Broken Symmetry, Boundary Conditions, and Band Gap Oscillations in Finite Single Wall Nanotubes

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Abstract

We have shown that the interplay between the broken symmetry of finite single-wall nanotubes (SWNT) and the boundary conditions affects the electronic properties of SWNTs in a profound way. For finite SWNTs $(p, q)$ characterized by $p = k + l, q = k - l, p - q = 2l, l = 0, 1, \cdots, k$, and $k = 1, 2, \cdots$, we found that the band gaps of finite SWNTs belonging to a certain $k$ exhibit similar well-defined oscillating patterns but with diminishing amplitudes from the armchair ($l = 0$) to the zigzag ($l = k$) SWNTs. These profound changes hold intriguing implications in the potential utilization of these finite NTs as the basic component of molecular scale devices.
Very recently, there is a series of interesting studies related to the feasibility of utilizing carbon nanotubes (NTs) of finite lengths as the basic component for molecular scale electronic and magnetic devices \[1, 2, 3, 4\]. Specifically, there have been experimental evidences of increasing band gap in NTs of decreasing length \[5, 6\]. Theoretical calculations \[10\] have shown that an armchair single-wall NT (ASWNT), while it is metallic when infinitely long, developed a band gap when it is short and this band gap exhibited a well-defined oscillation as a function of the length of the NT. Mehrez et al \[11\] found in a theoretical study different transport behavior for ASWNT-based magnetic tunnel junctions of different lengths. These studies had demonstrated that the finiteness of ASWNT has altered the fundamental properties of its electronic structure. However, the physics underlying these profound changes has not been delineated. To explore the full potential of NTs as molecular scale devices, it is imperative to first determine the nature of the electronic structure of all types of SWNTs of finite length, and then to have a clear understanding of its underlying physics. In other words, the logical question to be raised is whether these or any other profound changes are to be found for finite SWNTs of general chirality. In this Letter, we address this issue in terms of the symmetry breaking and the boundary condition.

For an infinite graphene sheet, each atom in the bonding network forms three $\sigma$-bonds with its three equivalent neighbors. In addition, the remaining itinerant electron associated with the atom may form a $\pi$-bond with the itinerant electron of any one of the 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 equivalent double bond distributions (see, for example, the pattern displayed in Fig. 1). These three bonding configurations are in resonance, thus leading to a network of equivalent resonant bonds for an infinite graphene sheet with no manifestation of any of the double bond 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 double bond pattern can survive under appropriate conditions. The scenario
can be understood as follows. Fig. 1 shows one of the possible double bond distribution. If the carbon atoms in the first section (row) are replaced by hydrogen atoms, an examination of the pattern in Fig. 1 indicates that that particular double bond distribution will survive if and only if the sheet is terminated by replacing the carbon atoms in the 3\textsuperscript{m}\textsuperscript{th} section \((m = 1, 2, \cdots)\) by hydrogen atoms. In this situation, there are \(3m - 2\) sections in the finite graphene sheet sandwiched between the top and bottom sections of passivating hydrogen atoms. In other words, a finite graphene sheet with "lengths" of \(3m - 2 = 3n + 1\) sections \((n = 0, 1, 2, \cdots)\) can sustain the double bond distribution, indicating the formation of the \(\pi\)-bond that in turn results in a large gap separating the bonding \(\pi\) state with the antibonding \(\pi^*\) state. On the other hand, for finite graphene sheets with lengths of \(3n\) and \(3n - 1\) sections, no characteristic double bond 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 ASWNTs with lengths of \(3n\) or \(3n - 1\) sections will only have relatively small gaps. Thus it is the existence or non-existence 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 [10].

To demonstrate our scenario of bonding patterns for finite ASWNTs of different lengths, we calculated the bond charge distribution for these ASWNTs, using the extended Hückel molecular orbital (EHMO) method [12] as it has been shown to give qualitatively correct result in comparison with ab initio calculations [10]. In the calculation, the C-C and C-H bond lengths were kept at commonly accepted values of 1.42Å and 1.09Å 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 on (see Fig. 1, note that bonds labeled by $3s + 2$ are double bonds, with $s = 0, 1, \cdots$). From the left panel of Fig. 2, it can be seen that, for the finite ASWNT with a length of 16 ($3n + 1$ type, with $n = 5$) sections, the bond charge distribution exhibits the characteristic pattern of the double bonds of a graphene sheet as shown in Fig. 1. The existence of the double bond configuration indicates the formation of the $\pi$-bonds, thus leading to a large band gap between the bonding $\pi$ state and the antibonding $\pi^*$ 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 double bond pattern. Hence ASWNTs with lengths of 14 ($3n - 1$ type) and 18 ($3n$ type) sections can only have relatively small gaps. We have also used the EHMO method to calculate 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 sections (to be discussed later), and in the inset of Fig. 3 for ASWNTs with both even and odd number of sections. The well-defined oscillatory behavior of the band gap as a function of the length of the NTs exhibited in both displays shows the direct correlation to the bond scenario presented above. This oscillatory pattern of the band gap of the finite ASWNT as a function of the length anchored by large band gaps of the order of magnitudes of eVs for lengths of $3n + 1$ sections represents a fundamental change in the electronic structure of ASWNTs from a pseudo-one dimensional metallic conductor when they are infinitely long to a zero-dimension large band gap semiconductor at selected lengths.

Having established the pivotal roles played by the finiteness of the ASWNT and its interplay with the boundary condition, it will be interesting to find out how these factors or any modification of them affect the electronic structure of a finite SWNT of general chirality. The totality of SWNTs $(p, q)$ can be divided into two groups. Group I is characterized by $p = k + l$, $q = k - l$, $l = 0, 1, 2, \cdots, k$, and $k = 1, 2, \cdots$, 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 Letter, we focus our study on finite SWNTs belonging to Group I. Specifically, we chose \( k = 6 \) to demonstrate the result of our study. The family of NTs in this subset includes the armchair NT \((6,6)\) (metallic when infinitely long), NTs \((7,5), (8,4), (10,2), (11,1)\) (semiconducting when infinitely long), the NT \((9,3)\) (semimetal when infinitely long), and the zigzag NT \((12,0)\) (metallic when infinitely long). We started our study by mapping the \((7,5)\) NT onto a flat surface as shown in Fig. 4. Imagining that the carbon atoms in the top section of the NT are passivated by a section of hydrogen atoms (not shown in Fig. 4), hydrogen-passivated finite \((7,5)\) NTs of different lengths can be obtained by terminating the sheet at different sections at the other end with hydrogen atoms. 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 outlined 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 mis-aligned. 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 whether they contain odd or even number of sections. Hence, in this respect, the finite ASWNT is the exception rather than the rule among all the finite NTs in group I. (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 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.

(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/dash bonds. These bonds are resonant bonds formed as a result of the resonance between two mis-aligned 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).

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 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 leads to the prediction that the band gap of $(7,5)$ NTs with even number of sections exhibits 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 ASWNT. We have also
calculated 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 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 both ZSWNTs have vanishing gap when longer than 4 sections while the former is semiconducting and the later is metallic when both are infinitely long. 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 family and these defects overwhelm the large gap associated with the double bond pattern.

Finally, we have calculated the resistance at the Fermi energy of the family of NTs with \( k = 6 \), using the Landauer’s formula \[13,14\]. In the calculation, we modeled the leads following the procedure of Mehrez et al \[11\]. The Hamiltonians of the samples were constructed using the EHMO method. The result is shown in Fig. 5. It can be seen that the resistance curves for these NTs of finite lengths also exhibit a well-defined oscillatory pattern. A side-by-side examination of the resistance curves in Fig. 5 and the corresponding band gap curves in Fig. 3 reveals a close correlation between the gap and the resistance.
In conclusion, we have shown that finite SWNTs in each family \((k)\) in group I exhibit similar pattern for band gap oscillations with diminishing amplitudes from ASWNT to ZSWNT. We have also established that these characteristic patterns for the band gap are the consequences of the interplay between the broken symmetry associated with the finiteness of the NTs and the boundary conditions. The fundamental change in the electronic structure of all the finite SWNTs in group I has very intriguing implications for utilizing these finite NTs as molecular scale devices. For example, our result indicates that it is more appropriate to use ZSWNTs as molecular scale conductors rather than ASWNTs. On the other hand, ASWNTs of selected lengths may be used as large band gap molecular scale semiconductors. Furthermore, the existence of the double bond pattern raises the possibility of fabricating nanoscale coils \([15]\). We have also studied the electronic structure of finite SWNTs in group II. It turned out that different physics is operational in that situation. The result of that study will be presented elsewhere.

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FIGURES

Fig. 1 A typical double bond pattern in a graphene sheet.

Fig. 2 The (average) bond charge vs the bond label.

Fig. 3 The band gap vs the length (the number of sections) for SWNTs containing even number of sections corresponding to the subset $k = 6$. The inset shows the band gap curve for the (6,6) ASWNTs containing both odd and even number of sections.

Fig. 4 The mapping of (7,5) SWNTs onto a flat surface and the double bond pattern. The stacking fault defects are highlighted as hexagons bordered by resonant (solid/dash) bonds.

Fig. 5 The resistance vs the length for the series of SWNTs (6,6), (7,5), and (8,4) containing even number of sections. The inset gives the resistance vs the length curve for the ASWNTs (6,6) containing both odd and even number of sections.
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Resistance ($h/2e^2$)

- (6–6)
- (7–5)
- (8–4)
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