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Propagating $S=\frac{1}{2}$ particles in $S=1$ Haldane-gap systems

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Inspired by the recent experiments on $Y_{2-x}Ca_xBaNiO_5$, we discuss the dispersion relation of the $S=\frac{1}{2}$ particles in the $S=1$ Heisenberg and valence bond solid model in the limit of small hopping amplitudes. The effective $S=\frac{1}{2}$ edge spins mix with the spin of the impurity resulting in one fourfold and two twofold degenerate bands. We briefly discuss the interaction between the $S=\frac{1}{2}$ particles arising from the background.

Recently, the family of the quasi-one-dimensional materials showing the Haldane gap[1] has been enlarged by the charge transfer insulator[2] Y_2BaNiO_5. In these materials the Ni^{2+} ions with $S=1$ are surrounded by oxygens forming an octahedron, NiO_6. These octahedra are linked and form well separated chains, making an ideal one-dimensional $S=1$ antiferromagnet. Susceptibility and neutron scattering measurements have observed a spin gap of $\approx$ 100 K (9 meV). The two relevant Ni orbitals are $3d_{3z^2-r^2}$ and $3d_{x^2-y^2}$. The latter is almost localized, while the $3d_{3z^2-r^2}$ orbital has finite overlap with $2p_z$ orbital[3] of the O.

The importance of Y_2BaNiO_5 is not only being another Haldane gapped system, but by replacing the off-chain Y^{3+} by Ca^{2+} one can dope the chain by holes; thus one can introduce carriers into a gapped spin liquid. The doped material, $Y_{2-x}Ca_xBaNiO_5$, has been studied by DiTusa *et al.* (Ref. 4). The addition of carriers lowers the resistivity and its temperature dependence cannot be described as thermal activation across the charge gap. Polarized x-ray absorption experiment showed that upon doping, the holes go to the $2p_z$ orbital of the O between the Ni^{2+} ions. Furthermore, new states with S between 1 and $\frac{3}{2}$ per impurity appeared inside the Haldane gap.

It is not clear at the moment, what a minimal microscopic model capable to describe the experiments can be. Neither is clear the importance of the disorder caused by replacing Y by Ca (the effect of the bond disorder was addressed in Refs. 5 and 6). If the disorder can be neglected, then, as far as the low energy physics is concerned, the effective model Hamiltonian can be that of the $S=1$ Heisenberg model, where additional $S=\frac{1}{2}$ objects are added (see Fig. 1). The question of localized $S=\frac{1}{2}$ impurities was discussed in Refs. 5 and 7. However, nothing can exclude that the holes can move, and it raises a very interesting question: what are the low energy properties of doped Haldane systems? For this reason here we discuss a simple Hamiltonian to describe such systems. It turns out that even in that simple Hamiltonian, to solve the propagation of one spin $S=\frac{1}{2}$ object is not trivial, and the interaction between the spin $\frac{1}{2}$ objects due to the $S=1$ background is rather complicated.

A similar problem is the propagation of $S=0$ holes in the Haldane gap systems.[8] However, it corresponds to a simultaneous hopping of two electrons, which can be favorable to one electron hopping only in limited circumstances.

To describe the interaction between the $S=1$ spins of the Ni^{2+} ions, we consider the following rotationally invariant spin Hamiltonian

$$H_0=J\sum_i\left[\mathbf{S}_i\cdot\mathbf{S}_{i+1}-\beta(\mathbf{S}_i\cdot\mathbf{S}_{i+1})^2\right]. \qquad (1)$$

We will concentrate on the special cases of $\beta=0$ and $\beta=-\frac{1}{3}$. The former is the Heisenberg model for $S=1$, while the latter is the valence bond solid (VBS) Hamiltonian, where the ground-state function is known.[9] Both Hamiltonians have a gap in the excitation spectrum. Since the holes break the valence bonds of the $S=1$ host, we get open chains segments between the $S=\frac{1}{2}$ objects (see Fig. 2). The ground state of an open chain is fourfold degenerate[10] in the thermodynamic limit. This can be simply explained by noticing that the construction of the VBS state of an open chain leaves effective $\frac{1}{2}$ spin objects at the ends of the chain. These edge spins can form a triplet and a singlet, and the energy splitting for N-site long chain is $\sim\exp(-N/\xi)$ and it disappears for $N\rightarrow\infty$, where ξ is the correlation length. One can actually see these edge states, and their extension is over several lattice sites.[11] For $\beta=-\frac{1}{3}$, the correlation length is 1/ln3, while for the Heisenberg model $\xi\approx7$. We denote the triplet wave function by $T_N^{\pm1,0}$ and singlet by S_N, where the superscript $\pm1,0$ denotes the z component of the triplet. For N even, the singlet is even and triplet is odd in parity, while for N odd the parities are reversed.

Now, let us turn to the Hamiltonian describing the effect of $S=\frac{1}{2}$ impurities. First of all, an impurity at site $i+\frac{1}{2}$ will change the effective J coupling to J_1 between the $S=1$ spins at site i and $i+1$ in the Hamiltonian in Eq. (1). Next, there is an interaction between the $\frac{1}{2}$ impurity and $S=1$ spins (see Refs. 5 and 7):

$$H_{J'}=2J'\sum_i\left(\mathbf{S}_i\cdot\boldsymbol{\sigma}_{i+1/2}+\mathbf{S}_{i+1}\cdot\boldsymbol{\sigma}_{i+1/2}\right), \qquad (2)$$

and finally, there are the Hamiltonians describing the effective hopping of the holes on the O sites:

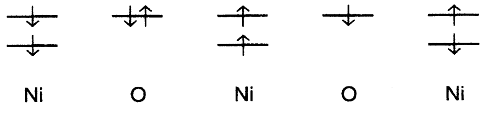

FIG. 1. Schematic diagram of the Ni–O chain with typical low-energy level occupation. The hole is on the second O.

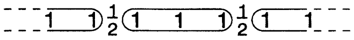

FIG. 2. Part of the $S=1$ chain with two $S=\frac{1}{2}$ spins. Between them the three $S=1$ spins form an open chain.

$$H_{\tilde{t}}=\tilde{t}\sum_i \hat{P}_i,$$

$$H_{\tilde{J}}=2\tilde{J}\sum_i \hat{P}_i(\mathbf{S}_i\cdot\boldsymbol{\sigma}_{i+1/2}+\boldsymbol{\sigma}_{i-1/2}\cdot\mathbf{S}_i), \tag{3}$$

where the factor 2 in front of the $\tilde{J}$ and J' is for convenience and $\boldsymbol{\sigma}$ is the spin operator of the $S=\frac{1}{2}$ spin. The operators $\hat{P}_i$ exchanges the occupation of the site $i+\frac{1}{2}$ and $i-\frac{1}{2}$, i.e., if the hole is on site $i+\frac{1}{2}$, the $\hat{P}_i$ will move it to $i-\frac{1}{2}$ if that site was empty. We do not allow two $S=\frac{1}{2}$ objects to occupy the same site, as it costs a lot of energy. Clearly, the Hamiltonian $H=H_0+H_{J'}+H_{\tilde{t}}+H_{\tilde{J}}$ is isotropic.

In the following we will restrict ourselves to the case when the parameters $\tilde{t}$ and $\tilde{J}$ describing the propagation of the $S=\frac{1}{2}$ objects are small compared to the Haldane gap, i.e., J of the host $S=1$ system. Furthermore, J_1 and J' are assumed small as well. In this limit the energetically large excitation of the $S=1$ host created during the motion can be neglected and we will work in the subspace where the wave function of the $S=1$ sequences are the singlet and triplet wave function described above. Our approach is similar to the variational wave function applied in Ref. 7.

Given the Hamiltonian and the constraints above, let us now turn to the calculation of the dispersion relation of a single hole. First, let us construct the trial wave function of the L-site periodic chain with one impurity:

$$|S_L\sigma k\rangle=\frac{1}{\sqrt{L}}\sum_j e^{ikj}|S_L\sigma;j+1/2\rangle,$$

$$|T_L\sigma k\rangle=\frac{1}{\sqrt{L}}\sum_j e^{ikj}|T_L\sigma;j+1/2\rangle, \tag{4}$$

where $|S_L\sigma;j+1/2\rangle$ and $|T_L\sigma;j+1/2\rangle$ denote the states with hole at site $j+\frac{1}{2}$.

Now it is a good point to say something about the addition of angular momenta. The state of the two edge $\frac{1}{2}$ spins and the impurity $\frac{1}{2}$ spin has one $S=\frac{3}{2}$ and two $S=\frac{1}{2}$ representations. Since our Hamiltonian is rotationally invariant, we expect one fourfold degenerate band with total spin $S=\frac{3}{2}$ (quartet) and two twofold degenerate bands with $S=\frac{1}{2}$ (doublet). The $S=\frac{3}{2}$ representation can be constructed as follows:

$$|Q_k^{+3/2}\rangle=|T_L^{+}\uparrow k\rangle,$$

$$|Q_k^{+1/2}\rangle=\sqrt{1/3}|T_L^{+}\downarrow k\rangle+\sqrt{2/3}|T_L^{0}\uparrow k\rangle,$$

$$|Q_k^{-1/2}\rangle=\sqrt{1/3}|T_L^{-}\uparrow k\rangle+\sqrt{2/3}|T_L^{0}\downarrow k\rangle,$$

$$|Q_k^{-3/2}\rangle=|T_L^{-}\downarrow k\rangle, \tag{5}$$

while the states belonging to the $S=\frac{1}{2}$ representations are

$$|D_k^{+1/2}\rangle=\sqrt{2/3}|T_L^{+}\downarrow k\rangle-\sqrt{1/3}|T_L^{0}\uparrow k\rangle,$$

$$|D_k^{-1/2}\rangle=\sqrt{2/3}|T_L^{-}\uparrow k\rangle-\sqrt{1/3}|T_L^{0}\downarrow k\rangle \tag{6}$$

and

$$|\bar{D}_k^{+1/2}\rangle=|S_L^{0}\uparrow k\rangle,$$

$$|\bar{D}_k^{-1/2}\rangle=|S_L^{0}\downarrow k\rangle. \tag{7}$$

The parity of the states defined above is different, and is determined by the parity of the $|T_L\rangle$ and $|S_L\rangle$. For example, if we define the reflection operator $\hat{R}$ so that it changes the spin at site j to $-j$, then $\hat{R}|Q_k\rangle=r|Q_k\rangle$, $\hat{R}|D_k\rangle=r|D_k\rangle$ and $\hat{R}|\bar{D}_k\rangle=-r|\bar{D}_k\rangle$, where $r=-1$ for L even and $r=+1$ for L odd.

The rotational invariance of the Hamiltonian implies that the Hamiltonian matrix among $|Q_k\rangle$ is diagonal, and there are matrix elements between the $|\bar{D}_k\rangle$ and $|D_k\rangle$ states only. Furthermore, since the parity of the states $|\bar{D}_k^{\pm1/2}\rangle$ and $|D_k^{\pm1/2}\rangle$ is different, the matrix elements with some Hermitian operator $\hat{A}$ commutable with $\hat{R}$ will satisfy $\langle D_k|\hat{A}|\bar{D}_k\rangle=-\langle D_{-k}|\hat{A}|\bar{D}_{-k}\rangle$. These arguments give

$$H|D_k\rangle=(\varepsilon_T+b_k)|D_k\rangle+ic_k|\bar{D}_k\rangle,$$

$$H|\bar{D}_k\rangle=-ic_k|D_k\rangle+(\varepsilon_S+d_k)|\bar{D}_k\rangle,$$

$$H|Q_k\rangle=(\varepsilon_T+a_k)|Q_k\rangle. \tag{8}$$

Here ε_S and ε_T are the energies of the $|S_L\rangle$ and $|T_L\rangle$, respectively, and for small values of the interaction parameters compared to J they depend only on J' apart from the finite-size effects mentioned earlier. Then, the dispersion relation is

$$\varepsilon_D^{\pm}(k)=\frac{b_k+\varepsilon_T+d_k+\varepsilon_S}{2}\pm\sqrt{\left(\frac{b_k+\varepsilon_T-d_k-\varepsilon_S}{2}\right)^2+c_k^2},$$

$$\varepsilon_Q(k)=\varepsilon_T+a_k. \tag{9}$$

We can give more precise statements about the parameters using the microscopic model of the hopping, Eq. (3). First, let us consider the hopping due to $H_{\tilde{t}}$. Since $H_{\tilde{t}}$ is a scalar operator in the spin space, it will have purely diagonal matrix elements: $\langle T^m\sigma k|H_{\tilde{t}}|T^{m'}\sigma' k\rangle=2\delta_{mm'}\delta_{\sigma\sigma'}\tilde{t}h_t^Q\cos k$ and $\langle S\sigma k|H_{\tilde{t}}|S\sigma' k\rangle=2\delta_{\sigma\sigma'}\tilde{t}h_t^D\cos k$. However, $H_{\tilde{J}}$ is a vector operator in the Hilbert space spanned by the $S=1$ spins, and we can use the Wigner-Eckart theorem to get the following identities: $\langle T^m\sigma k|H_{\tilde{J}}|T^m\sigma k\rangle=4m\sigma\tilde{J}h_J^Q\cos k$ and $\langle T^{+1}\downarrow;k|H_{\tilde{J}}|T^0\uparrow;k\rangle=2\sqrt{2}\tilde{J}h_J^Q\cos k$, furthermore $\langle S\sigma;k|H_{\tilde{J}}|S\sigma';k\rangle=0$. Similarly, $\langle T^{+1}\downarrow;k|H_{\tilde{J}}|S\uparrow;k\rangle=-i2\sqrt{2}\tilde{J}h_J^D\sin k$ and $\langle T^0\uparrow;k|H_{\tilde{J}}|S\uparrow;k\rangle=i2\tilde{J}h_J^D\sin k$. The same arguments can be applied for the matrix elements of $H_{J'}$ as well. Putting all together, we get

TABLE I. The coefficients of the VBS wave-function decomposition

N	1	2	3	4	5	...	∞
α_N	0	$\sqrt{1/2}$	$\sqrt{2/7}$	$\sqrt{7/20}$	$\sqrt{20/61}$	...	$\sqrt{1/3}$
β_N	1	0	$\sqrt{3/7}$	$\sqrt{6/20}$	$\sqrt{21/61}$	...	$\sqrt{1/3}$

$$a_k=2(h_t^Q\tilde{t}+h_J^Q\tilde{J})\cos k+J'g,$$

$$b_k=2(h_t^Q\tilde{t}-2h_J^Q\tilde{J})\cos k-2J'g,$$

$$c_k=2\sqrt{3}h_J^D\tilde{J}\sin k,$$

$$d_k=2h_t^D\tilde{t}\cos k, \tag{10}$$

where the coefficients h_t^Q, h_J^Q, h_t^D, h_J^D, and g depend on the wave functions $|S_L\rangle$ and $|T_L\rangle$ and their size dependence is governed by the ξ.

Here we will calculate these coefficients for the VBS model and the Heisenberg model.

VBS model: For the VBS model the task is essentially simplified due to the knowledge of how to construct the ground-state wave function. Actually, for our purposes, the following decomposition of the four lowest-lying wave functions turns out to be useful:

$$|T_N^+\rangle=\alpha_N|T_{N-1}^+0\rangle-\alpha_N|T_{N-1}^0+\rangle-\beta_N|S_{N-1}+\rangle,$$

$$|T_N^0\rangle=\alpha_N|T_{N-1}^+-\rangle-\alpha_N|T_{N-1}^-+\rangle-\beta_N|S_{N-1}0\rangle,$$

$$|T_N^-\rangle=\alpha_N|T_{N-1}^0-\rangle-\alpha_N|T_{N-1}^-0\rangle-\beta_N|S_{N-1}-\rangle,$$

$$|S_N\rangle=\sqrt{1/3}(|T_{N-1}^+-\rangle-|T_{N-1}^00\rangle+|T_{N-1}^-+\rangle)$$

and similarly

$$|T_N^+\rangle=-\alpha_N|0T_{N-1}^+\rangle+\alpha_N|+T_{N-1}^0\rangle-\beta_N|+S_{N-1}\rangle,$$

$$|T_N^0\rangle=-\alpha_N|-T_{N-1}^+\rangle+\alpha_N|+T_{N-1}^-\rangle-\beta_N|0S_{N-1}\rangle,$$

$$|T_N^-\rangle=-\alpha_N|-T_{N-1}^0\rangle+\alpha_N|0T_{N-1}^-\rangle-\beta_N|-S_{N-1}\rangle,$$

$$|S_N\rangle=\sqrt{1/3}(|-T_{N-1}^+\rangle-|0T_{N-1}^0\rangle+|+T_{N-1}^-\rangle),$$

where the coefficients α_N and β_N are given in Table I. It is easy to get this decomposition by inspection. We believe that it is trivial to get this result from the transfer-matrix[12] representation of the VBS wave function. The coefficients exhibit the following remarkable properties: $2\alpha_N^2+\beta_N^2=1$, and it means that in this decomposition is complete in the Hilbert space spanned by the four VBS wave functions. Furthermore, $\alpha_N=(2+3\alpha_{N-1}^2)^{-1/2}$, which allows us to calculate the coefficients recursively.

With the help of the wave-function decomposition presented above, it is straightforward to get the parameters for the hopping matrix elements:

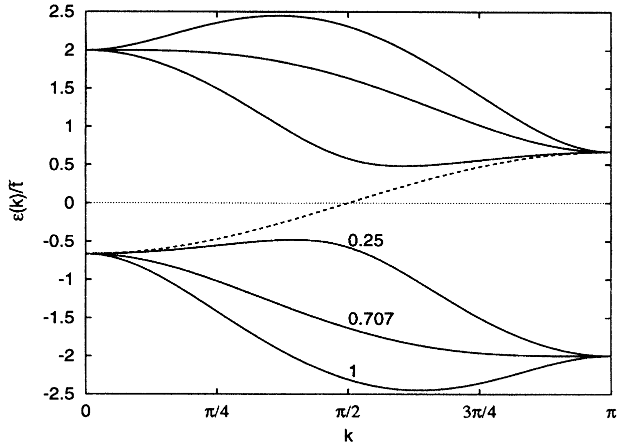

FIG. 3. Dispersion relation for different values of $\tilde{J}/\tilde{t}$ and $J'=J_1=0$. The dashed line is $\varepsilon_Q(k)$, the lower solid line is for $\varepsilon_D^-(k)$ and the upper for $\varepsilon_D^+(k)$. Energy is measured from $\varepsilon_S=\varepsilon_T$.

$$h_t^Q=\beta_L^2-2\alpha_L^2,$$

$$h_J^Q=\beta_L^2-\alpha_L^2,$$

$$h_t^D=1,$$

$$h_J^D=2\alpha_L/\sqrt{3},$$

$$g=2(\alpha_L^2+\beta_L^2), \tag{11}$$

furthermore $\varepsilon_S=-2J_1/3$ and $\varepsilon_T=(34-80\alpha_L^2)J_1/9$, where the energy is measured from $\varepsilon_T(J_1=0)=\varepsilon_S(J_1=0)$. Let us comment here that $h_t^D=1$ means that no walls were created during the motion for that special process.

For infinitely large system and $J_1=0$ the dispersion relation Eq. (9) is simplified to

$$\varepsilon_D^{\pm}(k)=\frac{2}{3}\tilde{t}\cos k-\frac{4}{3}J'\pm\frac{4}{3}\sqrt{3\tilde{J}^2\sin^2k+(\tilde{t}\cos k+J')^2},$$

$$\varepsilon_Q(k)=-\frac{2}{3}\tilde{t}\cos k+\frac{4}{3}J'. \tag{12}$$

We show some examples of the dispersion relation in Fig. 3. An interesting feature of the dispersion relation is that for large values of $\tilde{J}$ the minimum moves away from $k=\pi$ (when $\tilde{t}>0$) or $k=0$ (if $\tilde{t}<0$). It means that the holes will be described by a two-band model, which can have interesting features.

Heisenberg model: We also calculated the hopping matrix elements in Eq. (10) for small clusters of up to 15 sites for the more realistic Heisenberg model, where $\beta=0$. In that case the correlation length is comparable to the cluster size and the size dependence of the matrix elements is large. We have plotted the different matrix element on Fig. 4. Although the size is not large enough to get good values for $L\rightarrow\infty$ limit, we can conclude that $h_t^Q=-0.28\pm0.01$, $h_J^Q=0\pm0.005$, $h_t^D=0.81\pm0.01$, and $h_J^D=0.55\pm0.01$. Fur-

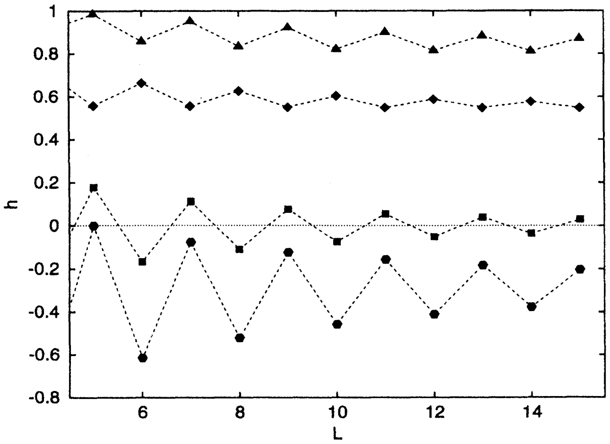

FIG. 4. The matrix elements h for the Heisenberg model: h_t^D (triangles), h_J^D (diamonds), h_J^Q (squares), and h_t^Q (hexagons) from the top to the bottom.

thermore, from Ref. 5 we know that $g=\alpha$ and $\varepsilon_S-\varepsilon_T\approx\alpha^2J_1$ for $J_1\ll J$, where $\alpha=1.0640$. We find these matrix elements to be ≈20% less then those of the VBS Hamiltonian.

A few words about the validity of the approach presented above. During the motion the spin $\frac{1}{2}$ object can destroy the hidden antiferromagnetic order[13] by creating walls. Taking this into account, it would give us corrections of the order $\tilde{t}^2/J$ and $\tilde{J}^2/J$ to the dispersion relation. Also with the increasing amplitude of the hopping, the upper bands will merge with the continuum of the states above the gap. On the other hand, the numerical calculation on small clusters shows that the qualitative features of the lowest band remain even when the hopping amplitudes are comparable with the magnitude of the Haldane gap.

Now, let us turn to the question of what happens if there are more than one $S=\frac{1}{2}$ impurities? We can follow the idea that for small values of the $\tilde{t}$ and $\tilde{J}$, the states above the gap are not excited and it is enough to consider the four low-lying states of the open chain for the wave function of the $S=1$ sequence in the wave functions. For example, a typical state is

$$|\ldots T^{+}_{i_1-i_0}\uparrow_{i_1}T^{0}_{i_2-i_1}\downarrow_{i_2}S_{i_3-i_2}\downarrow_{i_3}\ldots\rangle. \tag{13}$$

We can think of this wave function as a variational ansatz. Then, the interaction between the $S=\frac{1}{2}$ objects in this wave function comes from: (i) the hopping matrix elements, which depend strongly on the size of the open chains, i.e., on the distance of the nearest holes; (ii) the energy splitting of the singlet and triplet states of the finite chains between the holes. The interaction due to (i) is proportional to the hopping amplitudes $\tilde{t}$ and $\tilde{J}$ itself, while the strength of (ii) is determined by the J of the host system. These effects depend very much on the correlation length of the $S=1$ system, and they are the smallest for the VBS model. Actually in that case the energy splitting is zero and the interaction is due to (i) only. These interactions can in principle result in a bound state, unless the kinetic energy is large enough. Despite the strong constraints involved in construction of the variational wave function Eq. (13), it has still a substantial freedom and the properties of the system with more impurities remains to be solved.

As far as the experiments done on $Y_{2-x}Ca_xBaNiO_5$ are concerned, we have shown that there are states with S larger than the $S=\frac{1}{2}$ of the impurity in the Haldane gap. Unfortunately, the parameter range for the $Y_{2-x}Ca_xBaNiO_5$ based on simple electronic model seems to indicate that the hopping amplitudes are comparable with the interaction between the $S=1$ spins, where our approach is valid only qualitatively.

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