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Quantum spin liquids

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Abstract. This paper presents an overview of the properties of magnetic insulators, with emphasis on quantum effects. In particular, the consequences of strong quantum fluctuations on the low-energy properties of a number of systems are reviewed: the occurrence of a spin gap in spin-1 chains and other low-dimensional magnets; the presence of low-lying singlet excitations in several frustrated magnets; the interplay of orbital and spin fluctuations in orbitally degenerate Mott insulators. This review is intended as a pedagogical introduction to the field, and the formalism has been kept at a minimal level.

1. Introduction

The low-temperature properties of many systems, in particular transition metal oxides, can be very precisely described by an effective spin Hamiltonian known as the **Heisenberg model** [1]:

$$\mathcal{H} = \sum_{(i,j)} J_{ij} \boldsymbol{S}_i \cdot \boldsymbol{S}_j \tag{1}$$

In this expression, the three components of $\boldsymbol{S}$ satisfy the usual commutation rules of angular momentum ($[S^x, S^y] = \mathrm{i}S^z$, etc) and $\boldsymbol{S}^2 = S(S+1)$, where the spin S can be integer or half-integer. In these systems, the magnetic moments are carried by transition metal atoms, and charge fluctuations occur at energies much higher than the largest exchange integrals J_{ij} because of the strong Coulomb repulsion between electrons in localized orbitals. These systems are **Mott insulators** [1, 2].

The properties of the Heisenberg model dramatically depend on various parameters, in particular upon the following.

(a) **The size of the spin**. In general, magnetic moments have both an orbital and a spin contribution and, depending on the system, the resulting spin can be minimal ($S = 1/2$) or quite large (in principle up to $S = 15/2$ in rare earths).

(b) **The sign and the range of the couplings**. The coupling is most often positive (or **antiferromagnetic**) because of the kinetic exchange that allows an electron to hop to a neighbouring orbital already occupied by another electron as long as their spins are antiparallel. However, if the orbitals on neighbouring sites are orthogonal, this process is forbidden by symmetry, and the coupling is then negative (or **ferromagnetic**): being globally antisymmetric, the wavefunction of two electrons with parallel spins vanishes when the electrons are at the same point in space and, hence, minimizes the Coulomb repulsion between electrons. This last effect is known as Hund's rule in atomic physics, according to which spins tend to be parallel in the ground state of atoms with a partially filled level. The range of the coupling due to these processes is limited by the extent of the wavefunctions in which the electrons sit and, since the wavefunctions decrease exponentially, it is usually a very good approximation to consider only the first two or

three neighbours of an atom. The dipolar interaction, which decreases as $1/r^3$, i.e. much more slowly, is in most cases orders of magnitude smaller, hence negligible.

(c) **The dimensionality and geometry of the lattice**. All systems are, strictly speaking, three-dimensional (3D), but it often happens that the couplings in one or two directions are much larger than the other couplings, in which case the systems are effectively one- or two-dimensional. Furthermore, the topology of the lattice (e.g. square, triangular, etc in 2D) can have dramatic consequences on the properties of the system, as we shall see.

It is now clear that very different behaviours can occur depending on these parameters, even if several aspects are still only partially understood. In the following sections, we shall review our present understanding of this field, starting from systems whose properties can be essentially understood in classical terms to reach systems whose properties are completely determined by quantum mechanics.

2. Ordered systems

For 3D systems, the most common situation is the appearance of magnetic long-range order below a critical temperature T_c. This means that the relative orientation of spins is fixed, even at very large distances. The type of order depends on the coupling and, in general, the orientation changes from one site to another. For instance, in the case of a Bravais lattice, i.e. a lattice with only one site per unit cell, the order will correspond to a helical state (see figure 1) characterized by a pitch vector $\boldsymbol{Q}$, and the correlation function will behave like

$$\langle \boldsymbol{S}_i \cdot \boldsymbol{S}_j \rangle \propto M_s^2 \cos \boldsymbol{Q} \cdot (\boldsymbol{R}_i - \boldsymbol{R}_j). \tag{2}$$

The pitch vector $\boldsymbol{Q}$ is determined as the minimum of the Fourier transform $\tilde{J}(\boldsymbol{q})$ of the coupling constants:

$$\tilde{J}(\boldsymbol{q}) = \sum_j J_{ij} \exp\left[\mathrm{i}\boldsymbol{q} \cdot (\boldsymbol{R}_i - \boldsymbol{R}_j)\right]. \tag{3}$$

This includes the particular cases of **ferromagnetism** ($\boldsymbol{Q} = \boldsymbol{0}$) and **antiferromagnetism** or Néel order ($\boldsymbol{Q} = (\pi/a, \pi/a, \pi/a)$ on a cubic lattice of lattice parameter a). The coefficient M_s is usually called the staggered magnetization by extension of the terminology used for antiferromagnets (AF for short).

This picture is closely related to the so-called 'classical' limit, where $\boldsymbol{S}$ is considered as a classical vector of length S. In fact, in this limit the energy is indeed minimized on a Bravais lattice by choosing, for instance, $\boldsymbol{S}_i = (S \cos \boldsymbol{Q} \cdot \boldsymbol{R}_i, S \sin \boldsymbol{Q} \cdot \boldsymbol{R}_i, 0)$, in which case $\boldsymbol{S}_i \cdot \boldsymbol{S}_j = S^2 \cos \boldsymbol{Q} \cdot (\boldsymbol{R}_i - \boldsymbol{R}_j)$. Quantum effects enter as a renormalization of this function, since in general, $M_s^2 < S^2$. These quantum fluctuations can be treated in the context of a $1/S$ expansion, and they vanish in the limit $S \to +\infty$. A systematic way of performing this

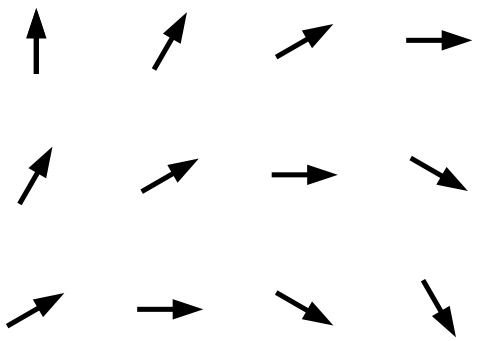

Figure 1. Example of helical order.

expansion is to use the Holstein–Primakoff representation of spin operators in terms of bosonic creation and annihilation operators:

$$S_i^z = S - a_i^+ a_i \qquad S_i^+ = \sqrt{2S - a_i^+ a_i}\, a_i \qquad S_i^- = a_i^+ \sqrt{2S - a_i^+ a_i} \tag{4}$$

and to classify the terms in the Hamiltonian in powers of $1/S$ [3].

Keeping only terms of order S^2 and S corresponds to the so-called 'linear spin-wave theory'. This already contains the basic aspects of quantum fluctuations in ordered systems.

The main consequence of long-range order is the presence of low-energy, hydrodynamic fluctuations, as in all systems with long-range order, and this is in essence classical. Specific quantum effects are important only at very low temperature, 'very low' meaning far below the ordering transition temperature. The quantum nature of the low-energy fluctuations, called spin-waves, then becomes important and, since they are bosonic in nature, as suggested by equation (4), they will lead to properties typical of bosons. For instance, the specific heat behaves as T^3 for 3D antiferromagnets at low temperatures, in close analogy to phonons.

How general is this picture? Until about 20 years ago, it was thought to be very general. All magnetic insulators appeared to present some kind of long-range order at sufficiently low temperature, and, apart from some very specific models [4], the presence of long-range order seemed to be a universal property of the Heisenberg model. In 2D, there is an analytical proof that the ground state of the AF, nearest-neighbour Heisenberg model has long-range order for $S \geqslant 1$ [5], and there is very strong numerical evidence that this is also the case for $S = 1/2$ [6]. Even in 1D and for $S = 1/2$, where quantum fluctuations are *a priori* largest, the Bethe ansatz solution [7] of the model shows that it is almost ordered, with low-lying excitations and with a spin–spin correlation function that decreases very slowly, as $1/r$ up to logarithmic corrections. In such a case, one talks of 'algebraic order'. This should be contrasted with the case of magnets above their critical temperature, where the spin–spin correlation function decays exponentially with the distance due to the destruction of long-range order by thermal fluctuations. The last 20 years have witnessed a true revolution in that field which will be described in the next sections. For simplicity, the discussion will be limited, unless specified otherwise, to the Heisenberg model with only nearest-neighbour interactions defined by the Hamiltonian:

$$\mathcal{H} = J \sum_{\langle i,j \rangle} \boldsymbol{S}_i \cdot \boldsymbol{S}_j \tag{5}$$

on various lattices and for different values of the spin S.

3. Gapped systems

By far the most remarkable event is the prediction by Haldane in 1983 [8] that the AF, $S = 1$ Heisenberg chain is disordered at zero temperature, with a correlation function that decreases exponentially at large distance:

$$\langle \boldsymbol{S}_i \cdot \boldsymbol{S}_j \rangle \propto (-1)^{|i-j|} \exp\left[-|\boldsymbol{R}_i - \boldsymbol{R}_j|/\xi\right]. \tag{6}$$

This result came as a great surprise since one expected the quantum fluctuations to be less severe than for $S = 1/2$, a system in which the correlation function decays very slowly. It is nevertheless in some sense the most natural one: in 1D antiferromagnets, the quantum correction $S^2 - M_s^2$ estimated from spin waves has an infrared divergence. Thus, the $1/S$ treatment is not valid, and 1D antiferromagnets cannot sustain long-wavelength spin waves. The paradox of $S = 1/2$ was lifted when it was realized that low-lying excitations are not spin waves but soliton-like topological excitations [9]. Such excitations can exist only for half-integer spins. Thus, all integer AF spin chains must be disordered. Haldane's prediction has been verified in many organic and inorganic compounds [10].

One very important corollary of the exponential decay of the correlation function is the presence of a spin gap: the system has no low-energy excitations. The ground state is a spin singlet, and the first triplet excitations show up at a finite energy $\Delta > 0$. The presence of a gap

is a natural consequence of the finite correlation length. The system behaves as a finite system of size ξ and, for a finite system, energy levels are quantized. The gap Δ is thus essentially the energy difference between the singlet ground state and the first excited triplet of a finite system. It is thus of the order of J/N (N is the number of sites of the cluster), i.e. $\Delta \propto J/(\xi/a)^d$ (where a is the lattice parameter and d is the dimensionality of the space). Magnetic systems with a finite correlation length at zero temperature and a spin gap are called **spin liquids**, by analogy with standard liquids, which, in contrast to solids, have only short-range order.

The most striking feature of these systems appears in their response to a magnetic field. Quite generally, systems with local magnetic moments develop a macroscopic moment $\boldsymbol{M}$ when put into a magnetic field $\boldsymbol{H}$ because this lowers the total energy by an amount:

$$E = -\boldsymbol{M} \cdot \boldsymbol{H}. \tag{7}$$

If the magnetic field is small, the moment is proportional to the field:

$$\boldsymbol{M} = \chi \boldsymbol{H}. \tag{8}$$

The coefficient χ is called the magnetic susceptibility. The typical behaviour of the susceptibility in standard systems is depicted in figure 2. It arises from an interplay between thermal fluctuations, which favour disorder to increase the entropy, and exchange interactions, which favour a certain relative orientation of the moments. The typical behaviours are the following.

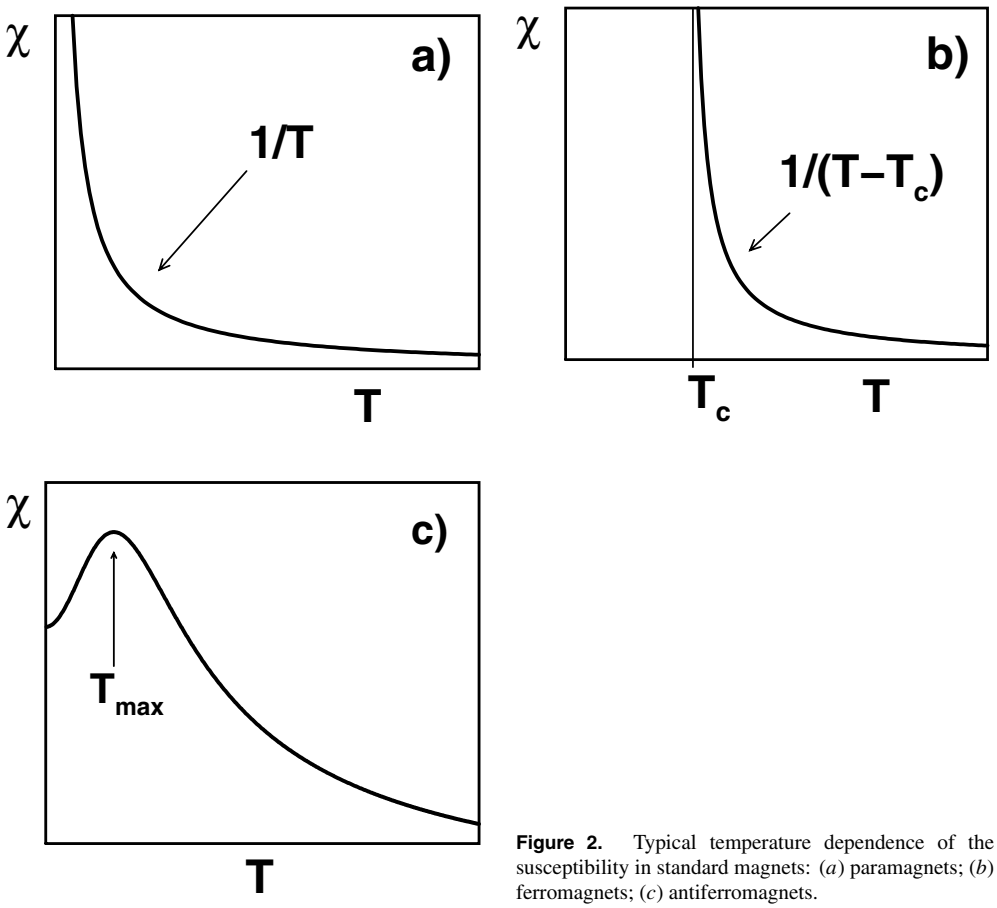

Figure 2. Typical temperature dependence of the susceptibility in standard magnets: (*a*) paramagnets; (*b*) ferromagnets; (*c*) antiferromagnets.

(a) **Paramagnetism**. With no coupling between the spins, these systems are controlled by thermal fluctuations, and the susceptibility follows the Curie law $\chi \propto 1/T$.
(b) **Ferromagnetism**. Below T_c, the system spontaneously acquires a macroscopic moment. Since this moment will align along the field in any infinitesimal field, the susceptibility is infinite below T_c and diverges at T_c.
(c) **Antiferromagnetism**. Antiferromagnetic order prevents the moments from aligning along the field. Thus, below a temperature T_{max} of the order of J, the ability of the system to polarize decreases, and the susceptibility decreases accordingly. It does not go to zero however because it is energetically favourable to adopt a configuration in which the moments are perpendicular to the field with a small component along the field (see figure 3).

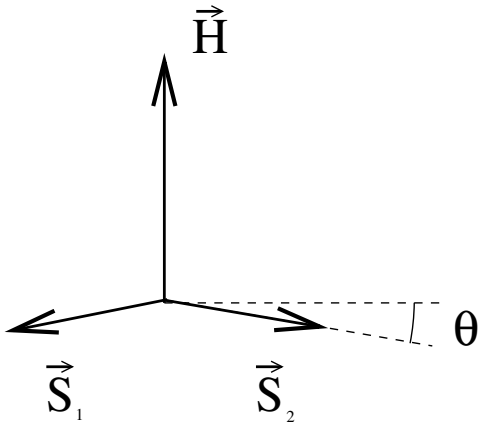

Figure 3. Spin configuration in a classical antiferromagnet in the presence of a magnetic field. The moments are related to the spins by $\boldsymbol{\mu} = -g\mu_B \boldsymbol{S}$. Thus, there is a small resulting moment in the direction of the field.

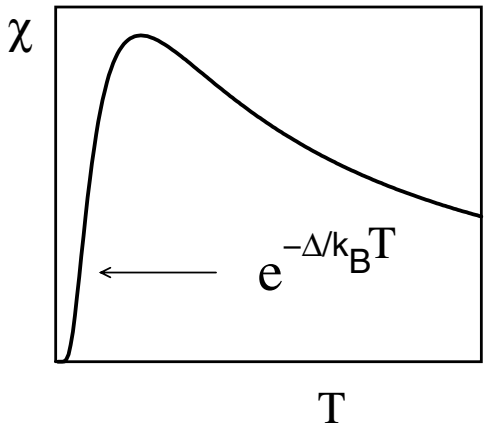

Figure 4. Typical temperature dependence of the susceptibility of a spin liquid.

In spin liquids, the susceptibility behaves very differently (see figure 4): it goes to zero exponentially at low temperature as $\chi \propto \exp[-\Delta/k_B T]$. The origin of the difference from antiferromagnets is that the low-energy configuration of figure 3 cannot be achieved in a quantum system with a finite correlation length. To understand this, let us consider the simple case of two spins in a magnetic field $\boldsymbol{H}$. Since the magnetic moment $\boldsymbol{\mu}$ carried by an atom is related to the spin by $\boldsymbol{\mu} = -g\mu_B \boldsymbol{S}$, the energy is given by

$$E = J\boldsymbol{S}_1 \cdot \boldsymbol{S}_2 + g\mu_B \boldsymbol{H} \cdot (\boldsymbol{S}_1 + \boldsymbol{S}_2). \tag{9}$$

If one treats the spins as classical vectors of length S, one can easily show that the energy is minimal when the spins adopt a symmetric configuration with respect to the field (see figure 3). The energy of such a configuration is given by:

$$E = -J\cos 2\theta - 2g\mu_B HS\sin\theta. \tag{10}$$

The minimum occurs when $\partial E/\partial\theta = 0$, which gives

$$\sin\theta = \frac{g\mu_B HS}{2J}. \tag{11}$$

In the ground state, the magnetization M is the sum of the projections of the moments along the field:

$$M = 2g\mu_B S\sin\theta = \frac{H(g\mu_B S)^2}{J}. \tag{12}$$

Thus, at zero temperature, the susceptibility is given by:

$$\chi = \frac{(g\mu_B S)^2}{J}. \tag{13}$$

Note that in the limit $H \to 0$, it is always advantageous to tilt the moments: for small θ, the energy can be expanded as

$$E = -J - 2g\mu_B HS\theta + 2J\theta^2 + \mathrm{O}(\theta^3). \tag{14}$$

The energy gain due to the field, which is linear in θ, always dominates over the loss of exchange energy, which is quadratic in θ.

For a quantum mechanical system, the Hamiltonian is given by:

$$\mathcal{H} = J\boldsymbol{S}_1 \cdot \boldsymbol{S}_2 + g\mu_B H(S_1^z + S_2^z) \tag{15}$$

and the ground-state magnetization is proportional to the mean value $\langle S_1^z + S_2^z \rangle$. But $\boldsymbol{S}_1 \cdot \boldsymbol{S}_2$ can be rewritten as a function of the total spin $\boldsymbol{S}_{\mathrm{tot}} = \boldsymbol{S}_1 + \boldsymbol{S}_2$ as

$$\boldsymbol{S}_1 \cdot \boldsymbol{S}_2 = \frac{1}{2}\left[(\boldsymbol{S}_1 + \boldsymbol{S}_2)^2 - \boldsymbol{S}_1^2 - \boldsymbol{S}_2^2\right] = \frac{1}{2}\boldsymbol{S}_{\mathrm{tot}}^2 - S(S+1) \tag{16}$$

and, accordingly, the Hamiltonian can be rewritten as

$$\mathcal{H} = -JS(S+1) + \frac{J}{2}\boldsymbol{S}_{\mathrm{tot}}^2 + g\mu_B HS_{\mathrm{tot}}^z. \tag{17}$$

Since S_{tot}^z and $\boldsymbol{S}_{\mathrm{tot}}^2$ commute with each other, the eigenstates can be classified according to the value of S_{tot} and S_{tot}^z:

$$\mathcal{H}|S_{\mathrm{tot}}; S_{\mathrm{tot}}^z\rangle = \left(JS(S+1) + \frac{J}{2}S_{\mathrm{tot}}(S_{\mathrm{tot}}+1) + g\mu_B HS_{\mathrm{tot}}^z\right)|S_{\mathrm{tot}}; S_{\mathrm{tot}}^z\rangle. \tag{18}$$

In this expression, S_{tot} can take all the values from 0 to $2S$, while S_{tot}^z can take all the values from $-S_{\mathrm{tot}}$ to S_{tot}.

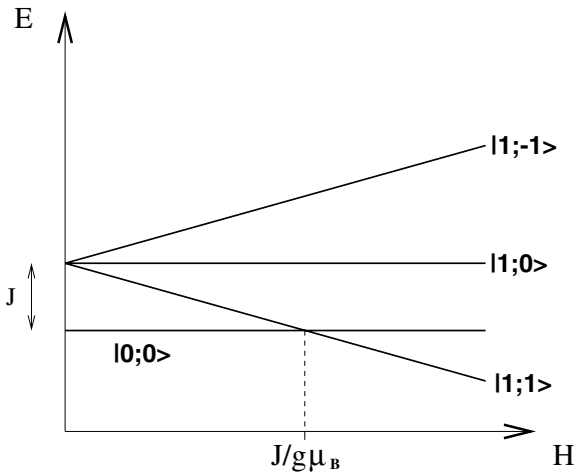

Figure 5. Magnetic field dependence of the energy of the lowest levels of two quantum spins coupled antiferromagnetically.

The energy of the first few states is plotted in figure 5 as a function of H. The ground state corresponds to $S_{\mathrm{tot}}^z = 0$ as long as $H < J/g\mu_B$. Thus, at small field, the magnetization is equal to zero. The susceptibility is thus equal to zero at zero temperature. As announced above, this effect is a pure quantum effect.

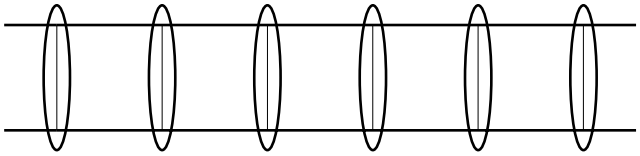

Figure 6. Spin ladder. The ellipses represent singlets on the rungs.

Since the first observation of a spin gap in a spin-1 chain, several systems with similar properties have been discovered. The example that has been most extensively studied in the mid 90's is that of the $S = 1/2$ spin ladders (figure 6) defined by the Hamiltonian:

$$\mathcal{H} = J_{\parallel} \sum_i \sum_{\alpha=1,2} \boldsymbol{S}_{i\alpha} \cdot \boldsymbol{S}_{i+1\alpha} + J_{\perp} \sum_i \boldsymbol{S}_{i1} \cdot \boldsymbol{S}_{i2}. \tag{19}$$

In that case, the presence of a gap is very intuitive in the limit $J_{\perp} \gg J_{\parallel}$. In the limit $J_{\parallel} = 0$, the ground-state wavefunction is just a product of singlets constructed on the rungs of the ladder:

$$|\psi\rangle = \prod_i [i1, i2] \tag{20}$$

where $[i1, i2]$ is the singlet constructed on rung i:

$$[i1, i2] = \frac{|\uparrow_{i1}\downarrow_{i2}\rangle - |\downarrow_{i1}\uparrow_{i2}\rangle}{\sqrt{2}}. \tag{21}$$

When $J_{\parallel}$ is small but not equal to zero, the ground-state wavefunction can be expanded in powers of $J_{\parallel}$, and it essentially retains the form of equation (20). To make an excitation, one has to break a singlet, and this costs a finite energy equal to $J_{\perp}$ minus a small correction due to the kinetic energy to be gained thanks to $J_{\parallel}$. It is however possible to show, using quantum field theory arguments, that there is a gap for all values of $J_{\perp}$ as long as $J_{\perp} > 0$. Several oxides ($SrCu_2O_3$, CaV_2O_5,...) are very good realizations of spin ladders [11]. Among the recent developments in that field, one can cite the study of an organo-metallic ladder $Cu_2(C_5H_{12}N_2)_2Cl_4$ in a magnetic field [12]. The interesting effect is that a strong magnetic field can close the spin gap by pulling down one of the first triplet excitations, similarly to in the example of two spins depicted in figure 5. In the same spirit, 2D systems with a spin gap have been discovered. The system CaV_4O_9 is particularly interesting because the building bricks are not dimers but four-site plaquettes [13]. The physics is nevertheless quite similar. The most recent example is the compound $SrCu_2(BO_3)_2$ [14]. It can be seen as a 2D arrangement of dimers, and the low-temperature physics is again quite similar. The properties under a high magnetic field are quite remarkable, however. The magnetization curve does not rise smoothly between the field that closes the gap and the saturation field but exhibits plateaux at some rational values of the magnetization. Work is in progress to explain this effect.

4. Frustrated magnets and low-lying singlets

From the previous discussion, one might feel that the alternative 'ordered or gapped' exhausts the physics of quantum magnets. This is far from the truth, however. It has been known for a long time that, in addition to lowering the dimensionality, there is another way to increase quantum fluctuations, namely by introducing **frustration**, that is a competition between exchange integrals. The classical example is the AF Heisenberg model on the triangular lattice. There is frustration because it is impossible to satisfy fully and simultaneously the three bonds of a given triangle, and one must settle for a compromise. In the case of the triangular lattice, recent numerical results strongly suggest that the system still develops helical long-range order by adopting a three sublattice configuration [15]. So in that case the quantum system retains the classical order in spite of strong quantum fluctuations.

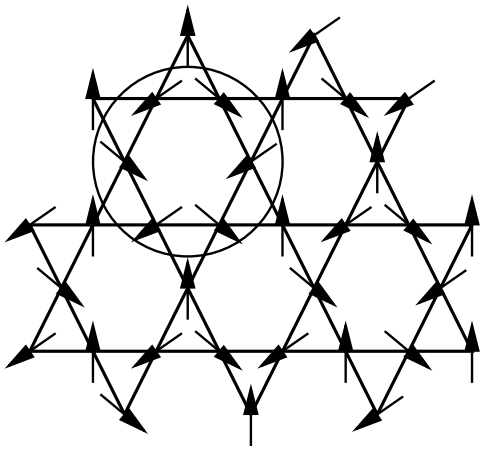

Figure 7. Kagomé lattice. An example of a classical ground state is shown. A rotation of the spins inside the circle around the common direction of the external spins does not change the energy and generates an infinity of degenerate ground states.

New physics has appeared in systems for which the classical case is already pathological, namely systems for which the classical ground state is infinitely degenerate. The most famous example is the AF Heisenberg model on the kagomé lattice (figure 7). Like the triangular lattice, this lattice is made of triangles, and if it is possible to find a configuration that minimizes the energy of every triangle, this will also minimize the total energy. Now the energy of a triangle can be written as:

$$E = J\ (\boldsymbol{S}_1 \cdot \boldsymbol{S}_2 + \boldsymbol{S}_2 \cdot \boldsymbol{S}_3 + \boldsymbol{S}_3 \cdot \boldsymbol{S}_1) = \frac{J}{2}\left[(\boldsymbol{S}_1 + \boldsymbol{S}_2 + \boldsymbol{S}_3)^2 - (\boldsymbol{S}_1{}^2 + \boldsymbol{S}_2{}^2 + \boldsymbol{S}_3{}^2)\right]. \tag{22}$$

$\boldsymbol{S}_1{}^2 + \boldsymbol{S}_2{}^2 + \boldsymbol{S}_3{}^2$ being a constant, and $(\boldsymbol{S}_1 + \boldsymbol{S}_2 + \boldsymbol{S}_3)^2$ being positive, the energy is minimal for configurations such that $\boldsymbol{S}_1 + \boldsymbol{S}_2 + \boldsymbol{S}_3 = \boldsymbol{0}$. On the triangular lattice, the constraints are such that, up to a global rotation of the spins, one can find only one global configuration that minimizes the total energy. This is not true, however, of the kagomé lattice, which is far less constrained and for which one can find an infinite number of such configurations [16].

To include quantum fluctuations is a highly non-trivial task in such a case. The first problem is that there is no longer a natural classical starting point since there are infinitely many possible reference states. One possible way of handling this problem is to compare the energy obtained starting from different classical states after inclusion of the zero-point contribution due to spin waves. This usually leads to a lifting of the classical degeneracy, an effect known as 'order from disorder' [17]. While this procedure is already well defined within linear spin-wave theory for cases with a finite degeneracy of the classical ground state, there is a specific problem when the degeneracy is infinite. This degeneracy leads to zero-energy modes in the linear spin-wave theory, hence again to a divergence of the quantum correction $S^2 - M_s^2$. One can cure this problem by including higher-order terms in the spin-wave expansion, but such an expansion in $1/S$ is somewhat questionable for small spins, such as, e.g. $S = 1/2$. By analogy with the Haldane chain, another likely scenario is the opening of a gap in the excitation spectrum.

The truth turns out to be even more interesting. Very extensive numerical simulations on the $S = 1/2$ AF Heisenberg model on the kagomé lattice have shown that there is indeed a singlet–triplet gap in the spectrum, but that this gap is filled by a large number of low-lying singlets [18], which number grows like $(1.15)^{N_{\text{sites}}}$. Great effort is currently devoted to the explanation of these results. The first idea to explain the origin of these singlets was the resonating-valence bond (RVB) theory first proposed by Anderson for the triangular lattice [19]. According to this theory, the system prefers to be in a configuration which is a product of singlets constructed on nearest-neighbour dimers, i.e. a valence-bond configuration, rather than to build long-range order, very much like for a ladder in the $J_\perp \gg J_\parallel$ limit. However,

in the case of the triangular lattice, there is no self-evidently better way of choosing the dimer covering. The system is thus expected to resonate between configurations constructed from different dimer coverings (see figure 8), hence the name RVB. Abandoned in the case of the triangular lattice, which is now believed to be ordered [15], this theory has become very popular again, first in the context of high- T_c cuprates [20], and, more recently, in the context of the kagomé antiferromagnet [21]. In this case, the idea is to explain the low-lying singlets as linear combinations of singlet dimer coverings of the kagomé lattice. In its simplest version, this explanation has a serious problem: the number of dimer coverings is equal $(2^{1/3})^{N_{\text{sites}}} \simeq (1.26)^{N_{\text{sites}}}$, which is much too large compared with the numerical estimate $(1.15)^{N_{\text{sites}}}$. This is not a final blow, however: fluctuations between these configurations might *a priori* lead to a spectrum with only $(1.15)^{N_{\text{sites}}}$ low-lying states. Analytical arguments proving that this is indeed the case have been put forward for a trimerized version of the model [22], and there is now numerical evidence that this is also the case for the standard kagomé lattice [23]. Therefore, it is now widely accepted that the low-energy physics of the AF Heisenberg model on the kagomé lattice is of the RVB type.

The particular property of such a spin liquid is the possession of low-lying singlet excitations in the singlet–triplet gap Δ. From an experimental point of view, if one still expects the magnetic susceptibility to behave like $\exp(-\Delta/k_B T)$, since only states with non-zero total spin can react to a magnetic field, the specific heat will have *a priori* a contribution from the singlets that could lead to a power-law dependence $C_v \propto T^{\alpha}$. The analysis of this singlet subspace turned out to be very difficult, however, and it has not yet been possible to reach a conclusion.

To date, there is no experimental realization of the $S = 1/2$, AF Heisenberg model on the kagomé lattice. The compounds known at the time of writing have a larger spin, and it is not clear that the physics is the same [24]. First, the presence of low-lying singlets for integer spins is not guaranteed. This observation is based on the fact that the properties of a triangle are very different for half-integer and integer spins: the ground state is a two-fold degenerate doublet for half-integer spins, and a non-degenerate singlet for integer spins. Furthermore, for larger spins, the singlet–triplet gap is probably very small, and might even vanish. The spin-glass behaviour reported in several $S = 3/2$ and $S = 5/2$ kagomé systems might actually be due to the combined effect of low-lying singlets and low-energy magnetic excitations.

Even if chemists do not succeed in the near future in synthesizing a $S = 1/2$ kagomé AF, this is probably not too serious because other systems are good candidates as well. First, other lattices lead to an infinite degeneracy of the classical ground state as is the case, for instance, for the pyrochlore lattice [25] (see figure 9), a 3D lattice built from tetrahedra, or other lattices based on tetrahedra [26]. It seems that the low-temperature properties of the pyrochlore systems synthesized to date are dominated by the on-site anisotropy, which reduces the symmetry of the coupling from Heisenberg to Ising and radically changes the physics [27]. But the synthesis of $S = 1/2$ systems, for which there can be no single-ion anisotropy, is under way in several groups, and progress in this direction is to be expected soon.

However, frustration or reduced dimensionality are not the only ways of producing spin liquids. Another possibility, which is attracting increasing attention, comes from Mott insulators with orbital degeneracy. This rather common situation occurs for systems with

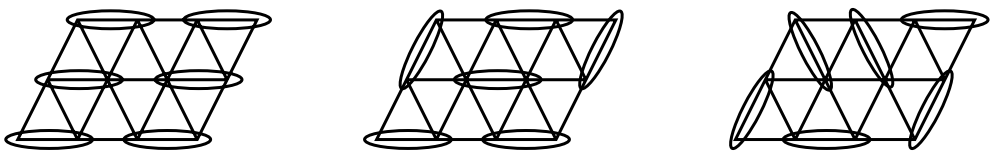

Figure 8. Examples of dimer coverings of the triangular lattice. The ellipses represent singlets on the dimers.

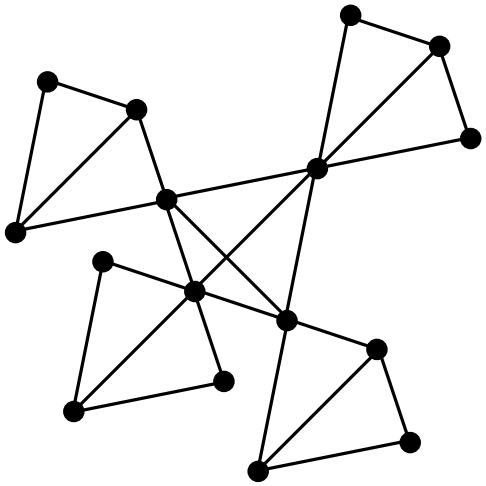

Figure 9. Pyrochlore lattice.

a partially filled band when the crystal field has only partially lifted the degeneracy of the atomic levels. A typical example is Cu^{2+} in an octahedral environment: the hole of the $3d^9$ configuration can go in any of the two e_g orbitals. In such systems, the Hamiltonian, known as the Kugel–Khomskii model [28], is of the type:

$$\mathcal{H} = J \sum_{\langle i,j \rangle} \left(2\boldsymbol{S}_i \cdot \boldsymbol{S}_j + \frac{1}{2} \right) \left(2\boldsymbol{\tau}_i \cdot \boldsymbol{\tau}_j + \frac{1}{2} \right) \tag{23}$$

where the pseudo-spin $\boldsymbol{\tau}$ describes orbital fluctuations. The general Hamiltonian also contains less symmetric terms, but the Hamiltonian of equation (23) is a good starting point for several compounds.

When $S = 1/2$ and $\tau = 1/2$ (two-fold degenerate orbital), the symmetry of the model is not simply $SU(2) \times SU(2)$ but $SU(4)$: for a spin 1/2, $2\boldsymbol{S}_i \cdot \boldsymbol{S}_j + \frac{1}{2}$ is the permutation operator. So the Hamiltonian of equation (23) consists of the permutation of objects with four colours, each colour corresponding to a spin-orbital configuration ($1 = \uparrow\uparrow$, $2 = \uparrow\downarrow$, $3 = \downarrow\uparrow$, $4 = \downarrow\downarrow$). There are several ways of taking a 'classical' limit of this model. For instance, one could consider $\boldsymbol{S}$ and $\boldsymbol{\tau}$ as classical vectors. In that case, it is easy to show that there is an infinite degeneracy. A more natural limit, that is a limit which does not break the symmetry between the four colours, is the AF four-state Potts model [29]. Again, the ground state is infinitely degenerate. In that sense, these models are similar to very frustrated spin systems, and the possibility of obtaining a spin liquid with RVB-like physics has been convincingly suggested [30]. $LiNiO_2$ could be the first example of this class [31].

5. Conclusion

There is increasing evidence that quantum effects play a major role in the low-temperature properties of various classes of magnetic systems. The usual picture of ordered moments with low-energy, hydrodynamic fluctuations breaks down in several situations owing to very large quantum fluctuations.

At that stage, the best way to classify the possible behaviours is probably to look at the spectrum of a finite system. Roughly speaking, three kinds of spectra are possible:

- **Ordered systems**. There is a finite gap, but this gap goes to zero when the system size goes to infinity, and the first excitations are magnetic ($S \geqslant 1$). They are arranged in a

tower-like fashion (Anderson's tower of states)‡. The collapse of these states gives rise to the spin waves in the thermodynamic limit.

- **Gapped systems**. The first excitations are also magnetic, but they remain at a finite energy Δ from the ground state when the system size goes to infinity. All thermodynamic quantities (susceptibility, specific heat,...) are activated at low temperature.
- **Low-lying singlets**. The magnetic excitations are gapped, but there is a continuum of low-lying singlets inside this gap. The magnetic susceptibility is activated, but the specific heat can have a power-law behaviour.

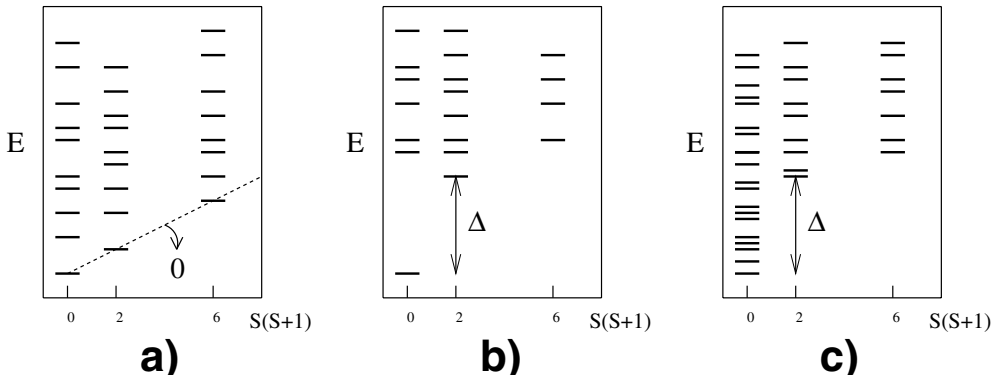

Figure 10. Typical spectrum for: (*a*) an ordered antiferromagnet; (*b*) a gapped system; (*c*) a frustrated system with low-lying excitations.

Many examples of systems in the second category are now known, the best studied examples being $S = 1$ chains and $S = 1/2$ ladders. The search for systems of the third kind, as well as better theoretical predictions regarding their properties, is a very active field of research at the moment, and is likely to remain so for a number of years. While it will be rewarding to observe this physics in actual systems, the pay-off might even be higher. A better understanding of spin liquids in general might help understand the underdoped phase of the high-T_c cuprates [32] and pin down the mechanism of superconductivity in these fascinating systems.

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‡ This is true for systems with $Q \neq 0$. Ferromagnets are simpler, but from this point of view pathological: the dispersion is quadratic around $Q = 0$.

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