

Local Probe of Fractional Edge States of $S = 1$ Heisenberg Spin Chains

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Spin chains are among the simplest physical systems in which electron-electron interactions induce novel states of matter. Here we propose to combine atomic scale engineering and spectroscopic capabilities of state of the art scanning tunnel microscopy to probe the fractionalized edge states of individual atomic scale $S = 1$ spin chains. These edge states arise from the topological order of the ground state in the Haldane phase. We also show that the Haldane gap and the spin-spin correlation length can be measured with the same technique.

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The basic electronic properties of large classes of materials, such as good metals and semiconductors, can be described with an independent electron picture because the Coulomb electron-electron interaction plays a marginal role. In contrast, the single-electron picture is not applicable to strongly correlated materials, such as Mott insulators and their descendants, which exhibit a variety of fascinating phenomena including high temperature superconductivity and colossal magnetoresistance [1,2]. Modeling the electronic properties of these strongly correlated materials can be notoriously difficult. However, different analytical and numerical tools, developed for this purpose, provide a great deal of insight for strongly correlated one-dimensional systems. The study of quantum spin chains played a central role in this context. Exact analytical solutions [3] and efficient numerical methods [4] revealed a plethora of collective phenomena that triggered new paradigms, such as quantum spin liquids [5,6], fractionalized spin excitations [7–9], and hidden topological order [10,11]. The gapped Haldane phase of integer spin antiferromagnetic (AFM) Heisenberg chains is a remarkable example of a novel quantum state induced by electron-electron interactions [5].

In analogy with the in-gap edge states of topologically ordered phases [8,9], the $S = 1$ AFM Heisenberg chain exhibits fractional $S = 1/2$ edge states, whose energy lies inside the Haldane gap. These in-gap states behave like two $S = 1/2$ spins that are localized at each end of the open chain [12–14], in spite of the fact that the elementary building blocks of the model are $S = 1$ spins.

The existence of these $S = 1/2$ edge states was revealed by electron spin resonance [12,13,15] and neutron scattering [16] experiments performed on quasi-one-dimensional $S = 1$ materials. Measurements of thermodynamic properties are also consistent with the existence of these end states [17–19]. However, these experiments can only probe a thermodynamically large number of open $S = 1$ chains of different lengths, which arise from chemical substitution of the $S = 1$ ion by a nonmagnetic ion.

In this Letter, we propose a radically different approach based on the recent progress in atomic scale manipulation and single atom inelastic electron tunneling spectroscopy (IETS) of spin excitations that can be measured with a scanning tunneling microscope (STM). The STM can be used as a tool for arranging the magnetic adatoms in a single linear chain [20–24]. The spectral features of the linear chain remain sharp if the magnetic adatoms are deposited on a thin insulating layer, like a single monolayer of Cu_2N coating a $\text{Cu}(100)$ substrate [20,24,25], that reduces the exchange coupling to the underlying metallic substrate and strongly attenuates charge fluctuations. Under these conditions, it is possible to perform atomically resolved spin IETS [20] [see Fig. 1(a)]. Indeed, STM-IETS measurements of Mn, Fe, or Co atoms deposited on a thin insulating layer revealed quantized spin values of $S = 5/2$, 2, and $3/2$, respectively, that are consistent with Hund's rules [25]. Experiments using the same Cu_2N substrate have revealed the low energy spectra of short ($N \lesssim 20$) chains

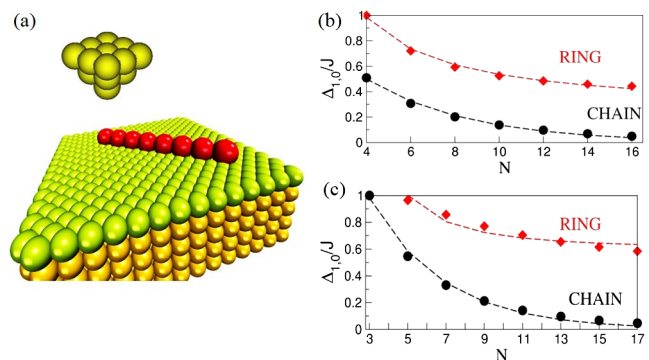


FIG. 1 (color online). (a) Scheme of an STM tip probing the spin excitation of a chain of magnetic adatoms deposited on top of the insulating layer as in Ref. [20]. (b), (c) Size (N) dependence of the singlet-triplet energy gap for PBC (diamonds) and OBC (circles) $S = 1$ Heisenberg model in absence of anisotropy for even (b) and odd (c) N . The dashed lines are fits to the predicted asymptotic (large N) behavior (see text for details).

of Mn [20], Co [26], and Fe [26,27] adatoms, which are well described by an AFM Heisenberg model with single-ion anisotropy terms [20,26–28].

Here, we demonstrate that IETS performed with an STM on a family of $S = 1$ spin chains of increasing lengths $N \leq 17$, which are well within the experimental range [20,24], provides a local probe for the $S = 1/2$ edge states of the Haldane phase. We also show that our results are robust against the unavoidable presence of single-ion anisotropy. Our proposal suggests that atomically engineered spin chains can be used as “quantum simulators” for probing exotic correlated states of matter, such as gapped quantum spin liquids.

We start by considering the Heisenberg Hamiltonian for a chain (ring) of N anisotropic $S = 1$ spins

$$H = \sum_{i=1}^N h_0(i) + J \sum_{i=1}^{N-1} \mathbf{S}_i \cdot \mathbf{S}_{i+1} + \kappa \mathbf{S}_N \cdot \mathbf{S}_1, \quad (1)$$

where

$$h_0(i) = D(S_i^z)^2 + E[(S_i^x)^2 - (S_i^y)^2] \quad (2)$$

is the single-ion anisotropy contribution to H , with axial anisotropy D and transverse anisotropy E . $J, \kappa \geq 0$ are the nearest neighbor antiferromagnetic exchange interatom energies and κ allows switching between open boundary conditions (OBC) for $\kappa = 0$, and a ring with periodic boundary conditions (PBC) for $\kappa = J$. The energy spectrum of H without anisotropy has been studied in the context of impurity bound states [29–31] and it was shown how the spin gap evolves from having a finite value in the thermodynamic limit when $\kappa = J$ (Haldane gap) to decaying exponentially in N for $\kappa = 0$. It was also shown how delocalized excitations for $\kappa = J$ become localized $S = 1/2$ edge states [29–31].

We first discuss the results for the isotropic case $D = E = 0$, which is a good starting point when J is much larger than single ion anisotropy [20,28]. We denote the eigenvectors of this Hamiltonian as $|m\rangle$ and the eigenvalues as E_m in increasing order, $E_{m-1} \leq E_m$, with $m = 0$ corresponding to the ground state. The low-energy eigenvalues and eigenstates are obtained by direct numerical diagonalization.

As shown in Figs. 1(b) and 1(c), the finite size scaling of this gap $\Delta_{1,0} = E_1 - E_0$ sheds light on the nature of the lowest energy excited states. For the ring, the size dependence of the energy gap is well fitted by the expression $\Delta_{1,0} = \Delta_H + \eta J/N^2$, ($\Delta_H \sim 0.4J$ is the Haldane gap and $\eta \sim 10$), as expected from the quadratic dispersion relation of the single-magnon excited states [32]. The finite size scaling of the singlet-triplet gap is qualitatively different for open chains

$$\Delta_{1,0} = \Delta_0 e^{-N/\xi}, \quad (3)$$

where $\xi \approx 4.65$ ($\xi \approx 3.85$) for even (odd) chains is the spin-spin correlation length and $\Delta_0 \approx 1.2J$ ($\Delta_0 \approx 2.14J$),

both in perfect agreement with previous results [33–35]. Of course, the spin of the ground state of even (odd) chains is $S = 0$ ($S = 1$), and the spin of the first excited states is $S = 1$ ($S = 0$). Other subtle differences in the excitations of even and odd short chains have been reported recently [36]. For a characteristic [20] exchange constant of 6 meV, the excitation energy for a chain of $N = 16$ $S = 1$ spins would be $\Delta_{1,0} \approx 230 \mu\text{eV}$, well within range of state of the art STM-IETS [25].

The exponential decay of Eq. (3) is known to arise [18] from the coupling of two $S = 1/2$ modes localized at the edges. The gap $\Delta_{1,0}$ corresponds to the effective coupling between both edge modes and the existence of these modes is illustrated by the site dependence of $\langle 1, \pm 1 | S_i^z | 1, \pm 1 \rangle$ shown in Fig. 2(a). The expectation value is $\pm(1/2)$ for the boundary atoms and it decays exponentially [37] towards the center of the chain with π oscillations that reflect the

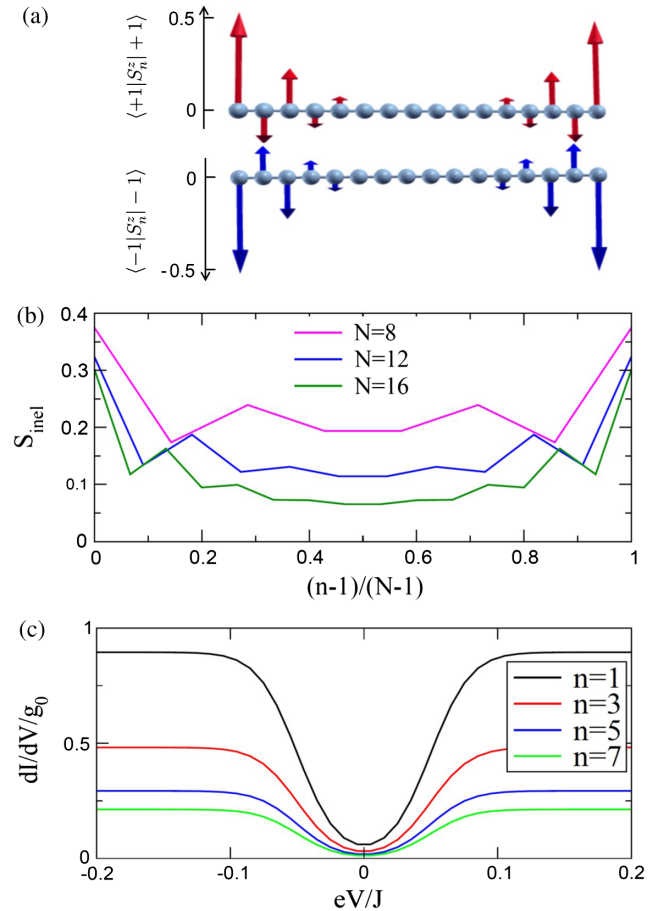


FIG. 2 (color online). (a) Expectation value $\langle S_i^z \rangle_m$ for the two triplet states with $S_z = \pm 1$. The spin density is peaked at the edges. (b) Inelastic signal $S_{\text{inel}} = \sum_a \sum_{m=1}^3 |\langle 0 | S_a^z | m \rangle|^2$ versus the normalized atomic position $(n-1)/(N-1)$ for chain sizes $N = 8, 12$, and 16 (from top to bottom). $D = E = 0$ in all cases. (c) IETS on atoms 1, 3, 5, and 7 for the $N = 16$ chain at $T = 0.01J$. The step of dI/dV is at $eV = \Delta_{1,0}$. The height of the step is controlled by S_{inel} shown in panel (b).

AFM nature of the exchange coupling. For chains with odd N , the expectation values $\langle 1, \pm 1 | S_i^z | 1, \pm 1 \rangle$ are the same, except for the fact that the $S = 1$ triplet becomes the ground state.

Making use of a spin polarized tip [24], the observation of the average magnetization shown in Fig. 2(a) would only be possible under two conditions. First, the $S = 1$ triplet should become the ground state, which in the case of even N chains would require the application of a magnetic field with $g\mu_B B > \Delta$. Second, the lifetime of the three states with different local magnetization should be longer than the detection time [24]. Because these conditions might be hard to meet, here we propose a different approach. Electron tunneling between the tip and the substrate of the setup illustrated in Fig. 1(a) can excite states of energy Δ (provided that the bias energy eV is larger than Δ) when they go through one of the magnetic atoms [20,28]. The opening of a new (inelastic) tunneling channel results in a stepwise increase of the conductance dI/dV . The width of these steps is proportional to the temperature T because of the thermal smearing of the Fermi surfaces of the tip and the substrate. Spin assisted tunneling arising from cotunneling exchange, makes IETS sensitive to spin excitations of the chain [28,38]. The inelastic tunneling current when the tip is placed on top of atom n reads [28]

$$I(n) = \mathcal{T} \sum_m P_m \sum_{m',a} |\langle m | S_n^a | m' \rangle|^2 i(\Delta_{m,m'}, eV), \quad (4)$$

where $a = \{x, y, z\}$ and \mathcal{T} is a dimensionless constant that scales linearly with the tip- n -adatom and adatom substrate coupling. P_m is the occupation of the $|m\rangle$ state and $\Delta_{m,m'} = E_m - E_{m'}$. $i(\Delta_{m,m'}, eV) = (G_0/e)[\mathcal{G}(\Delta_{m,m'} + eV) - \mathcal{G}(\Delta_{m,m'} - eV)]$ is the current of a single inelastic channel, where G_0 is the quantum of conductance and $\mathcal{G}(\omega) \equiv \omega(1 - e^{-\beta\omega})^{-1}$ is the phase space factor ($\beta = 1/k_B T$). Finally, the matrix elements of the spin operators of atom n , $\langle m | S_n^a | m' \rangle$, relate the current characteristics to properties of the quantum spin eigenstates. For small current flow, the occupations, P_m , are given by their thermal equilibrium values [39,40]. Because only the ground state is significantly occupied for $k_B T \ll \Delta_{1,0}$, the inelastic current provides information about excitation energies and matrix elements, $\langle 0 | S_n^a | m' \rangle$, connecting the ground state and certain excited states. The form factors that control the intensity of the step in the dI/dV curve for energy $\Delta_{1,0}$ are $\sum_{m',a} |\langle 0 | S_n^a | m' \rangle|^2$, where m' runs over the first excited $S = 1$ states, are shown in Fig. 2(b) for different sites n and chain lengths N . These matrix elements are enhanced near the edges and the edge/center ratio increases with N . We have verified that these matrix elements do not change upon application of a magnetic field $\vec{B} = (0, 0, B)$ with B up to 1 T.

The consequences of Fig. 2(b) in transport are illustrated in Fig. 2(c), which shows the calculated dI/dV in units of

$g_0 = G_0 \mathcal{T}$ for the different atoms in a chain of $N = 16$ spins. All of them have a step at $eV = \Delta_{1,0}$, but the intensity of the step is 3 times larger at the edge than at the center. This effect is more pronounced for odd N : the edge/center inelastic intensity ratio is equal to 8 for $N = 15$. In addition, by measuring $\Delta_{1,0}$ as a function of N , it is possible to extract the spin correlation length ξ [32] from a fit with Eq. (3). The same type of spectroscopy performed on a ring of equidistant spins would also allow us to measure the value of the Haldane gap.

We will now consider the effects of the single-ion anisotropy terms. Previous theory work has addressed this issue in the context of bulk-probe experiments [18,41]. Here, we tackle the effects of these terms on the STM-IETS probe. Experiments for transition metals on Cu_2N show that the exchange constant is much stronger than the single-ion anisotropy terms for Mn spin chains [20], but not for Fe or Co chains where the two energy scales are similar [24,26]. The difference between these

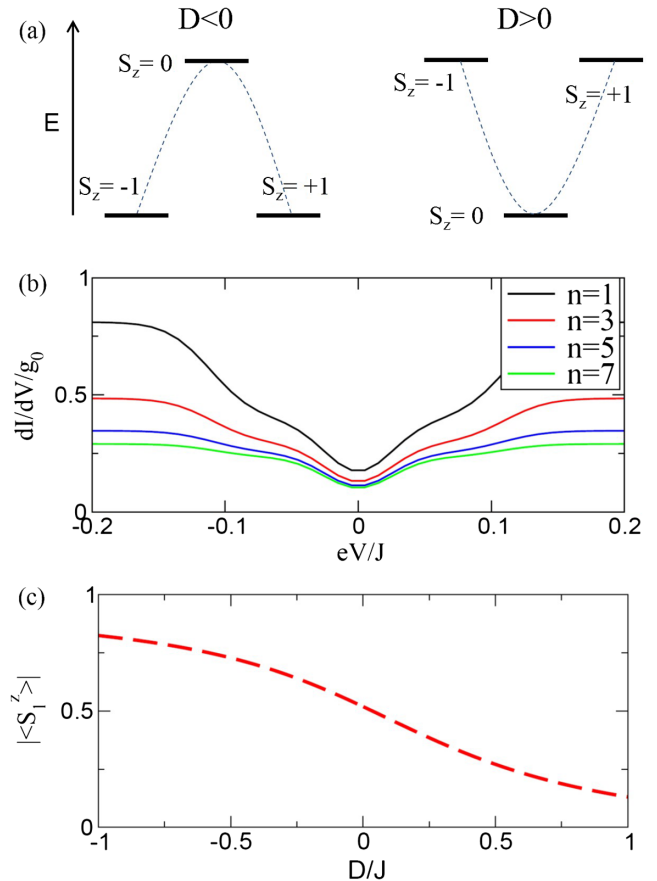


FIG. 3 (color online). (a) Scheme of the energy level diagram of each spin in the chain for $D < 0$ (left panel) and $D > 0$ (right panel) when $J/|D| \rightarrow 0$ and $E = 0$. (b) Low bias dI/dV along different positions $n = 1, 3, 5$, and 7 (top to bottom) of an $N = 16$ spin chain with anisotropy parameters $D = -0.2J$, $E = 0.05J$, and $T = 0.01J$. (c) Expectation value $|\langle S_1^z \rangle|$ (dashed red line) versus D/J .

two cases is that the orbital moment is quenched for the case of Mn atoms ($S = 5/2$), but it is not for the case of Fe or Co atoms.

As we show in Fig. 3(a), the uniaxial single-ion anisotropy, D , splits the $S = 1$ triplet into a $S^z = \pm 1$ doublet and an $S^z = 0$ singlet. Depending on the sign of D , either the singlet or the doublet are pushed down in energy. The in-plane anisotropy breaks the degeneracy of the $S^z = \pm 1$ doublet. The splitting, $\Delta_{1,0} \sim E$, between the resulting eigenstates, $(|S^z = 1\rangle \pm |S^z = -1\rangle)/\sqrt{2}$, can be observed with IETS as a fine structure in the inelastic step associated with transitions between the ground and the first excited states, provided $\Delta_{1,0} \gtrsim 5.4k_B T$, see Fig. 3(b).

As is clear from the rapid suppression of the IETS signal as the tip moves from the edges towards the center of the chain [see Fig. 3(b)], the local character of the edge excitations survives under the presence of small anisotropy terms D and E . This is not surprising because the edge states can only be removed by closing the Haldane gap. Therefore, the edge states are also robust against any other perturbation that is weak in comparison to J , such as second neighbor exchange. For large enough and negative D , the model undergoes a quantum phase transition into an Ising-like AFM ground state that does not have $S = 1/2$ edge states. Therefore, it is interesting to determine how the nature of the edge states changes as a function of increasing $|D|$. For that matter, we compute the local expectation value of the edge spin in the lowest energy triplet state, $\langle 1|S_1^z|1\rangle$, which should approach $1/2$ if there are fractionalized edge states. As is shown in Fig. 3(c), $\langle 1|S_1^z|1\rangle$ decreases and tends to zero for positive values of D , while it increases and tends to 1 for negative values of D . This behavior is consistent with the evolution towards a quantum paramagnet for $D > D_{c1} > 0$ and an Ising Néel antiferromagnet for $D < D_{c2} < 0$.

We now discuss promising materials to fabricate $S = 1$ spin chains under control and verify our predictions. So far, STM-IETS has revealed two different systems with $S = 1$ moments: Fe adatoms on InSb(110) [42] and Fe phthalocyanine (Pc) molecules on oxidized Cu. However, the strong coupling of laterally assembled Pc molecules seems unlikely and the manipulation of magnetic atoms on semiconducting surfaces remains to be demonstrated. The fabrication of spin chains with Mn, Co, and Fe atoms has been reported for the case of Cu_2N [20,24,26], and more complex structures, such as kinklike chains, have been created [27]. However, these ions have $S \neq 1$ moments. Given that the first row of transition metals has a +2 oxidation state on this surface, we expect that Nickel or Vanadium atoms on Cu_2N should be good experimental candidates to test the properties of $S = 1$ spin chains by STM-IETS. Naturally, progress in this field will enlarge the number of surfaces and chemical species that can be used to engineer quantum spin chains and explore quantum magnetism at the nanoscale. A particularly interesting

possibility could arise from the use of modified AFM molecular wheels and horseshoe [43] deposited on surfaces, which can be used to test the properties of closed and open chains, respectively.

Finally, we emphasize that the $S = 1/2$ character of the edge states implies that the level splitting induced by single-ion anisotropy is exponentially small in the chain length N [44]. In other words, the $S = 1/2$ edge states remain asymptotically isotropic for large N (> 20) in the presence of single-ion anisotropy. In contrast, excitations coming from $S = 1$ moments are split into three levels separated by gaps of order $D \pm E$ (the new energy levels for a single $S = 1$ moment are 0 and $D \pm E$).

In summary, we are proposing a way to probe fractionalized $S = 1/2$ edge states of an individual $S = 1$ spin chain, as well as to map the spectral weight of the edge states along the chain. The proposal relies on the spectroscopical capabilities of STM that allow measuring spin excitations with atomic spatial resolution. We have shown that this technique opens a direct access to the spectral properties of individual spin chains, which are fingerprints of exotic states of matter. This simple example illustrates the potential for using this experimental technique as a controllable artificial lab for testing fundamental properties of highly correlated systems.

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