

Spin gap antiferromagnets: materials and phenomena

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There are several interacting spin systems which have a gap in their spin excitation spectra. The gap does not occur due to anisotropies present in the system but is quantum mechanical in origin. We give a brief overview on different types of spin gap (SG) antiferromagnets, the models proposed to describe their physical properties and experimental realizations of such systems. Our special focus is on exactly-solvable models and rigorous theories which provide the correct physical picture for the novel phenomena exhibited by SG systems.

THE last decade has witnessed an unprecedented research activity on undoped and doped quantum antiferromagnets (AFMs) in low dimensions. Several new materials exhibiting a variety of novel phenomena have been discovered. The experimental effort is closely linked with theoretical ideas. The field of low-dimensional quantum magnetism provides a fertile ground for rigorous theory. Powerful techniques like the Bethe Ansatz (BA)¹ and bosonization are available to study ground and excited state properties. Models of interacting spin systems are known for which the ground state and in some cases their low-lying excitation spectra are known exactly. Theorems, furthermore, offer important insight into the nature of the ground and the excited states. The knowledge gained provides impetus to look for real materials so that experimental confirmation of theoretical predictions can be made. In this review, we discuss a special class of low-dimensional AFMs, the so-called spin gap (SG) systems, to illustrate the rich interplay between theory and experiments. The review is not meant to be exhaustive but focuses on some broad classes of phenomena exhibited by SG systems.

The SG AFMs are characterized by a gap in their spin excitation spectra. The magnitude of the gap, Δ , is the difference between the energies of the lowest excited state and the ground state. The excitation spectrum of an AFM is said to be gapless if $\Delta = 0$. In general, a gap appears in the spin excitation spectrum if some kind of anisotropy is present in the system. In SG AFMs, however, the gap is purely quantum mechanical in origin and cannot be ascribed to any anisotropy. The basic spin-spin interactions in AFMs are described by the Heisenberg Hamiltonian

$$H = \sum_{\langle ij \rangle} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j \quad (1)$$

where $\mathbf{S}_i$ is the spin operator located at the lattice site i and J_{ij} denotes the strength of the exchange interaction. Real magnetic materials are three-dimensional (3d) but behave effectively as low-dimensional systems if the dominant exchange interactions are intra-chain (1d) or intra-planar (2d). For most materials, the exchange interaction is confined to only the nearest-neighbour (n.n.) spins on the lattice. Also, J_{ij} 's have the same magnitude J for all the n.n. interactions. There are, however, spin systems in which further-neighbour interactions cannot be ignored and the exchange interaction strengths are inhomogeneous in character. In the next section, we discuss some possible origins of SG, the models proposed to describe such systems and experimental evidence for different mechanisms of SG.

Origins of spin gap

SG AFMs have spin-disordered ground states, i.e. the spin-spin correlations in the ground state are short-ranged. The ground states, in the absence of long range magnetic order, can broadly be described as quantum spin liquids (QSLs). The spin liquids are distinct from simple paramagnets, in certain cases one can define novel order parameters which have non-zero expectation values in the QSL states. Formation of such states is favoured by quantum fluctuations, the effect of which is prominent in low dimensions and for low values of the spin. In experiments, the presence of the gap Δ is confirmed through measurement of properties like susceptibility, χ , which goes to zero exponentially at low T as $\chi \sim \exp(-\Delta/k_B T)$. Some well-known examples of SG AFMs are: spin-Peierls (SP) systems, AFM compounds consisting of weakly coupled spin dimers, frustrated spin systems, spin ladders and Haldane gap (HG) AFMs. SP compounds are historically the first examples of magnetic systems exhibiting a SG. The SP transition was originally observed in some organic compounds. In 1993, Hase *et al.*² obtained the first experimental evidence of the SP transition in an inorganic compound, CuGeO_3 . The SP transition generally occurs in quasi-one dimensional (1d) AFM spin systems with half-odd integer spins and is brought about by spin-phonon coupling. Below the SP transition temperature T_{SP} , a periodic deformation of the lattice sets in

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such that the distances between neighbouring spins are no longer uniform but alternate in magnitude. This results in an alternation, $J(1+\delta)$ and $J(1-\delta)$, in the strengths of the n.n. exchange interaction strengths. The ground state is dimerized in which singlet spin pairs occupy the links with enhanced exchange couplings. The SP ground state is spin disordered and a finite energy gap exists in the $S=1$ spin excitation spectrum.

Some AFM compounds can be described as crystalline networks of spin dimers. Well-known examples of such systems are the compounds $ACuCl_3$ ($A=K, Tl$) in which a spin dimer arises from two antiferromagnetically coupled Cu^{2+} ions^{3,4}. The dimer ground state is a spin singlet with total spin $S=0$. The excited triplet state with total spin $S=1$ is separated from the ground state by an energy gap. The excitation created on a particular dimer propagates through the network of dimers due to the weak inter-dimer exchange coupling.

Frustrated spin systems

Quantum fluctuations in a spin system are enhanced due to the presence of frustration in the system. Frustration implies a conflict in minimizing the exchange interaction energies associated with different spin pairs. Such conflicts arise mainly due to lattice topology and the presence of competing further-neighbour interactions⁵. AFM systems with an odd number of bonds in the unit cell of the underlying lattice are frustrated spin systems. Examples include the triangular, kagomé, pyrochlore and FCC lattices. Consider three Ising spins located at the vertices of a triangular plaquette and interacting antiferromagnetically with each other. The energy of an interacting spin pair is minimized when the spins are antiparallel. The three interacting spin pairs cannot, however, be simultaneously made antiparallel so that one pair is in the parallel spin configuration in the lowest energy state. Such conflicts are absent when the elementary plaquette of the lattice contains an even number of bonds as in the case of the square lattice. Determination of the ground state of the AFM Heisenberg exchange interaction Hamiltonian (eq. (1)) on various lattices poses a formidable theoretical problem. The task becomes simpler if the spins are treated as classical vectors, i.e., the magnitude of spins $S \rightarrow \infty$. The energy of a triangle of spins is given by

$$E_t = \frac{J}{2}[(S_1 + S_2 + S_3)^2 - (S_1^2 + S_2^2 + S_3^2)]. \quad (2)$$

The ground state, i.e. the minimal energy spin configurations are obtained for $S_{\text{tot}} = S_1 + S_2 + S_3 = 0$. In the case of the full triangular lattice, the classical ground state has a three-sublattice order with each elementary plaquette of spins satisfying the constraint $S_{\text{tot}} = 0$. In the case of the kagomé lattice, which is constructed out of triangular

plaquettes, the classical ground state is infinitely degenerate⁶. In the first case, quantum fluctuations do not fully destroy the order in the ground state but reduce the sublattice magnetization significantly from its classical value. Recent calculations show that the $S=\frac{1}{2}$ Heisenberg AFM (HAFM) Hamiltonian on the triangular lattice has long range order (LRO) in the ground state^{7,8}. A rigorous proof of the existence of LRO is, however, still missing. Experimental realizations of the triangular lattice HAFM include VCl_2 , VBr_2 , $CdEu$, $NaNiO_2$, etc.⁹. In the case when the classical ground state is highly degenerate, i.e. spin-disordered, thermal/quantum fluctuations may select a subset of states as ground states leading to new forms of spin order. This is the phenomenon of ‘order from disorder’¹⁰. Another possibility is the opening up of a gap in the spin excitation spectrum. The $S=\frac{1}{2}$ HAFM on the kagomé lattice appears to be a SG system with a singlet-triplet gap in the spin excitation spectrum. An interesting feature of the SG system is the existence of a large number of singlet excitations in the gap, the number of which is proportional to $(1.15)^N$, where N is the number of sites in the lattice^{11,12}. The temperature dependence of the susceptibility is not affected by the presence of singlet excitations but the specific heat possibly has a power-law dependence, $C_v \propto T^\alpha$, due to contributions from the singlets. An experimental realization of a $S=\frac{1}{2}$ HAFM on the kagomé lattice is yet to be obtained. The compounds $SrCr_9Ga_{12}O_{19}$ is an example of a kagomé-lattice AFM with $S=\frac{3}{2}$. The dominant contribution to the low temperature specific heat of this compound appears to come from the singlet states.

The $S=\frac{1}{2}$ J_1-J_2 model in 1d, describing the Majumdar-Ghosh (MG) chain¹³, is the first example of a frustrated quantum spin model with further-neighbour interactions for which the ground state can be determined exactly. The Hamiltonian with periodic boundary conditions (PBC) is given by

$$H_{\text{MG}} = J_1 \sum_{i=1}^N S_i \cdot S_{i+1} + J_2 \sum_{i=1}^N S_i \cdot S_{i+2}, \quad (3)$$

where J_1 and J_2 are the n.n. and next-nearest-neighbour (n.n.n.) exchange interaction strengths. The exactly solvable MG point corresponds to $J_2/J_1 = \frac{1}{2}$. The exact ground state is doubly degenerate and the ground states are

$$\begin{aligned} \phi_1 &\equiv [12][34][56] \dots [N-1N], \\ \phi_2 &\equiv [23][45][67] \dots [N1] \end{aligned} \quad (4)$$

where $[lm]$ denotes a singlet spin configuration, $\frac{1}{\sqrt{2}}(\alpha(l)\beta(m) - \beta(l)\alpha(m))$, for spins located at the lattice sites l and m . The up and down spin states are denoted as α and β . A singlet state is also known as a valence bond (VB). The excitations in the model can be described in terms of scattering spin-(1/2) defects acting as domain walls between the two exact ground states¹⁴. The scattering states form a

continuum, the lowest branch of which is separated from the ground state by a gap. The MG chain is thus a SG AFM. The SG phase survives for $\alpha = J_2/J_1$ greater than a critical value $\alpha_{cr} \approx 0.2411$. For $0 < \alpha < \alpha_{cr}$, a gapless phase is obtained. If the n.n. exchange interactions are alternating in strength, as in a SP system, the ground state is nondegenerate with the VBs forming along the stronger bonds. The MG Hamiltonian has been used to study the properties of the SP compound CuGeO_3 . A large number of studies have been carried out on the frustrated $J_1 - J_2$ and $J_1 - J_2 - J_3$ models in 2d, where J_2 denotes the strength of the diagonal exchange couplings and J_3 that of n.n.n. interactions in the horizontal and vertical directions. The most general model studied so far is the $J_1 - J_2 - J_3 - J_4 - J_5$ model¹⁵. J_4 and J_5 are the strengths of the knight's-move-distance-away and further-neighbour diagonal exchange interactions respectively (Figure 1). The four columnar dimer (CD) states (Figure 2) are the exact eigenstates of the $J_1 - J_2 - J_3 - J_4 - J_5$ Hamiltonian for the ratio of interaction strengths

$$J_1 : J_2 : J_3 : J_4 : J_5 = 1 : 1 : \frac{1}{2} : \frac{1}{2} : \frac{1}{4}. \quad (5)$$

Each dotted line in Figure 2 represents a VB, i.e. a singlet spin configuration. There is no rigorous proof as yet that the CD states are the exact ground states though approximate theories tend to support the conjecture¹⁶. One can, however, prove that any one of the CD states is the exact ground state when the dimer bonds are of strength $7J$ and the rest of the exchange interactions are of strengths as specified in eq. (5). The excitation spectrum of the model is separated from the ground state by a gap.

The Shastry-Sutherland (SS) model¹⁷ is an example of a frustrated SG AFM in 2d. Figure 3, shows the lattice on which the model is defined. The n.n. and diagonal exchange interactions are of strengths J_1 and J_2 respectively. For J_1/J_2 less than a critical value ≈ 0.7 , the exact ground state consists of singlets along the diagonals. At the critical point, the ground state changes from the gapped disordered state to an antiferromagnetically ordered gapless state. The AFM compound $\text{SrCu}_2(\text{BO}_3)_2$ is an experimental realization

of the SS model¹⁸. Triplet excitations in the model are found to be almost localized. A single triplet excitation can propagate in the SS lattice only at the sixth order perturbation in J_1/J_2 .

Spin ladders

Spin ladders constitute one of the most well-known examples of SG AGMs. The simplest ladder model consists of two chains coupled by rungs (Figure 4). In general, the ladder may consist of n chains. In the spin ladder model, each site of the ladder is occupied by a spin (usually of magnitude $\frac{1}{2}$) and the spins interact via the HAFM exchange interaction Hamiltonian (eq. (1)). The n.n. intra-chain and rung exchange interactions are of strengths J and J_R respectively. When $J_R = 0$; one obtains two decoupled AFM spin chains for which the excitation spectrum is known to be gapless. For all $J_R/J > 0$; a gap opens up in the spin excitation spectrum¹⁹. The result is easy to understand in the simple limit in which the exchange coupling J_R along the rungs is much stronger than the coupling along the chains. The intra-chain coupling in this case may be treated as a perturbation. When $J = 0$; the exact ground state consists of singlets along the rungs. The ground state energy is $-(3J_R N/4)$, where N is the number of rungs in the ladder. The ground state has total spin $S = 0$. In first order perturbation theory, the correction to the ground state energy is zero. An $S = 1$ excitation may be created in the ladder by promoting one of the rung singlets to the $S = 1$ triplet state. The weak coupling along the chains gives rise to a propagating $S = 1$ magnon. In first order perturbation theory, the dispersion relation is

$$\omega(k) = J_R + J \cos k \quad (6)$$

where k is the momentum wave vector. The SG is given by

$$\Delta = \omega(\pi) \approx J_R - J. \quad (7)$$

The two-spin correlations decay exponentially along the chains showing that the ground state is a QSL. The family

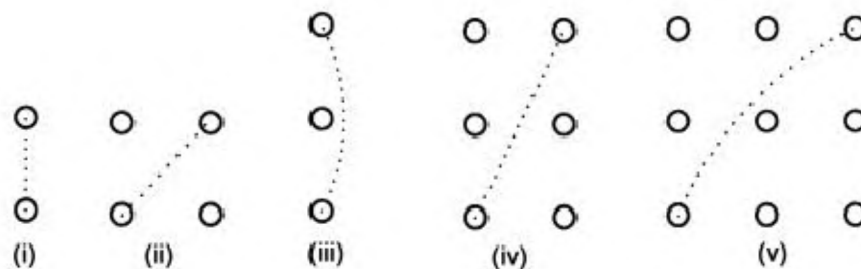


Figure 1. Five types of interaction in the $J_1 - J_2 - J_3 - J_4 - J_5$ model. The successive interactions are (i) n.n., (ii) diagonal, (iii) n.n.n., (iv) knight's-move-distance-away and (v) further-neighbour-diagonal.

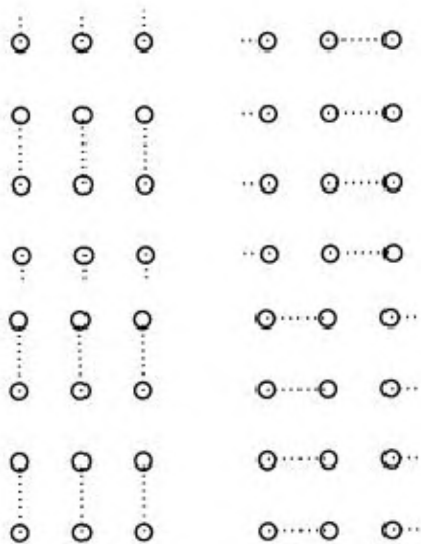


Figure 2. Four columnar dimer states. The dotted line represents a valence bond, i.e. a singlet spin configuration.

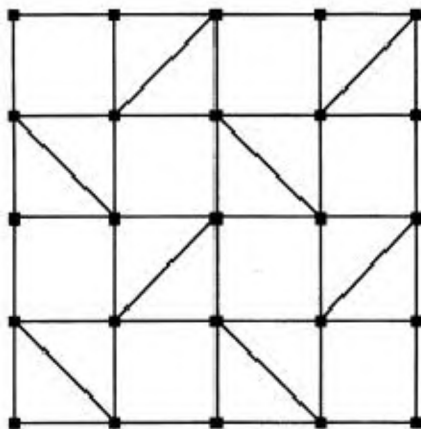


Figure 3. The Shastry-Sutherland model. The n.n. and diagonal exchange interaction strengths are J_1 and J_2 respectively.

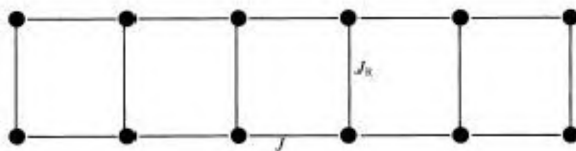


Figure 4. A two-chain spin ladder.

of compounds $\text{Sr}_{n-1}\text{Cu}_n\text{O}_{2n}$ consists of planes of weakly coupled ladders of $(n+1)/2$ chains²⁰. For $n=3$ and 5, one gets the two-chain and three-chain ladder compounds SrCu_2O_3 and $\text{Sr}_2\text{Cu}_3\text{O}_5$ respectively. The first compound is a SG AFM while the second compound has properties similar to those of the HAFM Hamiltonian in 1d, which has a gap-

less excitation spectrum. The experimental evidence is consistent with the theoretical prediction that in an n -chain ladder, the excitation spectrum is gapped (gapless) when n is even (odd)¹⁹. Bose and Gayen²¹ have studied a two-chain ladder model with frustrating diagonal couplings. The intra-chain and diagonal couplings are of equal strength J . For $J_R \geq 2J$, the exact ground state consists of singlets along the rungs with the energy $E_g = -(3J_R N/4)$. An excitation can be created by replacing one of the singlets by a triplet. The triplet excitation is localized and separated by an energy gap from the ground state. Xian²² later pointed out that as long as $(J_R/J) > (J_R/J)_c \simeq 1.401$, the rung dimer state is the exact ground state.

Ladders provide a bridge between 1d and 2d many body systems and are ideally suited to study how the electronic and magnetic properties change as one goes from a single chain to the square lattice limit. The significant interest in 2d many body systems is due to the unconventional properties of the CuO_2 planes in doped cuprate systems. The latter exhibit high temperature superconductivity in appropriate ranges of dopant concentration. Many of the unusual properties of the cuprate systems arise due to strong correlation effects. Ladders are simpler systems in which some of the issues related to strong correlation can be addressed in a rigorous manner. Doped ladder models are toy models of strongly correlated systems. In these systems, strong Coulomb correlations prohibit the double occupancy of a site by two electrons, one with spin up and the other with spin down. In a doped spin system, two processes are in competition: hole delocalization and exchange energy minimization. The latter is minimized in the antiferromagnetically ordered Néel-type of state. A hole moving in such a background gives rise to parallel spin pairs which raise the exchange interaction energy of the system. The questions of interest are: whether a coherent motion of the holes is possible, whether two holes can form a bound state and superconducting (SC) pairing correlations develop, etc. These issues are of significant relevance in the context of doped cuprate systems in which charge transport occurs through the motion of holes. In the SC phase, the holes form bound pairs with possibly d-wave symmetry. Several proposals have been made so far on the origins of hole binding but the actual binding mechanism is still controversial²³. The doped cuprate systems exist in a 'pseudo-gap' phase before entering the SC phase. In fact, some of the cuprate systems also exhibit a SG. The two-chain AFM ladder systems are SG systems and it is of interest to study how the gap evolves on doping. The possibility of binding of hole pairs in a two-chain ladder system was first pointed out by Dagotto *et al.*²⁴. In this case, the binding mechanism can be understood in a simple physical picture. Again, consider the case $J_R \gg J$, i.e. a ladder with dominant exchange interactions along the rungs. In the ground state, the rungs are mostly in singlet spin configurations. On the introduction of a single hole, a singlet spin pair is broken and the corresponding exchange inter-

action energy is lost. When two holes are present, they prefer to be on the same rung to minimize the loss in the exchange interaction energy. The holes thus form a bound pair. In the more general case, detailed energy considerations show that the two holes tend to be close to each other effectively forming a bound pair. For more than two holes, several calculations suggest that considerable SC pairing correlations develop in the system. The superconducting state can be achieved only in the bulk limit. Theoretical predictions motivated the search for ladder compounds which can be doped with holes. Much excitement was created in 1996 when the doped ladder compound²⁵ $\text{Sr}_{14-x}\text{Ca}_x\text{Cu}_2\text{O}_{41}$ was found to become SC under pressure at $x=13.6$. The transition temperature T_c is ~ 12 K at a pressure of 3 GPa: As in the case of cuprate systems, bound pairs of holes are responsible for charge transport in the SC phase. Experimental results on doped ladder compounds point out strong analogies between the doped ladder and cuprate systems²⁶. Bose and Gayen^{21,27,28} have derived exact, analytical results for the ground state energy and the low-lying excitation spectrum of the frustrated t - J ladder model doped with one and two holes. The undoped frustrated ladder model has already been described. The t - J Hamiltonian describing the ladder is given by

$$H_{t-J} = - \sum_{\langle i,j \rangle, \sigma} t_{ij} (\tilde{c}_{i\sigma}^+ \tilde{c}_{j\sigma} + H.C.) + \sum_{ij} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j. \quad (8)$$

The $\tilde{c}_{i\sigma}^+$ and $\tilde{c}_{i\sigma}$ are the electron creation and annihilation operators which act in the reduced Hilbert space (no double occupancy of sites),

$$\tilde{c}_{i\sigma}^+ = c_{i\sigma}^+ (1 - n_{i-\sigma}), \quad \tilde{c}_{i\sigma} = c_{i\sigma} (1 - n_{i-\sigma}), \quad (9)$$

where σ is the spin index and n_i , n_j are the occupation numbers of the i th and j th sites. The first term in eq. (8) describes the motion of holes. The hopping integral t_{ij} has the value t_R for hole motion along the rungs and the value t for both the intra-chain n.n. and diagonal hops. The latter assumption is crucial for the exact solvability of the eigenvalue problem in the one and two hole sectors. Though the model differs from the standard t - J ladder model^{29,30} (diagonal couplings missing in the latter model), the spin and charge excitation spectra exhibit similar features. For the frustrated t - J ladder, the dispersion relation of the two-hole bound state branch can be obtained exactly and analytically. The exact two-hole ground state is a bound state with centre of mass momentum wave vector $K=0$ and d -wave type symmetry. The ladder exists in the Luther-Emery phase in which the spin excitation is gapped and the charge excitation gapless. There is no spin-charge separation, a feature associated with Luttinger liquids in which both the spin and charge excitations are gapless. In the exact hole eigenstates, the hole is always accompanied by a spin- $\frac{1}{2}$. The hole-hole correlation function can also be cal-

culated exactly. When $J_R \gg J$, the holes of a bound pair are predominantly on the same rung. For lower values of J_R , the holes prefer to be on n.n. rungs so that energy gain through the delocalization of a hole along a rung is possible. The novel phenomena exhibited by undoped and doped spin ladders have motivated a large number of theoretical studies. Several ladder compounds have been discovered/synthesized to date. Detailed information on the theoretical and experimental investigations may be obtained from two exhaustive reviews on ladders^{19,26}.

Haldane gap antiferromagnets

We have so far been discussing SG systems with half-odd integer spins. From the Lieb-Schultz-Mattis (LSM)³¹ theorem one can show that the half-odd integer spin HAFM chain has a gapless excitation spectrum in the infinite chain length limit. The theorem does not extend to integer spin chains. Haldane³², based on his analysis of the nonlinear σ model mapping of the large S HAFM Hamiltonian in 1d, conjectured that the HAFM spin chains with integer spins have a gap in the excitation spectrum, i.e. they are SG AFMs. The ground state of an integer spin chain is disordered and the spin-spin correlation function has an exponential decay. Haldane's conjecture has now been verified both theoretically and experimentally³³. The spin-1 HAFM Hamiltonian has the same ground state features as the spin-1 Affleck, Kennedy, Lieb, Tasaki (AKLT) Hamiltonian for which the so-called valence bond solid (VBS) state is the exact ground state. Consider a 1d lattice each site of which is occupied by a spin-1: A spin-1 can be considered to be a symmetric combination of two spin- $\frac{1}{2}$'s. In the VBS state, each spin- $\frac{1}{2}$ component of a spin-1 forms a singlet (VB) with a spin- $\frac{1}{2}$ at a neighbouring site. The AKLT Hamiltonian is a sum over projection operators onto spin 2 for successive pairs of spins, i.e.

$$H_{\text{AKLT}} = \sum_i P_2(\mathbf{S}_i + \mathbf{S}_{i+1}). \quad (10)$$

The presence of a VB between each neighbouring pair of sites implies that the total spin of each pair of spins cannot be 2. Thus H_{AKLT} acting on Ψ_{VBS} , the wave function of the VBS state, gives zero. The eigenvalues of the projection operator being positive, Ψ_{VBS} is the ground state of H_{AKLT} with eigenvalue zero. The VBS state is spin-disordered with an exponentially decaying spin-spin correlation function. One can, however, define a non-local string order parameter which has a non-zero expectation value in the VBS state³⁴. The explicit form of the AKLT Hamiltonian is given by

$$H_{\text{AKLT}} = \sum_i \left[\frac{1}{2} (\mathbf{S}_i \cdot \mathbf{S}_{i+1}) + \frac{1}{6} (\mathbf{S}_i \cdot \mathbf{S}_{i+1})^2 + \frac{1}{3} \right]. \quad (11)$$

The excitation spectrum of H_{AKLT} cannot be determined exactly. Variational calculations show the existence of a gap in the excitation spectrum. Several Haldane gap (HG) AFMs have been discovered so far. These include the $S=1$ compound CsNiCl_3 (ref. 33), $\text{Ni}(\text{C}_2\text{H}_8\text{N}_2)_2\text{NO}_2$ (ClO_4) (NENP) (ref. 33), Y_2BaNiO_5 (ref. 35) and the $S=2$ compound (2,2'-bipyridine)trichloromanganese (III), MnCl_3 (bipyridine)³⁶. Experiments carried out on these compounds show that the VBS state provides the correct physical picture for the true ground state³³.

The doped spin-1 compound $\text{Y}_{2-x}\text{Ca}_x\text{BaNiO}_5$ provides an example of a QSL in 1d³⁵. The parent compound YBaNiO_5 is a charge transfer insulator containing Ni^{2+} ($S=1$) chains. The ground state of the system is spin-disordered and the spin excitation spectrum is separated by the HG from the ground state. The compound is doped with holes on replacing the off-chain Y^{3+} ions by Ca^{2+} ions. The holes mostly appear in oxygen orbitals along the NiO chains. There is no evidence of metal-insulator transition but the dc-resistivity ρ_{dc} falls by several orders of magnitude. This indicates that the holes are not fully mobile but delocalized over several lattice spacings. Inelastic neutron scattering (INS) experiments reveal the existence of new states within the HG. Several studies have been carried out to explain the origin of the sub-gap states³⁷. A recent neutron scattering experiment³⁸ provides evidence for an incommensurate double-peaked structure factor $S(q)$ for the sub-gap states. The INS intensity is proportional to the structure factor. For the pure compound, the structure factor $S(q)$; near the gap energy of 9 MeV, has a single peak at the wave vector $q=\pi$ indicative of AFM correlations. For the doped compound, $S(q)$ has an incommensurate double-peaked structure factor, for energy transfer $\omega \sim 3-7$ MeV, with the peaks located at $q=\pi \pm \delta q$. The shift δq is found to have a very weak dependence on the impurity concentration x , for x in the range $x \in [0.04, 0.14]$. Evidence of incommensurate peaks has also been obtained in the underdoped metallic cuprates. The peaks are four in number and occur at $(\pi \pm \delta q, \pi)$ and $(\pi, \pi \pm \delta q)$. The crucial difference from the nickelate compound is that δq is proportional to the dopant concentration x . The incommensurability has been ascribed to inhomogeneous spin and charge ordering in the form of stripes²³. Malvezzi and Dagotto³⁹ have provided an explanation for the origin of spin incommensurability in the hole-doped $S=1$ nickelate compound. They have shown that a mobile hole generates AFM correlations between the spins located on both sides of the hole and this is responsible for the spin incommensurability seen in experiments. Xu *et al.*³⁸ have given a different explanation for the origin of incommensurability. The holes doped into the QSL ground state of the $S=1$ chain are located on the oxygen orbitals and carry spin. They induce an effective ferromagnetic interaction between the Ni spins on both sides. The incommensurate peaks arise because of the spin density modulations developed around the holes with the size of the droplets controlled by the

correlation length of the QSL. Bose and Chattopadhyay⁴⁰ have developed a microscopic theory of the origin of spin incommensurability in keeping with the suggestions of Xu *et al.*

Quantum phase transitions

A quantum phase transition (QPT) occurs at $T=0$ and brings about a qualitative change in the ground state of an interacting many body system at a specific value g_c of some tuning parameter g . Examples of tuning variables include magnetic field h , pressure and dopant concentration. The origin of QPTs lies in quantum fluctuations just as thermal fluctuations drive thermodynamic phase transitions. In the case of second order thermodynamic phase transitions, the critical point is characterized by scale invariance and a divergent correlation length. Free energy and the different thermodynamic functions become non-analytic at the critical temperature $T=T_c$. The quantum critical point is also associated with scale invariance and a divergent correlation length with quantum fluctuations substituting for thermal fluctuations. The ground state energy becomes non-analytic at the critical value g_c of the tuning parameter. If one of the phases is gapped, the gap goes to zero in a power-law fashion as $g \rightarrow g_c$. Quantum and thermal fluctuations are equally important in the so-called quantum critical regime extending into the finite- T part of the T versus g phase diagram. The macroscopic physical properties in this regime are in many cases independent of microscopic details. A large number of theoretical and experimental studies have been carried out on QPTs in condensed matter systems⁴¹. Here we focus on a few specific examples of QPTs in SG AFMs. Organic spin ladder compounds provide ideal testing grounds for theories of QPTs. Consider the phase diagram of the AFM two-chain spin ladder in the presence of a magnetic field h . At $T=0$ and for $0 < h < h_{c1}$, the ladder is in the SG phase. At $h=h_{c1}$, there is a transition to the gapless Luttinger liquid phase with $g\mu_B h_{c1} = \Delta$, where g is the Landé splitting factor, μ_B the Bohr magneton and Δ , the magnitude of the SG⁴². At an upper critical field h_{c2} , there is another transition to the fully polarized ferromagnetic state. Both h_{c1} and h_{c2} are quantum critical points. The compound $(\text{C}_5\text{H}_{12}\text{N})_2\text{CuBr}_4$ has been identified as a $S=1/2$ two-chain spin ladder in the strong coupling limit. $J_K=13.3$ K and $J=3.8$ K with $h_{c1}=6.6$ T and $h_{c2}=14.6$ T⁴³. The magnetization data exhibit universal scaling behaviour in the vicinity of h_{c1} and h_{c2} , consistent with theoretical predictions. In the gapless regime $h_{c1} < h < h_{c2}$, the ladder model can be mapped onto an XXZ chain, the thermodynamic properties of which can be calculated exactly by the BA. The theoretically computed magnetization M versus magnetic field h curve is in excellent agreement with the experimental data. Other organic ladder compounds exhibiting QPTs are $(\text{SIAP})_2\text{CuBr}_4 \cdot 2\text{H}_2\text{O}$ (ref. 44) and $\text{Cu}_2(\text{C}_5\text{H}_{12}\text{N}_2)_2\text{Cl}_4$ (ref. 45). For inorganic spin ladder systems, the value of h_{c1} is too high to be experimen-

tally accessible. The synthesis of organic ladder compounds has paved the way for experimental observation of QPTs.

Another notable example of experimentally observed QPTs is that of field-induced 3d magnetic ordering in low-dimensional SG AFMs, KCuCl_3 (ref. 3) and TiCuCl_3 (ref. 4) which, as described earlier, consist of networks of dimers. The dimer ground state is a singlet for $h=0$. The triplet ($S=1$) excitation is separated from the singlet ground state by an energy gap, Δ . Application of an external magnetic field h leads to Zeeman splitting of the triplet excitation into three components: $S_z=+1, 0, -1$. At a critical external magnetic field h_{c1} , the lowest triplet component becomes energetically degenerate with the ground state. This results in a QPT at $h=h_{c1}$ to a 3d magnetically ordered state. The critical point $h=h_{c1}$ separates a gapped QSL state ($h < h_{c1}$) from a field-induced magnetically ordered state ($h > h_{c1}$). The triplet components can be regarded as diluted bosons and the QPT at $h=h_{c1}$ can be treated as a Bose-Einstein condensation (BEC) of low-lying magnons⁴⁶. Support for this idea comes from experimental findings on TiCuCl_3 . Recently, the excitation spectrum in the magnetically ordered state of TiCuCl_3 has been determined using INS⁴⁷. The observed data are consistent with the theoretical prediction of a gapless Goldstone mode characteristic of the BEC.

In the BE condensed state, the state of each dimer is found to be a coherent superposition of the singlet and the $S_z=+1$ triplet states. The phase in the superposition specifies the orientation of the staggered magnetization in the plane transverse to the magnetic field direction. The number of magnons in the condensed state is not, however, infinite as magnons cannot occupy the same sites in a spin system due to a hard-core repulsion between them. The interaction restricts the number of magnons to be large but finite. Recently, there is a resurgence of research interest in BEC because of its experimental realization in ultracold gases of dilute atoms. SG AFMs offer another testing ground for theories related to BEC. The definitive evidence of BEC in the compound TiCuCl_3 motivates the search for condensation phenomena in other SG systems.

Magnetization plateaus

The magnetization curve of a low-d AFM does not always show a smooth increase in magnetization, from zero value to saturation, as the magnetic field is increased in magnitude. In certain systems, the curve exhibits plateaus at certain rational values of the magnetization per site m . The phenomenon is analogous to the quantum Hall effect in which electrical resistivity exhibits plateaus as a function of the external magnetic field. Oshikawa, Yamanaka and Affleck (OYA) derived a condition for the occurrence of magnetization plateaus in quasi-1d AFM systems by generalizing the LSM theorem to include an external magnetic field⁴⁸. For general spin systems, the quantization condition can be written as

$$S_U - m_U = \text{integer}, \quad (12)$$

where $S_U = nS$, n being the number of spins of magnitude S in unit period of the ground state and $m_U = nm$ is the magnetization associated with the unit cell. The quantization condition is necessary but not sufficient as not all plateaus predicted by the condition exist in general. Hida⁴⁹ first predicted the existence of a magnetization plateau at $m = \frac{1}{6}$ in the magnetization curve of a $S = \frac{1}{2}$ AFM chain with period 3 exchange coupling. One can readily check that the quantization condition (12) is obeyed as in this case $S_U = \frac{3}{2}$ and $m_U = \frac{1}{2}$ ($n=3$, $S=\frac{1}{2}$, $m=\frac{1}{6}$). A gapped phase is essential for the appearance of a plateau (magnetization unchanging) in the m versus h curve. More than one plateau can occur if there is more than one gapped phase as h is changed.

High-field measurements reveal the existence of magnetization plateaus⁵⁰ in several AFM compounds. The $S = \frac{1}{2}$ material NH_4CuCl_3 exhibits plateaus⁵⁰ at $M = \frac{1}{4}$ and $\frac{3}{4}$ ($M = m/S$). The $S = \frac{1}{2}$ SG AFM $\text{SrCu}_2(\text{BO}_3)_2$ is the first example of a 2d spin system for which magnetization plateaus have been observed experimentally. The plateaus are obtained⁵¹ for $M = \frac{1}{3}$, $\frac{1}{4}$ and $\frac{1}{8}$. Momoi and Totsuka⁵² have suggested that the appearance of plateaus in $\text{SrCu}_2(\text{BO}_3)_2$ is due to a transition from a superfluid to a Mott insulating state of magnetic excitations. As pointed out earlier, the triplet excitations in the SS model, which describes $\text{SrCu}_2(\text{BO}_3)_2$, are almost localized. In the presence of a magnetic field and at special values of the magnetization, the triplet excitations localize into a superlattice structure to minimize energy so that the magnetization remains constant. As in the cases of KCuCl_3 and TiCuCl_3 , the compound $\text{SrCu}_2(\text{BO}_3)_2$ is a network of coupled dimers. A triplet excitation created on a dimer can propagate to a neighbouring dimer due to the inter-dimer exchange interaction. The delocalization of triplets is similar to that of electrons in crystals. In the presence of a magnetic field, the triplet excitation is split into three components with the $S_z=+1$ component being the lowest in energy. The $S_z=+1$ excitations can be regarded as bosons with a hard core repulsion. The repulsive interaction arises from the z -component of the exchange interaction and disallows the occupation of a single dimer by more than one boson. The xy -part of the exchange interaction is responsible for the hopping of the triplet excitation to neighbouring dimers. One thus has a system of interacting bosons in which itinerancy competes with localization. The transition from itinerancy to localization is analogous to the Mott metal-insulator transition in electronic systems. If repulsive interactions dominate, the triplet excitations (bosons) localize to form a superlattice. A direct measurement of the magnetic superlattice in $\text{SrCu}_2(\text{BO}_3)_2$ has been made by Kodama *et al.*⁵² using a high-field NMR facility. The superlattice corresponds to $M = \frac{1}{8}$ which requires a high magnetic field strength of 27 T for its observation. Superlattice structures

for higher M values have not been detected as yet because of the requirement of very high magnetic fields.

Summary and future outlook

SG AFMs exhibit a variety of novel phenomena, the observation and interpretation of which have been possible due to intimate links between theory and experiments. Rigorous theories and exactly solvable models have predicted phenomena which were later verified experimentally. Quantum magnetism is one of the few research areas in which rigorous theories go hand in hand with experimental initiatives. We have illustrated this interdependence through a few chosen examples. The MG model illustrates the origin of SG due to the presence of further-neighbour interactions. The SS and $J_1 - J_2 - J_3 - J_4 - J_5$ models extend the 1d model to 2d. Experimental realization of the SS model became a reality about twenty years after the original theoretical proposal was made. The AKLT model provides the correct physical picture of the ground states of integer spin chains. Knowledge of the ground state has given rise to testable predictions which were later verified experimentally. Spin ladders were originally studied as toy models of strongly correlated systems. Theories of undoped and doped ladder models motivated the search for real materials which led to success in several instances. The OYA theorem provides the condition for the existence of magnetization plateaus which is in agreement with experimental results. SG AFMs further exhibit novel quantum phenomena which illustrate how quantum effects influence ground and excited state properties. We have discussed only a few of these in the present review. Two SG AFM systems that we have not described include the compounds⁵⁴ CaV_4O_9 and the tellurate materials $\text{Cu}_2\text{Te}_2\text{O}_5\text{X}_5$ ($\text{X} = \text{Cl}$ or Br)⁵⁵. The first compound is defined on a 1/5-depleted square lattice which is a network of four-spin plaquettes connected by single links (dimer bonds). Each square plaquette is in a resonating valence bond (RVB) spin configuration in the ground state. In this case, the RVB state is a linear superposition of two VB configurations. In one configuration, the VBs (singlets) occupy the horizontal links of the square plaquette. In the other configuration, the VBs occupy the vertical links. More generally, a RVB state is a coherent linear superposition of VB states and is a well-known example of a QSL. The tellurate materials can be described as networks of spin tetrahedra. In both CaV_4O_9 and the tellurate materials, the existence of singlet excitations in the spin gap has been reported as in the case of the kagomé lattice HAFM.

The QPTs considered in this review are brought about by tuning magnetic field strengths. QPTs can also occur by tuning of exchange interaction strengths. In the case of the frustrated two-chain spin ladder model described earlier, a first order QPT takes place at $(J_{\text{R}}/J) = (J_{\text{R}}/J) \approx 1.401$ from the rung dimer state to the Haldane phase of

the $S = 1$ chain²². Kolezhuk and Mikeska⁵⁶ have constructed generalized $S = \frac{1}{2}$ two-chain ladder models with two-spin and four-spin exchange couplings for which the ground state can be determined exactly. QPTs to the various phases are obtained by varying the exchange interaction strengths. A lattice of coupled two-chain ladders provides another example of a QPT which is brought about by tuning the inter-ladder exchange interaction strength⁴¹ λ . For $\lambda < \lambda_c$, the spin lattice is in the SG phase. At $\lambda = \lambda_c$, a QPT to a long range magnetically ordered state occurs. Most of the spin models considered in this review exhibit QPTs at specific values of the exchange interaction strengths. One might think that experimental observation of such QPTs is not possible as exchange interaction strengths cannot be changed at will. There is now reason to believe that exchange interaction strengths can be controlled. Recent observations⁵⁷ of the superfluid to Mott insulator transition in a system of ultracold atoms defined in an optical lattice open up the exciting possibility of investigating phenomena associated with interacting many-body-systems in a controllable environment. The optical lattice is generated as a light-wave interference pattern using several criss-crossing laser beams. The lattice is equivalent to an energy landscape of mountains and valleys which can provide the confining potential to trap individual atoms in separate valleys. Proposals for implementation of spin Hamiltonians in optical lattices have been put forward with the aim to study the exotic quantum phases of interacting spin systems⁵⁸. The exchange interaction between spins belonging to atoms in neighbouring valleys can be modified by controlling the intensity, frequency and polarization of the trapping light. Spin Hamiltonians of interest can be engineered through design of appropriate optical lattice geometries. Practical implementation of some of these ideas may be possible in the not too distant future. Spin systems have recently been suggested as candidates for realization of quantum computation and communication protocols⁵⁹. The spin systems considered so far include some SG AFMs like the MG and HG chains, the two-chain spin ladder, etc.⁶⁰. Again, one anticipates intense research activity in the coming years on such problems. To sum up, the richness and vitality of the subject of SG AFMs are evident in the challenging problems of current research interest and also in the opening up of new avenues of research.

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