$S=\frac{1}{2}$ chain-boundary excitations in the Haldane phase of one-dimensional $S=1$ systems

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The $S=\frac{1}{2}$ chain-boundary excitations occurring in the Haldane phase of $S=1$ antiferromagnetic spin chains are investigated. The bilinear-biquadratic Hamiltonian is used to study these excitations as a function of the strength of the biquadratic term, β, between $-1\leq\beta\leq1$. At the Affleck-Kennedy-Lieb-Tasaki point, $\beta=-\frac{1}{3}$, we show explicitly that these excitations are localized at the boundaries of the chain on a length scale equal to the correlation length $\xi=1/\ln3$, and that the on-site magnetization for the first site is $\langle S_1^z\rangle=\frac{2}{3}$. Applying the density matrix renormalization group we show that the chain-boundary excitations remain localized at the boundaries for $-1<\beta<1$. As the two critical points $\beta=\pm1$ are approached the size of the $S=\frac{1}{2}$ objects diverges and their amplitude appears to vanish.
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Many different compounds exist which are believed to be quasi-one-dimensional $S=1$ antiferromagnetic systems. Among these are CsNiCl$_3$, which yielded the first experimental confirmation[1] of the Haldane gap,[2] as well as Ni(C$_2$H$_8$N$_2$)$_2$NO$_2$(ClO$_4$) (NENP)[3,4] which has been studied extensively and Y$_2$BaNiO$_5$,[5–7] a compound similar to the perovskites, which has garnered considerable attention recently due to the relative ease with which it is carrier doped. These compounds are thought to be in the so-called Haldane phase at low temperatures. This phase is characterized by a disordered singlet ground state with a gap to the lowest-lying excitations in the thermodynamic limit. In general, antiferromagnetically coupled linear $S=1$ systems are believed to be in the Haldane phase if the Hamiltonian describing the interaction between the spins is sufficiently close to the standard nearest-neighbor Heisenberg model. In particular it is known that if a biquadratic term linear in β is added:

$$H=J\sum_{i=1}^{L-1}[\mathbf{S}_i\cdot\mathbf{S}_{i+1}-\beta(\mathbf{S}_i\cdot\mathbf{S}_{i+1})^2],\qquad(1)$$

the system remains in the Haldane phase for $-1<\beta<1$. At the Affleck-Kennedy-Lieb-Tasaki[8] (AKLT) point, $\beta=-\frac{1}{3}$, this model is partly solvable and the exact ground state corresponds to a valence bond solid (VBS) of adjacent dimers[8] (Fig. 1) and throughout the Haldane phase the ground state is presumably closely related to the VBS state. If each $S=1$ spin is viewed as two $S=\frac{1}{2}$ spin in the symmetric triplet state then the VBS state corresponds to combining each of the two $S=\frac{1}{2}$ into a singlet with spins on the adjacent sites.

As was noted by Kennedy,[9] it is only when periodic boundary conditions are imposed that the ground state can be considered as a nondegenerate singlet. If the chain is broken (i.e., open boundary conditions) then the ground state is actually fourfold degenerate in the thermodynamic limit. One way to understand this fourfold degeneracy is to think of the open chain as a periodic chain with one coupling removed. At the AKLT point this corresponds to breaking one of the dimers, resulting in two free $S=\frac{1}{2}$ objects and a ground state that is fourfold degenerate in the thermodynamic limit, as

shown in Fig. 1. Hence, it was suggested[10] that such $S=\frac{1}{2}$ are real and experimentally observable. For a finite open chain the $S=\frac{1}{2}$ excitations couple and an exponentially low-lying triplet, above the singlet ground state, is found in the Haldane gap.[9] In the Haldane phase these $S=\frac{1}{2}$ objects can be shown to be located at the boundaries of the open chain and we shall refer to them as chain-boundary excitations.

The chain-boundary excitations may seem like a curiosity, but it is important to realize that the Haldane systems are gapped and hence, in the presence of impurities, the low-temperature physics will be determined by the interaction between these $S=\frac{1}{2}$ objects. In particular, there is considerable current interest in disordered $S=1$ chains[11–14] which in many cases are treated in terms of interacting $S=\frac{1}{2}$ objects. Hence, considerable effort has been devoted to the experimental verification of the above considerations. Electron-spin-resonance (ESR) studies on Cu doped NENP (Refs. 10 and 15) have confirmed the existence of these $S=\frac{1}{2}$ chain-boundary excitations. Subsequent studies of NENP doped with nonmagnetic impurities Zn, Cd, and Hg also showed evidence for $S=\frac{1}{2}$ excitations.[16] More recent specific heat measurements[17] on doped Y$_2$BaNiO$_5$ has been interpreted as low-lying $S=1$ excitations, but a more detailed analysis showed that an interpretation in terms of $S=\frac{1}{2}$ excitations also is possible.[18]

In light of the above remarks it seems important to understand how the chain-boundary excitations occur throughout the Haldane phase, a point we systematically investigate in the present paper. In order to include exact results we have studied the bilinear-biquadratic model, Eq. (1) and we take this model as representative of the Haldane phase. At the
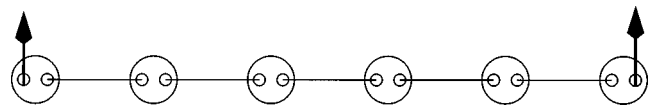

FIG. 1. Schematic representation of the VBS state for open boundary conditions. Large circles correspond to spin-1 sites and the smaller one to spin-$\frac{1}{2}$ states. The $S=\frac{1}{2}$ excitations at the boundaries are indicated by the bold arrows.

AKLT point the $S=\frac{1}{2}$ excitations can be studied using the exact results for the VBS state as we detail below, facilitating the analysis. Exponentially localized $S=\frac{1}{2}$ objects are shown to occur at each end of an open chain. Using the density matrix renormalization group (DMRG) we show that these $S=\frac{1}{2}$ chain-boundary excitations remain well defined in the Haldane phase as β is varied between $-1<\beta<1$, disappearing as the critical points $\beta=\pm 1$ are approached.

We now briefly discuss the physics of the Hamiltonian Eq. (1). Two critical points exist. The Uimin-Lai-Sutherland (ULS) point,[19] described by a $SU(3)_{k=1}$ Wess-Zumino-Witten (WZW) model, at $\beta=-1$, where the system displays a Berezinskii-Kosterlitz-Thouless phase transition with an exponentially diverging correlation length into a massless phase[20] for $\beta<-1$, and the Takhtajan-Babudjian (TB) point,[21] described by a $SU(2)_{k=2}$ WZW model, at $\beta=1$ where a second-order phase transition to a dimerized phase occurs. At the ULS point the system has gapless modes at $k=0,\pm 2\pi/3$ in contrast to the Heisenberg point, $\beta=0$, where the Haldane gap occurs at $k=\pi$. Consequently, as the ULS point is approached, a disorder point, which has been identified with the AKLT point,[22] occurs where the system develops short-range incommensurate correlations. The associated Lifshitz point, where the peak in the structure factor moves away from $k=\pi$, has been numerically estimated to occur at $\beta\simeq -0.438$.[22,23] At the TB point gapless modes occur at $k=0,\pi$ and hence, as β approaches 1 the peak in the structure factor remains at π.

Exact results: The VBS ground-state can be written[8,24,25]

$$|\Psi_{\mathrm{vbs}}\rangle=\prod_i g_i, \quad g_i=\begin{pmatrix} \frac{1}{\sqrt{2}}|0\rangle_i & -|+\rangle_i \\ |-\rangle_i & -\frac{1}{\sqrt{2}}|0\rangle_i \end{pmatrix}. \quad (2)$$

Here $|+\rangle_i,|0\rangle_i,|-\rangle_i$ corresponds to the three states of the $S=1$ on site i. If periodic boundary conditions are considered the trace should be taken whereas for open boundary conditions the matrix gives directly the four ground states. Using the above wave function it is now straightforward to evaluate $\langle S_1^z\rangle_{\mathrm{vbs}}$, the magnetization on the first site of the open chain, as a function of L. Since in the singlet ground state the on-site magnetization is always zero we find for the state with total magnetization $S_T^z=1$:

$$\langle S_1^z\rangle_{\mathrm{vbs}}(L)=\frac{\frac{2}{3}-2\times 3^{-L}}{1-3^{-L}}, \quad L \text{ even} \quad (3)$$

for even L, including all finite size corrections. As is evident from this expression this amplitude rapidly approaches 2/3 as $L\to\infty$. For odd L one finds for the state with total magnetization $S_T^z=1$:

$$\langle S_1^z\rangle_{\mathrm{vbs}}(L)=\frac{\frac{2}{3}+2\times 3^{-L}}{1+3^{-L}}, \quad L \text{ odd} \quad (4)$$

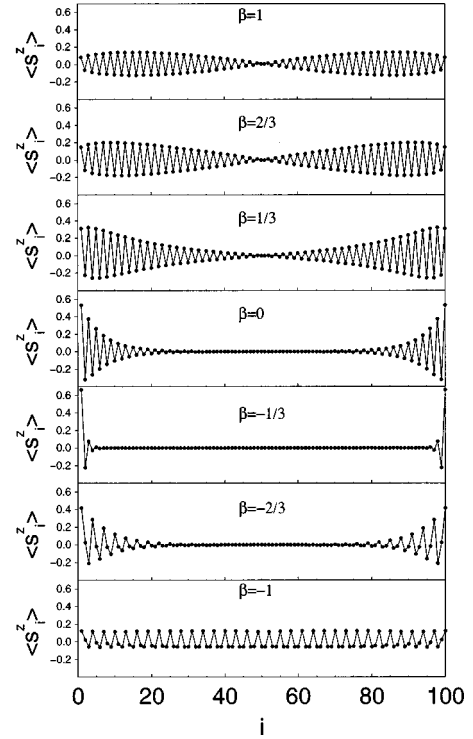with the general expression for any site and any L:

FIG. 2. The on-site magnetization $\langle S_i^z\rangle$ along the chain for different values of the biquadratic coupling, β. In all cases $S_T^z=1$ was used.

$$\langle S_i^z\rangle_{\mathrm{vbs}}(L)=(-1)^{i-1}\frac{\frac{2}{3}\left(\frac{1}{3}\right)^{i-1}-2(-1)^L 3^{i-1-L}}{1-(-3)^{-L}}. \quad (5)$$

Hence, in the thermodynamic limit one obtains the following result for $\langle S_i^z\rangle$ in the state $S_T^z=1$:

$$\langle S_i^z\rangle_{\mathrm{vbs}}=\frac{2}{3}\left(\frac{-1}{3}\right)^{i-1}=(-1)^{i-1}\frac{2}{3}e^{-(i-1)\ln 3}. \quad (6)$$

This *explicitly* shows that the on-site magnetization is decreasing exponentially away from the boundary of the chain with a length scale equal to the bulk-correlation length, $\xi=1/\ln 3$.[8,25] Within the framework of a free boson model,[26] an exponential decrease has been shown to occur at the Heisenberg point,[27] $\beta=0$, in accordance with numerical results,[28,29,27] in this case with a correlation length $\xi\sim 6$. Hence at the AKLT point the $S=\frac{1}{2}$ chain-boundary excitations are well-defined objects localized at the two ends of the chain on a length scale equal to the bulk correlation length. Presumably this picture holds in most of the Haldane phase as we shall verify numerically in the following.

DMRG results: Away from the AKLT point the ground state is not known and in order to study the behavior of the chain-boundary excitations we use the density matrix renormalization group (DMRG) method.[28] We refer the reader to Ref. 28 for a discussion of this method. The calculations were performed using the total z component of the spin, S_T^z, as a quantum number and a number of states, m, between 60 and 100 was kept. The obtained results were extrapolated to the $m\to\infty$, $L\to\infty$ limit where needed.

The bulk of our results are summarized in Fig. 2 where $\langle S_i^z\rangle$, the on-site magnetization, is plotted as a function of
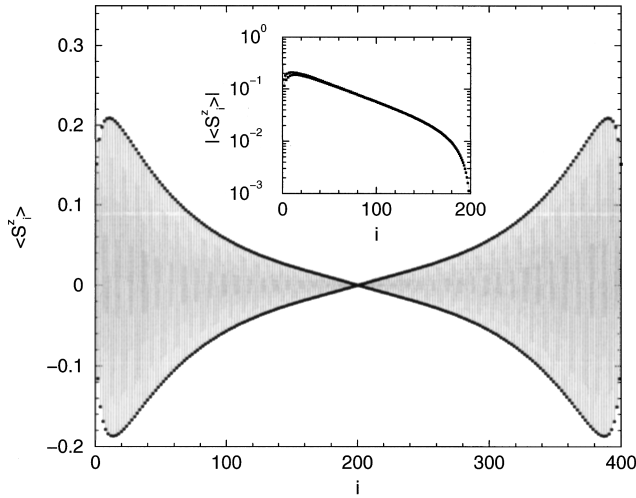
FIG. 3. The on-site magnetization in the $S_T^z = 1$ state for a 400 site chain with $\beta = \frac{2}{3}$. The inset shows the same data for half the chain on a log scale. The asymptotic exponential dependence is clearly visible. $m = 100$ was used.

site index, i, for 8 different values of β between $-1 \leq \beta \leq 1$. The calculations were in all cases performed in the $S_T^z = 1$ state with $m = 100$. If the lowest-lying excitations are indeed determined by the $S = \frac{1}{2}$ chain-boundary excitations, then selecting this state corresponds to polarizing the two $S = \frac{1}{2}$ objects, and one would expect a rather large signal at the ends of the chain. This is clearly the case for most intermediate values of β where well-defined excitations are visible at the boundaries. Decreasing β below the disorder point at $\beta = -\frac{1}{3}$ clearly induces short-range incommensurate (IC) real-space correlations as the period-3 ground state at $\beta = -1$ is approached, as can be seen in Fig. 2 for $\beta = -\frac{2}{3}, -1$. Increasing β beyond approximately $\beta \sim 0.2$ moves the maximum in the on-site magnetization, $\langle S_i^z \rangle$, away from the chain boundaries, $i = 1, L$. As β approached the critical point at $\beta = 1$ the on-site magnetization resembles more and more a double-doughnut shape which presumably is characteristic of the dimerized state the system enters.

Considering the results in Fig. 2 one may ask if the chain-boundary excitations remain localized at the boundaries as the critical points are approached. In order to obtain a partial answer to this question we have re-examined the results $\beta = \frac{2}{3}$ considering a system of size $L = 400$. Our results are shown in Fig. 3. An exponential decay is now clearly visible as detailed in the inset. Assuming that we can still identify the associated length scale with the bulk correlation length we obtain $\xi = 61(4)$. Hence, presumably the $S = \frac{1}{2}$ objects remain localized at the boundaries until the critical point $\beta = 1$ is reached where the correlation length diverges.

If the $S = \frac{1}{2}$ objects remain localized at the boundaries of the chain the first-site magnetization $\langle S_1^z \rangle$ should remain finite in the thermodynamic limit. If at some point the $S = \frac{1}{2}$ objects de-localize and spread out over the entire chain we would expect $\langle S_1^z \rangle$ to go to 0 in the thermodynamic limit with nontrivial finite-size corrections. As a measure of the presence of well-defined chain-boundary excitations we have therefore numerically studied $\langle S_1^z \rangle$ as a function of β. Two effects complicate the analysis: As $\beta \to \pm 1$ the correlation length rapidly diverges necessitating the use of larger and
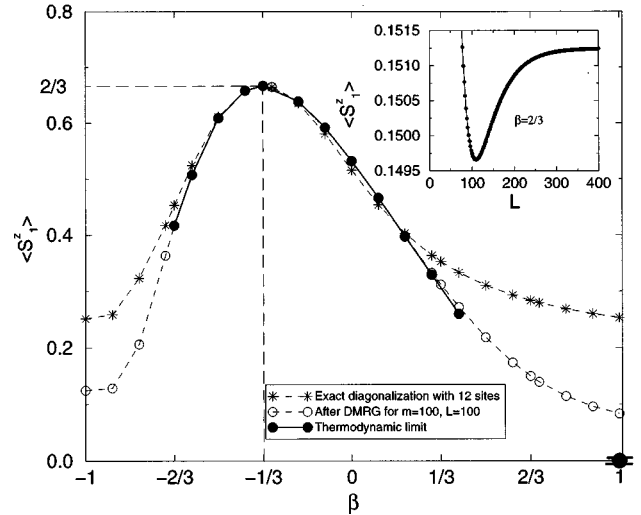

FIG. 4. The first site magnetization, $\langle S_1^z \rangle$, as a function of β between $-1 < \beta < 1$. The asterisks are data for 12 sites, the circles data for $L = 100, m = 100$, and the full circles extrapolations in m, L to the thermodynamic limit, in this latter case the estimated error bars were smaller than the symbols shown except at $\beta = 1$ where the error is shown. The inset shows the L dependence of $\langle S_1^z \rangle$ for $\beta = \frac{2}{3}$ calculated with $m = 100$.

larger system sizes as well as larger values of m, and secondly the incommensurate correlations arising beyond the AKLT point. Our results for several different values of L, m are shown in Fig. 4. The AKLT point constitutes an apparent maximum in this amplitude with a value of $\langle S_1^z \rangle = \frac{2}{3}$. Where possible, we have performed extrapolations in both m, L to obtain results representative of the thermodynamic limit (full circles in Fig. 4). The error obtained was smaller than the symbols except at $\beta = 1$ where the error bar is shown. At $\beta = -1$ we were not able to perform an extrapolation to the thermodynamic limit due to the incommensurability effects. The results are consistent with a nonzero value of $\langle S_1^z \rangle$ throughout the Haldane phase, vanishing as the two critical points are approached at $\beta = \pm 1$. The extrapolation to the thermodynamic limit is further complicated due to the fact that the $S = \frac{1}{2}$ objects strongly interact when $L \ll \xi$, leading to nontrivial finite-size corrections to $\langle S_1^z \rangle$. This is shown in the inset of Fig. 4 where $\langle S_1^z \rangle$ is plotted as a function of L for $\beta = \frac{2}{3}$. A clear minimum occurs at roughly 1–2 times the estimated correlation length. This minimum occurs for many values of β and is independent of m. We assume that this minimum corresponds to a system size separating regions with strongly and weakly interacting $S = \frac{1}{2}$ objects. Hence, only when $\xi \ll L$ are we able to extrapolate in m and L to the thermodynamic limit.

Summarizing, we have presented results that show that $S = \frac{1}{2}$ chain-boundary excitations occur throughout the Haldane phase as the biquadratic coupling is varied. These excitations are localized at the ends of the chain with a maximum in their amplitude of $\langle S_1^z \rangle = \frac{2}{3}$ occurring at the AKLT point, $\beta = -\frac{1}{3}$. It would be interesting to compare our results for $\langle S_i^z \rangle$, proportional to the local susceptibility, with NMR results in addition to the ESR results already available.

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