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1989 J. Phys.: Condens. Matter 1 5555

(http://iopscience.iop.org/0953-8984/1/32/028)

J. Phys.: Condens. Matter 1 (1989) 5555–5560. Printed in the UK

LETTER TO THE EDITOR

Bound excitons in quantum spin-1 chains with strong planar anisotropy

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Received 13 June 1989

Abstract. A strong-coupling expansion is used to study quantum spin-1 chains with strong planar anisotropy. In addition to providing accurate analytical results for the dispersion and intensity of a doubly degenerate excitonic mode, we find that an exciton–antiexciton bound state is formed that could be observed through the two-point longitudinal correlation function. The relevance of these results for the interpretation of neutron scattering experiments on $CsFeCl_3$ and $CsFeBr_3$ is discussed briefly.

We consider the class of quantum spin-1 chains described by the Hamiltonian

$$H = AH_0 - JV \qquad H_0 = \sum_n (S_n^z)^2 \qquad V = \sum_n (S_n^x S_{n+1}^x + S_n^y S_{n+1}^y + \delta S_n^z S_{n+1}^z) \tag{1}$$

which encompasses a number of quasi-one-dimensional magnetic systems of current interest. Throughout this work we will assume the coefficient A of the single-site anisotropy to be positive. Concerning the choice of J and δ we note that the spectrum of (1) is invariant under the transformation $(J, \delta) \rightarrow (-J, -\delta)$. This invariance of the spectrum follows from the fact that the transformation $S_n^x \rightarrow -S_n^x$ and $S_n^y \rightarrow -S_n^y$, at alternate sites, preserves the spin commutation relations while it changes the sign in front of $S_n^x S_{n+1}^x + S_n^y S_{n+1}^y$. Therefore one can always assume the exchange constant J to be positive. Then the isotropic ferromagnet corresponds to $\delta = 1$ and the antiferromagnet to $\delta = -1$. However, in the latter case, a sign alternation at consecutive sites should be incorporated into the two-point transverse correlation function, which amounts to a shift of the Brillouin zone according to $k \rightarrow k + n$; no such shift is necessary in the longitudinal correlation function.

There exist two distinct coupling regimes controlled by the dimensionless coupling constant $a = A/J$. Here we shall be interested in strong anisotropies, i.e. $a \gg 1$. Examples of spin-1 chains realised in this region are provided by $CsFeCl_3$ and $CsFeBr_3$ and are described by Hamiltonian (1) with ferromagnetic ($\delta = 1$) and antiferromagnetic ($\delta = -1$) exchange interactions, respectively. The corresponding values of a are thought to be $a = 4$ and $a = 4.7$ [1, 2]. A small inter-chain coupling is also present in the above compounds but will be neglected in this work for simplicity.

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0953-8984/89/325555 + 06 $02.50

The main features of this problem become transparent in the limit $a \to \infty$ where the ground state is such that the azimuthal spin vanishes at every site. Low-lying excited states are then constructed by exciting one spin to an azimuthal value $m = \pm 1$. If Λ is the total number of sites, there exist Λ distinct states with $m = 1$, which will be called excitons (e), and Λ states with $m = -1$, to be referred to as antiexcitons ($\bar{e}$). All these states are degenerate in the limit $a \to \infty$ with energy equal to A. However the degeneracy is removed to a large extent at finite a leading to two identical bands (e and $\bar{e}$) characterised by definite magnetisation ($m = \pm 1$) and parametrised as usual by the crystal momentum k.

The results of an approximate semiclassical theory based on a $1/n$ expansion [3, 4] are summarised by the two-point transverse dynamic correlation function

$$G^{\mathrm{tr}}(k, \omega) = \frac{1}{\Lambda} \sum_{mn} \int \frac{\mathrm{d}t}{2\pi} e^{ik(m-n)+i\omega t} \langle S_m^{\mu}(t) S_n^{\mu} \rangle = 2 f_k \delta(\omega - \omega_k)$$
$$\omega_k = A \left[1 - \frac{4 \cos k}{a} \right]^{1/2} \qquad f_k = \left[1 - \frac{4 \cos k}{a} \right]^{-1/2} \tag{2}$$

where the repeated index μ is summed over x and y, ω_k is the dispersion of the (anti)excitonic mode, and the amplitude f_k determines the corresponding intensity; the factor of 2 in $2f_k$ indicates that excitons and antiexcitons contribute with equal intensity. The result of (2) was derived also by Lindgard [5], using some sort of random phase approximation, and was recently used for the analysis of neutron scattering data from $CsFeBr_3$ [2]. Actually, Lindgard's result is more general in that it accounts for finite temperature and a small inter-chain coupling.

For sufficiently large a, the excitonic dispersion develops a mass gap that vanishes at $a = 4$ while it becomes imaginary for $a < 4$. Thus a phase transition is predicted at the critical coupling $a_c = 4$ below which the doubly degenerate excitonic mode bifurcates into the usual magnon and a massive resonance describing in-plane fluctuations [3, 4]. An immediate concern is the accuracy of (2) for the intermediate anisotropies of actual interest. A related question is whether or not the predicted critical coupling is accurate. In fact, as is often the case with semiclassical theories, the $1/n$ expansion does not predict the correct critical coupling in this problem. Numerical simulations indicate that the true critical coupling lies in the region $a_c \sim 1$. Therefore, for intermediate anisotropies, detailed numerical predictions based on (2) should be interpreted with caution, even though the overall qualitative picture is reasonable.

To remedy this situation we have carried out an independent calculation based on a direct strong-coupling expansion; that is, an expansion in inverse powers of a. A fourth-order calculation of the ground-state energy has already been reported in [4] and will not be repeated here. Instead we concentrate on quantities of immediate practical interest. Hence a third-order calculation of the excitonic dispersion yields

$$\omega_k = A[1 + \omega_1/a + \omega_2/a^2 + \omega_3/a^3 + \ldots]$$
$$\omega_1 = -2 \cos k \qquad \omega_2 = 1 + 2 \sin^2 k \qquad \omega_3 = \tfrac{1}{2}(1 + 8 \sin^2 k) \cos k - 2\delta \sin^2 k. \tag{3}$$

The corresponding intensity may be inferred from the amplitude f_k which has been calculated to second order with the result

$$f_k = 1 + 2 \cos k/a + (12 \cos^2 k - 2\delta \cos k - 7)/2a^2 + \ldots. \tag{4}$$

For $a \gg 4$, (3) and (4) coincide with the semiclassical results of (2). However, significant

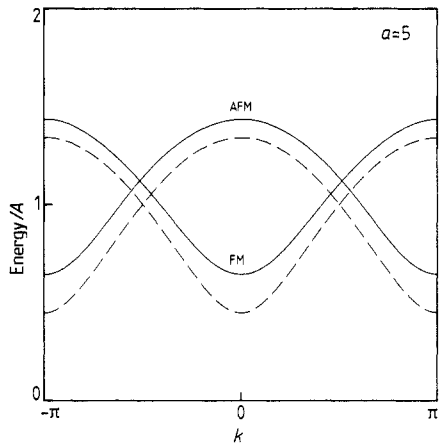

Figure 1. Excitonic dispersion for an intermediate anisotropy ($a = 5$). The dispersion is plotted for ferromagnetic (FM) and antiferromagnetic (AFM) exchange interaction. The full curves depict the result of the strong-coupling expansion, (3), and the broken curves correspond to the semiclassical result of (2).

discrepancies occur for intermediate anisotropies. In figure 1 we compare the dispersion (3) with the semiclassical result (2) for a typical intermediate coupling $a = 5$. The dispersion is depicted for both ferromagnetic ($\delta = 1$) and antiferromagnetic ($\delta = -1$) exchange interactions, having incorporated the shift $k \rightarrow k + n$ in the latter case.

One would think that the observed discrepancy would be due to the fact that (2) is only the leading approximation within a systematic $1/n$ expansion. Indeed, including $1/n$ corrections in (2) would improve its accuracy for strong anisotropies [4]. Nevertheless these corrections become increasingly singular in the region $a \simeq 4$, indicating that the semiclassical critical coupling $a_c = 4$ is actually inaccurate. To simplify the picture we consider the mass gap Δ of the excitonic mode calculated by setting $k = 0$ in (3):

$$\Delta = A[1 - 2/a + 1/a^2 + 1/2a^3 + \ldots]. \tag{5}$$

For $a \simeq 4$, the last term in (5) contributes about one per cent of the total value, which makes it reasonable to assume that the strong-coupling series is reliable in this region of couplings. Applied for $a = 4$, (5) gives $\Delta = 0.57A$, in disagreement with the semiclassical prediction of a vanishing mass gap. And, although (5) is too short a series to locate the critical coupling, it is consistent with $a_c \simeq 1$. Pushing the calculation to high orders would help locate the true critical coupling and elucidate the nature of the phase transition. The behaviour of this series is expected to be especially interesting in connection with the anticipated Haldane gap at $\delta = -1$ and $a = 0$. Note that the first few terms displayed in (5) are δ-independent; but this situation will change in higher-order terms.

The practical outcome of the preceding discussion is that neutron scattering data should be re-analysed in the light of (3) and (4), which are expected to provide an accurate description of the excitonic mode for strong as well as intermediate anisotropies. Here we consider briefly the excitonic dispersion of $CsFeBr_3$ for which [2] assigns the parameters $A = 29.8$ K, $J = 6.4$ K ($a = A/J = 4.7$) extracted essentially from a fit of the data against the semiclasical dispersion of (2). We thus use (2) with the above parameters as input 'experimental' data and perform a least-squares fit to the excitonic dispersion of (3). The resulting new parameters $A = 23$ K, $J = 7$ K ($a = A/J = 3.3$) are found to be in substantial disagreement with the assignment of [2]. The most notable feature of the new parameters is that the value of a is pushed below the semiclassical critical coupling

$a_c = 4$, where (2) is no longer valid. A more careful analysis should include a discussion of the intensity given in (4) and consider the effect of a small inter-chain coupling.

Having thus completed the description of the excitonic mode, we turn our attention to a second (mirror) mode observed through out-of-plane fluctuations in $CsFeBr_3$ [2]. A theoretical explanation of this mode has not been available [6]. In fact, a semiclassical calculation analogous to that leading to (2) would yield an expression for the two-point longitudinal correlation function $\langle S^z_m(t) S^z_n \rangle$ that is dominated by a dull exciton–anti-exciton continuum and provides no indication for a sharp mode in this channel. Yet is is conceivable that such a mode exists in the form of an exciton–antiexciton bound state and is missed by the semiclassical theory for more or less the same reason that the familiar Holstein–Primakoff expansion does not yield direct information for the two-magnon bound states known to exist in ferromagnets. However, this analogy with two-magnon states is somewhat misleading because two-body states in this problem come in three varieties: namely, exciton–exciton (ee) pairs with magnetisation $m = 2$; anti-exciton–antiexciton ($\bar{e}\,\bar{e}$) pairs with $m = -2$; and exciton-antiexciton ($e\bar{e}$) pairs with $m = 0$. The ee and $\bar{e}\,\bar{e}$ states share with two-magnon states the property that they may be observed only through four-point correlations. On the other hand, $e\bar{e}$ states contribute directly to the two-point longitudinal correlation function, because they carry the same magnetisation with the ground state ($m = 0$), and should be accessible to inelastic neutron scattering.

In order to ascertain the existence of bound states, we resort again to the strong-coupling expansion. First we consider the ee sector; the discussion of the $\bar{e}\,\bar{e}$ sector is identical, whereas the results for $e\bar{e}$ states will be inferred later by simple substitutions. Now, in the limit $a \to \infty$, the ee sector consists of states of the form $|n_1, n_2\rangle$ where the azimuthal spin is equal to $+1$ at sites n_1 and n_2 and vanishes at all other sites. Clearly, $|n_1, n_2\rangle = |n_2, n_1\rangle$ and $n_1 \neq n_2$, so there exist $\Lambda(\Lambda - 1)/2$ ee states all with energy $2A$. This degeneracy cannot be completely removed by sorting out states with definite crystal momentum. Hence we must perform degenerate perturbation theory which, to leading order, amounts to diagonalising the matrix $\langle n_1', n_2' | V | n_1, n_2 \rangle$ where V is the exchange operator defined in (1). The action of V on $|n_1, n_2\rangle$ is given by

$$V|n_1, n_2\rangle = |n_1 - 1, n_2\rangle + |n_1 + 1, n_2\rangle + |n_1, n_2 - 1\rangle + |n_1, n_2 + 1\rangle \tag{6a}$$

when n_1 and n_2 are not neighbours, and

$$V|n, n+1\rangle = \delta|n, n+1\rangle + |n-1, n+1\rangle + |n, n+2\rangle. \tag{6b}$$

In the right-hand sides of (6*a*) and (6*b*) we have neglected states that do not belong to the manifold $|n_1, n_2\rangle$, as is appropriate to leading order.

The main point of this calculation is that the operator V defined by (6) can be diagonalised by a Bethe *ansatz*, in close analogy with calculations of two-magnon states in anisotropic chains of arbitrary spin [7, 8]. Specifically the eigenvalue problem

$$V\Psi = \varepsilon\Psi \qquad \Psi = \sum_{n_1 < n_2} C_{n_1, n_2} |n_1, n_2\rangle \tag{7}$$

is solved by the Bethe *ansatz*

$$\begin{aligned} C_{n_1, n_2} &= \exp \mathrm{i}(k_1 n_1 + k_2 n_2 + \varphi/2) + \exp \mathrm{i}(k_1 n_2 + k_2 n_1 - \varphi/2) \\ \varepsilon &= 2(\cos k_1 + \cos k_2) \end{aligned} \tag{8}$$

provided that the wavenumbers k_1, k_2 and the phase shift φ are related by

$$\cot(\varphi/2) = \delta \sin[(k_1 - k_2)/2] / \{2\cos[(k_1 + k_2)/2] - \delta \cos[(k_1 - k_2)/2]\}. \tag{9}$$

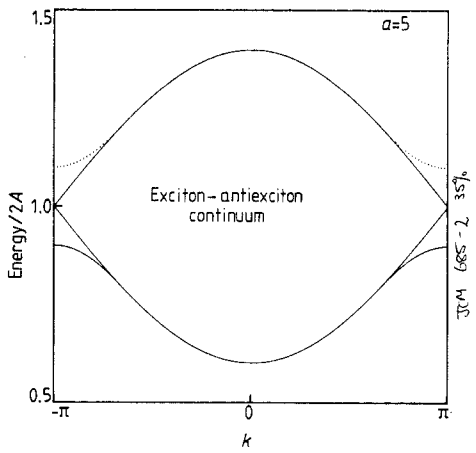

Figure 2. Dispersion of the exciton–antiexciton bound state, (12), for $a = 5$. The bound state emerges below the continuum for the antiferromagnet (full curve, $\delta = -1$) and above the continuum for the ferromagnet (dotted curve, $\delta = 1$).

This information, together with the periodic boundary conditions $C_{n_1,n_2} = C_{n_2,n_1+\Lambda}$, suffices for a complete description of the ee or $\bar{e}\bar{e}$ sector along the lines of [7, 8].

Thus the leading approximation to the energy of an ee or $\bar{e}\bar{e}$ pair is given by $\Omega_{k_1k_2} = A(2 - \varepsilon/a)$, i.e.

$$\Omega_{k_1k_2} = 2A[1 - (1/a)(\cos k_1 + \cos k_2)]. \tag{10}$$

The majority of solutions correspond to real wave number k_1 and k_2 for which (10) yields a two-body continuum with boundaries given by $\Omega_k^{\pm} = 2A\,[1 \pm (2/a)\cos(k/2)]$ where $k = k_1 + k_2$ is the total crystal momentum. We also find solutions for complex k_1 and k_2 leading to ee and $\bar{e}\bar{e}$ bound states with dispersion

$$\Omega_k^{ee} = \Omega_k^{\bar{e}\bar{e}} = 2A\{1 - (1/a)[(\delta/2) + (2/\delta)\cos^2(k/2)]\} \qquad 2\cos^{-1}(\delta/2) \leqslant |k| \leqslant \pi. \tag{11}$$

This dispersion describes a stable mode, for momenta near the zone boundary, which merges smoothly with the continuum at $|k| = 2\cos^{-1}(\delta/2)$. Note that the bound state is stable throughout the zone for $|\delta| \geqslant 2$, whereas no such state is formed in the XY limit $\delta = 0$.

The $e\bar{e}$ sector is spanned by states of the form $|n_1, \bar{n}_2\rangle$ where the bar indicates that the azimuthal spin at site n_2 is equal to -1. The study of this sector appears to be complicated by the fact that $|n_1, \bar{n}_2\rangle$ is not symmetric under exchange of n_1 and n_2. However, it is not difficult to see that the (anti)symmetric combinations $|n_1, n_2\rangle^{\pm} = |n_1, \bar{n}_2\rangle \pm |n_2, \bar{n}_1\rangle$ both satisfy (6) with the simple substitution $\delta \to -\delta$. Therefore a Bethe *ansatz* may be used in this case, too. The boundaries of the $e\bar{e}$ continuum are the same as those of (10) and an $e\bar{e}$ bound state is formed with dispersion.

$$\Omega_k^{e\bar{e}} = 2A\{1 + (1/a)[(\delta/2) + (2/\delta)\cos^2(k/2)]\} \qquad 2\cos^{-1}(\delta/2) \leqslant |k| \leqslant \pi. \tag{12}$$

This dispersion is plotted in figure 2 for $a = 5$. It is seen that the bound state emerges above the continuum in the ferromagnet ($\delta = 1$) and below the continuum in the antiferromagnet ($\delta = -1$).

The calculated $e\bar{e}$ bound state appears as a sharp mode in the two-point longitudinal dynamic correlation function $G^{zz}(k, \omega)$ and is thus tentatively identified with the 'mirror' mode picked up by out-of-plane fluctuations in the experiment of [2]. A convincing identification would require an explicit calculation of $G^{zz}(k, \omega)$. This calculation is

actually possible, by exploiting the detailed structure of the Bethe wavefunctions of (6)–(9), but will not be given in this short communication. However, the general features of the anticipated result may be envisaged by a simple inspection of figure 2. For values of k near the zone boundary, a sharp mode will appear at $\omega = \Omega_k^{e\bar{e}}$ separated from the contribution of the e–ē continuum by a finite frequency gap. As k approaches the zone centre, this gap tends to zero because the bound state gradually merges with the continuum.

Finally one should keep in mind that (12) is only the leading approximation of the bound-state dispersion within a systematic strong-coupling expansion. Therefore a consistent comparison of (12) with experiment would require that the parameters of the model be extracted from an excitonic dispersion calculated with comparable accuracy, i.e. one should use $\omega_k = A(1 - 2\cos k/a)$ instead of the more accurate expression given in (3). Of course, a more satisfactory procedure would be to calculate higher-order corrections to (12), but those appear difficult to obtain because of the inherent degenerate perturbation theory. We hope to return to some of these questions in a future more detailed publication.

We are grateful to M Steiner for valuable correspondence concerning the experimental work of [1, 2] and H Neuberger for some theoretical suggestions. This work was supported in part by the US Department of Energy and by an EEC grant (ESPRIT-3041).

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