Tight-Binding Electronic Band Structure Calculation Studies of Periodically Perturbed (n,n) Carbon Nanotubes

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Tight-binding electronic band structure calculations on perturbed (n,n) carbon nanotubes have been performed. Our study shows that periodic local perturbations influence the electronic band structures of (n,n) carbon nanotubes in different ways depending on the symmetry of the perturbation. We focus on reflection-symmetry-breaking local perturbations and analyze possible band crossings at the Fermi level at the Γ point in small-radius (n,n) carbon nanotubes with selected spatial periods. We find perturbations on the order of 1 eV are required to cause the nanotube to be metallic in the presence of the perturbations. This finding provides valuable information regarding sensor and electronic-device applications of perturbed (n,n) carbon nanotubes.

I. INTRODUCTION

Recently, carbon nanotubes have been successfully functionalized, and the nanotubes have shown unique physical properties [1]. Depending on the nature of the functional groups, hydrophobic carbon nanotubes can be soluble in water [2], and the electronic properties can be modified. Considering the successful demonstration of nano-electronic devices made of carbon nanotube-based structures [3], functionalization would add a possibility of improving the physical properties of the nanotubes or giving them entirely new properties. Indeed, experimental investigations reveal that various types of functional groups on the tube sidewalls are possible [2,4]. Functionalization would change the electronic properties of carbon nanotubes, but the issue has not been systematically addressed theoretically. Therefore, it is highly desirable to find a quantitative relation between the perturbations by functional groups and the electronic band structures to clarify the role played by the functional groups in the nanotubes. To get an insight regarding the issue, we adopt a simple tight-binding model and analyze electronic band structures of periodically perturbed carbon nanotubes. Although functional groups are usually attached randomly to the nanotube sidewall, our calculations are focused on periodic perturbations to systematically analyze the effects of the perturbations.

II. CALCULATION

In typical π-electron tight-binding models, only interactions between nearest neighbors are taken into account. The on-site energy is usually set to a constant, and we let the on-site energy be zero for simplicity. The unperturbed tight-binding Hamiltonian is of the form

$$H = - \sum_{<i,j>} V_{pp\pi}^{ij} a_i^\dagger a_j + \text{c.c.}, \tag{1}$$

where i and j atoms form a nearest neighbor pair. Depending on the models, the hopping integral, $V_{pp\pi}^{ij}$, is determined. For instance, in an isotropic one-parameter tight-binding model, $V_{pp\pi}^{ij}$ is -2.77 eV [5]. In non-isotropic tight-binding models, where curvature effects are taken into account, $V_{pp\pi}^{ij}$ depends on the orientation of the bond [6–8]. There are three different types of orientations of the bonds for chiral carbon nanotubes, and there are two different types of orientations for armchair (n,n) carbon nanotubes. We choose $V_{pp\pi}^{ij}$ with the constraint that the average of $V_{pp\pi}^{ij}$ is -2.77 eV. As in Ref. 8, γ_1 is $V_{pp\pi}^{ij}$ for bonds along the circumferential direction of armchair (n,n) nanotubes, and γ_2 and γ_3 are $V_{pp\pi}^{ij}$ for other slanted bonds (see Figure 1). The values of γ_1, γ_2 and γ_3 used in the calculations are summarized in Table 1. The values fit momentum-space positions of Fermi points of perfect armchair (n,n) nanotubes to those calculated from first-principles [9]. When the nanotube is functionalized, the Hamiltonian is perturbed because of the interaction between the nanotube and the functional group. We introduce the following perturbation

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Table 1. Fermi point shift [9], tight-binding parameters γ_1, γ_2 and γ_3 and the ratio of γ_2 to γ_1. The Fermi point shift is in units of $\frac{\pi}{L}$, where L is the length of the unit cell, $\sqrt{3} \times$ C-C bond length.

Type	Fermi point shift	γ_1 (eV)	$\gamma_2 = \gamma_3$ (eV)	$\frac{\gamma_2}{\gamma_1}$
(3,3)	0.0807	−2.316	−2.997	1.294
(4,4)	0.0465	−2.520	−2.895	1.149
(5,5)	0.0330	−2.596	−2.857	1.101
(6,6)	0.0233	−2.648	−2.831	1.069
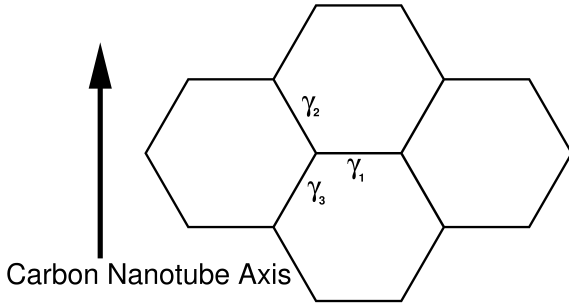
Fig. 1. Tight-binding hopping integrals, γ_1, γ_2 and γ_3. The integral for bonds along the circumferential direction of armchair (n,n) nanotubes is γ_1. By symmetry, the integrals for slanted bonds, γ_2 and γ_3, are the same.
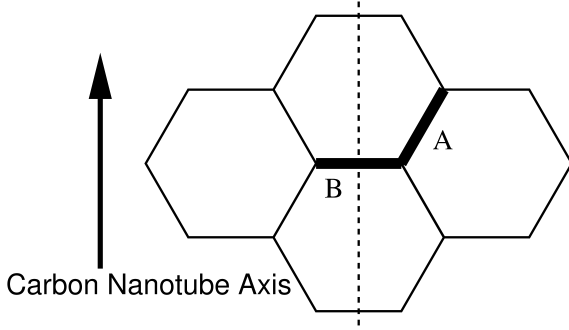

Fig. 2. Schematic diagram for functional groups. The functional group attached to the bond A breaks reflection symmetry about the plane containing the nanotube's symmetry axis. The functional group attached to the bond B preserves reflection symmetry. Any single functional group is either reflection-symmetry-breaking or reflection-symmetry-preserving.

Hamiltonian, which is assumed to govern the interaction between the nanotube and the functional group,

$$H_{\text{perturbation}} = \Delta \, a_\alpha^\dagger a_\beta + \text{c.c.}, \tag{2}$$

where α and β refer to atoms to which a functional group is attached (see Figure 2). The functional group is either reflection-symmetry-breaking or reflection-symmetry-preserving, as is illustrated in Figure 2.
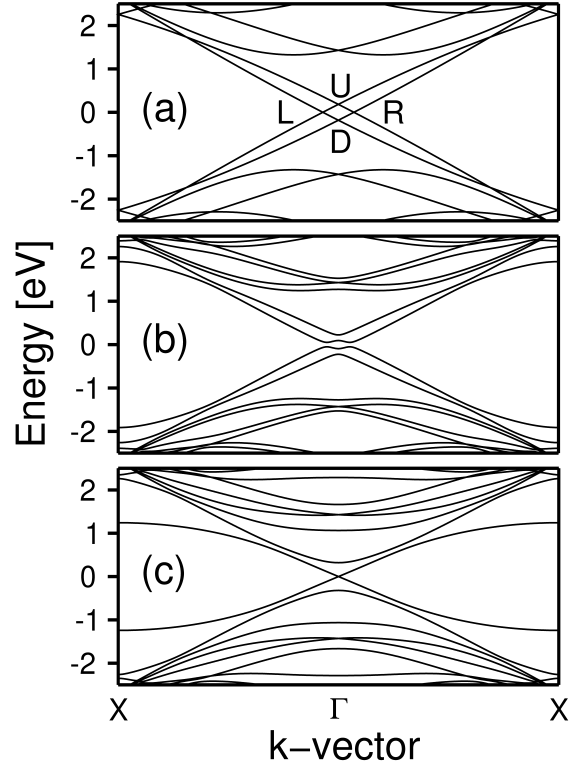

Fig. 3. (a) Electronic band structure of a (6,6) carbon nanotube with 3 primitive unit cells as a unit cell. U and D indicate band crossings at the Γ point, and L and R indicate band crossings at the Fermi points. (b),(c) Electronic band structures of a (6,6) carbon nanotube with a reflection-symmetry-breaking perturbation per 3 primitive unit cells. The value of the parameter Δ is $\Delta_{\text{zero gap}}$ in (b) and $\frac{1}{2}\Delta_{\text{zero gap}}$ in (c), where $\Delta_{\text{zero gap}}$ is 3.671 eV for the (6,6) carbon nanotube.

III. RESULTS AND DISCUSSION

We calculate the electronic band structures of (3,3), (4,4), (5,5) and (6,6) carbon nanotubes with the tight-binding method described in the previous section. The electronic band structures are based on that of a graphene sheet. Except for the position of band crossing at the Fermi level, the overall features of the band structure are not very different from those calculated with isotropic tight-binding models. Figure 3(a) and Figure 4(a) are the same electronic band structure of a (6,6) carbon nanotube, with 3 primitive unit cells as a unit cell defining first Brillouin zone, calculated with tight-binding method.

It has been known that the position of the Fermi point of a graphene sheet is shifted in carbon nanotubes due to curvature effects [6]. If a similar shift is to happen in the case of carbon nanotubes, the curvature effects should be included in the tight-binding Hamiltonian, and there has been some theoretical suggestions on including the effects [6–8]. In terms of symmetry, modification of an isotropic hopping parameter of the one-parameter tight-binding
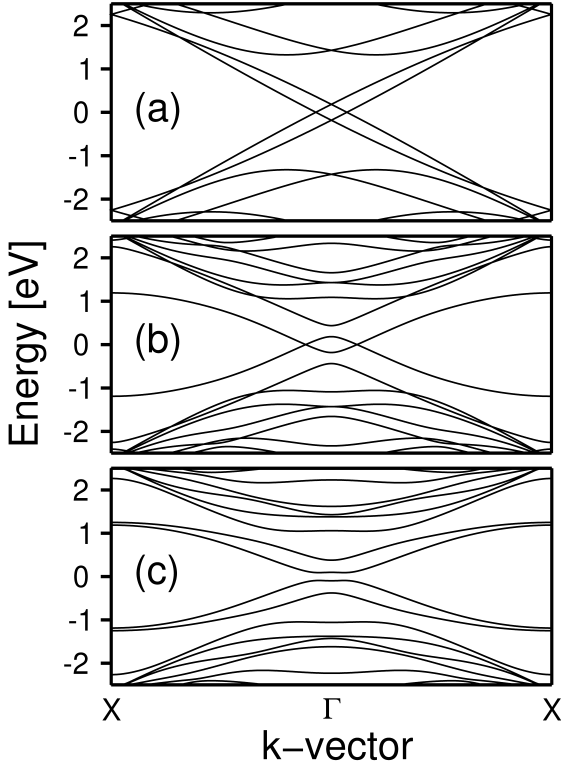
Fig. 4. (a) Electronic band structure of a (6,6) carbon nanotube with 3 primitive unit cells as a unit cell. (b) Electronic band structures of a (6,6) carbon nanotube with a reflection-symmetry-preserving perturbation per 3 primitive unit cells. (c) Electronic band structure of a (6,6) carbon nanotube with a unit cell of the same length, which has a reflection-symmetry-breaking perturbation and a reflection-symmetry-preserving perturbation on opposite sides. The value of the parameter Δ in (b) and (c) is 3.671 eV.
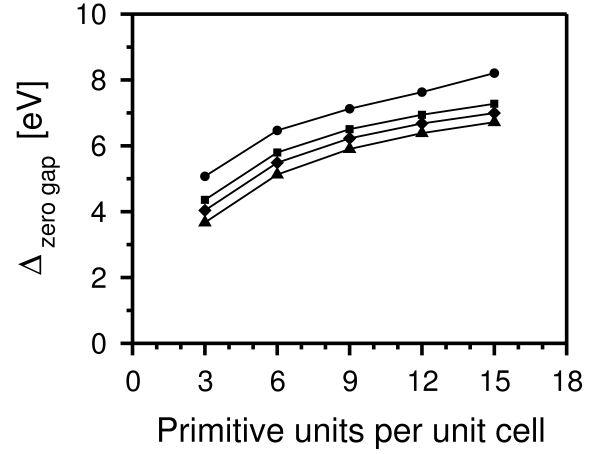
Fig. 5. Plots of $\Delta_{\text{zero gap}}$ versus primitive units per unit cell in the case of (3,3), (4,4), (5,5) and (6,6) nanotubes. The primitive units per unit cells are 3, 6, 9, 12 and 15. Note that the x-axis data are only valid for multiples of 3. Circles, squares, diamonds and triangles correspond to (3,3), (4,4), (5,5) and (6,6) nanotubes, respectively.

model is one way to include the Fermi point shift. Without the shift, the Fermi point of an (n,n) tube is exactly at $k = \frac{2\pi}{3L}$, where L is the length of the unit cell, or $\sqrt{3} \times$ the C-C bond length. Suppose that a (n,n) carbon nanotube is perturbed periodically, with the period being a multiple of three primitive units. The Fermi point of the unperturbed tube is at the Γ point because the Brillouin zone is folded. Moreover, because of the Fermi point shift, the Fermi points, L and R in Figure 3(a), are close to the Γ point, and there are band crossing points, U and D in Figure 3(a), at the Γ point just above and below the Fermi level after the Brillouin zone is folded. With a periodic perturbation, there are splittings of degeneracies at the Γ point, regardless of the symmetry of the perturbation, but the crossings at the Fermi level are preserved in the case of a reflection-symmetry-preserving perturbation. Therefore, depending on the symmetry of the perturbation, the perturbed nanotube is either metallic or semiconducting.

With a reflection-symmetry-breaking perturbation,

degeneracies at and near the Fermi level are all split. We can easily conclude that the reflection-symmetry-breaking perturbation renders the nanotube semiconducting. That is true if the perturbation is very weak. However, if the splitting is comparable to the energy difference between two band crossings at the Γ point, which is the distance between U and D in Figure 3(a) for a (6,6) carbon nanotube, there is a possibility that the energy gap closes. To investigate the possible gap closing, we systematically perturb Hamiltonian in our tight-binding model. As we increase the value of the parameter Δ, the distance between U and D decreases, becomes zero, and increases. We define $\Delta_{\text{zero gap}}$ as the parameter Δ for which the distance between U and D becomes zero. That is, the energy band gap closes at $\Delta = \Delta_{\text{zero gap}}$. Figure 3(b) and (c) show electronic band structures of a (6,6) carbon nanotube, which has reflection-symmetry-breaking perturbations per 3 primitive unit cells. The value of the parameter Δ is $\Delta_{\text{zero gap}}$ and $\frac{1}{2}\Delta_{\text{zero gap}}$ in Figure 3(b) and (c), respectively, where $\Delta_{\text{zero gap}}$ is 3.671 eV for the (6,6) carbon nanotube.

Figure 4(b) shows the electronic band structures of the (6,6) carbon nanotube, which has a reflection-symmetry-preserving perturbation per 3 primitive unit cells. We have chosen 3.671 eV for Δ for the calculation of the band structure. The perturbed nanotube with reflection symmetry is metallic as expected. If we apply a symmetry-breaking perturbation and a symmetry-preserving perturbation together, the total perturbation is symmetry-breaking, and we expect an energy band gap opening. Figure 4(c) shows the electronic band structure of the (6,6) carbon nanotube, which has a reflection-symmetry-breaking perturbation and a reflection-symmetry-preserving perturbation on opposite sides per 3 primitive unit cells. We have chosen 3.671 eV

Table 2. Ranges of Δ for energy band gaps of less than 1 meV in very weak perturbations.

Type	3 units	6 units	9 units	12 units	15 units
(3,3)	0.0195	0.0390	0.0586	0.0781	0.0974
(4,4)	0.0266	0.0532	0.0800	0.1063	0.1331
(5,5)	0.0337	0.0674	0.1010	0.1347	0.1681
(6,6)	0.0407	0.0816	0.1224	0.1629	0.2040

Table 3. Ranges of Δ for energy band gaps of less than 1 meV near the Γ point.

Type	3 units	6 units	9 units	12 units	15 units
(3,3)	0.0076	0.0081	0.0089	0.0108	0.0157
(4,4)	0.0125	0.0126	0.0122	0.0122	0.0126
(5,5)	0.0174	0.0172	0.0164	0.0156	0.0152
(6,6)	0.0235	0.0243	0.0228	0.0213	0.0203

for Δ in both the perturbations for the calculation of the band structure, for which the energy band gap opens as expected.

The nanotube in Figure 3 and Figure 4 has a unit cell corresponding to 3 primitive unit cells. We have also calculated $\Delta_{\text{zero gap}}$ for (3,3), (4,4) and (5,5) nanotubes to see the dependence of $\Delta_{\text{zero gap}}$ on the radius of the nanotube. To analyze the dependence of $\Delta_{\text{zero gap}}$ on the period of perturbation, we have performed the following calculations. For each nanotube, we have changed the length of the unit cell in which a perturbation is applied to on bond (bond B in Figure 2) and have calculated $\Delta_{\text{zero gap}}$. Figure 5 shows the plot of $\Delta_{\text{zero gap}}$ versus primitive units per unit cell for each nanotube. The perturbations are of order 1 eV. The values of $\Delta_{\text{zero gap}}$ are larger for smaller radius nanotubes, which is not surprising because curvature effects are larger for smaller radius nanotubes. Note that curvature effects are considered when positions of Fermi points are fitted to those calculated from first-principles. Although $\Delta_{\text{zero gap}}$ increases with primitive units per unit cell, the relation is not linear.

Table 2 and Table 3 summarize the ranges of the perturbation for the energy band gap less than 1 meV. The values indicate the sensitivity of the energy gap closing. In the case of very weak perturbations, the range is roughly proportional to the size of the unit cell, and the ratio of the range to the size is about 20 meV per 36 atoms. In the case of the energy gaps at the Γ point, the range is about $8 \sim 24$ meV, and the range is not proportional to the size of the unit cell.

If carbon nanotubes are perturbed periodically, the electronic band structure can be manipulated in a very interesting manner. Although we focus on local periodic perturbations, carbon nanotubes can also be perturbed by substrates, external fields, other nanotubes, and so on. Depending on the symmetry and the spatial period of the perturbation, the electronic properties of carbon nanotubes may dramatically change. Therefore, the properties may be exploited for specific nano-electronic device applications or nano-sensor applications.

IV. CONCLUSIONS

The tight-binding electronic band structures of small-radius (n,n) armchair carbon nanotubes are calculated. The periodic local perturbations, which break reflection symmetry, open energy band gaps. The gap closes for an appropriate perturbation. We have calculated perturbations for the band crossings at the Fermi level at the Γ point with selected spatial periods. We find relations among perturbations, unit cell sizes, and the radii of the nanotubes. Our findings can be used for further nano-device applications.

ACKNOWLEDGMENTS

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