Broken symmetry, boundary conditions, and band-gap oscillations in finite single-wall carbon nanotubes

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The interplay between the broken symmetry and the boundary conditions alters profoundly the electronic properties of carbon single-wall nanotubes (SWNTs) of finite-lengths. For SWNTs (p,q) characterized by $p = k+l$, $q = k-l$, $0 \leq l \leq k$, and $k = 1, 2, \ldots$, the energy gaps for finite SWNTs belonging to a given family k exhibit strikingly similar oscillating patterns for *even* NT sections, but the gap maxima for SWNTs of different lengths exhibit different periodicities with the amplitudes of oscillations diminishing from the armchair, to chiral, and to the zigzag SWNTs.

A number of exciting discoveries on carbon nanotubes (CNTs) have been unfolding recently. In the arena of molecular electronics, two fundamental issues are (i) the properties of nanotubes (NTs) of finite lengths and (ii) the role of metal electrodes. Experimental techniques to control the length of carbon single-wall nanotubes (SWNTs) have been developed for sometime[1–3] and there have been measurements on the electronic and transport properties of finite-length nanotubes.[3–5] Of particular interest is the experimental evidence of an increase in the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) as the NT is shortened. However, it is difficult to experimentally study the variation of HOMO-LUMO gaps for a series of NT lengths. Theoretical studies have addressed this issue for an armchair single-wall nanotube[6] (ASWNT) and a general chiral[7] NT. Rochefort *et al.*,[6] using a variety of theoretical methods, have reported that an ASWNT, while it is metallic when infinitely long, developed a band gap when it is short. The band gap maxima exhibit well-defined oscillations as a function of the length of the NT with a period of $3a/2$ ($a =$ lattice constant of the graphene sheet) reminiscent of the gap oscillations in π-conjugated organic semiconducting polymers.[8] On the other hand, Zhu *et al.*,[7] using a nearest-neighbor π-bond tight-binding model, found that band gaps of most chiral NTs, exhibited a monotonic decrease as a function of the length. Since, in their calculation, the length of the tube is expressed in the unit of the translational vector, they only obtain a coarse-grained result and cannot possibly capture gap oscillations that may be present at a finer scale.

Experimentally, well-defined oscillations in the local density of states (LDOS) along the axis of the SWNT at the Fermi energy E_f have been observed.[5] They have been explained using a ''particle-in-a-box'' model. In this model,[9,10] a simple relationship exists between the tube length L and the wavelength λ of the standing-wave (state) in the tube ($\lambda = 2L/l$ with l being an integer). For an infinite ASWNT, band crossing occurs at E_f with $k_f = 2\pi/3a$ or $\lambda_f = 3a$, leading to a period of $3a/2$ for LDOS oscillations at E_f as observed in the experiment. If one were to use this model to interpret HOMO-LUMO gap oscillations, one notes that the

HOMO-LUMO gap minimum exists in the vicinity of E_f for a finite ASWNT, leading to a period $3a/2$ for HOMO-LUMO minimum. However, Rochefort *et al.*'s result had indicated that, while there is a well-defined periodicity for HOMO-LUMO gap maximum, there is no such periodic pattern for the gap minimum. Hence the simple standing-wave picture of electrons cannot be used to explain the HOMO-LUMO gap oscillations for SWNTs.

The available theoretical calculations are either inadequate or incomplete in providing the explanations for the observed HOMO-LUMO gap oscillations. In fact, these calculations do not address how the electronic structure of a finite nanotube of general chirality differs from an ASWNT. In this work, we provide a complete picture for the oscillatory characterstics of HOMO-LUMO gaps of not only armchair but also zig-zag and chiral nanotubes. HOMO-LUMO gaps are calculated within the framework of the extended Hückel molecular orbital method,[11] which has been shown to give results in agreement with the *ab initio* results.[6] We demonstrate that there exists a correlation between bond-charge oscillations and gap oscillations that arises from an interplay between the broken symmetry and boundary conditions. It is shown that the band-gap oscillations, when examined at the sectional scale of carbon nanotubes (each section containing a ring of atoms defined by the diameter of the tube), exhibit strikingly similar characteristics for all SWNTs belonging to the same family (with the gap maximum repeating every six sections). However, when examined at the actual length-scale, gap maxima for different types of SWNTs were found to exhibit different periodicities [$3a \cos(30° - \phi)$, ϕ being the chiral angle]. These results are shown to hold intriguing implications in the potential utilization of finite NTs as the basic component of molecular scale optoelectronic devices.

For an infinite graphene sheet, each atom in the bonding network forms three σ bonds with its three equivalent neighbors. In addition, the remaining itinerant electron may form a π bond with the itinerant electron of any one of its three neighbors, resulting in the formation of a double bond between the atom and that particular neighbor. Because of the equivalence of the three neighbors due to the symmetry of the infinite graphene sheet, there are in fact three such
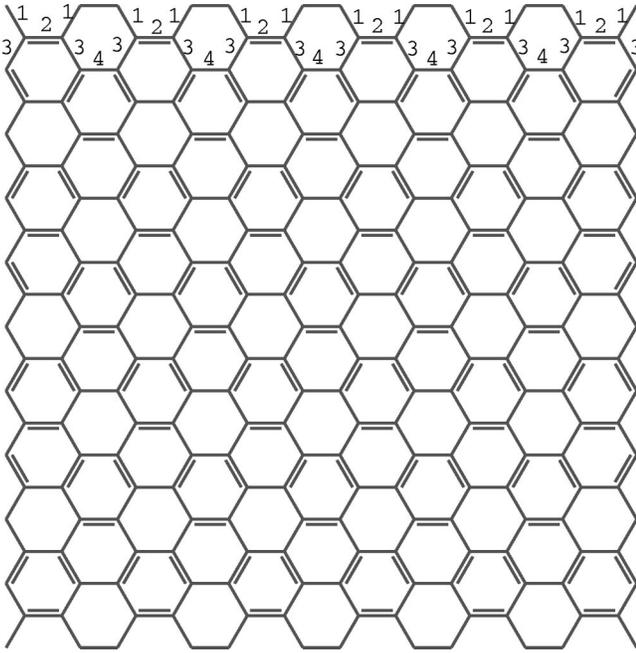
FIG. 1. A possible DB distribution of a graphene sheet. The bonds are labeled continuously from the top to the bottom by integers (bonds labeled by 1 to 4 are indicated explictly in the figure). Note that the bonds denoted by $3s+2$ ($s=0,1,2,\ldots$) are double bonds, while others are single bonds.
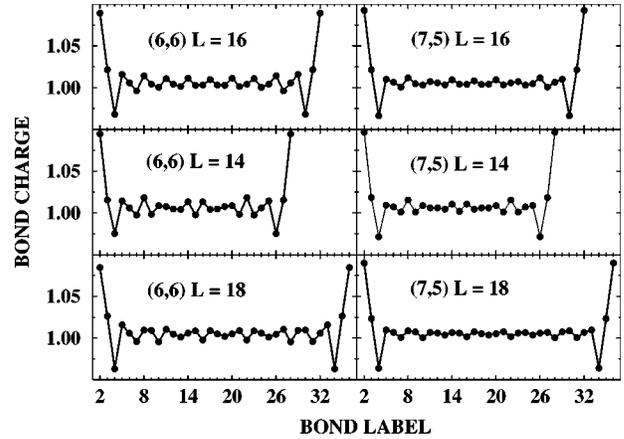

FIG. 2. The (average) bond charge vs the bond label (see Fig. 1 for the labeling scheme) for (6,6) and (7,5) NT's of different lengths. Note that $L=16$, 14, and 18 correspond to $3n+1$ ($n=odd$), $3n-1$ ($n=odd$), and $3n$ ($n=even$) types of NT.

equivalent double-bond (DB) distributions. These three bonding configurations are in resonance, leading to a network of equivalent resonant bonds for an infinite graphene sheet with no manifestation of any of the DB patterns. When the infinite graphene sheet is rolled up into an infinite nanotube, nothing is changed as far as the bonding pattern is concerned. The situation is, however, entirely different for a nanotube of finite length. In this case, the DB pattern can survive under appropriate conditions. The scenario can be understood as follows. Figure 1 shows one of the possible DB distributions. If the carbon atoms in the first section (row) are replaced by hydrogen atoms, an examination of the pattern in Fig. 1 indicates that, for the particular DB distribution in Fig. 1 to survive, one must hydrogen terminate the sheet at the other end such that the length of the sheet corresponds to $3n+1$ sections ($n=0,1,2,\ldots$) of carbon. In this situation, the DB distribution is sustained, indicating the formation of the π bond that in turn results in a large gap separating the bonding π state with the antibonding π^* state. On the other hand, for finite graphene sheets with ''lengths'' of $3n$ and $3n-1$ sections, no characteristic DB distribution of the graphene sheet can be maintained and hence only small gaps exist. When the finite graphene sheet is rolled up into a tube with its circumference along the horizontal direction as shown in Fig. 1, a finite ASWNT is obtained. The analysis of the broken symmetry associated with the *finiteness* of the graphene sheet and the boundary condition imposed on the finite sheet immediately leads to the conclusion that ASWNTs with lengths of $3n+1$ sections will possess large band gaps while ASWNT's with lengths of $3n$ or $3n-1$ sections will only have relatively small gaps.

Thus it is the existence or nonexistence of the double-bond configuration as a result of the interplay between the broken symmetry associated with the *finiteness* of the ASWNT and the boundary condition that is responsible for the well-defined oscillatory behavior of the band gap of ASWNTs reported in Ref. 6.

We tested our scenario of bonding patterns for finite ASWNTs of different lengths by computing the bond charge using the scheme outlined in Ref. 12. In the calculation, the C-C and C-H bond lengths were kept at commonly accepted values of 1.42 Å and 1.09 Å, respectively. The left panel of Fig. 2 gives the bond charge of the three different types ($3n+1$, $3n-1$, and $3n$) of (6,6) finite ASWNTs vs the bond label. Here, the bonds in Fig. 1 are labeled by integers continuously from the top to the bottom. For example, bonds connecting atoms in the first section (hydrogen) and those in the second section (carbon) are labeled by 1, bonds connecting carbon atoms within the second section by 2, bonds connecting carbon atoms between the second and third section by 3, and so forth. From the left panel of Fig. 2, it can be seen that, for a finite ASWNT with a length of 16 ($3n+1$ type with $n=5$) sections, the bond charge distribution exhibits the characteristic pattern of the DB of a graphene sheet shown in Fig. 1, leading to a large band gap between the bonding π state and the antibonding π^* state. On the other hand, for finite ASWNTs with lengths of 14 ($3n-1$ type with $n=5$) sections and 18 ($3n$ type with $n=6$) sections, the bond charge distribution does not follow the correct DB pattern. Hence ASWNTs with lengths of 14 and 18 sections can only have relatively small gaps. We have verified this explicitly by computing the band gap of the finite (6,6) ASWNT as a function of its ''length.'' The result is displayed in Fig. 3 for finite ASWNTs with even number of NT sections (to be discussed later), and in the inset of Fig. 3 for ASWNTs with both even and odd number of NT sections. The well-defined oscillatory behavior of the band gap as a function of NT lengths exhibited in both displays (including the inset) demonstrates the direct correlation to the bond scenario presented above. Note that the band gap is large when-
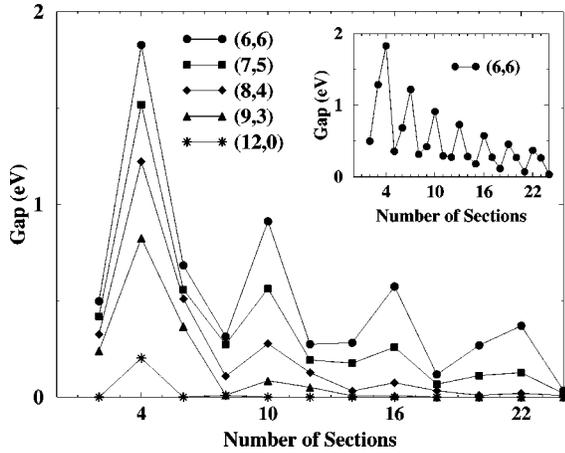
FIG. 3. The band gap as a function of (*even*) NT sections for SWNTs belonging to the $k=6$ family. The inset shows the band-gap oscillations as a function of NT sections (*odd* as well as *even*) for (6,6) ASWNT. Note that the oscillation of the energy gap exhibits maxima every three sections in the case of an ASWNT and every six sections in the case of chiral NTs.
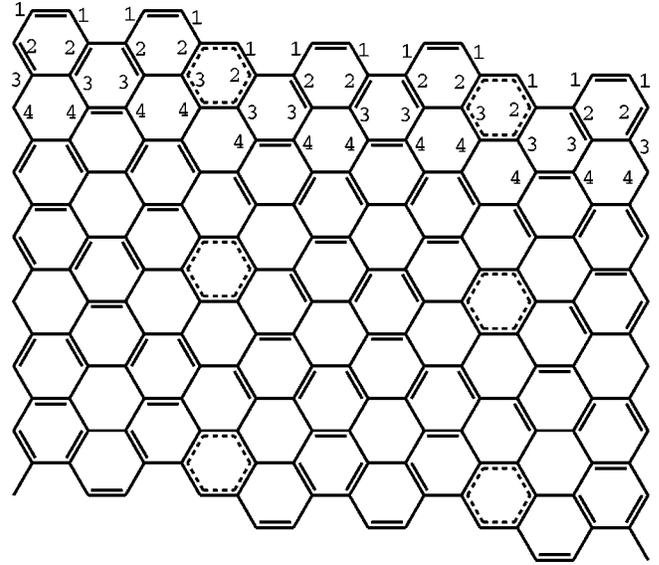

FIG. 4. An unwrapped (7,5) SWNT showing double bonds and resonant bonds (dashed line). Resonant bonds are at the location of the stacking-fault defects. Atoms in sections 1–4 are marked explicitly to indicate the NT sections.

ever the tube length satisfies the $3n+1$ rule, where n can be either odd or even for an ASWNT. It should also be noted that the energy-gap oscillations exhibit maxima recurring every three sections (see the inset of Fig. 3). This is equivalent to a $3a/2$ periodicity, similar to the result obtained by Rochefort *et al.*[6]

The totality of SWNTs (p,q) can be divided into two groups. Group I is characterized by $p=k+l$, $q=k-l$, $l=0,1,2,\ldots,k$, and $k=1,2,\ldots$, with $p-q=2l$ while group II by $p=k+l$, $q=k-l-1$, and $l=0,1,2,\ldots,k$, with $p-q=2l+1$. In this work, we focus our study on the energy gap oscillations of finite SWNTs belonging to Group I only.[13] Specifically, we chose $k=6$ to demonstrate the result of our study. The family of NTs in this subset can be either metallic [(6,6), (9,3), and (12,0)] or semiconducting [(7,5), (8,4), (10,2), and (11,1)] when infinitely long. We started our study by mapping the (7,5) NT onto a flat surface as shown in Fig. 4. By considering the carbon atoms in the top section of the NT to be passivated by a section of hydrogen atoms (not shown in Fig. 4), one can obtain hydrogen-passivated finite (7,5) NTs of different lengths by terminating the sheet corresponding to different sections by hydrogen atoms at the other end. A close examination of Fig. 4 reveals three interesting properties for (7,5) NTs of finite length. (i) Similar hydrogen terminations at both ends of the finite (7,5) NTs can only be achieved for such NTs of even number of sections. Referring to Fig. 4, the first section of the (7,5) NT is defined by the carbon atoms with dangling bonds (denoted by integer 1). It can be seen that there are two steps in the first section where the adjacent atoms are misaligned. While each carbon atom in the first section is connected to one passivating hydrogen atom at the top (not shown in Fig. 4), the corner atom, one at each step, is connected to two atoms in the second section (denoted by integer 2). On the other hand, every atom in the second section is connected to one atom in the third section (denoted by integer 3). This alternating pattern persists throughout the sheet from the top to

the bottom. As a result, different boundary conditions exist at the top and at the bottom for (7,5) NTs with odd number of sections, while similar boundary conditions exist at both ends of finite (7,5) NTs with even number of sections. In fact, this scenario is also true for the other SWNTs in group I except ASWNTs (k,k). From Fig. 1, it can be seen that similar boundary conditions exist at both ends for ASWNTs regardless of whether they contain odd or even number of sections. Hence, in this respect, the finite ASWNT is an exception rather than a rule. (ii) Figure 4 shows that, for (7,5) NTs with even number of sections, the double-bond pattern [with some "defects" to be discussed in (iii)] can be maintained for those containing $3n+1$ sections (with odd n). Such a pattern, however, does not exist for those containing $3n-1$ (with odd n) sections or $3n$ (with even n) sections. This picture is consistent with the situation discussed for the ASWNT, as there are again the same three types of finite NTs with the same identical properties. It also means that a well-defined oscillatory pattern, consistent with the rule characterizing the oscillatory behavior of the ASWNTs, must exist for the band gap of (7,5) NTs containing even number of sections as a function of the length. However, unlike the case of ASWNT, the maxima of gap oscillations recur every six sections instead of every three sections. Since the angle between the axial direction of the ASWNT and that of a chiral NT is $30°-\phi$, ϕ being the chiral angle, the periodicity of the oscillation of the energy gap maxima is simply $6(a/2)\cos(30°-\phi) = 3a\cos(30°-\phi)$. (iii) For the (7,5) NTs, the top boundary (first section) is characterized by two steps where adjacent atoms are misaligned, creating what are akin to two "stacking" faults (see Fig. 4). The defects associated with the stacking faults are highlighted as hexagons bordered by solid/dashed bonds. These bonds are resonant bonds formed as a result of the resonance between two misaligned equivalent bonding configurations (see Fig. 4). We

have calculated the bond charges of the defect configuration. We found the bond charges for the resonant bonds to lie between those of the single bonds and double bonds. These findings confirm our picture regarding the nature of the defect configuration. The effect of the presence of these defects in the double-bond pattern is to reduce the magnitude of the band gap (see Fig. 3).

To verify the property outlined in (ii), we have calculated the bond charges of (7,5) NTs of various lengths. The results for (7,5) NTs of length 16 (type $3n+1$ with $n=5$) sections, 14 (type $3n-1$ with $n=5$) sections, and 18 (type $3n$ with $n=6$) sections are shown in the right panel of Fig. 2. The results are similar to the case of an ASWNT with the bond charge distribution for 16 sections exhibiting the double-bond pattern shown in Fig. 4 while those for the other two cases (14 and 18 sections) do not, confirming the picture presented in (ii) in the preceding paragraph. The consequences of the three properties enunciated above lead to the prediction that the band gap of (7,5) NTs with even number of sections must exhibit a regular oscillatory pattern similar to the one for ASWNTs, namely, large gaps for NTs of $3n+1$ sections (with odd n) and relatively small gaps for NTs of $3n-1$ (with odd n) sections or $3n$ (with even n) sections. However, because of the presence of the stacking-fault defects, the amplitudes of oscillations are smaller compared to the corresponding ones for an ASWNT. We have verified our ideas by calculating the band gaps for the (7,5) NTs with even number of sections. The result displayed in Fig. 3 indeed shows that the band gap of finite (7,5) SWNTs exhibits a similar oscillatory pattern as that of the finite ASWNTs but with smaller amplitudes of oscillations, just as predicted using the three properties discussed above.

The argument presented in the discussion of the three properties for (7,5) NTs applies also to (8,4), (9,3), (10,2), (11,1), and (12,0) NTs. However, this series of NTs will have increasing number of defects from (7,5) to (12,0). Therefore, similar oscillatory patterns, but with diminishing amplitudes of oscillations, are expected for these NTs. The result of our calculation shown in Fig. 3 has indeed also confirmed this prediction. The same argument is also valid for all the other families of SWNTs in group I. We have studied families of NTs in this group for other k values. We found similar results as expected. For example, the band gaps of the SWNTs in the family corresponding to $k=5$, including the series of NTs (5,5), (6,4), (7,3), (8,2), (9,1), and (10,0), show exactly the same behavior as that for the family corresponding to $k=6$. In particular, there is hardly any difference between the oscillating pattern for the zigzag SWNT (ZSWNT) (10,0) in the $k=5$ family and that for the ZSWNT (12,0) in the $k=6$ family. It is interesting to note that, although the former is semiconducting and the latter is metallic when they are infinitely long, both ZSWNTs have vanishing gap for tubes longer than six sections, suggesting that they will be conductors at those lengths. The reason for them to have indistinguishable behavior when they are short must be attributable to the fact that they both have the largest number of stacking-fault defects in their respective familied and these defects overwhelm the large gap associated with the double-bond pattern.

In conclusion, we have shown that there is a fundamental change in the electronic properties of finite-length carbon SWNTs. For example, ASWNTs at selected lengths behave as semiconductors, in contrast to the metallic behavior of infinite ASWNTs. On the other hand, infinite ZSWNTs that can be either metallic or semiconducting behave as molecular-scale conductors. These results are expected to have profound implications in the utilization of finite-length CNTs as optoelectronic devices. Finally, we would like to remark that the energy gap as a function of the NT length exhibits a different behavior for group II SWNTs.[13] These results will be discussed in a forthcoming publication.

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