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)\(^3\), which has been studied extensively and Y\(_2\)BaNiO\(_5\)\(^\pm\), 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 spins is sufficiently close to the standard nearest neighbor Heisenberg model. In particular it is known that if a biquadratic term linear in \( \beta \) is added:

\[
H = J \sum_{i=1}^{L-1} \left[ S_i \cdot S_{i+1} - \beta (S_i \cdot S_{i+1})^2 \right], \tag{1}
\]

the system remains in the Haldane phase for \(-1 < \beta < 1\). At the Affleck-Kennedy-Lieb-Tasaki\(^8\) (AKLT) point, \( \beta = -\frac{1}{2} \), 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 \( s = 1/2 \) spin in the symmetric triplet state then the VBS state corresponds to combining each of the two \( s = 1/2 \) 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 non-degenerate singlet. If the chain is broken (i.e. open boundary conditions) then the ground-state is actually four-fold degenerate in the thermodynamic limit. One way to understand this four-fold 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 \( s = 1/2 \) objects and a ground-state that is four-fold degenerate in the thermodynamic limit, as shown in Fig. 1. Hence, it was suggested\(^10\) that such \( s = 1/2 \) are real and experimentally observable. For a finite open chain the \( s = 1/2 \) 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 \( s = 1/2 \) 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 \( s = 1/2 \) 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 \( s = 1/2 \) objects. Hence, considerable effort has been devoted to the experimental verification of the above considerations. Electron-spin-resonance (ESR) studies on Cu doped NENP\(^10\),\(^15\) have confirmed the existence of these \( s = 1/2 \) chain-boundary excitations. Subsequent studies of NENP doped with non-magnetic impurities Zn, Cd and Hg also showed evidence for \( s = 1/2 \) 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 \( s = 1/2 \) 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), with the physical systems corresponding to $\beta = 0$, and we take this model as representative of the Haldane phase. At the AKLT point the $s = 1/2$ excitations can be studied using the exact results for the VBS state as we detail below, facilitating the analysis. Exponentially localized $s = 1/2$ objects are shown to occur at each end of an open chain. Using the density matrix renormalization group (DMRG) we show that these $s = 1/2$ chain-boundary excitations remain well-defined in the Haldane phase as $\beta$ is varied between $-1 \leq \beta \leq 1$, 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, described by a $\text{SU}(3)_{k=1}$ 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 for $\beta < -1$, and the Takhtajan-Babujian (TB) point, described by a $\text{SU}(2)_{k=2}$ 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, 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 $\beta \approx -0.438$. At the TB point gapless modes occur at $k = 0, \pi$ and hence, as $\beta$ approaches $1$ the peak in the structure factor remains at $\pi$.

**Exact Results:** The VBS ground-state can be written\(^6,24,25\)

$$ \Psi_{\text{vbs}} = \prod_i g_i, \quad g_i = \left( \frac{1}{\sqrt{2}} | 0_i \rangle - | +_i \rangle - | -_i \rangle \right). $$

(2)

Here $| +_i \rangle, | 0_i \rangle, | -_i \rangle$ corresponds to the three states of the $s = 1$ on site $i$. If periodic boundary conditions are considered the trace should be taken. Using the above wave-function it is now straightforward to evaluate $< S_i^z >_{\text{vbs}}$, the magnetization on the first site of the open chain, as a function of $L$. One finds for the state with total magnetization $S_i^z = 1$:

$$ < S_i^z >_{\text{vbs}} (L) = \frac{\frac{2}{3} - 2 \cdot 3^{-L}}{1 - 3^{-L}}, \quad \text{L even} \quad \text{for even } L, \text{ including all finite size corrections. As is evident from this expression this amplitude rapidly approaches } 2/3 \text{ as } L \rightarrow \infty. \text{ For odd } L \text{ one finds for the state with total magnetization } S_i^z = 1:\n
$$

$$ < S_i^z >_{\text{vbs}} (L) = \frac{\frac{2}{3} - 2 \cdot 3^{-L}}{1 - 3^{-L}}, \quad \text{L even} \quad \text{for even } L, \text{ including all finite size corrections. As is evident from this expression this amplitude rapidly approaches } 2/3 \text{ as } L \rightarrow \infty. \text{ For odd } L \text{ one finds for the state with total magnetization } S_i^z = 1:\n
$$



**figure 2:** The on-site magnetization $< S_i^z >$ along the chain for different values of the biquadratic coupling, $\beta$. In all cases $S_i^z = 1$ was used.

$$ < S_i^z >_{\text{vbs}} (L) = \frac{\frac{2}{3} - 2 \cdot 3^{-L}}{1 - 3^{-L}}, \quad \text{L odd} \quad \text{with the general expression for any site and any even } L:\n
$$

$$ < S_i^z >_{\text{vbs}} (L) = (-1)^{i-1} \frac{\frac{2}{3} + 2 \cdot 3^{-L}}{1 - 3^{-L}}. \quad \text{L even} \quad \text{with the general expression for any site and any odd } L:\n
$$

Hence, in the thermodynamic limit one obtains the following result for $< S_i^z >$ in the state $S_i^z = 1$:

$$ < S_i^z >_{\text{vbs}} (L) = \frac{2}{3} \left( \frac{1}{3} \right)^{i-1} \frac{1}{1 - 3^{-L}}. \quad \text{L odd} \quad \text{with the general expression for any site and any odd } L:\n
$$

$$ < S_i^z >_{\text{vbs}} (L) = \frac{2}{3} \left( \frac{1}{3} \right)^{i-1} \frac{1}{1 - 3^{-L}}. \quad \text{L even} \quad \text{with the general expression for any site and any even } L:\n
$$

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, $\xi = 1/\ln 3^{6,25}$. Within the framework of a free boson model, the same exponential decrease has been shown to occur at the Heisenberg point, $\beta = 0$, in accordance with numerical results. Hence at the AKLT
point the $s = 1/2$ 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, $S^z$, 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 $\langle S^z \rangle$, the on-site magnetization, is plotted as a function of site index, $i$, for 8 different values of $\beta$ between $-1 \leq \beta \leq 1$. The calculations were in all cases performed in the $S^z = 1$ state with $m = 100$. If the lowest-lying excitations are indeed determined by the $s = 1/2$ chain-boundary excitations, then selecting this state corresponds to polarizing the two $s = 1/2$ 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 $\beta$ where well-defined excitations are visible at the boundaries. Decreasing $\beta$ below the disorder point at $\beta = -1/3$ 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 $\beta = -2/3$, $-1$. Increasing $\beta$ beyond approximately $\beta \sim 0.2$ moves the maximum in the on-site magnetization, $\langle S^z \rangle$, away from the chain-boundaries, $i = 1, L$. As $\beta$ 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 $\beta = 2/3$ 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 $s = 1/2$ objects remain localized at the boundaries until the critical point $\beta = 1$ is reached where the correlation length diverges.

If the $s = 1/2$ objects remain localized at the boundaries of the chain the first-site magnetization $\langle S^z_i \rangle$ should remain finite in the thermodynamic limit. If at some point the $s = 1/2$ objects de-localize and spread out over the entire chain we would expect $\langle S^z_i \rangle$ to go to 0 in the thermodynamic limit with non-trivial finite-size corrections. As a measure of the presence of well-defined chain-boundary excitations we have therefore numerically studied $\langle S^z_i \rangle$ as a function of $\beta$. Two effects complicate the analysis: As $\beta \to \pm 1$ the correlation length rapidly diverges necessitating the use of larger and 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 $\langle S^z_i \rangle = 2/3$. Where possible, we have performed extrapolations in both $L, m$ to obtain results representative of the thermodynamic limit. These are shown as the solid line in Fig. 4. The results are consistent with a non-zero value of $\langle S^z_i \rangle$ 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 $s = 1/2$ objects strongly interact when $L \ll \xi$, leading to non-trivial finite-size corrections to $\langle S^z_i \rangle$. This is shown in the inset of Fig. 4 where $\langle S^z_i \rangle$ is plotted as a function of $L$ for $\beta = 2/3$. A clear minimum occurs at roughly 1-2 times the estimated correlation length. We assume that this minimum corresponds to a system size separating regions with strongly and weakly interacting $s = 1/2$ objects.

Summarizing, we have presented results that show that $s = 1/2$ 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 $\langle S^z_i \rangle = 2/3$ occurring at the AKLT point, $\beta = -1/3$. It would be interesting to compare our results for $\langle S^z_i \rangle$, proportional to the local susceptibility, with NMR results in addition...
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I. Affleck, Th. Jolicœur and K. Penc and thank IDRIS to the ESR results already available.

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figure 4: The first site magnetization, < S_1^z >, as a function of β between −1 < β < 1. The stars are data for 12 sites (•), the circles data for L = 100, m = 100 (○), and the plusses extrapolations in m, L to the thermodynamic limit (+). The inset shows the L dependence of < S_1^z > for β = 2/3 calculated with m = 100.

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