Magnetic light scattering in low-dimensional quantum spin systems

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Abstract

An overview of one- and two-dimensional quantum spin systems based on transition-metal oxides and halides of current interest is given, such as spin-Peierls, spin-dimer, geometrically frustrated and ladder systems. The most significant and outstanding contributions of magnetic light scattering to the understanding of these materials are discussed and compared to results of other spectroscopies and thermodynamic measurements.

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Chapter 0

Preface

This article reviews recent progress in magnetic light scattering in one- and two-dimensional quantum spin systems. These systems received considerable interest from both theoretical and experimental points of view. Following the investigations of the two-dimensional superconducting cuprates and the search for related transition metal oxides a fascinating field of copper oxide compounds, vanadates, manganites and nickelates opened up. These compounds show effects of strong electronic correlations and in particular magnetism in low dimensions.

The theory of magnetism in one dimension, on the other hand, has a history reaching back to the origin of quantum mechanics. This is due to the fact that a spin chain allows more easily analytical or numerical solutions. It was found that the suppression of “trivial” long-range order sets the stage for an enormous complexity of possible ground states, exotic quasiparticles and many-body states. Understanding these effects is the most intriguing challenge at present.

A central concept in describing these low-dimensional quantum spin systems is that of a spin liquid. This ground state is dominated by strong quantum fluctuations, pronounced spin-spin correlations and a suppression of long-range magnetic order. The Heisenberg chain with isotropic-antiferromagnetically coupled spins (s=1/2) represents such a state in the sense that the spin-spin correlations decay algebraically. It is therefore often denoted as a critical spin liquid. An interesting situation occurs when transitions lead to a sudden change of the excitation spectrum, e.g., the opening of an excitation gap or the formation of long-range magnetic order. These quantum phase transitions are driven or controlled by the exchange coupling parameters, the exchange topology or by spin vacancies. The excitation gap may be realized with or without a spontaneously broken translational symmetry.

The spin-Peierls transition and the related charge ordering instability discovered in the inorganic compounds CuGeO$_3$ and NaV$_2$O$_5$, respectively, represent the case of broken translational symmetry. These compounds allow to investigate the excitation spectrum going from a homogeneous gapless to a dimerized state just as a function of temperature. In the two-leg spin ladder system SrCu$_2$O$_3$
and the chain/ladder system \( \text{Sr}_{14}\text{Cu}_{24}\text{O}_{41} \) an excitation gap is realized without breaking translational symmetry. These compounds are discussed as model systems for an electronic mechanism of high temperature superconductivity. The steady improvement of understanding also leads to surprising reinterpretations of compounds that have been investigated for years. The formerly canonical example of a spin ladder, the vanadium compound \((\text{VO})_2\text{P}_2\text{O}_7\), is now recognized as a spin chain with strongly alternating coupling constants. This result has profound consequences for the interpretation of its low energy excitations. Very important compounds that bridge one and two dimensions and still do not show long-range magnetic order are the spin frustrated system \( \text{SrCu}_2(\text{BO}_3)_2 \) and the 1/5-depleted square lattice system \( \text{CaV}_4\text{O}_9 \).

Light scattering experiments or other spectroscopic methods like inelastic neutron scattering have been used to investigate both the above cited and many more compounds. One of the most significant aspects of light scattering experiments is the observation of magnetic singlet bound states. These states originate from strong triplet-triplet interaction and characterize the excitation spectrum of the spin system. Recent theoretical progress has enabled a more detailed understanding of these effects. Parameters like dimerization, frustration, interchain coupling, and spin-phonon coupling have an important impact on the ground state and the excitations of a quantum spin system.

This review is organized as follows: After a brief description of the excitations and the phase diagram of quantum spin systems given in Chapter 1, important low-dimensional spin systems, recent experimental results and their interpretations are discussed in Chapter 2. Up to now no comprehensive review on this rapidly growing field exists that also considers material aspects. Therefore we try to balance between well established results and very recent developments. In Chapter 3 magnetic light scattering in low-dimensional spin systems is reviewed. The following Chapters 4 and 5 discuss magnetic bound states and quasielastic scattering. Chapter 6 finally sums up some aspects of the present knowledge in this field and gives an outlook to future developments.

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Chapter 1

Excitations in low-dimensional spin systems

In strongly correlated electron systems with integer number of electrons per site the low energy excitations are usually given by the spin degrees of freedom. This situation is properly described by the Heisenberg exchange spin Hamiltonian. If, in addition, the exchange is restricted to low dimensions, then spin chains, spin ladders, and respective systems with a more complex exchange geometry are realized. These systems exhibit a number of unusual properties which are related to strong quantum fluctuations. These properties will be addressed in the following.

One-dimensional s=1/2 spin systems (spin chains) with uniform nearest neighbor exchange coupling show according to the Lieb-Schultz-Mattis theorem a degeneracy of the singlet ground state with triplet excitations. Assuming negligible spin anisotropies even for T=0 the ground state is gapless and not magnetically ordered. It is described by the Bethe Ansatz. The spin-spin correlations are algebraically decaying typical for a quantum critical state. Triplet excitations in this system are not described as magnons (bosons) but as massless domain wall-like s=1/2 spinons (fermions). These spinons are created as pairs, e.g., by an exchange process. Their dynamical structure factor is therefore given by a gapless two-particle continuum restricted by a lower and an upper dispersing boundary. In Fig. 1.1 a sketch of the spinon creation and the spinon continuum is given. The spectral weight of the continuum is dominant close to its lower boundary.

A quantum phase transition from a gapless critical state into a gapped state (disordered spin liquid) is induced by dimerization, i.e. an alternation \( \delta \) of the coupling constants to nearest neighbors \( J_{nn}^\pm = (1 \pm \delta)J_{nn} \) along the chain or by a sufficient frustration \( \alpha = J_{nnn}/J_{nn} \) due to next nearest neighbor antiferromagnetic exchange \( J_{nnn} \). With dimerization the spinons are confined into massive triplet excitations. This confinement of spinon and antispinon composite objects (triplets) is discussed similar to the quark confinement in particle physics. The resulting quantum disordered ground state is characterized by short-ranged exponential
decaying spin-spin correlations. In many cases the system is allowed to be
described as an arrangement of spin dimers. The resulting lifted degeneracy
of triplet and singlet excitations leads to an energy gain of the system. Fig. 1.2
shows a sketch of the excitation processes in a dimerized chain with the respec-
tive energy dispersion. The dimerization or alternation of the coupling constants
connects $k=0$ and $k=\pi$ therefore a small part of the continuum spectral weight
($\propto \delta^2$) is also expected for $k \leq \pi/2$. In Fig. 1.2 this contribution is neglected. A
(T=0) phase diagram of dimerized and frustrated spin chains is given in Fig. 1.3.
The points ($\delta=0,\alpha=0$) and ($\delta=0,\alpha=0.5$) correspond to the Bethe Ansatz and the
Majumdar-Ghosh point. For $\delta=0$ and $\alpha_{c}<0.3$ the gap remains numerically small.

The simplest representative of the quantum disordered state, however, is the
two-leg spin ladder with an approximately equal or larger exchange coupling along
the rungs with respect to the coupling along the legs of the ladder. The singlet
ground state is composed of spin dimers on the rungs. Here, the term spin liquid
is even more appropriate as it is not based on a broken translational symmetry.
An excitation in this picture of strong dimerization corresponds to the breaking
of one dimer. The energy related to this process is the singlet-triplet gap $\Delta_{01}$, see
Fig. 1.2. A coupling of more than two chains to three-, four- or five-leg ladders
leads to the experimentally proven conjecture that ladders with an even number
of legs have a spin gap while odd-leg ladders are gapless. \(^2\)

\(^2\)It should be mentioned that the combined effect of dimerization and interchain interaction
may also lead to a vanishing spin gap in a quantum spin system. In a certain parameter space
of a two-leg ladder with additional frustration, 4-spin cyclic exchange or interchain interactions,
Figure 1.2: Sketch of spin excitations on a dimerized chain. Breaking a dimer a) - b) corresponds to the singlet/triplet gap $\Delta_{01}$ with the respective triplet dispersion shown on the right hand side. The continuum of “free” triplets is reached for energies $E > 2\Delta_{01}$. For small $k$ there exist a finite curvature of the dispersion relation.

In the limit of a large number of coupled chains a two-dimensional Heisenberg system is obtained and the magnitude of the respective spin gap is going to zero. This limit may also be used to understand the two-dimensional high temperature superconductors (HTSC). Weakly doped two- and three-leg ladders have been theoretically investigated in this context. However, also in two dimensions spin dimer ground states with a gapped excitation spectrum are realized. This happens either if the exchange topology is modified to favor a dimer ground state, e.g., in removing 1/5 of the spins from a square lattice, or due to strong frustration (next nearest neighbor interaction).

The triplet-triplet interactions that are responsible for the opening of the gap also lead to magnetic bound states, i.e. triplet excitations that are bound to singlet, triplet or quintuplet states. The former two states are characterized by a well-defined excitation with an energy reduced with respect to the energy of the two-particle continuum of “free” triplets. If interchain or magnetoelastic interactions are dominant bound states consist of soliton-antisoliton pairs. Neglecting these effects the binding energy of a bound state in a dimerized spin chain originates from frustration. The maximum number of bound states of a spin chain is restricted to one singlet and one triplet state. In spin ladders with an additional diagonal frustration the number of bound states and their binding energy is less limited and increasing with frustration. In Fig. 1.4 the excitation spec-

quantum phase transitions to gapless phases have been observed. On the other hand, there is theoretical evidence for a spin gap in doped three-leg ladders for a certain set of exchange coupling constants.
Figure 1.3: Phase diagram (T=0) of spin chains in dependence of dimerization \( \delta \) and spin frustration \( \alpha \). For \( \delta = 0 \) and \( \alpha \leq \alpha_c = 0.2412 \) (dark grey bar) a gapless quantum critical ground state exists. The remaining dashed region denotes the phase space of the gapped quantum disordered state.

However, the spectrum of a homogeneous two-leg \( s=1/2 \) ladder is shown with a singlet and a triplet bound state at the lower boundary of the two-particle continuum. A quantum phase transition at a critical frustration into a gapless phase is understood as a condensation process of large many-particle bound states together with a general softening of the excitation spectrum. More generally, magnetic bound states may therefore be used to study the triplet-triplet interaction, determine the coupling parameters and the phase diagram of the system.

If defects, either as localized non-magnetic vacancies or as mobile carriers, are introduced into a quantum spin system its excitation spectrum may change drastically. In a 2D square lattice doping with mobile carriers destroys long-range Néel order and leads to the opening of a pseudo gap in the spin and charge excitations. The effect of localized spin vacancies in dimerized spin chains or in spin ladders is different. Here, a transition from a gapped into an ordered and gapless Néel-type state is induced by a seemingly negligible amount of vacancies. This effect is based on the doping of only weakly bound spinons by every vacancy. Thereby additional excitations are introduced in the gap corresponding to staggered moments for sites far from the vacancy and increasing spin-spin correlations. Interchain interaction leads to the occurrence of magnetic order at finite temperature.

The coexistence of true long-range magnetic order and dimerization is possible if spatial variations of the competing order parameters are taken into account. This means that the excitation spectrum of such a system has two features, the gapped triplet mode due to dimerization and the gapless “spin wave mode”. The emergence of antiferromagnetism keeps the structure and the energy scales of
these modes essentially unchanged as the transfer of spectral weight from the gapped to the spin wave mode is realized with only a small reduction of the gap and an increase of the spin wave velocity. The latter mode is damped with a broadening proportional to the square of the wave vector. Similar arguments have recently been used to describe the interplay or competition of disorder-induced antiferromagnetism and superconductivity in Heavy Fermion compounds. Comprehensive experimental studies concerning the effect of spin vacancies exist for spin ladder and dimerized spin chain systems. Some results including light scattering data will be presented in the next chapter.

The effect of mobile carriers on the gapped excitation spectrum of a spin liquid is directly related to the problem of an electronic mechanism for HTSC and not yet understood completely. In the 2D CuO$_2$ square lattice the doped holes are believed to form self-organized slowly fluctuating arrays of metallic stripes in which the motion of holes shows a locally quasi-one-dimensional character. A spin gap or pseudo gap is then the result of the spatially confined Mott-insulating regions of the material in the proximity of the metallic stripes. This effect has been described by the term “topological doping”. Corresponding theoretical studies of weakly doped two- and three-leg ladders confirm these ideas in the sense that a
tendency toward a binding effect of holes either into a superconducting condensate or charge ordered ground state exists. The excitation spectrum of the latter system is of special interest as it is separated into a gapless Luttinger-liquid (odd channel) and an insulating gapped spin liquid phase (even channel). In some sense this spectrum represents or mimics the scenario of spin and charge separation discussed for HTSC. A quantum phase transition into a superconducting state with d-wave character has been predicted for the three-leg ladder at higher doping levels.

In a very simplified picture the two channels of the three-leg ladder may be understood as a “plain” ladder coupled to a chain. Holes hop back and forth from the chain to the ladder system. In the ladder they prefer to form pairs minimizing the number of broken dimers. Hopping back into the chain system this correlation is “partially transferred” into the conducting channel. The experimental part of this problem is far from being completely settled and therefore under progress. Although only few spin ladder systems are available unusual experimental results pointing to $k$-dependent relaxation rates different from the undoped material exist. In the following chapter a thorough review of the presently known inorganic low-dimensional compounds will be given focusing on the questions discussed above.
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Important inorganic quantum spin systems

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2.3 Quasi-Two-Dimensional Compounds
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2.3.3 High Temperature Superconductors
2.3.4 The diluted square lattice system $\text{K}_2\text{V}_3\text{O}_8$

2.4 Low-Dimensional Cuprates: new compounds related to high-temperature superconductors
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3.2 Light scattering in high temperature superconductors

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3.4 Spinon Light Scattering in CuGeO$_3$

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4.2.2 Deficiency and substitutions on the Na Site
4.2.3 Theoretical considerations

4.3 Bound states in (VO)$_2$P$_2$O$_7$

4.4 Bound states in SrCu$_2$(BO$_3$)$_2$
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