Solitons in Carbon Nanotubes

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The symmetries of spontaneous lattice distortions in carbon nanotubes are investigated. When the degeneracy of the ground states remains discrete, there are solitons or domain walls connecting the different symmetry broken vacua. These solitons, similarly to the case of polyacetlene, are fractionally charged states. In addition to the topological domain walls, there are polaron states with discrete energies within the energy gap. The energies and shapes of these localized mid-gap states should be accessible via STM spectroscopy.

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The electronic properties of carbon nanotubes have recently become the subject of much attention [1]. Single wall nanotubes, in particular, provide a clean realization of quantum wires, as well as the opportunity to both engineer electronic device properties and study fundamental questions in low dimensional physics. Even within an independent electron approximation, the properties of the single wall tubes are rather rich and useful. Depending on how a graphene sheet is wrapped so as to make the tube, the system can be either an insulator or a metal [1].

A great deal of work has been done towards understanding the role of electron-electron interactions in the tubes. Studies have been carried out by using the bosonization scheme [3–6], as well as by mapping the problem with short range interactions into a two-leg Hubbard model [7]. Within the bosonization studies, power law correlations were found for the order parameter of different electronic instabilities, such as charge density wave (CDW), spin density wave (SDW) and superconductivity (SC).

A different perspective is explored in this paper. Here we consider the effect of lattice deformations in the electronic properties of the nanotubes. The effects of stress induced long wavelength distortions have been elegantly studied by Kane and Mele using a tight binding model [8]. Also, Peierls like distortions have been previously investigated by studying displacements along the bond directions, and by assuming no spatial or quantum fluctuations of these distortions [9]. In this paper we show what exactly the symmetries of the displacement order parameters are, study the role of fluctuations in this order parameter, and discuss topological solitons and polarons in carbon nanotubes.

Let us motivate the study of the symmetries of lattice distortions by raising a question: are there fractionally charged solitons in carbon nanotubes? If there is a discrete number of degenerate ground states corresponding to different lattice distortions, topological excitations should exist connecting the degenerate vacua, and fractionally charged excitations should be present in the domain walls. These ideas are familiar from another one-dimensional carbon based system: polyacetylene [10]. The carbon nanotubes are structurally more complex than polyacetylene, and this complexity will be reflected in the nature of the dimerization patterns that arise from breaking the lattice symmetries. Consider for example the patterns shown in Figure 1 for armchair nanotubes (the tube axis is on the horizontal line).

![Dimerization patterns for armchair nanotubes](image)

FIG. 1. Dimerization patterns for armchair nanotubes.

The ALT structures have dimerizations similar to polyacetylene. However, pairs of rows along the axis have displacements in the opposite direction. There is a $\mathbb{Z}_2$ symmetry, and there should be, at the domain walls between the two-fold vacua, quantum states with fractional charge $\pm e/2$ per spin degree of freedom for each of the two species of Dirac fermions present in the problem [11]. The armchair tubes have, in the low energy spectrum, two species of Dirac fermions, while polyacetylene has just one. The vacuum flow of charge for the two species of Dirac fermions goes in opposite directions, and it can be interpreted as flowing charge $e/2$ from one species to the other. (The precise discussion on the fractional charge will be done later in the paper).

The Kekulé bond-alternated structure contains short (double line) and long bonds (single line) between neigh-
boring carbon atoms. The patterned cells are labelled A, B and C according to the relative position of the single and double lines in the hexagons. If one visualizes the Kekulé structure as a tiling or coloring of the hexagons in the nanotube with the three labels or colors A, B and C, there should be three degenerate vacua corresponding to permutations of the coloring scheme. The domain walls between these three vacua should be described by topological solitons with fractional charge \( \pm e/3 \) per spin degree of freedom.

The conclusions above are based on displacements only along the bonds. In order to fully understand the validity of these naive arguments, we need to look more carefully at more general lattice distortions and their actual symmetries. We will show that the Kekulé distortion actually has a continuous \( U(1) \) symmetry, and fluctuations, both thermal and quantum, play an extremely important role.

The ALT structure, on the other hand, is truly two-fold symmetric. Let us start from a tight-binding Hamiltonian for a graphite sheet:

\[
H = -\sum_{r \in \mathbf{R}} \sum_{j=1}^{3} \left[ t + \delta t_j(r) \right] c_{1}^{\dagger}(r) c_{2}(r + \tau_j) + H.c., \tag{1}
\]

where \( r \) spans the triangular lattice, and the vectors \( \tau_j \) \((j = 1, 2, 3)\) connect a carbon atom to its three nearest neighbors in the other sublattice. The distortions of the lattice alter the bond lengths, and thus the hopping matrix elements change by \( \delta t_j(r) \).

In the absence of the distortions, the spectrum is given by \( E(k) = \pm t \left| h(k) \right| \), where \( h(k) = \sum_{j=1}^{3} e^{i k \cdot \tau_j} \). The spectrum contains two Dirac points at \( k_{\pm} = (\pm \frac{2\pi}{3}, 0) \). The dispersion \( h(k) \) can be linearized near the Dirac points, i.e., \( k = k_{\pm} + p \), so the energy near these points is \( E(p) \approx \pm \nu_F |p| \), with a Fermi velocity \( \nu_F = \frac{2t}{d} \) \((d = a/\sqrt{3})\) is the distance between neighboring carbon atoms). The nanotubes are obtained from the graphite sheets by wrapping around a certain direction, identifying the lattice points \((0, 0)\) and \((N, M)\). In the \( N = M \) armchair tubes, the two Dirac points \( k_{\pm} \) always lie on the \( p_y = 0 \) sub-band.

The Kekulé distortion - The size of the unit cell is tripled due to the dimerizations, because the hexagons A, B and C become distinct. This corresponds to coupling points in the original BZ which are separated by \( \mathbf{G} = k_{+} - k_{-} \), such as the two Dirac points.

Consider displacements of carbon atoms that can be written (in terms of the undistorted lattice positions \( r \)) as \( A_r = A e^{-i G \cdot r} \) and \( B_r = B e^{i G \cdot r} \). Complex numbers are used to represent the displacement vectors, and \( A_r \) and \( B_r \) are in separate sublattices (see Fig. 2(a)). Notice that the textures in the two sublattices spiral in opposite directions. The Kekulé distortion triples the size of the unit cell, hence the displacements of the three neighbors to any carbon atom are related by a rotation of \( \pm 2\pi/3 \). It is useful at this point to introduce the cubic roots of unit \( z_j = e^{i k_{+} \cdot \tau_j} = e^{i \frac{2\pi}{3} (j-1)} \), and \( \bar{z}_j = e^{i k_{-} \cdot \tau_j} = e^{-i \frac{2\pi}{3} (j-1)} \). Is is also convenient to think of \( \tau_j \) as complex numbers \( \tau_j = -i d z_j \). Notice that \( \sum_{j=1}^{3} \bar{z}_j = \sum_{j=1}^{3} z_j^2 = 0 \) and \( \sum_{j=1}^{3} z_j^3 = 3 \) in this notation one can write \( B_{r+\tau_j} = B e^{i G \cdot r} \bar{z}_j \).

![FIG. 2. Displacement vectors for the carbon atoms. (a) Textured displacements in the Kekulé and (b) uniform displacements in the ALT structures.](image)

The change in bond length \( d_j(r) \), at site \( r \) and in the direction of \( \tau_j \) is

\[
\frac{\delta d_j(r)}{d} = \left| \frac{\tau_j}{d} - \frac{A_r}{d} + \frac{B_{r+\tau_j}}{d} \right| - 1 \\
\approx -\frac{1}{2} \frac{\bar{r}_j}{d} \left( \frac{A_r}{d} + \frac{B_{r+\tau_j}}{d} \right) + H.c.
\]

Using the properties of \( z_j \), it is simple to show that the expression above leads to

\[
\frac{\delta d_j(r)}{d} = i \bar{\epsilon} z_j e^{i G \cdot r} - i \epsilon \bar{z}_j e^{-i G \cdot r} \tag{2}
\]

where \( \epsilon = d_{G+2\bar{B}} \) is the effective lattice displacement vector that alters bonds. The other combination, namely \( \eta = d_2 B - \frac{2}{3} \bar{B} \), changes bond angles without stretching them, only costing elastic energy without any electronic gain. Therefore, \( \eta = 0 \) or \( A = B \) is chosen.

The elastic energy per hexagon is

\[
\delta E = \frac{1}{N} \sum_r \sum_{j=1}^{3} \frac{1}{2} K (d_j(r) - d)^2
\]

Using Eq. (2) and the properties of the cubic roots of unit, \( z_j \), one easily finds \( \delta E = 3 K d^2 |\epsilon|^2 \). This energy cost is independent of the phase, i.e., the direction of the distortion of the carbon atoms. This is consistent with a continuous \( U(1) \) symmetry, not a discrete \( \mathbb{Z}_3 \). Terms that lower the symmetry appear to higher orders in the expansion of the changes in bond length (as well as bond angle). The non-linearities, however, are more pronounced in the hopping overlaps, which are exponentially sensitive to the changes in distance.

Consider a change in bond hopping which is related to the change in bond length by an exponential: \( t_j = \frac{1}{2} \bar{\epsilon} z_j e^{i G \cdot r} - \frac{1}{2} \epsilon \bar{z}_j e^{-i G \cdot r} \). This corresponds to a change in bond length

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\]
\[
t e^{-\alpha \sqrt{d_j(r)}/d}.
\]
Expanding to second order, and using \( d_j(r) \) as given by Eq. (2), one finds
\[
\frac{\delta t_j(r)}{t} = \lambda_j e^{iG \cdot r} + \lambda' \ e^{iG \cdot r} + \alpha^2 |e|^2 \text{,}
\]
where \( \lambda_j = \left( -i \alpha e - \frac{a^2 \epsilon^2}{2} \right) z_j \).

The wavevector \( \mathbf{G} = \mathbf{K}_+ - \mathbf{K}_- \) mixes the two species of Dirac fermions. Substituting Eq. (3) into Eq. (4), one obtains
\[
H = \sum_p \Psi^\dagger(p) \begin{bmatrix} h & 0 \\ 0 & -h \end{bmatrix} \Psi(p), \quad h = \begin{pmatrix} p & \Delta \\ \Delta & -p \end{pmatrix}
\]
where \( \Psi^\dagger = (\psi_{+,S}^\dagger \psi_{-,S}^\dagger \psi_{-,A}^\dagger \psi_{+,A}^\dagger) \), and
\[
\psi_{\pm,S/A}(p) = \frac{1}{\sqrt{2}} \left[ c_1(\mathbf{K} \pm + \mathbf{p}) \pm c_2(\mathbf{K} \pm - \mathbf{p}) \right]
\]
are the symmetric and antisymmetric linearized fermion operators near the Dirac points. The order parameter is \( \Delta/t = -3\alpha \epsilon + 3\alpha^2 \epsilon^2 / 2 \).

The mean field gap \( |\Delta| \) that opens is given by \( |\Delta|^2 / t^2 = 9\alpha^2 |e|^2 / 2 + 9\alpha^3 i (\epsilon^3 - \epsilon^3) \), and the cubic terms in \( \epsilon \) restore a \( Z_3 \) symmetry. Notice, however, that these terms are smaller than the rotational symmetric leading term by a factor of the order \( |\Delta|/t \). Minimizing the elastic and electronic energy for the filled levels, one finds (ignoring the non-linear effects) \( |\Delta| = v_F \Lambda \text{ exp} \left( -\frac{2\pi}{\sqrt{3n}} K \epsilon^2 / \Delta \right) \), where \( v_F \Lambda \) is an energy cut-off scale of the order of the band-width \( t \).

Using typical parameters for graphite sheets \( t \approx 2.4 \text{ eV}, K \approx 19.4 \text{ eV} / \text{Å}^2, \alpha \approx 3.7, \) and \( d \approx 1.42 \text{ Å} \), one finds \( |\Delta| \propto t \ e^{-2.1n} \), so for a \( (5,5) \) tube the gap is of the order \( 1K \), as previously found [3]. The anisotropy which restores the \( Z_3 \) symmetry is a factor \( |\Delta|/t \) lower than the gap scale, and it only becomes apparent at temperatures of the order of \( 20\mu K \). This is a very low scale, and so the symmetry for the Kekulé distortion is effectively \( U(1) \).

Even at \( T = 0 \) quantum fluctuations can restore the \( U(1) \) symmetry. This can be studied using a simple rotor model, where the arm of the rotor is the magnitude of the displacement of the carbon atoms from equilibrium. One finds that the anisotropy is irrelevant even for small \( N \) tubes (the estimated \( N_c \) is less than 2, smaller than that for realistic tubes).

Phase fluctuations of the order parameter \( \Delta(x) \) imply a charge accumulation \( \Delta Q_{\pm} = \pm \frac{e}{2\pi} \Delta \phi \text{[2]} \), where \( \Delta \phi \) is the phase twist of \( \Delta(x) \). The accumulation due to twisted phases of \( \Delta(x) \) coming from the \( S,A \) channels have opposite signs. Notice that these continuous phase twists, and the accompanied charge compensation between the symmetric and antisymmetric channels, can be understood in terms of a neutral boson. This is indeed the same situation that emerges when nearest neighbor electronic interactions are included, and the system is in the so called CDW2 phase of Krotov, Lee and Louie [3]. The charge transferred between \( S/A \) is not quantized because the symmetry is a continuous \( U(1) \).

The ALT distortion - We will show that the symmetry for the ALT distortion is truly a discrete \( \mathbb{Z}_2 \) symmetry. The change in bond length \( d_j \) in the direction of \( \tau_j \) is now the same for all lattice points (see Fig. [3]), in contrast to the textured structure that was treated previously. One has
\[
\frac{\delta d_j}{d} = iz_j\bar{u} - i\bar{z}_j u,
\]
where \( u = \frac{A-B}{2d} \). Analogously to the previous case of lattice distortion, the elastic energy per hexagon can be related to \( u \): \( \delta E = 3 \ (K + K_\theta) \ d^2 |u|^2 \), where in this case there is an extra contribution due to changes in bond angle, as well as bond length \( (K_\theta \) is defined using \( d \) to convert from angle to length displacements - see Ref. [14] for values in graphene). Again, this energy cost is independent of the phase, i.e., the direction of the distortion of the carbon atoms.

The correction to the Hamiltonian due to the new hopping amplitudes, however, is not independent of the direction of the displacements. It is not necessary to keep the changes in bond hopping beyond lowest order. Similarly to the previous case, one can show that the Hamiltonian is
\[
H = v_F \sum_p \tilde{\Psi}^\dagger(p) \begin{bmatrix} h_A & 0 \\ 0 & -h_{-A} \end{bmatrix} \tilde{\Psi}(p)
\]
where \( h_A = \begin{pmatrix} 0 & p - A \\ \bar{p} - A & 0 \end{pmatrix} \), \( A = 2i\alpha u/d \).

The spinor \( \tilde{\Psi} = (\psi_{+,1}^\dagger, \psi_{+,2}^\dagger, \psi_{-,1}^\dagger, \psi_{-,2}^\dagger) \), where \( \psi_{\pm,1/2} \) are the fermions near \( K_b \) in the two sub-lattices.

For the \( p_y = 0 \) band, the distortion opens the largest gap for real values of \( u \), in which case \( A = -\bar{A} \) and \( \Delta = v_F |A| = 3\alpha t \ |u| \). There only two vaccua, corresponding to positive or negative real \( u \) \((Z_2)\), as in polyacetylene. Notice that \( h_A = h_{-A} \), and the spectrum has positive and negative energies in pairs. If \( u \) is purely imaginary, i.e., if the displacement is orthogonal to the tube axis, then there is no gap and hence no electronic gain from the negative energy states. There is only elastic cost for imaginary \( u \), so the minimum energy path connecting the two vaccua should be like in polyacetylene: a real \( u \) changes sign.

Quantum numbers for ALT domain walls - The accumulation of fractional charge in domain walls between the two-fold vaccua is \( e/2 \) per spin degree of freedom, and the \( \pm \) species contribute with opposite phase shifts (one may allow a small imaginary part in \( u \) to see this relative phase), hence the two quantum states have opposite charge. If filled or occupied, they have charge \( \pm e/2 \) and \( \mp e/2 \) respectively. One can interprete the imbalance as transfer of charge \( e/2 \) from one specie of Dirac fermion to the other.

In the case of polyacetylene, the presence of the two spins \( (N_s = 2) \) masks the fractionally charged states.
Instead, states with quantum numbers such as charge \( e \) and spin \( S = 0 \) appear in the spectrum, as a consequence of having \( N_s = 2 \) spin species. In the nanotubes, in addition to two spin states \( (N_s = 2) \) there are two species of fermions \( (N_f = 2) \) to begin with. Because \( N_T = N_s N_f = 4 \), the quantum numbers of the zero energy states in the nanotubes cannot be distinguished from those of electrons. For example, one can assemble from the fractionally charged states an excitation with charge \( 2e \) and spin \( S = 0 \) on the domain wall.

**Midgap states and STM probes** - In contrast to polyacetylene chains, the nanotubes can be individually laid on a substrate, and locally probed via STM\[14\]. One would then expect that the midgap states with \( E = 0 \) corresponding to domain walls (kinks and anti-kinks) could be probed by tunneling of electrons from an STM tip. The position dependent tunneling density of states would probe the shape of the soliton, as well as the energy of the state.

In addition to the topological zero energy states connecting the two ground states, there are also polaronic excitations. The difference between the polarons and the domain walls is that the polarons correspond to depletions or dimples in the order parameter without switching between the two ground states.

It is very simple to obtain the energy levels for the electronic excitations, as well as the polaron and kink formation energies. We start by recognizing that the Hamiltonian for the ALT distortions Eq. \( (14) \) together with elastic energy cost \( \delta E = 3 \left( K + K_0 \right) u^2 \) is simply a static version of the Gross-Neveu model for a real \( u \) background field \( (13) \). The energies of the electronic states and the formation energies are

\[
\omega_n = \Delta \cos \left( \frac{n \pi}{2N_T} \right) \quad , \quad E_n = \Delta \frac{2N_T}{\pi} \sin \left( \frac{n \pi}{2N_T} \right)
\]

where \( 1 \leq n \leq N_T - 1 = 3 \) for the polarons, and \( n_0 = N_T \) for an infinitely separated kink-anti-kink soliton pair (notice that the topological electronic state has zero energy). One would hope that both the topological and the polaronic states could be probed by STM spectroscopy, with both energy and spatial resolution of the solitonic states.

**Interaction effects** - We would like to briefly discuss the effects of electron-electron interaction in the above conclusions. The results obtained in this paper by considering the effects of lattice displacements should be complementary to the studies of the electron-electron interaction effects using bosonization (Refs. 14, 15). The interaction effects also open energy gaps, of the same order of magnitude as the one discussed in this paper (see ref. 14, for example). The one major difference between the electron-phonon interaction we discuss in this paper, and the electron-electron interaction discussed elsewhere, is that the CDW order parameter for the ALT distortion has a discrete \( Z_2 \) symmetry. Because of the lower symmetry, we expect the soliton and polaron solutions with mid-gap energies discussed here.

In conclusion, we have studied the symmetries of spontaneous lattice deformations in carbon nanotubes. We have shown that the Kekulé distortion has a continuous \( U(1) \) symmetry, contrary to a naive expectation of a discrete \( Z_3 \). Consequently, thermal and quantum fluctuations destroy any long-range order. The ALT structure, however, has a discrete \( Z_3 \) symmetry. We discuss the implications of topological domain walls between the two-fold ground states, the fractionally charged states on the walls, and the consequences of having \( N_T = N_s N_f = 4 \) in masking the fractional states. We obtain the energies of the kink states, as well as polaron states, by recognizing that the Hamiltonian for the ALT distortion is a version of Gross-Neveu model with a static real background field. We argue that the mid-gap states could be probed by STM spectroscopy, resolving experimentally both the energies and the shapes of the solitonic states.

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