Electron spin resonance shift in spin ladder compounds

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We analyze the effects of different coupling anisotropies in spin-1/2 ladder on the Electron Spin Resonance (ESR) shift. Combining a perturbative expression in the anisotropies with temperature dependent Density Matrix Renormalization Group (T-DMRG) computation of the short range correlations, we provide the full temperature and magnetic field evolution of the ESR paramagnetic shift. We show that for well chosen parameters the ESR shift can be in principle used to extract quantitatively the anisotropies and, as an example, discuss the material BPCB.

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Quantum magnetism is a fascinating branch of solid state physics, and more recently of quantum gases in optical lattices. Due to the competition between the exchange interactions between spins localized on different lattice sites, many fascinating quantum phases can occur ranging from ferromagnetically or antiferromagnetically ordered states to spin liquids. Recently spin systems have also allowed one to address questions usually related to itinerant quantum systems such as Bose-Einstein condensation (BEC) and Tomonaga-Luttinger liquid physics.

For potential application it is particularly important to have efficient probes to characterize the properties of magnetic systems. Fortunately powerful probes, such as neutron scattering or nuclear magnetic resonance exist and give important physical information. However in systems which are particularly sensitive to the symmetry of exchange interactions (such for example the ones where BEC can be realized), a direct probe of small asymmetries of the coupling constants is desirable. An ideal probe for this purpose is the Electronic Spin Resonance (ESR) which allows one to investigate the frequency shift of the paramagnetic resonance induced by small anisotropies. In order to interpret the experimental observations an efficient theoretical analysis of the corresponding spectra is mandatory. Therefore theoretical interpretations have been developed for a long time, their range of applicability is generally limited to several models in a restricted domain of parameters: low temperature region of spin-1/2 antiferromagnetic chains, high temperature limit of spin-1/2 antiferromagnetic chains, low temperature region of spin-1 Haldane chain compound, spin-1/2 chains with nearest and next nearest neighbor interactions, strongly dimerized spin-1/2 ladders analysed in a single rung picture.

In this letter we present a flexible theory of the ESR spectra. Combining an analytical expression of the ESR shift with a numerical evaluation of short range correlations we give the full dependence of the ESR shift with the magnetic field and the temperature. We apply this approach to the case of spin-1/2 ladders using temperature dependent density matrix renormalization group (T-DMRG). We show in particular that the ESR technique can be used to distinguish the nature of different anisotropies quantitatively.

A spin-1/2 ladder in a magnetic field with interaction exchange anisotropies can be described by the Hamiltonian which consists of two parts. The first part includes the isotropic exchange interaction and the Zeeman term. The spin operator is defined by , where is the Pauli matrix acting on the spin located on leg and rung , and is the total spin. Here are the antiferromagnetic couplings along the legs and the rungs of the ladder, is the Landé factor, is the Bohr magneton and is the strength of the static magnetic field. Note that by this has the unit of energy.

The anisotropic exchange interaction contains different spatial anisotropies in the exchange interactions along the legs and the rungs, respectively. , , represents the principal axis coordinates of more general interactions.
instead of $J'_{\alpha,p} S_{i,p}^x S_{j,k}^x$ in (2) (for dipolar interaction typically) with $A_{\alpha q'}^q$, $\alpha = \parallel, \perp$, are symmetrical tensors in every coordinate basis $x, y, z$ (denoted $q, q' = x, y, z$) aligned with the magnetic field $h = h z$. In the $a_\alpha, b_\alpha, c_\alpha$ coordinates, one denotes $z = (z_{\alpha,a}, z_{\alpha,b}, z_{\alpha,c})$.

The ESR frequency shift $\delta \omega$ is defined as the difference between the ESR paramagnetic frequency resonance, and the Zeeman frequency:

$$h \delta \omega = h \omega_r - H.$$  

(3)

Here $\omega_r$ is the resonance frequency and $H = g\mu_B h$. Assuming that the anisotropies are small, i.e. $|J'_{\parallel,p}|, |J'_{\perp,p}| \ll J_\parallel, J_\perp$, we determine (3) based on a first order perturbation theory in the anisotropy. At this order, the ESR shift is represented by a static correlation function $h \delta \omega$

$$h \delta \omega = \sum_{\alpha = \parallel, \perp} f_\alpha(z) Y_\alpha(T, H).$$  

(5)

corresponding to the effect induced by the anisotropy in the parallel ($\alpha = \parallel$) and the perpendicular ($\alpha = \perp$) interaction exchange. The temperature and magnetic field dependence of the shift (5) are determined by the short range correlations $Y_\alpha(T, H)$:

$$Y_\parallel(T, H) = \frac{\langle (S_{1,1}^z S_{1,1+1,1}^z - S_{1,1}^z S_{1,1+1,1}^z) \rangle_0}{\langle S_{1,1}^z \rangle_0},$$  

(6)

$$Y_\perp(T, H) = \frac{\langle (S_{1,2}^z S_{1,2+1,2}^z - S_{1,2}^z S_{1,2+1,2}^z) \rangle_0}{\langle S_{1,2}^z \rangle_0}. $$  

(7)

Computing these correlations is in general involved [20]. Here we use the T-DMRG method which allows us to determine the ESR shift. Note that this approach is quite general and can be extended to other systems.

For the considered spin ladder we fix the direction of the magnetic field $z$ with respect to the system orientation, the factors $f_\alpha(z)$ depend only on the anisotropic coupling constants $J'_\alpha$:

$$f_\alpha(z) = t_\alpha \sum_{p=x,y,z} J'_{\alpha,p}(1 - 3 z_{\alpha,p}^2),$$  

(8)

with $t_\parallel = 1$ and $t_\perp = 1/2$. Assuming that all the isotropic coupling is included in $H^0$, i.e. $\sum_p J'_{\alpha,p} = 0$, we obtain $f_\alpha(z) \sim -3 t_\alpha z A_{\alpha,z}z'$. Hence $f_\alpha(z)$ measures the anisotropy $A_{\alpha q'}^q$ along the magnetic field orientation $z$ and has extrema when $z \parallel a_\alpha, b_\alpha$ or $c_\alpha$.

In the following we first discuss the properties of $Y_\alpha(T, H)$ for different coupling ratios $j = J_\parallel/J_\perp$. We then focus on the compound BPCB and analyze its ESR measurements.

At low magnetic field $H \ll H_{c1}$ both $Y_\parallel$ and $Y_\perp$ grow linearly with $H$ (Fig. 1), i.e. $Y_\parallel, Y_\perp \propto H$ ($H_{c1} < H_{c2}$) are the two critical fields between which the system is gapped (19). In a strong magnetic field $H \gg H_{c2}$ the system becomes totally polarized and $Y_\parallel, Y_\perp \approx 1/2$. Between these two limits the behavior of $Y_\parallel$ and $Y_\perp$ is very subtle and clearly depends on the coupling ratio $j$. In the zero interladder coupling limit $j = 0$, the two ladders decouple. $Y_\perp$ reduces to $Y_\perp \approx \langle S_{1,1}^z \rangle_0$, and $Y_\parallel$ can also be calculated analytically [10, 21]. The system is gapped below $H_{c2}$ and $Y_\parallel, Y_\perp$ are monotonic functions of $H$ as shown in Fig. 1(a).

For finite interladder couplings $j > 0$, the system is gapped for $H < H_{c1}$ and has a $S^z = S^2 = 0$ ground state. Thus we expect that $Y_\parallel$ and $Y_\perp$ show special signatures at $H_{c1}$ when the gap is closed and the excitations become accessible. In this range of magnetic field $H \approx J_\perp, y_\parallel$ can exhibit a non-monotonical behavior at low temperatures and strong couplings ($j = 3.6, 10$...
in Fig. 1(c-d)). In contrast $Y_\perp$ shows an intermediate plateau like feature at low coupling (cf. $j = 0.5$ in Fig. 1(b)) and a strong rise with a subsequent plateau at a value 0.5 for stronger coupling.

The features at large $j$ are roughly understood using a strong coupling approach. In this limit for $H_1 < H < H_{c,2}$ (gapless regime) and $k_BT < J_{\perp}$, the Hilbert space per rung can be approximated keeping only the two lowest states, i.e. the triplet $|↑↑⟩ = |↑↑⟩$ and singlet $|s⟩ = (|↑↓⟩ - |↓↑⟩)/√2$ state. Mapping these onto two effective spin-1/2 states $|↑⟩ \rightarrow |↑⟩$ and $|s⟩ \rightarrow |↓⟩$, the system $H^0$ becomes equivalent to an effective anisotropic spin chain $H_{XXZ}$

$$H_{XXZ} = J_\parallel \sum_i (\tilde{S}^x_i \tilde{S}^x_{i+1} + \tilde{S}^y_i \tilde{S}^y_{i+1} + \Delta \tilde{S}^z_i \tilde{S}^z_{i+1}) - \tilde{H} \tilde{S}^z_i,$$

with $\Delta = 1/2$ and $\tilde{H} = H - J_\perp - J_\parallel/2$. Within this approximation

$$Y_{\perp} = \frac{1}{2}, \quad Y_{\parallel} = \frac{1}{8} + \frac{1}{2} \frac{\langle \tilde{S}^z_i \rangle^2}{\langle \tilde{S}^z_i \rangle^2} / \frac{\langle \tilde{S}^x_i \tilde{S}^x_{i+1} \rangle}{\langle \tilde{S}^x_i \rangle^2} - \frac{\langle \tilde{S}^x_i \tilde{S}^x_{i+1} \rangle}{\langle \tilde{S}^x_i \rangle^2}.$$

In particular, this approximation recovers the almost constant behavior of $Y_{\perp}$ in the gapless regime at low temperature. In contrast, although $Y_{\parallel} \approx 1/2$ for $H \gg H_{c,2}$, this quantity shows a dip in the gapless regime and a plateau when $0 \ll H < H_{c,1}$. These effects are present in Fig. 1(c,d) in both the strong coupling approximation and the full ladder at low temperature. The use of Eq. (5) for the discrimination between the two kinds of anisotropies $J_{\parallel,p}$ and $J_{\perp,p}$ is very efficient in this range of parameters $H \approx J_{\parallel}$ and $k_BT \approx J_{\parallel}$ for which very distinct behavior contributions from $Y_{\parallel}$ and $Y_{\perp}$ can be well separated. Note that when $j$ decreases these contributions become less distinguishable (see Fig. 1(b)).

Recently ESR measurements performed on BPCB extracted the fitting parameters are

$$f_{1/2}/k_B = -1.5 \pm 0.1 \text{ K}, \quad f_{1/2}/k_B = 0.4 \pm 0.1 \text{ K} \quad (10)$$

for the corresponding orientation of each ladder respectively. Similarly, considering only anisotropies along the rungs $J_{\perp,p}$ we get

$$f_{1,1}/k_B = -1.3 \pm 0.1 \text{ K}, \quad f_{1,2}/k_B = 0.3 \pm 0.1 \text{ K} \quad (11)$$

Once extracted, these parameters determine the shift at all temperatures and values of the magnetic field. As shown in Fig. 2 both anisotropies are able to reproduce very well all the experimental measurements available. The discrepancies between the ESR measurements and the prediction lie within the uncertainties due to extraction of the peak location from the measured ESR spectra. Indeed, the shift is related to the first frequency momentum of the peak instead of its maximum location which is not well defined when the peak is broadened. These discrepancies are clearly seen for temperatures $T \approx J_{\parallel}/k_B = 3.6$ K in Fig. 2(c) which shows the magnetic field location of the peak at $\omega_c = 2\pi \cdot 96$ GHz extracted from extrema of the measured ESR spectra (Fig. 4 of Ref. [17]) versus the temperature. Let us note that the magnitude of the extracted parameters considering only rung anisotropy is in agreement with the anisotropy $f_{1,1}/k_B = -1.1$ K and $f_{1,2}/k_B = 0.4$ K extracted in Ref. [17] for a single rung model. However, taking the full ladder into account enables in principle the determination of the repartition of the anisotropy along the rung and the leg using suited experimental measures.

Since the measurements in Ref. [17] are done in a region where $Y_{\parallel}$ and $Y_{\perp}$ are not very distinct, the fit cannot uniquely determine their contributions. The optimal fit is shown in Fig. 2(b,c). More precise measurements around $T \approx 3$ K, for which $Y_{\parallel}$ and $Y_{\perp}$ behave very distinctly (see Fig. 1(c)), could be used for a clear separation of the effects of both anisotropies. The differences expected at that temperature are shown in Fig. 3. Note that one should make a compromise between the separation of the two components $Y_{\parallel}$ and $Y_{\perp}$ and the occurrence of a well resolved ESR resonance peak. The extraction of the anisotropies $J_{\alpha,p}$ and their corresponding orientation $a_\alpha, b_\alpha, c_\alpha$ would require measurements for different magnetic field directions.

In summary, we proposed a general theory to determine the frequency shift of ESR in spin-1/2 ladder compounds. By taking advantage of the wide applicable scope of the perturbative formula, combined with numerical evaluation of the static correlation functions at arbitrary temperatures, we computed the shift in a wide range of parameters.
Figure 3. Theoretical prediction of the ESR shift $\delta \omega$ versus the magnetic field at $T = 3$ K for the two ladders orientations. The predictions are plotted in dotted, dashed and full lines considering only the rung, leg anisotropy with the fitting parameters (10), (11) and with the best fitting parameters given in Fig. 2 respectively. The shaded area represents the standard deviation of the ESR experiments in Ref. [17] from our theoretical prediction. Note that for the experimental configuration of Ref. [17], the anisotropies along the magnetic field for ladder 1 could be well separated from the ESR measurements at $T = 3$ K.

Figure 2. (color online): Magnetic field dependence of (a) the ESR paramagnetic resonance frequency $\omega_r$, (b) the ESR resonance frequency shift $\delta \omega$. (c) Temperature dependence of the magnetic field at which the ESR paramagnetic resonance at $\omega_r = 2\pi \cdot 96$ GHz occurs. Symbols denote experimental data taken from [17] and lines theoretical predictions of the best fitting parameters $f_{11}/k_B = 0.1$ K, $f_{12}/k_B = -1.4$ K and $f_{12}/k_B = 0.2$ K, $f_{22}/k_B = 0.2$ K if not stated otherwise. The results corresponding to the two differently oriented ladders 1 and 2 are plotted in black and grey (online red), respectively. In (a) the linear Zeeman component of the ESR frequency resonance is represented by full lines (for the Landé factors $g_1$ and $g_2$). We show in (b) the theoretical prediction of the ESR shift at $T = 1.3$ K for the ladder 1 considering only the leg (black dotted lines) or the rung anisotropy (black dashed lines) with the fitting parameters (10) and (11), respectively. These fits show only small deviations with the best fit in this range of temperature and magnetic field.

range of temperature and magnetic field and showed how the ESR technique can distinguish the nature of different anisotropies. The predicted ESR shift is in very good agreement with experimental data for BPCB. Based on our results, we propose a new set of experiments to better resolve the different anisotropies.

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