2U/3)\Sigma_u S_u^2 + (U/6)\Sigma_u n_u.$$

U being positive, a magnetic ground state may be expected. Accordingly, the system would somehow pick a global quantisation axis, the same for all sites, which means a **spontaneous breaking** of the global SU(2) spin symmetry. H_{hub} is also invariant with respect to the phase change $\exp(i\varphi)c_{us}$ of the one-particle wavefunction (U(1) symmetry), which transposes to nothing but charge conservation. When the relative strength of the intra-atomic correlation U over the hopping energy t_{uv} is weak, the states of the electrons are well described by the **Fermi liquid** theory, as far as we may think of a one-to-one correspondence of the electronic states with that of the free fermions and if we may ignore the bosonic excitations such as magnons [33]. Numerical diagonalisation suggest nevertheless that, at least in small finite systems, the statistical distribution of energy levels gets characteristic of a quantum chaos when increasing the U/t_{uv} ratio to about unity. Another interesting limit is that of large U/t_{uv} values. At half filling, i.e. one electron per site, there are no low energy hopping processes and we get a **Mott insulator** phase. The low energy excitations are then that of spins one-half $\mathbf{S}_u$ interacting via the effective antiferromagnetic exchange interaction $-2\Sigma_{u,v<v}J_{uv}\mathbf{S}_u.\mathbf{S}_v$ where $J_{uv}=-4t_{uv}^2/U$. This generalise to many sites, the interatomic exchange interaction obtained for the hydrogen molecule. Slightly away from half-filling, the antiferromagnetic correlation are destroyed by the additional electrons or holes which, to get more mobile, tend to favour a ferromagnetic local spin environment. As a matter of fact, with N-1 electrons where N is the number of sites (one hole) the ground state in the extreme limit of infinite U, is the fully polarised ferromagnet with total spin S=(N-1)/2) as stated by the **Nagaoka theorem**. A present widespread belief is that superconductivity could emerge from adding or extracting electrons to a Mott insulator.

Actually the Hubbard Hamiltonian is difficult to analyse. An exact solution was obtained in one dimension [34] and the rigorous demonstration that in higher dimensions it may lead to a ferromagnetism in non-singular instances i.e. finite ranged hops, finite Coulomb interaction U and dispersive (single-electron) bands is recent [35]. A number of approximate methods, more or less sophisticated, were developed to investigate it. The simplest approach refers to the **Hartree-Fock** approximation: using the functional-integral technique, the partition function of H_{hub} can be written (in the static approximation) in terms of N auxiliary variables μ_u as $Z=\int d\mu_u \exp[(-\beta F(\mu_u)]$ with $F(\mu_u)=F_0-(1/\beta)\mathrm{TrLn}(1-VG_0)+\Sigma_u U\mu_u^2/4$, where the free energy F_0

and the green function G_0 are related to the one-electron Hamiltonian H_0 and V is the non uniform potential $V=-(U/2)\Sigma_u\mu_u(n_{u\uparrow}-n_{u\downarrow})$. At zero temperature, the integral is replaced by a saddle-point approximation and the μ_u are determined by minimising $F(\mu_u)$, which is equivalent to performing the local Hartree-Fock approximation: $\mu_u=<n_{u\uparrow}-n_{u\downarrow}>$. The main contributions to F come from a one-site term $F_1=\Sigma_u\Delta\mu_u^2$ and a two-site term $F_2=-2\Sigma_{u,v<v}J_{uv}\mu_u.\mu_v$ with $\Delta=(U/4)\{1+(U/N)\Sigma_{\mathbf{kq}}[f(\varepsilon_{\mathbf{k}})-f(\varepsilon_{\mathbf{k+q}})]/(\varepsilon_{\mathbf{k}}-\varepsilon_{\mathbf{k+q}})\}$, where $f(\varepsilon_{\mathbf{k}})=1/(\exp[(\varepsilon_{\mathbf{k}}-\varepsilon_F)/k_BT]+1)$ is the Fermi function, and $J_{uv}=-(U^2/4N)\Sigma_{\mathbf{kq}}\exp(-i\mathbf{q}.(\mathbf{r}_v-\mathbf{r}_u))[f(\varepsilon_{\mathbf{k}})-f(\varepsilon_{\mathbf{k+q}})]/(\varepsilon_{\mathbf{k}}-\varepsilon_{\mathbf{k+q}})$. F_1 transposes to the formation of a pseudo-moment on a site and F_2 to the inter-site coupling between the pseudo-moments, which should now be treated on the same footing, in contrast to ionic systems.

CRYSTALLINE ELECTRIC FIELD INTERACTIONS

Other electrostatic interactions exist in a solid where indistinguishability is not involved, therefore acting on the orbital motion of the electrons without giving rise to an effective coupling between spins. In a metal, these interactions are already taken into account when computing the hopping $t_{\alpha uv}$ matrix elements. In an ionic solid, these interactions concern all the electric charges external to the ion and are described by an electrostatic potential $V(\mathbf{r})$, which is invariant only with respect to the crystallographic symmetry of the environment of the ion in the solid. As a consequence, the rotational invariance of the orbital states of the ion gets broken. According to its strength, as compared to the interactions giving rise to the Hund's rules, the effect of $V(\mathbf{r})$ is either only a perturbation removing the orbital degeneracy of well separated ionic orbital states or to mix states of different orbital moments leading to spectral terms mixing and even configuration mixing. The full treatment of the problem is a priori complex since the charge distribution associated with the neighbouring ions may overlap that of the electrons under consideration. These external charge distributions are called ligands and their effects are computed by means of the **ligand field** theory [36].

If the overlapping effects may reveal negligible, the effects of the electrostatic potential $V(\mathbf{r})$ are handled by the **Crystal Field** theory. In that case $V(\mathbf{r})$ satisfies the Laplace's equation and may be expanded as $V(r,\theta,\phi)=\Sigma_l\Sigma_{-l<m<l}\, a_l^m\, r^l\, Y_l^m(\theta,\phi)$ on the basis of the spherical harmonics $Y_l^m(\theta,\phi)$. The number of terms that need to be considered in this expansion is very small and in many cases the constants a_l^m can be treated as adjustable parameters. The reason for this is that the matrix elements of $V(\mathbf{r})$ are computed on wavefunctions, which contains themselves spherical harmonics. If $\psi_a(\mathbf{r})$ and $\psi_b(\mathbf{r})$ are two wavefunctions of orbital momentum l' then the matrix elements of $V(\mathbf{r})$ with $l > 2l'$ will vanish by orthogonality of the spherical harmonics since the product $\psi_a(\mathbf{r})\psi_b(\mathbf{r})$ does not contain harmonics of order higher than $2l'$.

Similarly the symmetry of the wavefunctions by inversion in coordinate space implies to restrict the expansion to spherical harmonics of even parity. The computations of the matrix elements of V(**r**) are finally accomplished in standard ways through appropriate operator techniques by making use of the **Wigner-Eckart theorem** as set up in the theory of group representations [37]. In particular, if the mixing of spectral terms, defining manifolds of constant values L and S of $\mathbf{L}=\Sigma_i \mathbf{l}_i$ and $\mathbf{S}=\Sigma_i \mathbf{s}_i$, was to be negligible then the **equivalent operator method** applies [38]. This method makes use of the fact, implied by the Wigner-Eckart theorem, that within an L manifold the matrix elements of operators which are functions of orbital variables x,y and z are proportional to those of similar functions of the components L_x, L_y and L_z of **L**, provided the non commuting character of these operators are taken into account. The crystalline electric field Hamiltonian writes then as a function of powers of **L** and its components.

The way a set of original states decompose under the effect of the crystalline electric field potential V(**r**) into new states depend of course on the original states themselves as well as on the strength of V(**r**) but also on the group of symmetry characterising the environment of the ion. The **group theory** is then of considerable help [39]. If $\psi_a(\mathbf{r})$ is an eigenstate of V(**r**) then any wavefunction $\psi_b(\mathbf{r})=O\psi_a(\mathbf{r})$, obtained by applying on $\psi_a(\mathbf{r})$ a symmetry operator O which leaves V(**r**) invariant, is also an eigenstate for the same eigenenergy. Therefore $\psi_b(\mathbf{r})$ must be a linear combination of the orthogonal set of wavefunctions spanning the subspace of states having this eigenenergy. Assuming this subspace is g-fold degenerate we have $\psi_b(\mathbf{r})=\Sigma_{\alpha=1,g}\Gamma(O)_\alpha{}^b\psi_\alpha(\mathbf{r})$. The matrix Γ(O) are said to form an **irreducible representation** of the crystal symmetry group. Each irreducible representation is associated with a given eigenstate and the dimensionality of the representation is equal to the degeneracy of this eigenstate. The number and nature of the irreducible representations associated with the various symmetry groups may be tabulated by means of the **character tables**. A character is merely the trace of the matrix of a representation and is therefore independent on the basis of the wavefunctions used to compute the matrix. It is solely characteristic of the symmetry operator considered. As to know how rotationally invariant states decompose under a crystal field potential, it then suffices to know how the representations of the rotation group decompose into that of the crystal symmetry group, which is done by just inspecting the corresponding character tables without ever having to know about the wavefunctions. This is the powerful feature of the group theory which allow to get an insight of the expected energy spectrum of the crystal field without any calculations. It must be emphasised however that the group theory cannot tell about the ordering of the different eigenenergy and of their relative separations.

A relevant feature of the crystalline electric field potential V(**r**) is that it is invariant with respect to the **time reversal**. Unlike the usual spatial symmetry operators, the time inversion operator T is anti-unitary. It reverses the angular momentum as well as the spin of a particle, so that it anticommutes with the operators associated with these dynamical variables, but it commutes with the rotation operators. T^2 is equivalent to a 2π rotation operator. A spinor of an half-odd integer spin is not invariant with respect to a 2π rotation but only with respect to a 4π rotation. This implies that T^2 differs from the identity operator $\mathbb{1}$ and is equivalent to $(-1)^n \mathbb{1}$ for a system of n electrons. If now n is even, T may transform a state into itself, which is impossible if n is odd. Consequently any system with an odd number of electrons where the interactions are invariant with respect to the time reversal, as e.g. the crystalline electric field potential, must have a ground state which is necessarily at least two-fold degenerate. This is known as the **Kramers degeneracy** [25]. A system with an even number of electrons can in contrast have a non-degenerate ground state. The invariance with respect to the time reversal implies furthermore that opposite expectation values of orbital moments should occur with equal probability. Consequently the trace of all the components L_x, L_y and L_z of the angular momentum operator $\mathbf{L}$, which anticommute with T, must vanish within each of the crystalline electric field energy level whereas the trace of $\mathbf{L}^2$, which commutes with T, has not to vanish. We may intuitively understand as fast quantum fluctuations of the orbital moments associated with the time reversal.

A solid is actually made of a background lattice of nuclei at positions $\mathbf{R}_\mu$ each surrounded by N electrons that feel a potential $V(\mathbf{R}_\mu,\mathbf{r})$ depending on the $\mathbf{R}_\mu$. Assuming that $E_0(\mathbf{R}_\mu)$ is the ground state energy of the electrons associated with a given set of positions $\mathbf{R}_\mu$, the potential energy of the nuclei writes $U(\mathbf{R}_\mu)=E_0(\mathbf{R}_\mu)-C(\mathbf{R}_\mu)$ where $C(\mathbf{R}_\mu)$ is the Coulomb interaction between the nuclei. We recognise here the Born-Oppenheimer adiabatic approximation that allow to separate the electronic and nuclear motions in a solid. A slight change of the positions away from given $\mathbf{R}_\mu$ will modify the potential $V(\mathbf{R}_\mu,\mathbf{r})$ seen by the electrons and change the electronic ground state energy $E_0(\mathbf{R}_\mu)$. A degeneracy if any will then be lifted to the first order of perturbation through matrix elements that transform according to the representation $\Gamma_{GS} \times \Gamma_V \times \Gamma_{GS}$, where Γ_{GS} is the irreducible representation of the symmetry group of the crystal associated with the ground state and Γ_V the irreducible representation associated with a mode of vibration of the lattice of nuclei. $\Gamma_{GS} \times \Gamma_V \times \Gamma_{GS}$ can be reduced to the sum $\Sigma_p\Gamma_p$ of the irreducible representations Γ_p. Assuming now that the positions $\mathbf{R}_\mu$ are those minimising the potential energy $U(\mathbf{R}_\mu)$, these matrix elements should all vanish. Any integral $\int d\mathbf{r} f_p(\mathbf{r})$ where $f_p(\mathbf{r})$ is a function that transform according to an irreducible representation Γ_p vanish if Γ_p is not the trivial representation Γ_1. At inspecting the character tables of all the space groups, a mode of vibration is always found that leads to a sum $\Sigma_p\Gamma_p$ containing Γ_1. Consequently the $\mathbf{R}_\mu$ cannot be those minimising $U(\mathbf{R}_\mu)$, if the ground state is degenerate. If the ground state is not degenerate then $\Gamma_{GS} \times \Gamma_V \times \Gamma_{GS} = \Gamma_V$ and the matrix element vanish and if there is a Kramers degeneracy, time reversal symmetry should be taken into account which also lead to vanishing matrix elements: this is the **Jahn-Teller** theorem [25], which states that in any non-linear molecule or non-unidimensional solid there cannot be a degeneracy in the electronic ground state save the Kramers degeneracy.

SPIN-ORBIT INTERACTIONS

A spin-orbit coupling interaction exists between the spin and the orbital kinetic moment of an electron, which was historically revealed from the Dirac equation in the nonrelativistic limit up to $(v/c)^2$. We may, to some extent, interpret it as the interaction of the spin of the electron with the magnetic field $\mathbf{H} = \mathbf{E} \times \mathbf{v}$ seen by the electron in its reference frame, where is $\mathbf{E}$ the electric field governing the electron orbital motion. A correction by a factor 1/2 should then be taken into account, associated with the relativistic effect of Thomas precession. This effect is a property of the Lorentz transformation that, to order up to $(v/c)^2$, writes: $B(\mathbf{v}+\delta\mathbf{v})=R(\delta\theta)B(\delta\mathbf{v})B(\mathbf{v})$, where $\delta\theta=(\delta\mathbf{v} \times \mathbf{v})$, $B(\mathbf{v})$ denotes a boost to a velocity $\mathbf{v}$ and $R(\delta\theta)$ is a rotation of $\delta\theta$ about $\delta\theta$. It tells that an accelerating particle moving at relativistic speeds appears to precess in orientation.

In an isolated ion or atom, the spin-orbit coupling interaction may lead to different types of coupling of the electronic kinetic moments according to its strength, which increases as one goes from light to heavier elements. Up to the lanthanide series it remains however smaller than the electrostatic interactions between the electrons so that the spin and the orbital moments of the electrons will first couple separately to give rise to the spectral term energy levels defined by the different values of the total spin $\mathbf{S}=\Sigma_i\mathbf{s}_i$ and total orbital $\mathbf{L}=\Sigma_i\mathbf{l}_i$ moments. The spin-orbit coupling will then act as a perturbation which will split each spectral term level (L,S) into multiplets characterised by the different values J of the total kinetic moment $\mathbf{J}=\mathbf{L}+\mathbf{S}$ which ranges from $|L-S|$ to L+S. This defines the **Russell-Saunders coupling** approximation. Assuming a stationary vector potential and a spherical symmetric scalar potential, the spin-orbit interaction writes $\Sigma_i\xi_i\mathbf{l}_i.\mathbf{s}_i$, which within an (L,S) manifold may also write $A\mathbf{L}.\mathbf{S}$, thanks to the Wigner-Eckart theorem. A is negative or positive according to whether the considered electronic shell is more or less than half filled. The matrix elements of the spin-orbit coupling within a manifold (L,S) are all diagonal and write $A[J(J+1)-L(L+1)-S(S+1)]/2$, using the formula $2\mathbf{L}.\mathbf{S}=\mathbf{J}^2-\mathbf{L}^2-\mathbf{S}^2$. As a consequence the energy difference between two successive multiplets (L,S,J) and (L,S,J+1) is given by A(J+1), which is known as the **Landé interval rule**. J value of the ground state multiplet is $|L-S|$ for a shell less than half filled because A is positive, and L+S for a shell more than half filled, A being negative. This may stand as a **third Hund's rule**. The magnetic moment associated with a given multiplet (L,S,J) is computed in an easy way as $g_J\mu_B\mathbf{J}$ where the **Landé factor** g_J is calculated as $1+[J(J+1)+S(S+1)-L(L+1)]/2J(J+1)$, using the relation $g_J\mathbf{J}^2=\mathbf{J}.(\mathbf{L}+2\mathbf{S})=\mathbf{J}^2+\mathbf{S}^2+(\mathbf{J}^2-\mathbf{L}^2-\mathbf{S}^2)/2$ valid only within the (L,S,J) manifold. For heavier elements such as actinides, the spin-orbit coupling becomes of the same order of magnitude as the electrostatic interactions between the electrons. In that case, the spin-orbit interaction which now commutes neither with **S** nor with **L** will mix the spectral terms, invalidating the Russell-Saunders coupling approximation. One has then to diagonalise simultaneously the electrostatic and spin-orbit coupling interactions, which refers to the so-called **intermediate coupling** scheme. If finally the spin-orbit coupling interaction was to be larger than the electrostatic interactions, it would at first couple the individual electronic spin and orbital moments to give rise to the individual kinetic moment $\mathbf{j}_i=\mathbf{l}_i+\mathbf{s}_i$ which would then couple through the electrostatic interactions to give rise to the total kinetic moment $\mathbf{J}=\Sigma_i\mathbf{j}_i$. This defines the **j-j coupling** scheme. Whatever the case, the total kinetic moment $\mathbf{J}=\Sigma_i(\mathbf{l}_i+\mathbf{s}_i)$ is a constant of motion since it is the generator of the group of rotations, under which isolated ions are invariant.

In a metal, the spin-orbit interaction is automatically taken into account by computing the band structure $\varepsilon_{\mathbf{k}s}{}^{\alpha}$ from a fully relativistic single electron Hamiltonian H_0, in the sense of the Dirac equation for the electron in an electromagnetic field. According to its strength in the usual metals, its main effect is to raise the degeneracy of the band states at points **k** of high symmetry in the reciprocal space. An important observation to make is that H_0 is still time reversal invariant and since it describes a single electron in an average potential we have the Kramers degeneracy $\varepsilon_{\mathbf{k}s}{}^{\alpha}=\varepsilon_{-\mathbf{k}-s}{}^{\alpha}$ at all the points **k** in the reciprocal space, which transposes to a spin dependent electron hopping without creation of a spin polarisation. When a symmetry inversion exist then we also have $\varepsilon_{\mathbf{k}s}{}^{\alpha}=\varepsilon_{-\mathbf{k}s}{}^{\alpha}$.

The spin-orbit coupling interactions might be considered to operate solely within an ion or within the displaced charge of a local spin polarisation in a metal (one-site approximation), as far as the inter-atomic "spin-other-orbit" coupling interactions are negligible, which is the case in most materials. If however these interactions come into play as within a pair interchange of electrons between different atoms, they give rise, to first order of perturbation, to the **antisymmetric exchange** interactions $-2\Sigma_{\mu,\nu<\mu}\mathbf{D}.(\mathbf{S}_\mu \mathrm{x} \mathbf{S}_\nu)$ [40]. At higher order of perturbation, anisotropic **pseudo-dipolar** and higher order coupling interactions are obtained. No non-exchange effects of the spin-orbit coupling interaction may occur, at least to first-order of perturbation, since the interaction involve an angular momentum operator, the trace of which cancels owing to the time reversal symmetry.

MAGNETOELASTIC INTERACTIONS

On phenomenological grounds, the elasticity of a material is described by a symmetric **strain tensor** $u_{\alpha\beta}$ which defines the response of the material to an applied **stress tensor** $\sigma_{\gamma\delta}$.

As far as the strains are small, the non linear effects associated with the anharmonic higher order terms of the expansion of internuclera potential $U(\mathbf{R}_\mu)$ with respect to $(\mathbf{R}_\mu-\mathbf{R}_\mu^0)$ are negligible: $u_{\alpha\beta}$ is then linear in $\sigma_{\gamma\delta}$ (Hooke's law) and the elastic free energy writes $(1/2)\Sigma_{\alpha\beta\gamma\delta}C_{\alpha\beta\gamma\delta}\sigma_{\alpha\beta}\sigma_{\gamma\delta}$ or $(1/2)\Sigma_{\alpha\beta\gamma\delta}M_{\alpha\beta\gamma\delta}u_{\alpha\beta}u_{\gamma\delta}$ where $C_{\alpha\beta\gamma\delta}$ and $M_{\alpha\beta\gamma\delta}$ are 4th order tensors defining the **elastic constants** and **elastic moduli** of the substance. $e_{\alpha\beta}$ (and therefore $\sigma_{\gamma\delta}$) is symmetric so that $C_{\alpha\beta\gamma\delta}=C_{\beta\alpha\gamma\delta}=C_{\alpha\beta\delta\gamma}=C_{\gamma\delta\alpha\beta}$: the number of independent components of $C_{\alpha\beta\gamma\delta}$ (or of $M_{\alpha\beta\gamma\delta}$) is considerably reduced: 21 for a triclinic single crystal to 3 for a cubic single crystal - if A is a matrix representing one of the symmetry elements of the considered substance then for any tensor T: $T_{\alpha\beta\ldots\delta}=\varepsilon(\det A)^x A_{\alpha\pi}A_{\beta\rho}\ldots A_{\delta\zeta}T_{\pi\rho\ldots\zeta}$ where $x=0$ ($x=1$) for polar (axial) tensors and ε is the time reversal signature [41]. In the case of a **polycrystal**, an averaging over the crystallite distribution should be performed and the elasticity of the grain boundaries should be taken into account but this is too difficult. In practice isotropy conditions are assumed. The elastic free energy may then write $S_L\Sigma_{\alpha\beta}(\sigma_{\alpha\beta}-\delta_{\alpha\beta}\Sigma_\lambda\sigma_{\lambda\lambda}/3)^2 + K_L\Sigma_\lambda\sigma_{\lambda\lambda}{}^2/2$ where $\delta_{\alpha\beta}$ is the Kronecker symbol, K_L the **compressibility** and S_L the **shear elasticity**. On increasing the temperature the non linear effects take place through the phonon-phonon couplings and there is a progressive softening of the elastic constants (or moduli). Another outcome of the anharmonic higher order terms in $U(\mathbf{R}_\mu)$ is to give rise to a **free thermal expansion** of the material, which for a polycrystal is given as $\alpha_L(T)=(\partial l/\partial T)/l=(1/3)(\partial V/\partial T)/V=KC_L(T)\gamma_L/3V$ where C_L is the phonon specific heat and γ_L the Gruneisen coefficient ($\gamma_L=-\partial\ln(\Theta_D)/\partial\ln V$ and Θ_D is the Debye temperature). Anisotropic $\alpha_L{}^{\alpha\beta}(T)$ thermal coefficients are obtained in the case of a single crystal ($\alpha_L{}^{\alpha\beta}(T)$ being symmetric, it has 3 independent components for triclinic, monoclinic and orthorhombic symmetry and 2 independent components for tetragonal, rhomboedral and hexagonal symmetry - it is isotropic as in a polycrystal for a cubic symmetry).

As already seen above with the Jahn-Teller effect, a part of the elasticity in a magnetic material will depend on the magnetic states of the electrons and a coupling will exist between the elastic and magnetic degrees of freeom in the material, which will define the **magnetelasticity** of the material. On phenolomenolgical grounds, the strain tensor $u_{\alpha\beta}$ gets dependent on both the stress tensor and the magnetisation state of the material. An additional free energy should be considered to take account of the associated magnetoelasticity. In the case of a ferromagnet, the lowest order term invariant with respect to the time reversal is linear in the stress $\sigma_{\alpha\beta}$ and quadratic in the magnetisation components M_γ. It writes $-\Sigma_{\alpha\beta\gamma\delta}\Lambda_{\alpha\beta\gamma\delta}\sigma_{\alpha\beta}M_\gamma M_\delta$ where $\Lambda_{\alpha\beta\gamma\delta}$ is a 4th order tensor defining the **magneto-elastic constants** ($\Lambda_{\alpha\beta\gamma\delta}=\Lambda_{\beta\alpha\gamma\delta}=\Lambda_{\alpha\beta\delta\gamma}$ but $\neq\Lambda_{\gamma\delta\alpha\beta}$). A next term is $-\Sigma_{\alpha\beta\gamma\delta\pi\rho}\phi_{\alpha\beta\gamma\delta\pi\rho}\sigma_{\alpha\beta}\sigma_{\gamma\delta}M_\pi M_\rho$ (arising e.g. from the morphic effects associated with the dipolar interactions) [4]. For a **polycrystal** we would write the magneto-elastic free energy as $S_M\Sigma_{\alpha\beta}\sigma_{\alpha\beta}M_\alpha M_\beta(1-\delta_{\alpha\beta})+K_M\Sigma_\lambda\sigma_{\lambda\lambda}M_\lambda{}^2$ (with S_M and K_M the magnetic contribution to the shear elasticity and compressibility) if isotropy conditions can be assumed. Of course, this is never rigorously the case: the existence of a magnetisation always lead to the lower ∞/mmm cylindrical symmetry. Assuming that it has no texture, the elasticity of a polycrystalline ferromagnetic material is actually characterised by 5 elastic constants (instead of 2 due the lowering of symmetry) and 3 magneto-elastic constants. Quite essential is also to emphasise that the interplay between the elastic and magnetic degrees of freedom implies that the elastic and magneto-elastic constants get dependent on the applied field and stress, making the analysis of the elasticity of a ferromagnetic material extremely delicate. When the magnetisation distribution in the material is not ferromagnetic, the lowest order term of the magneto-elastic free energy, invariant with respect to the time reversal, writes $-\Sigma_{\mathbf{k}}\Sigma_{\alpha\beta\gamma\delta}\Lambda_{\mathbf{k}\alpha\beta\gamma\delta}\sigma_{\alpha\beta}M_{\mathbf{k}\gamma}M_{\mathbf{-k}\delta}$ where $\mathbf{M_k}$ is the **k**-Fourier transform of the distribution. On increasing the temperature, the variations in the magnetic behaviours of the materials are mirrored in the elastic properties. A **thermal expansion** of **magnetic origin** $\alpha_M(T)$ comes out and, in certain instances, magnetic Gruneisen coefficients γ_M can be defined to relate $\alpha_M(T)$ and the magnetic specific heat $C_M(T)$.

The magneto-elastic effects are due to the strain dependence of the previous basic magnetic interactions. A detailed description of the different underlying mechanism is of course out of place but a qualitative picture of a few cases can be given. A first mechanism of interest, which may lead to large isotropic effects, is that connected with the onset of a pseudo-moment in itinerant electron magnetism [42]: this onset causes a local electronic charge displacement at the expense of the cohesion energy of the metal under concern. A large negative internal pressure then arises, which is minimised by an essentially isotropic volume expansion. Accordingly, in any **metal**, a change of the spin polarisation (e.g. with the temperature or an applied field) should be reflected in volume changes. Conversely the application of a pressure should perturb the magnetic properties of the metal. Clearly the effects will be the most drastic when there is a **magnetic instability**: the phonon frequency and sound velocity of the material show then strong anomalies and in some cases pressure or temperature induced first order magnetic transitions can be observed. When a magnetic order sets up, a volume expansion of about $1\%/\mu_B^2$ (in 3d transition metal based compounds) is experimentally found. If to a first approximation the anisotropy in the strains can be neglected, the corresponding magneto-elastic free energy may write $-\omega\Sigma_{\mathbf{k}}A_{\mathbf{k}}\mathbf{M_k}^2$ where $\omega=\Delta V/V$ is the volume strain and $\mathbf{M_k}$ the **k**-Fourier transform of the magnetisation density $\mathbf{M(r)}$. A thermal expansion of magnetic origin is then deduced: $\alpha_M(T)=(1/3B)\Sigma_{\mathbf{k}}A_{\mathbf{k}}(<\mathbf{M_k}^2>_T-<\mathbf{M_k}^2>_0)$ where B is the bulk modulus and $<>_T$ means a statistical average at temperature T. In the weak ferromagnets the small **k** components of the magnetic fluctuations are predominant and $\alpha_M(T)$ may be approximated by $N(A_0/3B)[\mathbf{M_L}^2(T)-\mathbf{M_L}^2(0)]$ where $\mathbf{M_L}^2(T)$ is the mean square local amplitude of the magnetic fluctuations. On increasing the temperature, $\mathbf{M_L}^2(T)$ decreases in the ordered state and increases above the Curie temperature leading to a negative $\alpha_M(T)$ within a given temperature range. When then the magnitude of $\alpha_M(T)$ is close to $\alpha_L(T)$ we get an invar material. Another instance where strong magneto-volume effects are met is in the materials showing **f electron instabilities** (intermediate or fluctuating valence systems): the ionic radii of an f element differ markedly according to its valence state and in case of valence fluctuations severe strain effects are induced, giving rise to huge magnetovolume anomalies and magnetostriction, soft modes of phonons and even localised phonons [43].

In the **materials with** well defined **ionic spins** S_μ, the dependence of the **exchange integrals** $J_{\mu\nu}$ upon the (μ,ν) inter-nuclear separations in the inter-atomic exchange interactions $-2\Sigma_{\mu,\nu<\mu}J_{\mu\nu}\mathbf{S}_\mu.\mathbf{S}_\nu$ may also lead to strong magneto-volume effects. We may formulate these effects (contraction or expansion) by considering a slight variation ∂V of volume out of the value V minimising the elasticity of the material in the absence of the exchange interactions [44]. The gain in magnetic energy at temperature T is then $-2\Sigma_{\mu,\nu<\mu}(\partial J_{\mu\nu}/\partial V)\delta V<\mathbf{S}_\mu.\mathbf{S}_\nu>_T$ while the cost in elastic energy is $(\delta V/V)^2/6K_L$ (isotropic conditions). A new equilibrium volume is reached when the two energy compensate each other i.e. for $\partial V_{eq}{}^M/V=VK_L\Sigma_{\mu,\nu<\mu}(\partial J_{\mu\nu}/\partial V)<\mathbf{S}_\mu.\mathbf{S}_\nu>_T$, as from which a magnetic expansion $\alpha_M(T)=(1/3)(\partial V_{eq}{}^M/\partial T)/V=K_L\Sigma_{\mu,\nu<\mu}(-\partial LnJ_{\mu\nu}/\partial LnV)$ $\partial(-2J_{\mu\nu}<\mathbf{S}_\mu.\mathbf{S}_\nu>_T)/\partial T$ is deduced. If a single parameter $J_{\mu\nu}$ dominate then $\alpha_M(T)$ is proportional to the magnetic specific heat $C_M(T)$ and a magnetic Gruneisen coefficient can be defined as $\gamma_L=-\partial lnJ_{\mu\nu}/\partial lnV$. In warming from the ordered to the disordered state there will be an expansion of magnetic origin if $\partial J_{\mu\nu}/\partial V$ is negative whilst when $\partial J_{\mu\nu}/\partial V$ is negative there will be a contraction which, if sufficiently large, will also lead to the invar phenomenon. When **anisotropic**, the inter-atomic exchange interactions give also rise to a **linear magnetostriction** i.e. a deformation of the solid at constant volume, involving the shear elasticity S_L of the material.

Another origin of the magneto-elasticity of a magnetic material that we shall briefly mention is that connected with the **crystalline electric field potential** [9]: this potential breaks the rotational invariance of the orbital states of the electrons and stabilises a highly aspherical electronic charge density about each nucleus. A cost in electrostatic energy exist in rotating the charge density which will be minimised thanks to the elasticity of the material through appropriate (anisotropic) strains. Conversely, an applied (anisotropic) stress, through the strains it will induce, will change the effect of the environment on the electrons under concern which should modify the asphericity of the charge distribution. A way to account for both effects is to assume that in the expansion $V(r,\theta,\phi)=\Sigma_l\Sigma_{-l<m<l}\, a_l{}^m\, r^l\, Y_l{}^m(\theta,\phi)$ of the crystalline electric field potential on the basis of the spherical harmonics, the $a_l{}^m$ **environment parameters** are **strain dependent**. One speaks then of a single ion effect because it solely involves the interaction of an ion with its environment - multi-ion effects should be considered if the rotation of the electronic

charge distribution of a given ion has such an effect on the environment that the charge distributions of the neighbouring ions are also affected. In many materials, the quadrupolar magnetoelastic effects associated with the spherical harmonics of order l=2 are dominant. Isotropic effects are again obtained but the largest effects are now anisotropic distortions (mirroring the magnetic symmetry of the moment distribution).

OUTCOMES OF THE BASIC INTERACTIONS: QUALITATIVE APPROACH

A wealth of ground states and low energy excitations of magnetic nature emerge from the basic interactions described above, depending upon the considered systems. Tthe electrons under concern might be localised as in ionic spin systems, partly delocalised by hybridisation with itinerant electrons as in anomalous rare earth based systems, delocalised to within the extent of a molecule as in molecular or organic systems or fully itinerant as in metals. Within a given model the relative strength of the interactions might vary to a large extent, a geometrical frustration may come out,... A description of all the instances is clearly not possible, even at a qualitative level, and only a few expected outcomes could be recalled in connection with the most familiar magnetic behaviours of ferromagnetism and antiferromagnetism.

All the interactions under concern are invariant with respect to the time reversal. An expected outcome of the exchange interactions is however to stabilise definite orientations of the spin of the electrons relatively to each other, i.e. a collective state of the electrons that is not invariant with respect to the time reversal. We shall then have a spontaneous breaking of the time reversal symmetry in the spin space and, owing to the spin-orbit coupling interaction, in the orbital space. Another observation that may be made is that the crystalline electric field is explicitly not invariant with respect to the spatial rotations. We shall then have an anisotropy of the orbital magnetism and, owing to the spin-orbit coupling interaction, of the spin magnetism.

Spin magnetism and magnetic ordering

A physical system is said to have a **spontaneously broken symmetry** when the symmetry of its low energy states is lower than that of the interactions describing it. At the origin of this phenomenon is the fact that the symmetry lowering allows the formation of correlations that may minimise the overall energy of the system. A qualitatively different behaviour emerges then at low temperature, giving birth to a symmetry-violating **order parameter** operator which in statistical average is non zero solely in the broken symmetry states of the system. An overwhelming variety of physical systems exhibit such a symmetry breaking phase transition, among which we may quote the ferroelectricity and broken inversion symmetry, the nematic liquid crystal and broken local rotational symmetry, the He^3 liquid and broken gauge symmetry, etc. A **magnetic order** is associated with the **breaking** of the **time reversal symmetry** and corresponds to a freezing of the relative orientations of given spins with respect to each other. Global changes of orientation involving all the spins coherently are not necessarily frozen and, in particular, no absolute orientation of the spins exist if there is no anisotropy.

An order parameter is essential in giving insights about the nature of the spectrum of the low-lying **collective excitations** in the ordered state and of the **fluctuations** in the disordered state. Onsets of **topological defects** inherent to the rigidity associated with the order as well as the mechanism of the **transition** at the critical temperature at which the order sets up are also intimately related to it [45]. A basic distinction is made according to whether the order parameter commutes with the exchange interactions or it does not, as both possibilities exist in the strict thermodynamical limit.

Commuting order parameters are those generating a group of transformations under which the interactions are invariant. A broken symmetry state in this case is an eigenstate of the interactions and can be a ground state. An important group of interest in that respect is the group SO(3) of the rotation transformations. Continuous, compact, connexe and non-Abelian, it has three generators which in the spin space are the components S_x, S_y and S_z of the total spin **S** under concern: the operator associated with a rotation of angle ϕ around an axis Ω writes as $\exp[i(\phi\, \Omega.\mathbf{S})]$ - $\mathbf{S}=\Sigma_\mu \mathbf{S}_\mu$ for a system of ionic spins $\mathbf{S}_\mu$. If the order parameter is one of the S_x, S_y or S_z generators we have a **ferromagnetic order**. Such an order may emerge from e.g. exchange interactions of the form $H_{exch}=-2\Sigma_{\mu,\nu<\mu}[J_{\mu\nu}{}^z S_\mu{}^z S_\nu{}^z+J_{\mu\nu}{}^\pm(S_\mu{}^+ S_\nu{}^- + S_\mu{}^- S_\nu{}^+)/2]$ with $J_{\mu\nu}{}^z \geq |J_{\mu\nu}{}^\pm|>0$ and where $S_\mu{}^\pm=S_{\mu x}\pm iS_{\mu y}$.

H_{exch} is invariant with respect to the full SO(3) group solely when $J_{\mu\nu}{}^z=J_{\mu\nu}{}^\pm$. Any of the generators S_x, S_y or S_z can then be an order parameter and the ferromagnetic state is (2S+1)-fold degenerate. If the eigenstate ψ associated with the maximum eigenvalue S of S_z is a ferromagnetic ground state, the other ferromagnetic ground states ψ' are obtained by applying the ladder operator $S^-=\Sigma_\mu S_\mu{}^-$ to it: $\psi'=(S^-)^n\psi$ (n=1,2,...2S). A branch of true collective excitations is deduced from that degeneracy: the **spin waves**, which are generated by no more than applying locally out of phase ladder operators $S_{\mathbf{k}}{}^-=\Sigma_\mu \exp(-i\mathbf{k}.\mathbf{r}_\mu)S_\mu{}^-$ to the ground state ψ. Consisting in small spiral precessions of the (z-) quantisation axis of the total spin S, the spin waves give rise **to a gradient in the relative orientations of the individual spins** $\mathbf{S}_\mu$. The stronger the gradient the larger the cost in exchange energy, leading to **k**-dependent spin wave energy $\varepsilon(\mathbf{k})$. Left-handed (**k**) and right-handed (-**k**) precessions can be intuitively expected to cost the same energy, except in the non-centrosymmetric materials, therefore as the momentum **k** goes to zero (long wavelength limit) $\varepsilon(\mathbf{k})$ may be predicted to vanish **quadratically** in the components k_α (α=x,y,z) of **k**: $\varepsilon(\mathbf{k})=\Sigma_{\alpha\beta}D_{\alpha\beta}k_\alpha k_\beta$ where $D_{\alpha\beta}$ is a symmetric tensor of rank 2.

As soon as $J_{\mu\nu}{}^z>|J_{\mu\nu}{}^\pm|$, the invariance with respect to the full SO(3) group is lost: H_{exch} is invariant with respect to only the rotations around the z-axis, which form an Abelian sub-group of SO(3) with S_z as its generator. Since all the representations of an Abelian group are one dimensional, the ground state is unique and, in the case of ferromagnetism, is the eigenstate ψ, associated with the maximum eigenvalue S of S_z, or the eigenstate $T\psi$, where T is the time inversion operator, associated with the minimum eigenvalue -S of S_z. Applying the ladder operator $S^-=\Sigma_\mu S_\mu{}^-$ to ψ will now cost a finite energy $\varepsilon_{ani}=g\mu_B Sh_{ani}$ where h_{ani} can be understood as an effective magnetic field that would, from isotropic exchange ($J_{\mu\nu}{}^z=J_{\mu\nu}{}^\pm$), lead to the same anisotropy as that associated with the inequality $J_{\mu\nu}{}^z>|J_{\mu\nu}{}^\pm|$. Above that energy the out of phase ladder operators $S_\mathbf{k}{}^-$ lead again to spin waves modes of excitation whose energy in the long wavelength limit writes now $\varepsilon(\mathbf{k})=g\mu_B S[h_{ani}+\Sigma_{\alpha\beta}(D_{\alpha\beta}/g\mu_B S)k_\alpha k_\beta]$.

Actual ferromagnets have in fact no perfect rotational symmetry even though the exchange interactions are isotropic because the spins experience also the crystal symmetry through the spin-orbit coupling interaction and a finite effective field h_{ani} will always be measured in the dispersion relation $\varepsilon(\mathbf{k})$ for the spin waves, getting only a different meaning: the magnetocrystalline anisotropy field. Of interest is also to observe that despite anisotropic interactions, the excitation spectrum consists of spin waves which are created from the eigenstate ψ of S_z by means of the $S_\mu{}^-=S_{\mu x}-iS_{\mu y}$ generators for the individual spins i.e. the initial SO(3) symmetry of a free spin is involved. On general grounds, a **dimensionality** is ascribed to the **order parameter**, defined as the number of generators of the group of transformations from which the object whose dynamics is under concern emerge. When continuous that group allows to built collective modes of excitations from the ground state. When not continuous (discrete symmetry) the order parameter is said to be one-dimensional and no collective modes of excitations may be built from the ground state. Examples are Ising or Potts models. Critical fluctuations at a transition show universal behaviours depending crucially on that dimensionality.

Order parameters that do not commute with the exchange interactions are not constants of motion and therefore none of the associated unsymmetric states can be a ground state. So the question is: how come the spontaneously broken symmetry and the answer could be: wavepacket pinning via the zero point motion or existence of quasidegenerate joint states or else collapse to the ground state of very low energy states in the thermodynamical limit. A familiar example of a non commuting order parameter is the "staggered" spin $S_\aleph{}^z=\Sigma_\mu\aleph_\mu S_\mu{}^z$ where $\aleph_\mu=\pm1$ is a Boolean function that distributes the sites μ over two equal size interpenetrating sublattices A and

B. $S_\aleph^z$ defines an **antiferromagnetic order** and may emerge from exchange interactions of the form $H_{exch}=-2\Sigma_{\mu,\nu<\mu}[J_{\mu\nu}^zS_\mu^zS_\nu^z+J_{\mu\nu}^\pm(S_\mu^+S_\nu^-+S_\mu^-S_\nu^+)/2]$ with $J_{\mu\nu}^z<0$ and $|J_{\mu\nu}^z|\geq|J_{\mu\nu}^\pm|>0$. The case $|J_{\mu\nu}^z|\leq|J_{\mu\nu}^\pm|$ and $J_{\mu\nu}^z>0$ or <0 leads to other non conserving order parameters or in a 2D system of spins to binding processes of topological singularities.

When $|J_{\mu\nu}^\pm|=0$ the ground state is the antiferromagnetic state $\psi=\Pi_\mu|S_\mu,M_\mu=\aleph_\mu S>$ but as soon as $|J_{\mu\nu}^\pm|\neq0$ the pairwise spin-flip operators $S_\mu^+S_\nu^-+S_\mu^-S_\nu^+$ mixes ψ with other states: $S_\aleph^z$ commutes with $-2\Sigma_{\mu,\nu<\mu}J_{\mu\nu}^zS_\mu^zS_\nu^z$ but not with $-2\Sigma_{\mu,\nu<\mu}J_{\mu\nu}^\pm(S_\mu^+S_\nu^-+S_\mu^-S_\nu^+)/2$. Applying spin-flip operators on a given state transform it into a state with the same total azimuthal quantum number M so that the eigenstates of H_{exch} can be labelled by M and expanded as $\psi^M=\Sigma_\alpha f_\alpha^M\varphi_\alpha^M$ on the basis of the states $\varphi_\alpha^M=\Pi_\mu|S_\mu m_\mu^\alpha>$ with $\Sigma_\mu m_\mu^\alpha=M$ (α is a label that distinguishes between different spin configurations).

Now in each subspace of fixed M, there exist a non degenerate eigenstate ψ_0^M of lowest energy. If $J_{\mu\nu}^\pm>0$, ψ_0^M is the state with $f_\alpha^M>0$ for any spin configuration α. ψ_0^M is proven to be of minimum energy when $f_\alpha^M\geq0$ for all α by making use of the fact that $-2\Sigma_{\mu,\nu<\mu}J_{\mu\nu}^\pm(S_\mu^+S_\nu^-+S_\mu^-S_\nu^+)/2$ has solely nonpositive matrix elements - if f_α^M vanishes for some α then it vanishes for all α in the same M sector so that in effect the strict inequality $f_\alpha^M>0$ should hold for all α - ψ_0^M is non degenerate because it is simply not possible to have ψ_1^M with all $f_\alpha^M>0$ orthogonal to ψ_0^M i.e. such that $<\psi_1^M|\psi_0^M>=0$). If $J_{\mu\nu}^\pm<0$, the lowest energy state ψ_0^M in a subspace of fixed M is the state $\psi_0^M=\Sigma_\alpha(-)^{\Gamma(\alpha)}f_\alpha^M\varphi_\alpha^M$ with $f_\alpha^M>0$ for any α and where $\Gamma(\alpha)=\Sigma_\mu(1-\aleph_\mu)(S_\mu+m_\mu^\alpha)/2$ defines the **Marshall sign criterion.** ψ_0^M with the Marshall sign criterion is proven to be of minimum energy in the case $J_{\mu\nu}^\pm<0$ in the same way as when $J_{\mu\nu}^\pm>0$, by observing that a rotation of an angle π about the z-axis of all the spins S_μ of the sublattice B, i.e. for which $\aleph_\mu=-1$, transforms the states $|S_\mu m_\mu^\alpha>$ into $(-)^{\Gamma(\alpha,\mu)}|S_\mu m_\mu^\alpha>$ with $\Gamma(\alpha,\mu)=(1-\aleph_\mu)(S_\mu+m_\mu^\alpha)/2$ and changes solely the sign of $J_{\mu\nu}^\pm$ in H_{exch}) [46]. Since the sign criterion thus deduced does depend solely on the fact that the matrix element of the spin-flip part of the exchange interactions are nonpositive, the states of lowest energy $\psi^\infty{}_0^M$ in the M sector associated with the interactions $H^\infty{}_{exch}=-2J\Sigma_{\mu,\nu<\mu}S_\mu^zS_\nu^z-2J^\pm\Sigma_{\mu,\nu<\mu}(S_\mu^+S_\nu^-+S_\mu^-S_\nu^+)/2$ (μ in A and ν in B)$=-(J-J^\pm)S_A^zS_B^z-J^\pm S_A.S_B$ should have the same quantum numbers as the states ψ_0^M, because the sign criterion of the two states is the same and therefore their overlap, involving a sum of positive numbers, cannot vanish. It is then an easy matter to show that the ground state of H_{exch} has quantum numbers M=0 and $S=\Sigma_\mu S_\mu$ (when $J_{\mu\nu}^\pm>0$) or S=0 (when $J_{\mu\nu}^\pm<0$).

$\psi_0^{M=0}$ is a quantum superposition of macroscopically distinct states, the spin configurations α, which may be pictured as a system of spins spatially correlated antiferromagnetically but orientationally delocalised. It is invariant with respect to the time reversal symmetry and is not an eigenstate of $S_\aleph^z$. A **spontaneously broken symmetry** can nevertheless occur **in the thermodynamical limit** as an effect of a recombination of states via the zero point motion that pin the spins in the antiferromagnetic spin configuration $\Pi_\mu|S_\mu,M_\mu=\aleph_\mu S>$. All allowed values of S (from S=0 to $S=\Sigma_\mu S_\mu=NS_\mu$ where N is the total number of spins) have indeed members $\psi_{QDJS}{}^{M=0}$ (quasi-degenerate joint states) in the M=0 sector at energy that scales as sJ/N for S=s, where J is the strength of the exchange interactions. We assume here that the ground state is the singlet state S=0 but the same arguments hold for the other case $S=\Sigma_\mu S_\mu$. As a consequence the macroscopic coherence between the different spin configurations will have a finite forth and back **tunnelling** time τ of the order of N/J. Coherence is destroyed by the environment effects such as the coupling of the electronic spins with the nuclear spins via the hyperfine interactions and N should be very small to get a measurable τ. Assuming there is in addition a magnetocrystalline anisotropy $(K/N)(\Sigma_\mu\aleph_\mu S_\mu{}^z)^2$ we have $\tau^{-1} \sim \varepsilon_{QDJS}\exp(-\zeta N^2S^2K/J)$. As N increases the states $\psi_{QDJS}{}^{M=0}$ collapse to the ground state and give rise to a long living antiferromagnetic wavepacket. τ for ordinary macroscopic samples is larger than the age of the universe by many orders of magnitude).

Collective excitations associated to non-commuting order parameters show also differences with respect to the commuting case. A branch of **spin wave** excitations may be generated by applying locally out of phase ladder operators $S_\mathbf{k}{}^-=\Sigma_\mu\exp(-i\mathbf{k}.\mathbf{r}_\mu)S_\mu{}^-$ to the antiferromagnetic state $\Pi_\mu|S_\mu,M_\mu=\aleph_\mu S>$. We get a dispersion relation $\varepsilon(\mathbf{k})$ that cancels at the ferromagnetic momentum $\mathbf{k}=0$ (the spins of the sublattices A and B precesses then with same phases) and at the antiferromagnetic momentum $\mathbf{k}=\pi$ (the spins of the sublattices A and B precesses then with opposite phases). $\varepsilon(\mathbf{k})$ vanishes **linearly** in the components k_α (α=x,y,z) of $\mathbf{k}$ (and not quadratically) at these points i.e. we have $\varepsilon(\mathbf{k})=\pm[\Sigma_{\alpha\beta}D_{\alpha\beta}k_\alpha k_\beta]^{1/2}$ as $\mathbf{k}$ goes to 0 and $\varepsilon(\mathbf{k})=\pm[\Sigma_{\alpha\beta}D_{\alpha\beta}(k_\alpha-\pi_\alpha)(k_\beta-\pi_\alpha)]^{1/2}$ as $\mathbf{k}$ goes to π, where $D_{\alpha\beta}$ is a symmetric tensor of rank 2: when the true ground state of the system is symmetric, it makes no sense to distinguish between left-handed and right-handed precessions as these precessions transform into each other by the time reversal. Collective excitations deduced from the ground state with a linear spectrum are characteristic of all the systems with an order parameter that do not commute with a Hamiltonian. A familiar example associated with the notion of crystalline states and spontaneous breaking of continuous translational symmetry is the acoustic phonon that shows a linear dispersion relation as a result of the non commutation of the mean position X of the crystal with the kinetic energy which is a function of the total momentum P of the crystal.

Whenever an interaction **breaking the time reversal symmetry** exists, as that associated with an applied magnetic field, an orbital moment may be induced. If the ground state of the system under interest is degenerate the orbital moment will be large whatever is the value of the applied magnetic field as small as it might be, but the induced orbital moment will in general not align along the applied field direction. Since the crystalline electric field potential is not rotationally invariant, the orbital moment tends to align rather along given crystallographic directions associated with the local crystal symmetry. At increasing the strength of the applied field a rotation of the orbital moment towards the applied field direction may however be obtained through a coupling of the orbital ground state with excited orbital states. A finite value of the applied field is necessary to achieve the rotation, that corresponding to the magnetic energy necessary to compensate the **anisotropy energy**. This energy is one of the basic parameters to be maximised in a hard magnet and minimised in a soft magnet. Coupling the ground state with the excited states is furthermore expected to change the amplitude of the orbital moment, which defines a **magnetisation anisotropy**. If now the ground state is a non degenerate state associated with a **trivial representation** Γ_1 of the local crystal symmetry group then no orbital moments may at all be induced except solely through a coupling with the excited states under large applied magnetic fields: there is an **orbital quenching**.

When an ordering sets up in the spin space, the orbital magnetism experiences the associated breaking of the time reversal symmetry through the spin-orbit coupling interaction. If the spin-orbit coupling interaction is the strongest, it will at first couple the spin and the orbital moment within an ion, so that within the Russell-Sanders approximation, these moments will remain parallel. The exchange interactions will tend to induce on a given ion a large expectation value of S_z and therefore of L_z according to a given axis of quantification, whereas the crystalline electric field potential will tend to align the axis of quantification along particular crystallographic directions. Exchange interactions and crystalline electric field potential compete if the relative orientations associated with the former does not coincide with the absolute orientation associated with the latter. An **anisotropy energy** develops which to the first order may be interpreted as the change in **energy of the crystalline electric field** potential due to the rotation from one direction (the easy axis) to another (the hard axis) of the highly asymmetric electronic charge cloud associated with an eigenfunction of L_z. This is e.g. the case for the 4f electrons in the Rare Earth based compounds. On the other hand, if the spin-orbit coupling is the weakest, the spin moments will at first order relatively to each other and the orbital states will decompose according to the local symmetry. Acting as a perturbation, the spin-orbit coupling interaction will then couple the orbital ground state with the excited orbital states in a way similar to that of an applied field $\mathbf{H}_{s.o}$ having the same gradient of orientation as that associated with the relative orientations of the spins. An orbital moment will then be induced which in turn will pin the spin moment in an absolute direction through the spin-orbit coupling interaction. At applying a magnetic field, the spin moments will rotate towards the applied field and the mixing of the orbital ground state with the excited orbital states will change owing to the rotation of the spin-orbit coupling effective field $\mathbf{H}_{s.o.}$ An **anisotropy energy** develops again which may be interpreted now as the cost in the **spin-orbit coupling energy** to rotate the orbital moment along the hard axis of magnetisation. This is the case for the d electrons especially in the 3d transition metal based compounds.

OUTCOMES OF THE BASIC INTERACTIONS: APPROXIMATE METHODS

Usually the different ground states are deduced from the exchange interactions approximately, in somehow more or less sophisticated "mean field approaches" which merely consists in replacing the interactions by an effective field. With a system of N ionic spins $\mathbf{S}_\mu$ interacting via the bilinear exchange $-2\Sigma_{\mu,\nu<\mu}J_{\mu\nu}\mathbf{S}_\mu.\mathbf{S}_\nu$, it is thus customary to assume that the Fourier components $\mathbf{S}_\mathbf{k}=\Sigma_\mu \exp(-i\mathbf{k}.\mathbf{r}_\mu)\mathbf{S}_\mu$ of the spin distribution fluctuates independently (this is referred to as the **random phase approximation**). In this approximation, the exchange interaction takes the "Zeeman" form $-\Sigma_\mathbf{k}\mathbf{H}_{-\mathbf{k}}.\mathbf{S}_\mathbf{k}$ where the effective field $\mathbf{H}_{-\mathbf{k}}=J_{-\mathbf{k}}<\mathbf{S}_{-\mathbf{k}}>_T$ with $J_\mathbf{k}=(1/N)-2\Sigma_{\mu,\nu<\mu}J_{\mu\nu}\exp(-i\mathbf{k}.(\mathbf{r}_\mu-\mathbf{r}_\nu))$ seen by the **k** Fourier component of the spin distribution depends self-consistently on that distribution at a given temperature T. It is then an easy matter to show that the magnetic susceptibility would be $\chi(\mathbf{k})=C/[(T-Tc)+(1-J_\mathbf{k}/J_\mathbf{Q}]$ at high temperature. $\chi(\mathbf{k})$ shows a divergence by decreasing the temperature to the critical value $Tc=CJ_\mathbf{Q}/(g\mu_B)^2$ where **Q** is the wavevector for which $J_\mathbf{k}$ is maximum. At low temperature, the system could be expected to order in a structure defined by the Fourier component $\mathbf{S}_\mathbf{Q}$ (**Q** is then said to be the propagation vector of the low temperature phase) but not necessarily [47].

Another approach is to make use of judicious variational magnetic states. An example is the variational spin density wave states $\psi(\mathbf{q},\phi_\mathbf{k},n_{\mathbf{k}\sigma})=\Pi_{\mathbf{k}\sigma}\alpha_{\mathbf{k}\sigma}{}^+|0>$ considered in the case of the Hubbard model $-\Sigma_{uvs}t_{uv}c_{us}{}^+c_{vs}+(U/2)\Sigma_{us}n_{us}n_{u-s}$ for itinerant electrons. $\psi(\mathbf{q},\phi_\mathbf{k},n_{\mathbf{k}\sigma})$ is constructed from the magnetic quasi-particles operators $\alpha_{\mathbf{k}\sigma=+}=\cos(\phi_\mathbf{k})c_{\mathbf{k}s=+}+\sin(\phi_\mathbf{k})c_{\mathbf{k+q}s=-}$ and $\alpha_{\mathbf{k}\sigma=-}=-\sin(\phi_\mathbf{k})c_{\mathbf{k}s=+}+\cos(\phi_\mathbf{k})c_{\mathbf{k+q}s=-}$ and its variational parameters are the ordering wavevector q, the angles $\phi_\mathbf{k}$ and the occupation numbers $n_{\mathbf{k}\sigma}$ that define for each state σ the Fermi surfaces that enclose the occupied states. $\psi(\mathbf{q},\phi_\mathbf{k},n_{\mathbf{k}\sigma})$ is a Fock state that factorises any quartic term $<c_u{}^+c_vc_p{}^+c_q>$ into $<c_u{}^+c_v><c_p{}^+c_q>-<c_u{}^+c_q><c_p{}^+c_v>$. It is then again an easy matter to calculate the energy $\psi(\mathbf{q},\phi_\mathbf{k},n_{\mathbf{k}\sigma})$ and minimise it with respect to the variational parameters. We get the **Stoner criterion** for the unstability of the paramagnetic state towards the formation of a magnetic state: $2U\chi(\mathbf{q})=1$ where $\chi(\mathbf{q})$ is the magnetic susceptibility of the electrons without the interactions U. $\chi(0)=(1/2)\Sigma_{\mathbf{k}}\partial f(\varepsilon_{\mathbf{k}})/\partial\varepsilon_{\mathbf{k}}$, would describe a uniform ferromagnetic spin order, while $\chi(\mathbf{q})=(1/2)\Sigma_{\mathbf{k}}[f(\varepsilon_{\mathbf{k+q}})-f(\varepsilon_{\mathbf{k}})]/(\varepsilon_{\mathbf{k+q}}-\varepsilon_{\mathbf{k}})$ would describe a spin density wave order. $f(\varepsilon)=(\exp(\varepsilon/k_BT)+1)^{-1}$ is the Fermi function. $\chi(0)$ scales with the density of orbital states at the Fermi level while $\chi(\mathbf{q})$ is optimised by the Fermi surface geometry (nesting and quasi-nesting). As in the case of the mean field approaches, the Stoner criterion overestimates the magnetic ordering and underestimate the effects of the spin fluctuations [41]: an order may be expected if the Stoner criterion is satisfied but not necessarily. Another family of variational states used in the context of itinerant electrons are the Gutzwiller states, which are however more difficult to handle because they do not factorise the quartic interactions. A few exact theorem about the ground states have been formulated. We shall quote the **Lieb's theorem** which shares similarities with the Marshall sign criterion for a system of ionic spins with antiferromagnetic interactions and which states that the ground state ψ_0 of the Hubbard model with hopping parameters t_{uv} that connect only between the sites of two interpenetrating sublattices A and B with respective number of sites N_A and N_B has a total spin $S=|N_A-N_B|/2$ at half-filling and that ψ_0 is unique up to a trivial (2S+1)-fold rotational degeneracy (when $N_A=N_B$ the ground state is, as in the case of the ionic spins interacting antiferromagnetically, the singlet state S=0) [48].

A step beyond in the difficulties is the question of the dynamical correlations which depend on the excited energy and states of the system. Use can been made of the ground state correlations to built excitations on condition to keep in mind that these excitations are perhaps not the only ones. According to the **Goldstone theorem**, if there is a spontaneously broken symmetry in a system with short range interaction, i.e. decaying faster than the inverse square power of the distance, then there always exist a branch of excitation called Goldstone modes, or Goldstone bosons when second quantised, built from the ground state correlations and that vanishes to the ground state energy for a given momentum. The converse statement is false i.e. the existence of gapless excitations in a system does not imply that there is a spontaneously broken symmetry in this system - if the spontaneously broken symmetry emanates from long range interactions then there are "edge" effects that can lead to a gap in the excitation spectrum. A subtle instance is when the system show also a local gauge invariance: the massless Goldstone modes are "gauged away" - as examples the dynamical Coulomb correlations of electrons in a metal get frozen below the plasma frequency and a superconductor has no gapless excitations - in a field theory context that gap is interpreted in terms of mass generation: the Higgs boson mechanism [49]. Goldstone modes in magnetism are the spin waves, which in the case of the ferromagnetism or the antiferromagnetism of a system of ionic spins were found to emerge from the ground state by means of the out of phase ladder operators.

An almost traditional way of dealing with the **spin waves** is to use the **Holstein-Primakoff** representation: bosons operators b_μ are built from the spin operators S_μ as

$S_\mu^+=(2S_\mu-n_\mu)^{1/2}b_\mu$, $S_\mu^-=b_\mu^+(2S_\mu-n_\mu)^{1/2}$ and $S_\mu^z=-n_\mu+S$ with $n_\mu=b_\mu^+b_\mu$ where the local z_μ-quantisation axis is taken to be that of the spin at site μ in the configuration obtained in the classical limit of large S_μ. A disadvantage of this representation is that owing to the square root function, an expansion is always made and truncated at a certain order, which is valid solely when $<n_\mu>$ is much smaller than $2S_\mu$. Using these operators, ferromagnetic exchange interactions $-2J\Sigma_{\mu,\nu<\mu}\mathbf{S}_\mu.\mathbf{S}_\nu$ ($J>0$) expands as $-S_\mu^2JNM/2 + \Sigma_\mathbf{k}\omega_\mathbf{k}b_\mathbf{k}^+b_\mathbf{k}$ + higher order terms (in $b_\mathbf{k}$) where N is the number of spins, M is the number of nearest neighbours of a spin, $b_\mathbf{k}=(1/\sqrt{N})\Sigma_\mu\exp(-i\mathbf{k}.\mathbf{r}_\mu)b_\mu$ and $\omega_\mathbf{k}=S_\mu JM(1-2(1/M)\Sigma_{\mu,\nu<\mu}\exp(-i\mathbf{k}.(\mathbf{r}_\mu-\mathbf{r}_\nu))$ or more shortly $\omega_\mathbf{k}=S_\mu JM(1-\gamma_\mathbf{k})$ $-S_\mu^2JNM/2$ is the ground energy obtained in the classical limit of large S_μ, the second term in the expansion describes non-interacting spin waves and the higher order terms the interactions between the spin waves incorporating the non linear processes of creation and annihilation of the spin waves. With antiferromagnetic exchange interactions (i.e. $J<0$) the following expansion is obtained $S_\mu^2JNM/2 + (\Sigma_\mathbf{k}\omega_\mathbf{k}(a_\mathbf{k}^+a_\mathbf{k}+1/2)+S_\mu JNM/2)$ + higher order terms, with $\omega_\mathbf{k}=S_\mu(-J)M(1-\gamma_\mathbf{k}^2)^{1/2}$, by first rotating by an angle π the spins of one of the sublattices, then performing the Holstein-Primakoff transformation and finally diagonalising, by a Bogoliubov transformation $a_\mathbf{k}^+=\cosh(\phi_\mathbf{k})b_\mathbf{k}-\sinh(\phi_\mathbf{k})b_{-\mathbf{k}}^+$ with $\tanh(2\phi_\mathbf{k})=-\gamma_\mathbf{k}$, the non interacting spin-wave term $JS_\mu M\Sigma_\mathbf{k}[b_\mathbf{k}^+b_\mathbf{k}+(b_\mathbf{k}^+b_{-\mathbf{k}}^++b_\mathbf{k}b_{-\mathbf{k}})/2]$. Unlike the ferromagnetic case, a quantum zero point energy $E-S_\mu^2JNM/2=(1/2)(-J)S_\mu M\Sigma_\mathbf{k}[(1-\gamma_\mathbf{k}^2)^{1/2}-1]$ emerge, which leads to a lower ground energy: the zero point quantum fluctuations, as already discussed above, reduce the energy of an antiferromagnet.

At low temperature the statistical average of the order parameters will show a thermal decrease associated with the spin wave excitations. In a ferromagnet the decrease is given as $\Delta M_F=S-<\Sigma_\mu S_\mu^z>=<\Sigma_\mu n_\mu>=\Sigma_\mathbf{k}n_\mathbf{k}$ where $n_\mathbf{k} = (\exp(\omega_\mathbf{k}/k_BT)-1)^{-1}$ is the Bose function. In an antiferromagnet the decrease writes $\Delta M_{AF}=S-<\Sigma_\mu \aleph_\mu S_\mu^z>=<\Sigma_\mu b_\mathbf{k}^+b_\mathbf{k}>$(with one sublattice of spins rotated by π about the z-axis)$=\Sigma_\mathbf{k}(n_\mathbf{k}+1/2)(1-\gamma_\mathbf{k}^2)^{-1/2}-N/2$. A divergent summation is found for the low dimensional system in both cases as k goes to zero (**infrared singularity**): $\Delta M_F=T/JSk+\ldots$for $d=1$ and $\Delta M_F=TLn(k)/JS+\ldots$for $d=2$ while $\Delta M_F=(-1/8)(T/JS\pi)^{3/2}\zeta(3/2)$ for $d=3$, where $\zeta(z)=\Sigma_n n^{-z}$ is the Rieman zeta function - $\Delta M_{AF}=(1-\gamma_\mathbf{k}^2)^{-1/2}/2k+\ldots$for $d=1$, $\Delta M_{AF}=TLn(k)/(-J)S\sqrt{2}-(1-\gamma_\mathbf{k}^2)^{-1/2}/2+\ldots$for $d=2$ and $\Delta M_{AF}=6^{-7/2}T^2/J^2S^2-(1-\gamma_\mathbf{k}^2)^{-1/2}/2+\ldots$for $d=3$ [48]. Consequently, the initial assumption of the Holstein-Primakoff representation that the fluctuations of the order parameter are small does not hold for the low dimensional systems.

On more general grounds, the **Mermin and Wagner's theorem** [50] proves that short range exchange interactions cannot give rise to a non vanishing order parameter at any finite temperature in one and two dimensions (d=1 or 2). Order parameters that are concerned by the theorem are those with continuous degrees of freedom and not the one dimensional order parameters associated with a discrete symmetry such as those of the Ising or Potts models. On the other hand the theorem does not apply at zero temperature. A long range antiferromagnetic ordering in the ground state of 2D systems was thus demonstrated to be possible for spins $S\geq 3/2$ [51]. It can also be shown that a system does not possess a long-range order in its ground state if there is a gap in the excitation spectrum but the converse is false i.e. the existence of gapless excitations does not imply a long-range order. An illustrative example is provided by the antiferromagnetic spin chains whose physics is quite unusual. With integer spins there is a gap in the excitation spectrum (**Haldane gap**) and the ground state is quantum disordered [52] but has an hidden string order parameter associated with the breacking of a discrete Z2xZ2 symetry. With half-odd integer spins, gapless excitations are found from the exact Bethe ansatz solution with the dispersion relation $\omega_k=(\pi/2)|\sin k|$ [53] but the equal time spin-spin correlations decay as the inverse of the distance and therefore do never diverge. One speaks then of quasi long range order as in all the cases where there is a power law decay of the spin-spin correlations with the distance. **Gaplessness** is now understood in terms of quantum interference of **topological Berry phases** [54]. A theorem due to Lieb, Schultz and Mattis tells also that there exists an excited twisted orthogonal state, which in the thermodynamical limit collapses to the ground state: an admixture able to break a symmetry and to generate further new phases according to the interactions [48]. At present, the interest on the low dimensional systems focuses at coupled chains or ladder systems as the mean to investigate how the d=1 to the d=2 crossover takes place. A ladder system of spins 1/2 with an odd number of chains is thus found to behave like a unique chain of spins 1/2 while with an even number of chains it shows a gap in the excitation spectrum as with the integer spin chain.

We shall end here by emphasising that spontaneous broken symmetry is not the only way for a magnetic system to change its behaviour at low temperature. Other alternatives exist by which a continuous transition to a qualitatively different behaviour could occur without a symmetry breaking. An example is the Kondo transition [45]. Another type of transitions that could be considered is the analogue of the liquid-gas transition as is the case with the Mott transition [45]. We shall finally mention the quantum transitions at zero temperature which in an itinerant electron system are expected to induce non fermi liquid behaviours [55].

CONCLUSION

We do not purport to have given an overview of the field of condensed matter magnetism. As already emphasised above, the task would have been impossible. Our aim was rather to show the richness of the field and to stress on its impact in terms of applications as well as on its theoretical interest in terms of a useful class of many body quantum statistical phenomena. A lot has been learned from its investigations and considerable progress has been achieved but many aspects of the field requires further investigations. Experiments are in that respect of utmost relevance. Macroscopic behaviours can now be measured in various ways : magnetisation, specific heat, ac and dc susceptibility measurements with more and more sophisticated miniaturised techniques. A deeper insight requires however to probe magnetism at the spatial scale of an atom within the largest time window to probe as completely as possible all the dynamical spin correlations. A number of local probes exist that do give information on the spin dynamics either based on resonant spectroscopy (NMR, ESR, Mössbauer effect,...) or on the spin dependent emission associated with the decay of implanted unstable elements (Muon spin rotation and depolarisation or muon spin resonance, 173-247 keV γ-γ cascade of the radioactive ^{111}In->^{111}Cd decay,...) but structural informations on the spin configuration are not obtained by these methods. The unique way to probe both the structural and dynamical correlations in a material was for a long time limited to elastic and inelastic scattering of neutrons. With the advent of synchrotron radiation facilities, new complementary doors are opened in that the experiments allow to go into more fine details (separation of the spin and orbital contributions to the magnetism by magnetic X-ray scattering, double selectivity in terms of orbitals and in terms of atomic species by magnetic circular dichroism,...).

References

[1] Zilstra H. "Permanent Magnets", Wohlfarth E.P., Ferromagnetic Materials volume 3 (North Holland, Amsterdam, 1986)

[2] Chin G.Y. and Wernick J.H., "Soft Magnetic Metallic Materials", Wohlfarth E.P.,

[3] Zvezdin A.K. and Kotov V.A. Modern magnetooptics and magnetooptical phenomena materials (Institute of Physics, Bristol, 1997)

[4] Heinrich B. and Bland G.A., Ultra-thin Magnetic Structures (SpringerVerlag, Berlin, 1994) Ferromagnetic Materials volume 2 (North Holland, Amsterdam, 1982)

[5] Béranger G., Duffaut F., Morlet J. and Tiers J.-F., Cent ans après la découverte de l'Invar...Les alliages de Fer et de Nickel (Technique et Documentation, Paris, 1996)

[6] De Lacheisserie E., Magnetostriction: Theory and Applications (CRC Press, USA, 1993)

[7] Kahn O., Molecular Magnetism (VCH, New York, 1993)

[8] Gignoux D. and Schmitt D. "Magnetic Properties of Intermetallic Compounds, Gschneidner J.A.Jr. and Eyring L., Handbook on the Physics and Chemistry of Rare earths volume 20 (Elsevier Sciences, Amsterdam, 1995) p.293

[9] Morin P. and Schmitt D. "Quadrupolar Interactions and Magneto-Elastic Effects in rare-Earth Intermetallic Compounds, Wohlfarth E.P. and Buschow K.H.J., Ferromagnetic Materials volume 5 (North Holland, Amsterdam, 1989)

[10] Binder K. and Young A.P., *Reviews of Modern Physics*, 54 (1986) 801

[11] Chandra P. and Coleman P. "New Outlooks and Old Dreams in Quantum Antiferromagnetism", Strongly Interacting Fermions and High Tc Superconductivity, Zinn-Justin J. and Douçot B. (North-Holland, Amsterdam, 1993)

[12] Boccara N., Symétries brisées (Hermann, Paris, 1976)

[13] Toulouse G. and Pfeuty P. Introduction au Groupe de Renormalisation et à ses applications (Presses Universitaires de grenoble, 1975)

[14] Baxter R.J., Exactly Solved Models in Statistical Mechanics (Academic Press, London, 1981)

[15] Gunther L. and Barbara B., Quantum Tunneling of Magnetisation-QTM'94 (Kluwer Academic, Dordrecht, Boston and London, 1995)

[16] Nakamura K., Quantum Chaos - A new paradigm of nonlinear dynamics (Cambridge University Press, 1993)

[17] Anderson W. and Brinkman W.F., "Theory of Anisotropic Superfluidity in He^3", The Helium Liquids: Proc. of the 15th Summer School in Physics, 1974, Armitage J.G.M. and Farquhar I.E. (Academic Press, New York, 1975)

[18] Abragham A., Les principes du Magnétisme Nucléaire (Presses Universitaires de France, Paris, 1961)

[19] Schulman L.S., Techniques and Applications of Path Integration (J. Wiley & Sons, New York, 1981)

[20] Bogoliubov N.N., Logounov A.A. and Todorov I.T., Introduction to Axiomatic Quantum Field Theory (W.W. Benjamin, New York, 1975)

[21] Wilczek F., Fractional Statistics and Anyon Superconductivity (World Scientific, Singapore, 1990)

[22] Fradkin E., Field Theories of Condensed Matter - Frontiers in Physics 82 (Addison-Wesley, Redwood City - California, 1991)

[23] Balachandran A.P., "Classical Topological and Quantum Statistics", Fractional Statistics in Action, Wilczek F., *International Journal of Modern Physics B* 5 (1991) n°16-17

[24] Haldane F.D.M., *Phys. Rev. Lett.* **67** (1991) 937 - Bernard D. and Wu Y.-S., "A note on Statistical Interactions and the Thermodynamical Bethe Ansatz", New Developments of Integrable Systems and Long-Ranged Interaction Models, Ge M.-L. and Wu Y.-S. (Word Scientific, 1994) p. 10-20

[25] Herpin A., Théorie du Magnétisme (Presses Universitaires de France, Paris, 1968)

[26] Herring C., "Direct exchange between well separated atoms", Magnetism vol IIB, Rado G.T. and Suhl H. (Academic Press, New York, 1966)

[27] Anderson P.W., *Phys. Rev.* **79** (1950) 350, *Phys. Rev.* **115** (1959) 2, *Solid State Phys.* **14** (1963) 99

[28] Zener C., Phys.Rev. **82** (1951) 403, Anderson P.W. and Hasegawa H., *Phys. Rev.* **100** (1955) 675, De Gennes P.-G., *Phys. Rev.* **118** (1960) 141

[29] Ruderman M.A. and Kittel C., *Phys. Rev.* **96** (1954) 99, Yosida K., *Phys. Rev.* **106** (1957) 893, Kasuya T., *Prog. Theor. Phys.* **16** (1950) 45

[30] Anderson P.W., *Phys. Rev.* **115** (1959) 2, Kasuya T., *Journal of Alloys and Compounds* **192** (1993) 11

[31] Hubbard J., *Proc. of the Roy. Soc.* **A276** (1963) 238, *Proc. of the Roy. Soc.* **A277** (1963) 237

[32] Montorosi A., The Hubbard Model (Word Scientific, 1992)

[33] Negele J.W. and Orland H., Quantum Many-particle Systems (Addison-Wesley, Redwood City - California, 1988)

[34] Mattis D.C., The Many Body Problem - An Encyclopedia of Exactly Solved Models in One Dimension (Word Scientific, 1993)

[35] Mielke A. and Tasaki H. *Commun. Math.Phys.* **158** (1993) 341

[36] Ballhaussen C.J., Introduction to Ligand Field Theory (Mc Graw Hill, New York, 1962)

[37] Judd B., Operator Techniques in Atomic Spectroscopy (Mc Graw Hill, New York, 1963)

[38] Hutchings M.T., "Equivalent Operator Method" Solid State Physics vol. 16 (Academic Press, New York, 1964) p.227

[39] Tinkham M., Group Theory and Quantum Mechanics (Mc Graw Hill, New York, 1964)

[40] Moriya T., *Phys. Rev.* **120** (1960) 91

[41] Landau L., Elasticité, Physique Théorique tome 8 (Editions MIR, Moscou, 1971)

[42] Moriya T., Spin Fluctuations in Itinerant Magnetism, Solid State Sciences 56 (Springer-Verlag, Berlin, 1985)

[43] Lüthi B., *J. Magn. Magn. Mat.* **52** (1985), 70, Lüthi B. and Yoshizawa M., *J. Magn. Magn. Mat.* **63&64** (1987), 274

[44] Campbell I.A. and Creuset G., "Magnetovolume effects", Metallic Magnetism, Capellman (SpringerVerlag, Berlin, 1987)

[45] Anderson P.W., Basic Notions of Condensed Matter Physics - Frontiers in Physics 55 (Addison-Wesley, Redwood City - California, 1984)

[46] Marshall W., *Proc. Royal Soc. London* Ser. A **232** (1955) 48 - Lieb E. and Mattis D.C., *J. Math. Phys.* **3** (1962) 749

[47] White R.M., Quantum theory of Magnetism (Mc Hraw Hill, USA, 1970)

[48] Auerbach A., Interacting Electrons and Quantum Magnetism (Springer-Verlag, Berlin, 1994)

[49] Coleman S., Aspects of Symmetry (Cambridge University Press, 1985)

[50] Mermin N.D. and Wagner H., *Phys. Rev. Lett.* **17** (1966) 1133

[51] Jordao Neves E. and Fernando Perez J., Phys. Lett. **114** A (1986) 331

[52] Haldane F.D., *Phys. Rev. Lett.* **50** (1983) 1153 - Golinelli O., Jolicoeur Th. and Lacaze R., *J. Condens. Matter.* **5** (1993) 1399 - Affleck J., *Phys. Rev. Lett.* **57** (1986) 1048

[53] Des Cloiseaux J. and Pearson J.J., *Phys. Rev.* **128** (1962) 2131

[54] Shapere A. and Wilczek F., Geometric Phases in Physics (World Scientific, 1989)

[55] Coleman P., *Physica* B **206** (1995) 872 - Onuki Y., *Physica* B **206** (1995) 862,