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 vaccua. These solitons, similarly to the case of polyacetelene, 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 midgap states should be accessible via scanning tunneling microscopy spectroscopy.

I. INTRODUCTION

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.[2]

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 Meele 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] The objective of this paper is to identify what exactly the symmetries of the displacement order parameters are, in order to understand the nature of the possible topological solitons in the nanotubes. Understanding the correct symmetries of the order parameter is fundamental in determining the fractional charge associated with the topological solitons. We also study the role of quantum fluctuations in the CDW order parameter.

Let us motivate the study of the symmetries of lattice distorsions 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 vaccua, and fractionally charged excitations should be present in the domain walls. These ideas are familiar from another one-dimentional carbon based system: polyacetylene.[10] The carbon nanotubes are structurally more complex than polyacetelene, 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 Fig. 1 for armchair nanotubes (the tube axis is aligned horizontally).

The ALT structures have dimerizations similar to polyacetelene. However, pairs of rows along the axis have displacements in the opposite direction. There is a $\mathbf{Z}_2$ symmetry, and there should be, at the domain walls between the twofold vaccua, 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 polyacetelene has just one. The vaccum 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 frac-

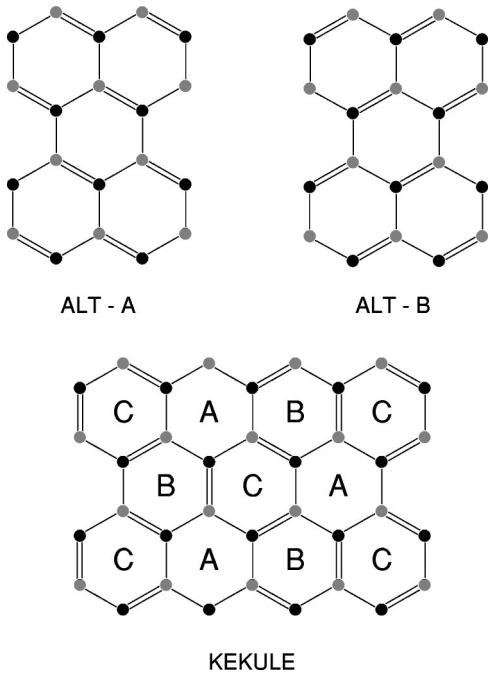

FIG. 1. Dimerization patterns for armchair nanotubes.

tional charge will be done later in the paper.)

The Kekulé bond-alternated structure contains short (double line) and long bonds (single line) between neighboring carbon atoms. The patterned cells are labeled *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 vaccua corresponding to permutations of the coloring scheme. The domain walls between these three vaccua should be described by topological solitons with fractional charge $\pm e/3$ per spin degree of freedom for each specie of Dirac fermion.

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. One of the results of this paper is that, in reality, the Kekulé distorsion has a continuous U(1) symmetry. Therefore, the naive conclusion that there should be fractional charge $\pm e/3$ should not hold. The ALT structure, on the other hand, is truly twofold symmetric, and does sustain topological excitations with charge $\pm e/2$.

The paper is organized as follows. In Sec. II we discuss the Kekulé-type distortions, and show that one can construct a continuous order parameter that represents the tripling of the unit cell. To date, considerations of Peierls-like instabilities in the armchair nanotubes were limited to threefold symmetric distortions only.[9] In this paper we argue that the right symmetry for the CDW order parameter is a continuous U(1). The effective U(1) symmetry, in contrast to the discrete $\mathbf{Z}_3$ which is naively expected, does not lead to a quantized value of the fractional charge associated with topological excitations connecting the different vaccua. Instead, the phase of the order parameter varies continuosly, and the local accumulation of charge is simply the gradient of the phase field, with no quantization condition as in the discrete symmetry case. In Sec. III we discuss the simpler dimerization pattern in the ALT structures. These patterns have a truly discrete $\mathbf{Z}_2$ symmetry, and therefore will have topological excitations with fractional charge $\pm e/2$ for each flavor ($N_f = 2$ species of Dirac fermions) and each spin ($N_s = 2$). We also discuss, in addition to the topological solitons, polaronic states that correspond to a local depletion of the CDW order parameter but without switching between the two degenerate vaccua of the ALT distortion. The polaronic states have energies withing the CDW gap (midgap states), which are calculated, and could be in principle measured by scanning tunneling microscopy (STM) spectroscopy. Finally, we briefly discuss in Sec. IV the effects of electronic interactions, and in the Appendix the effects of curvature.

II. KEKULÉ DISTORTIONS AND THE SYMMETRY OF THE PEIERLS ORDER PARAMETER

In this section we will study the Kekulé distortion in the nanotubes. We will do so in the most general way, by allowing displacements of carbon atoms along arbritary directions, not only along bonds. We will calculate the changes in the electronic energies due to such distortions, as well as the elastic cost associated with these general displacements. In this way, we will be able to identify the correct symmetry group of the Kekulé distortions in nanotubes, which will allow us to determine if there are fractionally charged domain walls connecting discrete vaccua.

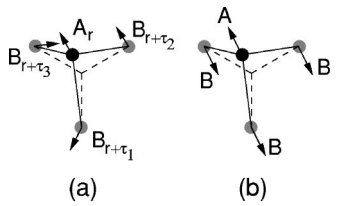

FIG. 2. Displacement vectors for the carbon atoms. (a) Textured displacements in the Kekulé and (b) uniform displacements in the ALT structures.

We start with a tight-binding Hamiltonian for a graphite sheet:

$$H = -\sum_{\mathbf{r}\in\mathbf{R}} \sum_{j=1}^{3} [t + \delta t_j(\mathbf{r})] c_1^\dagger(\mathbf{r}) c_2(\mathbf{r}+\tau_j) + \text{H.c.}, \quad (1)$$

where $\mathbf{r}$ spans the triangular lattice, and the vectors τ_j ($j = 1,2,3$) connect a carbon atom to its three nearest neighbors in the other sublattice. The fermion operators c_1 and c_2 act in the two sublattices of the graphite sheet. The distortions of the lattice alter the bond lengths, and thus the hopping matrix elements change by $\delta t_j(\mathbf{r})$.

In the absence of the distortions, the spectrum is given by $E(\mathbf{k}) = \pm t|h(\mathbf{k})|$, where $h(\mathbf{k}) = \Sigma_{j=1}^{3} e^{i\mathbf{k}\cdot\tau_j}$. The spectrum contains two Dirac points at $\mathbf{K}_\pm = (\pm 4\pi/3a, 0)$. The dispersion $h(\mathbf{k})$ can be linearized near the Dirac points, i.e., $\mathbf{k} = \mathbf{K}_\pm + \mathbf{p}$, so the energy near these points is $E(\mathbf{p}) \approx \pm v_F|\mathbf{p}|$, with a Fermi velocity $v_F = \frac{3}{2} td$ ($d = a/\sqrt{3}$ is the distance between neighboring carbon atoms). The nanotubes are obtained from the graphite sheet by wrapping around a certain direction, identifying the lattice points (0, 0) and (*N*, *M*). This wrapping introduces a set of quantization conditions on the momenta. In the $N = M$ armchair tubes, the two Dirac points $\mathbf{K}_\pm$ always lie on an allowed subband of states. The subband (which we identify as $p_y = 0$ if the momentum parallel to the tube axis is p_x) corresponds to states that are uniform along the circunference of the tube (the p_y direction). In addition to the periodic boundary condition, the wrapping of the tube brings in curvature effects; these are briefly discussed in the Appendix.

In 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 Brillouin zone, which are separated by $\mathbf{G} = \mathbf{K}_+ - \mathbf{K}_-$, such as the two Dirac points.

Consider displacements of carbon atoms that can be written (in terms of the undistorted lattice positions $\mathbf{r}$) as $A_\mathbf{r} = Ae^{-i\mathbf{G}\cdot\mathbf{r}}$ and $B_\mathbf{r} = Be^{-i\mathbf{G}\cdot\mathbf{r}}$. Complex numbers are used to represent the displacement vectors, and $A_\mathbf{r}$ and $B_\mathbf{r}$ 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

$$z_j = e^{i\mathbf{K}_+ \cdot \tau_j} = e^{i(2\pi/3)(j-1)}$$

and

$$\overline{z_j} = e^{i\mathbf{K}_- \cdot \tau_j} = e^{-i(2\pi/3)(j-1)}.$$

It is also convenient to think of τ_j as complex numbers $\tau_j = -idz_j$. Notice that $\Sigma_{j=1}^3 z_j = \Sigma_{j=1}^3 z_j^2 = 0$ and $\Sigma_{j=1}^3 z_j^3 = 3$. In this notation one can write $B_{\mathbf{r}+\tau_j} = Be^{i\mathbf{G}\cdot\mathbf{r}}\overline{z_j}$.

Given the displacement vectors $A_\mathbf{r}$ and $B_\mathbf{r}$ for the carbon atoms in the two sublattices, one can proceed and calculate the change in bond length $d_j(\mathbf{r})$, at site $\mathbf{r}$ and in the direction of τ_j:

$$\frac{\delta d_j(\mathbf{r})}{d} = \left| \frac{\tau_j}{d} - \frac{A_\mathbf{r}}{d} + \frac{B_{\mathbf{r}+\tau_j}}{d} \right| - 1 \approx -\frac{1}{2}\frac{\overline{\tau_j}}{d}\left(\frac{A_\mathbf{r}}{d} + \frac{B_{\mathbf{r}+\tau_j}}{d} \right) + \text{H.c.}$$

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

$$\frac{\delta d_j(\mathbf{r})}{d} = i\overline{\epsilon} z_j e^{i\mathbf{G}\cdot\mathbf{r}} - i\epsilon\overline{z_j} e^{-i\mathbf{G}\cdot\mathbf{r}}, \tag{2}$$

where

$$\epsilon = \frac{A + \overline{B}}{2d}$$

is the effective lattice displacement vector that alters bonds. The other combination, namely, $\eta = (A - \overline{B})/2d$, changes bond angles without stretching them, only costing elastic energy without any electronic energy gain. The reason is that the electronic overlaps are independent of angle for the π orbitals, and thus only depend on how much the bonds are stretched. Therefore, $\eta = 0$ or $A = \overline{B}$ is chosen.

The elastic energy per hexagon is

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

Using Eq. (2) and the properties of the cubic roots of unit, z_j, one easily finds

$$\delta E = 3Kd^2 |\epsilon|^2. \tag{3}$$

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 $\mathbf{Z}_3$. Terms that lower the symmetry appear to higher orders in the expansion of the changes in bond length (as well as bond angle). The nonlinearities, however, are more pronounced in the hopping overlaps, which are exponentially sensitive to the changes in distance.

Consider a change in bond hopping that is related to the change in bond length by an exponential: $t_j(\mathbf{r}) = te^{-\alpha \delta d_j(\mathbf{r})/d}$. Expanding to second order, and using $d_j(\mathbf{r})$ as given by Eq. (2), one finds

$$\frac{\delta t_j(\mathbf{r})}{t} = \lambda_j e^{i\mathbf{G}\cdot\mathbf{r}} + \overline{\lambda}_j e^{-i\mathbf{G}\cdot\mathbf{r}} + \alpha^2 |\epsilon|^2, \tag{4}$$

where $\lambda_j = [-i\alpha\overline{\epsilon} - (\alpha^2/2)\epsilon^2] z_j$.

The wave vector $\mathbf{G} = \mathbf{K}_+ - \mathbf{K}_-$ mixes the two species of Dirac fermions. Substituting Eq. (4) into Eq. (1), one obtains

$$H = \sum_p \Psi^\dagger(p) \begin{bmatrix} \mathbf{h} & 0 \\ 0 & -\mathbf{h} \end{bmatrix} \Psi(p), \quad \mathbf{h} = \begin{pmatrix} p & \Delta \\ \overline{\Delta} & -p \end{pmatrix}, \tag{5}$$

where

$$\Psi^\dagger = (\psi_{+,S}^\dagger \psi_{-,S}^\dagger \psi_{+,A}^\dagger \psi_{-,A}^\dagger)$$

and

$$\psi_{\pm,S/A}(\mathbf{p}) = \frac{1}{\sqrt{2}} [c_1(\mathbf{K}_\pm + \mathbf{p}) \pm c_2(\mathbf{K}_\pm + \mathbf{p})]$$

are the symmetric and antisymmetric linearized fermion operators near the Dirac points. The order parameter is

$$\frac{\Delta}{t} = -3i\alpha\overline{\epsilon} + \frac{3}{2}\alpha^2\epsilon^2.$$

The mean field gap $|\Delta|$ that opens is given by

$$|\Delta|^2/t^2 = 9\alpha^2|\epsilon|^2 + 9\alpha^3 i(\epsilon^3 - \overline{\epsilon}^3), \tag{6}$$

and the cubic terms in ϵ restore a $\mathbf{Z}_3$ symmetry.

Let us now start a detailed discussion of what, effectively, is the symmetry of the Kekulé distortion, as well as the size of the gap due to the dimerization. Although the second term in the right side of Eq. (6) does restore the discrete symmetry, these terms are smaller than the rotational symmetric leading term by a factor of the order $|\Delta|/t$. Basically, the terms that restore the $\mathbf{Z}_3$ are down from the first term in the right side of Eq. (6) by a factor $\alpha|\epsilon|$, which itself is of order $|\Delta|/t$.

The ratio of the gap $|\Delta|$ to the bandwidth is obtained in the following way. Minimizing the sum of the elastic and electronic energy for the filled levels, one finds (ignoring the nonlinear effects)

$$|\Delta| = v_F \Lambda \exp\left(-\frac{\pi}{\sqrt{3}\alpha^2} \frac{Kd^2}{t} N \right),$$

where $v_F\Lambda$ is an energy cutoff scale of the order of the bandwidth t. Using typical parameters for graphite sheets

$$t \approx 2.4\,\text{eV},$$

$$K \approx 19.4\,\text{eV/Å}^2,$$

$$\alpha \approx 3.7,$$

$$d \approx 1.42\,\text{Å},$$

one finds $|\Delta| \propto te^{-2.1N}$, so for a (5,5) tube the gap is of the order 1 K, as previously found.[9] The anisotropy that restores the $\mathbf{Z}_3$ symmetry is a factor $|\Delta|/t$ lower than the gap scale, and it only becomes apparent at temperatures of the order of 20 μK. This is a very low scale, and so the symmetry for the Kekulé distortion is effectively U(1), occurring on a temperature scale of the order of 1 K.

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 displace-

ment 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). This result is obtained as follows. Focusing on the linear pieces, one obtains a problem equivalent to a U(1) or O(2) rigid rotor, whose length is $|\epsilon|$. Slow spatial rotations of the displacement vector cost very little energy, and can be calculated from the Hamiltonian Eq. (5) for slow phase twists in Δ. The presence of the nonlinear terms introduces a cosine potential and turns the problem into a clock model. The energy scale for rotations, however, is still much smaller $[O(\epsilon^2)]$ than that for closing the gap altogether and opening it again at the new angle $[O(\epsilon)]$. In simple terms, the shape of the potential energy is that of a mexican hat with three little bumps along its bottom. Now consider the kinetic energy for rotations of the lattice displacement vector. Here only the angular component of the rotor motion is accounted for, and the massive fluctuations of the length of the rotor arm are neglected. The kinetic rotation energy for a carbon atom is given by $E_K = 1/2 M_C d^2 |\epsilon|^2 \dot{\phi}^2$. Using this, a Lagrangian for the fluctuating field $\phi(t,x)$ can be written

$$\mathcal{L} = \frac{1}{2}\left(\frac{2N}{a} M_C d^2 |\epsilon|^2\right)(\partial_t \phi)^2 - \frac{1}{2} v_F (\partial_x \phi)^2 - h_3 \cos[3(\phi + \pi/2)]. \tag{7}$$

Let us define

$$K_{\text{eff}}^2 = \frac{2N}{a} M_C d^2 |\epsilon|^2 v_F \approx \frac{2}{\sqrt{3}} N \frac{M_C}{m_e} |\epsilon|^2,$$

where the numerical value for $m_e v_F d/\hbar$ was substituted above. Because of the exponential dependence of $|\epsilon|$ on N, $K_{\text{eff}} \propto (M_C/m_e)\sqrt{N} e^{-2.1N}$. Hence, the quantum fluctuations are controlled by the diameter of the tube through N. However, K_{eff} is typically quite small. For example, numerical estimates for $N=5$ yield $K_{\text{eff}} \approx 5 \times 10^{-4}$. Therefore, $8\pi K_{\text{eff}} < 3^2$ for any N (with a possible exception to the pathological $N=1$ case), and the cosine term is irrelevant. Along the same lines of thought, one can study the role of vortices. If $K_{\text{eff}} < 2/\pi$ vortices are relevant, which in practice is always the case. Notice that, even in principle, there is no range of N such that both the vortices and the anisotropy are irrelevant, since the anisotropy is threefold and $3 < p_c = 4$.[13] The conclusion here is that, even at $T=0$, the symmetry for the Kekulé distortions are, contrary to previous studies,[9] continuous U(1) due to quantum fluctuations.

Let us discuss the implications of the continuous phase fluctuations of the U(1) order parameter in the local accumulation of charge. Phase fluctuations of the order parameter $\Delta(x)$ imply a charge accumulation $\Delta Q_{\pm} = \pm (e/2\pi)\Delta\phi$,[12] 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 has 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).

In conclusion, we find that the Kekulé distortions have a continuous U(1) symmetry, and therefore will not have fractionally charged states with $\pm e/3$ charge as the naive expectation, based on dimerizations along bonds only, would imply.

III. THE ALT DISTORTION

In this section we will show that the symmetry for the ALT distortion is truly a discrete $\mathbf{Z}_2$ symmetry. This will imply that there will be fractionally charged states with charge $\pm e/2$ for each of the species of Dirac fermions present in the low-energy description of the problem. We will also discuss the energies of the midgap polaronic states associated with local suppression of the ALT dimerizations, but which are not topological in nature.

In the case of the ALT distortion, the change in bond length d_j in the direction of τ_j is now the same for all lattice points [see Fig. 2(b)], in contrast to the textured Kekulé structure that was treated previously. One has

$$\frac{\delta d_j}{d} = i z_j \bar{u} - i \bar{z}_j u, \tag{8}$$

where

$$u = \frac{A-B}{2d}.$$

Analogously to the previous section, 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_θ 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

$$H = v_F \sum_{\mathbf{p}} \tilde{\Psi}^\dagger(\mathbf{p}) \begin{bmatrix} \mathbf{h}_A & 0 \\ 0 & -\mathbf{h}_{-A}^- \end{bmatrix} \tilde{\Psi}(\mathbf{p}), \tag{9}$$

where

$$\mathbf{h}_A = \begin{pmatrix} 0 & p - A \\ \bar{p} - \bar{A} & 0 \end{pmatrix}, \quad A = 2i\alpha u/d.$$

The spinor

$$\tilde{\Psi}^\dagger = (\psi_{+,1}^\dagger, \psi_{+,2}^\dagger, \psi_{-,1}^\dagger, \psi_{-,2}^\dagger),$$

where $\psi_{\pm,1/2}$ are the fermions near $\mathbf{K}_\pm$ in the two sublattices:

$$\psi_{\pm,1/2}(\mathbf{p}) = c_{1,2}(\mathbf{K}_\pm + \mathbf{p}).$$

For the $p_y=0$ band, the distortion opens the largest gap for *real* values of u, in which case $A=\bar{A}$ and

$$\Delta_0 = v_F|A| = 3\alpha t|u|.$$

The energy gap scale for this distortion is estimated to be 1 K [essentially, the electronic energy gain and the elastic energy loss are both similar to the U(1) Kekulé scale]. There are only two vaccua ($\mathbf{Z}_2$), corresponding to positive or negative real u, as in polyacetelene. Notice that $\mathbf{h}_A=\mathbf{h}_{-\bar{A}}$, 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 polyacetelene: a real u changes sign.

A. Quantum numbers for ALT domain walls

The accumulation of fractional charge in domain walls between the twofold 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 interpret the imbalance as transfer of charge $e/2$ from one specie of Dirac fermion to the other.

In the case of polyacetelene, the presence of the two spins ($N_s=2$) masks the $\pm e/2$ fractionally charged states. As a consequence of having $N_s=2$ spin species, states with quantum numbers such as charge e and spin $S=0$, which combine two $Q=e/2$, $S=1/2$ states, appear in the spectrum. In the nantotubes, in addition to the two spin states ($N_s=2$) there are the two species of fermions ($N_f=2$). Because $N_T=N_sN_f=4$, 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. Therefore, even though the ''fundamental'' constituents are fractionally charged objects, they appear in quartets that have the same quantum numbers as electrons. These quartets are ''confined'' together because they are forced to sit on the same domain wall that gives origin to each of the four quantum states.

B. Midgap states and STM probes

In contrast to polyacetelene chains, the nanotubes can be individually laid on a substrate, and locally probed via STM.[15] One would then expect that the midgap states with $E=0$ corresponding to domain walls (kinks and antikinks) could be probed by tunneling of electrons from a 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. More precisely, the polarons are self-consistent solutions for a position-dependent real order parameter $\Delta(x)$ such that $\Delta(-\infty)=\Delta(\infty)=\pm\Delta_0$, whereas the solitons or kinks are solutions such that $\Delta(-\infty)\times\Delta(\infty)=-\Delta_0^2$ (the sign switches).

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 distorsions Eq. (9) together with elastic energy cost $\delta E=3\ (K+K_\theta)d^2|u|^2$ is simply a static version of the Gross-Neveu model for a real u background field.[16–18] The energies of the electronic states and the formation energies are thus given by

$$\omega_n=\Delta_0\cos\left(\frac{n\pi}{2N_T}\right),\quad E_n\Delta_0\frac{2N_T}{\pi}\sin\left(\frac{n\pi}{2N_T}\right),$$

where $1\leqslant n\leqslant N_T-1=3$ for the polarons, and $n_0=N_T$ for an infinitely separated kink-antikink soliton pair (notice that the topological electronic state has zero energy). By means of STM spectroscopy, one should be able to probe both the energies (the ω_n above) and the shapes of the solitonic states.

IV. INTERACTION EFFECTS

The effects we described above were all derived taking into account the coupling between the electrons and lattice distortions. We have not included the effects of the electron-electron interactions. Let us discuss here what we expect when the electronic interactions are included. There are two issues that we need to address. The first one is whether the effects we discuss in this paper could arise from electronic interactions alone. If not, the second issue is whether the effects survive in the presence of electronic interactions.

To address the first issue, we can connect our results to some of the results found previously using bosonization (or ''g-ology'') in Refs. 3–7. To be more specific, let us directly compare some of our results to those by Krotov, Lee, and Louie using g-ology.[3] There they found that two of the possible instabilities that led to energy gaps were charge-density waves, termed CDW1 and CDW2. Basically, CDW2 corresponds to coupling between the two Dirac points in the armchair spectrum ($\mathbf{K}_\pm$), which is equivalent to our Kekulé distortion. They found that there was a continuous U(1) symmetry for the order parameter, and that the density fluctuations associated with slow twists of the order parameter phase did not couple to the electromagnetic field. In other words, they found that the low-energy excitations were neutral. This is exactly the same situation that we found considering the Kekulé distortions, where the order parameter had a continuous symmetry, and the charge accumulation in the symmetric and antisymmetric channels canceled each other. The reason that the results coincide is that electron-phonon or nearest neightbor electron-electron interactions (used, in addition to on-site interactions, in Ref. 3) lead to the same effective theory for the g-ology. Therefore, in this case, the electron-electron interactions and the electron-phonon interactions reinforce each other in opening a CDW gap.

However, there is a difference between what is found for the CDW1 phase of Ref. 3 and the case of the ALT distortion, even though both are instabilities that do not couple the

two Dirac points. The CDW1 order parameter has a continuous U(1) symmetry, whereas the ALT dimerization has a discrete $\mathbf{Z}_2$ symmetry. Although the electron-lattice coupling effectively generates an interaction between the electrons, a naive *g*-ology treatment in the case of the lattice distortions would miss the fact that the order parameter for the electronic instability has a direct (and physical) connection to a discrete symmetry that stems from the lattice displacements. So, even though both the electron-lattice coupling and electron electron interactions tend to open CDW gaps, their symmetry is different.

Therefore, the answer to the first question raised is that even though interactions alone lead to CDW instabilities, they in general do not have the same symmetries as those generated by the mechanisms we discuss here. The lower symmetry has important consequences, such as the soliton and polaron solutions with midgap energies discussed in this paper.

Let us now turn to the second issue about whether the effects of the lattice distortion survive in the presence of electronic interactions. Because the interactions also lead to a CDW instability, one would expect that they reinforce the effect found with the lattice distortions. Since the CDW symmetry due to the ALT distortion ($\mathbf{Z}_2$) is lower than that of the CDW1 [U(1)], the combined effects of electron-electron interactions and lattice distortions should give rise to a discrete $\mathbf{Z}_2$ (the lower) symmetry at a temperature scale of at least 1 K as found with the lattice distortions alone.

Finally, we would like to touch on the question of whether other instabilities due to electronic interactions, such as SDW or SC, could appear before the CDW. As found in Ref. 3, the prevailing instabilities depend on the details of the interaction potential. In addition, one would have to reconsider these findings if the lattice distortion effects are combined to the electron-electron interaction effects. Although the CDW1 and CDW2 states can be dominant instabilities depending on the interaction parameters, and the same should remain true when combined with the effects of lattice distortions, determining whether the physical interaction parameters fall within this parameter space window is beyond the scope of this paper.

V. CONCLUSIONS

We raised in this paper the question of whether there are fractionally charged states in carbon nanotubes, and carried out a detailed analyses to address the problem. We have studied the symmetries of spontaneous lattice deformations in carbon nanotubes, so as to determine whether or not there is a discrete number of ground states associated with lattice deformations, and consequently fractionally charged quantum states associated with domain walls between such discrete vaccua.

We have shown that the Kekulé distortion has a continuous U(1) symmetry, contrary to a naive expectation of a discrete $\mathbf{Z}_3$. This implies that the continuous phase fluctuations of the U(1) order parameter imply a charge accumulation $\Delta Q_{\pm} = \pm (e/2\pi)\,\Delta\phi$, which is not quantized. Therefore, there are no charge $\pm e/3$ states as naively expected from a $\mathbf{Z}_3$ symmetry for carbon atom displacements solely along the original bond directions. In principle there are small anisotropies that reduce the U(1) symmetry to $\mathbf{Z}_3$ when higher-order terms in the atomic displacements are included. However, we showed here that these anisotropies are only evident at energies five orders of magnitude smaller than the CDW gap scale. In addition, even at $T=0$, quantum fluctuations restore the U(1) symmetry in spite of the presence of the anisotropy.

We have also shown that the ALT structure has a discrete $\mathbf{Z}_2$ symmetry. We discuss the implications of topological domain walls between the twofold 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. Quartets of $Q = \pm e/2$ fractionally charged constituents appear together so that the combined quantum numbers are the same as those for electrons. We obtain the energies of the kink states, as well as the polaron states, by recognizing that the Hamiltonian for the ALT distorsion is a version of a Gross-Neveu model with a static real background field. These midgap states could be probed by STM spectroscopy, resolving experimentally both the energies and the shapes of the solitonic states.

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APPENDIX: CURVATURE EFFECTS

In this appendix we discuss how the curvature of the nanotubes affect the spontaneous lattice distortions considered in this paper. The tube curvature causes the hopping amplitudes to be different in the directions parallel and perpendicular to the tube axis. There is a simple way to account for these effects within the formulation we used when discussing the ALT structures, which are zero wave-vector lattice distortions. Consider a displacement u (as used in Sec. III) that is perpendicular to the tube axis. The orthogonality between the displacement u and the tube axis implies that $u = -\bar{u}$. Such displacement vector u stretches the bonds perpendicular and parallel to the tube axis unevenly, which correctly mimics the effects of curving the graphite sheet.

The effect of u on the electronic spectrum can be obtained from Eq. (9) with

$$A = 2i\alpha\, u/d,$$

which is now real. The spectrum is obtained from the eigenstates of the submatrices $\mathbf{h}_A$ and $\mathbf{h}_{-\bar{A}}$, which for real A give

$$E(p) = \pm |p \mp A|,$$

and correspond to shifting the two Dirac points by

$$K_{\pm} \rightarrow K_{\pm} \pm A.$$

These results are well known, and they can be obtained by just solving the tight-binding Hamiltonian for the graphite sheet with two different hopping amplitudes t and $t_{\perp}$ (see, for

example, Ref. 7). The reason for the above derivation in terms of the displacements u is that we can now combine the effects of the tube curvature and the Kekulé distortion in a very simple way.

The elastic energy cost of the Kekulé distortion remains the same to lowest order in the curvature because the uniform displacement u and the Kekulé displacement ϵ correspond to orthogonal modes, since they have different wave vectors. The extra energy cost of having a nonzero ϵ is, therefore, still $\delta E = 3Kd^2|\epsilon|^2$. The electronic spectrum, however, is changed due to u. The new Hamiltonian for the combined distortions is

$$H = \sum_p \Psi^\dagger(p) \begin{bmatrix} \mathbf{h} & 0 \\ 0 & -\mathbf{h} \end{bmatrix} \Psi(p), \tag{A1}$$

$$\mathbf{h} = \begin{pmatrix} p-A & \Delta \\ \overline{\Delta} & -p-A \end{pmatrix}, \tag{A2}$$

with

$$\Psi^\dagger(\psi^\dagger_{+,S}\psi^\dagger_{-,S}\psi^\dagger_{+,A}\psi^\dagger_{-,A})$$

as defined in Sec. II, and to lowest order in ϵ, $\Delta/t = -3i\alpha\overline{\epsilon}$. The new spectrum is given by

$$E = \pm A \pm \sqrt{p^2 + |\Delta|^2},$$

and it is easy to show that the shift in energy A leads to the cancellation of the logarithmic divergence $\ln \Lambda/\Delta$ from integrating the negative energy states, which is replaced by $\ln \Lambda/A$. Hence, there is no longer a spontaneous distortion with wave vector $G = K_+ - K_-$. Because of the curvature, with its associated shift in the Dirac points, the instability moves away from the commensurate wave vector $K_+ - K_-$. Instead, there will be an incommensurate distortion with wave vector $G' = K_+ - K_- + 2A$. For this new wave vector there will still be the logarithmic divergence for small Δ. In more physical terms, the singularity just moves to a new (incommensurate) phonon wave vector G'. The elastic energy cost remains almost unchanged, and can just be obtained from the phonon dispersion (see, for example, Ref. 14) at the new incommensurate wave vector G'.

In the incommensurate problem the symmetry of the order parameter is a continuous U(1). The absence of commensuration with a discrete symmetry washes away any anisotropy. The gradient of the phase of the order parameter gives continuous fluctuations of the charge density. So the conclusion reached in this paper that there are no fractionally (quantized) charged solitons for lattice distortions other than the ALT structures is unchanged.

Finally, we would like to discuss whether the curvature effects could restore a discrete symmetry for the Kekulé distortion, should there be any mechanism favoring a commensurate distortion. The answer is negative, because even if there is an anisotropy that tries to pin the phase of the order parameter Δ, this anisotropy is irrelevant, as we showed in Sec. II using the sine-Gordon Lagrangian Eq. (7). Therefore, the only effect of the tube curvature on the Kekulé structure is not to restore the anisotropy, but just to suppress the distortion at the wave vector G as described in this appendix.

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