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Electronic band structure of doped single-walled carbon nanotube of small diameter

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We briefly visit the extended Su-Schrieffer-Heeger(SSH) model Hamitonian for different geometries that that of graphene and carbon nanotubes. Electron doping has become accessible to model Hamiltonian, furnishing us with simpler example of doped systems in carbon nanotubes. The electronic structures of carbon nanotubes vary as the number of electron increases. The energy gap values decrease as electron doping increases for weakly doped case. However, in the system doped with five and six electrons, the energy gap narrowing almost stops and is rather negligible in further heavily doped cases.

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1. Introduction

Over the years, nanoscale materials have exhibited a number of outstanding properties from both theoretical and experimental point of view in various fields and will be studied extensively as long as the demand of device prevails and finally becomes negligible with the emerging for future technologies. The first step in this field has been taken by Iijima [1] who has discovered carbon nanotubes attracting much attention due to their unusual features. Carbon nanotubes are quasi-one-dimensional materials made by graphite sheet twisted up into cylinder with a narrow size diameter on nanoscale. A variety of carbon nanotubes are produced from some type of hybridized orbitals that a carbon atom can form. Carbon nanotubes are also constructed by sp^2-hybridized network: the three hybridized orbitals that consist of one 2s orbital and two-2p orbitals and those three orbital are arranged in one plane and extended in the direction of each apex of a regular triangle. Electronic structure of a single-walled carbon nanotube (SWCNT) can be determined in terms of a pair of integers (n,m): zigzag and armchair are named for m=0 and m=n, respectively. The zigzag nanotubes show semi-metallic character unless n-m is divisible by three while armchair nanotubes show entirely metallic character in which n-m either divisible or not divisible by three. Similarly multi-walled carbon nanotubes (MWCNT) can be formed by a few stacked graphite sheets [2].

The fascinating electronic and transport properties of doped carbon nanotubes clearly make them an important building block in applications. The controlled p-n doping and reversible adsorption-desorption of gas molecules, which strongly interact with nanotubes electronic states, are key issues in obtaining the carbon nanotube-based devices with desirable material [3]; whereas the overall mechanical and electronic properties of the pristine nanotubes are basically preserved after doping. Doping on carbon nanotubes neither destroys the hexagonal graphene carbon network nor demolishes the electronic band structures, although the local geometric structure near the doping site and the electronic properties around Fermi level could be significantly modified by: shifting the position of Fermi level, changing energy gap width, introducing impurity states in the region of Fermi level, leading to spin-polarized electron density of state at Fermi level and some others as following; constituting p–n junctions, enhancing or weakening the electron resistance, enhancing the third-order optical nonlinearity, etc [4].

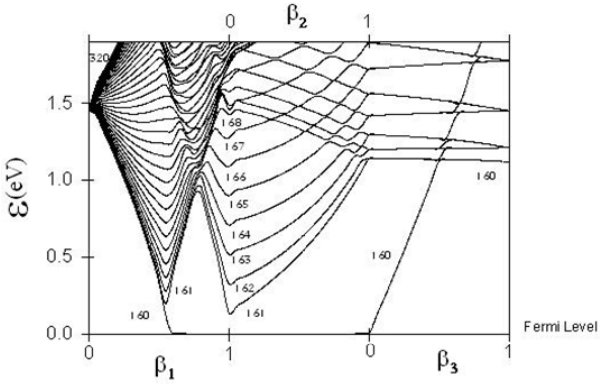

Fig. 1. Electronic band structure evaluation from graphene to open ended (4,0) SWCNT and to (4,0) SWCNT with periodic boundary condition for N=8 and K=40 containing 320-carbon atoms with no doping (N_e=N). Numbers, βs, abscissa axis (bottom line) and lines represent states, fractional values of hopping integral, Fermi Energy Level and eigenvalues, respectively.

In particular, the idea of doping carbon nanotubes is taken up with the nanometals, alkali metals, transition metals, and clusters in theoretical and experimental studies [5,6]. The best method to alter the electronic properties of nanostructures is to dope them, which assist removal of electrons from the fullerene molecules or nanotubes; the most commonly used form of doping is known as intercalation (or exohedral doping). Alkali metal intercalated C_{60} compounds exhibit metallic conductivity and superconductivity at transition temperatures can only be improved by the high temperature superconductors. The alkali metals (Na, K, Rb, Cs) are typical electron donors and much of the work on doped fullerenes to date has been carried out on the alkali metal intercalation compounds of C_{60} and C_{70} [7-10].

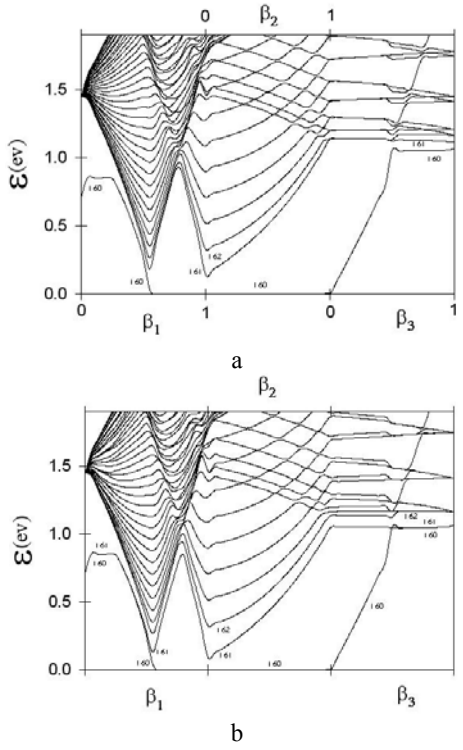

Fig. 2. Weakly doped cases for a) N_e=1 and b) N_e=2.

In the present paper, we have mainly discussed the electronic properties of the doped small diameter (4,0) carbon nanotube. It is well known that the geometrical structure of the doped system influences their electronic structures and vice versa. In order to deal with this problem, we work with extended Su-Schrieffer-Heeger(SSH) Model Hamitonian which is a so-called tight-binding calculation [11] and then we start to form open-ended (4,0) nanotube by gradually twisting the graphite sheet. In addition, we create the (4,0) nanotube with periodic conditions when open-ended (4,0) turns to be an infinitely long tube. Moreover, to observe the formation of each shape, we consider fractional value of a parameter which leads to continuous evaluation from geometry to geometry. Finally, we will discuss the electronic structure of (4,0) nanotube as a typical thin nanotube with and without electrons doping.

2. Method

The well-known extended SSH Model Hamiltonian for carbon nanotubes is given by

$$H_{SSH} = \sum_{\langle i,j\rangle,\sigma} \left[-t_0 + \alpha\left(u_i^{(j)} - u_j^{(i)}\right)\right]\left(c_{i,\sigma}^{+} c_{j,\sigma} + h.c.\right) + \frac{\kappa}{2}\sum_{\langle i,j\rangle}\left(u_i^{(j)} - u_j^{(i)}\right)^2 \tag{1}$$

where $<i,j>$ is the nearest-neighbor carbon–carbon atom pairs and t_0 is the hopping integral of the undimerized system. The second term represents the dimerization due to σ skeleton with free involving π-electrons. α and κ are the electron-lattice coupling and effective spring constant, respectively. The operator $c_{i,\sigma}^{+}(c_{i,\sigma})$ creates (annihilates) a π-electron at the *i*-th carbon atom with spinσ. The quantity, $u_i^{(j)} - u_j^{(i)}$, is the change of the length of the bond between *i*- and *j*-th atoms.

The total energy of the system

$$E_T = \sum_{i,\sigma}{}' \varepsilon_{i,\sigma} + \frac{1}{2\gamma}\sum_i v_i^2 \tag{2}$$

where $\varepsilon_{j,\sigma}s$, are the eigenvalues of Hamiltonian and the self-consistent equation for the lattice is read as

$$v_i = 2\gamma\left[\frac{\alpha C}{\gamma} + \sum_{j,\sigma}{}' B_{i+1,j,\sigma}^{+} B_{i,j,\sigma}\right] \tag{3}$$

In Eq. (3), the **B**s are the eigenvectors of the Hamiltonian and $\gamma = \alpha^2/\kappa$. By summing up both sides of Eq.(3) with the condition $\sum v_i = 0$ we obtain

$$C = \frac{1}{N_b}\frac{\gamma}{\alpha}\sum_{j,\sigma}{}' B_{i+1,j,\sigma}^{+} B_{i,j,\sigma} \tag{4}$$

which is called Lagrangian multiplier. In Eq. (4), the prime indicates the sum over the occupied states of electrons and N_b is the total number of π-bonds. Number of electron N_e in doping is varied within $N_e \le N + 6$ in which *N* is the number of carbon atoms of (4,0) and we calculate for all the possible N_e. The numerical calculation procedure is as follow: **1)** The extended SSH Hamiltonian matrix given by Eq.(1) is calculated with arbitrary initial values of v_i's **2)** By substituting Hamiltonian into the Schrödringer's equation one finds $\varepsilon_{j,\sigma}s$ and **B**s. **3)** Eqs.(2)-(4) are numerically calculated. **4)** The calculations in the first and

third procedures are repeated until the difference between the two successive iterations of v_i values becomes sufficiently small as $\leq 10^{-6}$.

3. Results and discussion

On a more geometrical framework, the connection between trans-polyacetylene (t-PA) and graphene geometry is needed in order to get further insight as a form of continuous evaluation. The graphene is created by parallel t-PA that has a zigzag structure with interchain coupling. Let N and K be the number of sites at the zigzag edge and rows along the width and length of graphene, respectively. In this case, the diameter and the length of nanotube are represented by the integers N and K. We introduced three β parameters, β_1, β_2 and β_3, varying within smoothly between 0 and 1. In order to get continuous evaluation we multiplied the hopping integral by those parameters, that responsible for graphene, open-ended (4,0) nanotube and (4,0) nanotube with periodic boundary condition. Another way of expressing the evaluation is as follow: Formation of graphene starts with β_1=0 and ends up with β_1=1 while β_2=β_3=0. Twisting graphene takes the form of open-ended nanotube with β_1=1 and β_2=0 and stops at β_1=β_2=1 while β_3=0. As we increase β_3 from 0 to 1, keeping β_1=β_2=1, open-ended nanotube converts a tube with periodic boundary conditions and the entire process is completed at β_1=β_2=β_3=1.

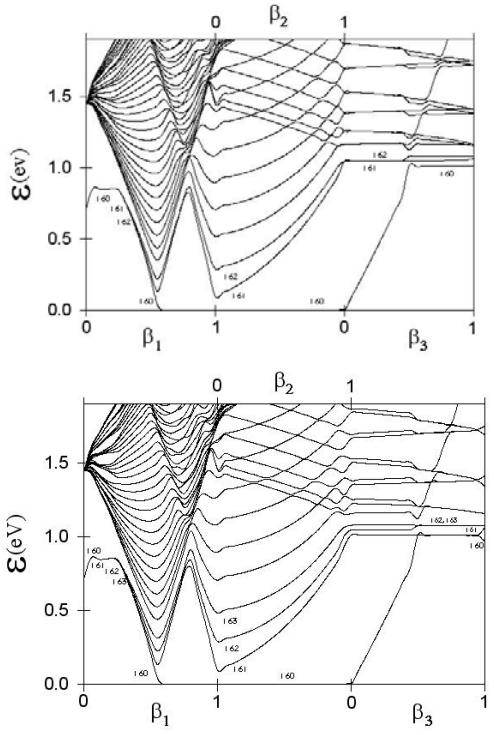

Fig. 3. Heavily doped cases for a) N_e=3 and b) N_e=4.

It is well-known that the lattice and electronic structures of carbon nanotubes change to a great extent when the number of carbon atoms increases. In the calculation, we take N=8 and K=40 for (4,0) SWCNT containing 320-carbon atoms. We first compute the energy-band gap in the conventional case of graphene, open-ended (4,0) nanotube and (4,0) nanotube with periodic boundary condition without doping by taking t_0, α and κ as 2.5 eV, 6.31 eV/Å and 49.7 eV/ Å^2 [12]. It is worth mentioning that these parameters are the same for those of three geometries since the origin of the parameter is the same. Fig.1 depicts the plot of the obtained band structures for graphene and (4,0) SWCNTs. To summarize it: a part of energy-band gap close to Fermi level was taken. In the figure, the ordinate axis is represented by eigenvalues of the Hamiltonian. This real space representation has 320-state. However, here, only half of the entire states appear since Hamiltonian is completely symmetric. Moreover, the energy gap is defined as the difference between the minimum of eigenvalues of lowest unoccupied molecular orbital (LUMO) and the maximum of those of highest occupied molecular orbital (HOMO) states. In all figures, as a matter of fact, we interpret only LUMO and Fermi energy levels from the point of view of the energy band gap. There are no localized states when all states start at $\beta_{1,2,3}$=0. Later, two sates 160th from LUMO and 159th from HOMO meet at Fermi level for β_1=0.6. These energy levels split and 160th and 159th become delocalize at β_1=β_2=1 and β_3=0. Hereafter, the numbered states 160 and 161 meet at β_1=β_2=1 and β_3=0.55 and assemble downward from LUMO. The gap as larger that found in an insulator is about 2x1.1169 eV [2,8].

To understand the effect of electron doping, first we dope (4,0) with an electron. The energy spectra of doped (4,0) structure is compared as depicted in Fig. 2(a). The state 160 splits downward from states, in which all states start from the same point, and get closer to Fermi level at $\beta_{1,2,3}$=0. The 160th state drops to zero, which is a Fermi energy level at β_1=0.6. At this point between the two states being 161 and 158, the energy difference is about 0.7546eV while both states differences remain as 0.2804 eV at β_1=1 and β_2=β_3=0 similar to undoped case. Some localized states appear in the system when they start to convert the open-ended tubes to the tube with periodic boundary condition at β_1=β_2=1 and β_3=0.0 while the states 159 and 160 splits from each other and are delocalized. The state 160 ends up at $\beta_{1,2,3}$=1 and constitutes one part of energy band gap, and the energy level differences between 159th and 160th is 2.1304 eV, which is a so-called gap value.

Doping with one or two electrons is sometimes known as weakly doped system [8-10]. We now dope the system with two-electrons as the doping proceeds further. Two bunch of energy level structure appear at the beginning of the evaluation, that is, $\beta_{1,2,3}$=0 and both states 160 and 161 become localized until β_1=0.45 and β_2=β_3=0 as shown in Fig. 2(b). State 161 goes back to the LUMO level while 160th state goes down to Fermi level. Minimum energy gap is about 0.2582 eV at β_1=0.55 and β_2=β_3=0 exclusion of the state 160. The state 150 and 160 are delocalized

between β_1=0.55, β_2=β_3=0 and β_1=β_2=1 and β_3=0.05. On the other hand, state 161 makes contribution to energy gap as lower as possible about 0.183 eV. Those state 160 and 161 meet at β_1=β_2=1 and β_3=0.45 and become delocalized until β_3=1 in which energy gap is about 2.1262 eV. It is noticed that the gap values decreases as the electron doping increases at $\beta_{1,2,3}$=1.

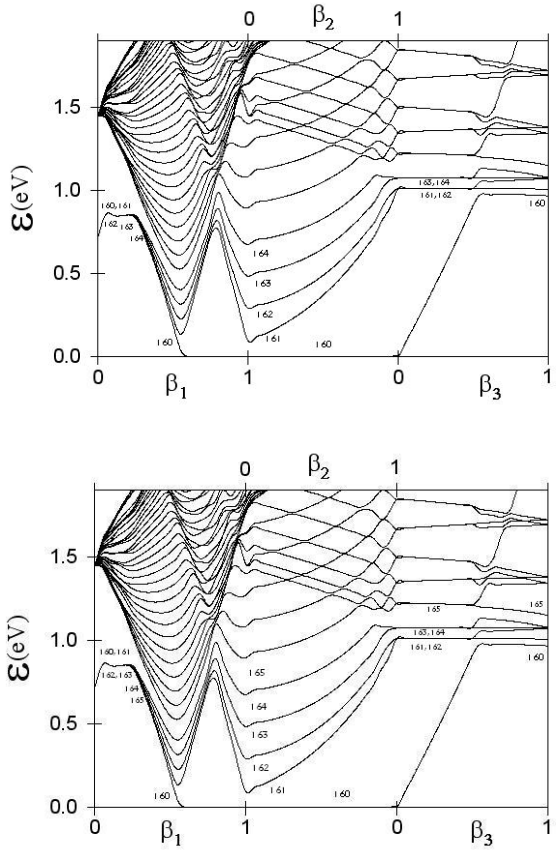

Fig. 4. Most heavily doped cases for a) N_e=5 and b) N_e=6.

Let us now consider one of the heavily doped systems with the inclusion of three electrons as seen in Fig. 3(a). It is worth mentioning that the position of new bunch of states does not change any further after one-electron doping. Thus, those three states, collectively at $\beta_{1,2,3}$=0 with the energy gap value being about 1.4344 eV correspond to t-PA. States 160, 161 and 162 are now localized states until β_1=0.40 and β_2=β_3=0. As a matter of fact, 161th and 162nd are delocalized states until β_1=β_2=1 and β_3=0 and become delocalized state at β_1=β_2=1 and β_3=0.45. On the other hand, 159th and 160th states become localized between β_1=0.6, β_2=β_3=0 and β_1=β_2=1,β_3=0.05. In addition to it, the energy gap contribution from the state 161 is about 0.2634 eV at β_1=0.55 and β_2=β_3=0 without state 160. When we go further, the gap value gets smaller as 2.0198 eV and the contribution to the gap value is specifically obtained from state 160, but the order of the energy value difference close to LUMO is very small.

We can now dope the system with four electrons to obtain changes in the electronic structure of graphene and (4,0) SWCNTs. In Fig. 3(b), four states 160-163 begin from the same point at β_1=β_2=β_3=0 and those states are localized up to β_1=0.25 and β_2=β_3=0. After that point, state 160 goes down to Fermi level and meets state 159 at β_1=0.60 and β_2=β_3=0 and then go further together up to β_1=β_2=1 and β_3=0.5. Delocalization ends up for 159th and 160th state between β_1=β_2=1 and β_3=0.05-0.45 but states 160 and 161 are localized at β_1=β_2=1 and β_3=0.45 and are delocalized at β_1=β_2=1 and β_3=0.95. When the open ended tube is converted to the tube with periodic boundary condition at $\beta_{1,2,3}$=1, the contribution of energy gap values comes from state 160 with very small difference as compared to state 161, which is about 1.9382 eV.

Here, we are going to consider both doping cases since there are no significant differences between doping the system with five and six electrons. In case of five electrons doping as depicted in Fig.4(a), five states start together as localized states at $\beta_{1,2,3}$=0 and split as a delocalized sates with β_1=0.3 and β_2=β_3=0. This is not changed when the system is doped with six electrons as shown in Fig. 4(b). In both cases, the energy gap value is obtained 1.9352 eV, which corresponds to the difference between the states 159(lower part of Fermi level) and 160 (upper part of Fermi level). It can be easily noticed that there is no significant gap value difference between four and more electron doping. We hence believe that on a more pure treatment, the connection between four and more electron doping is not needed in order to get further insight into the form of electronic structure of (4,0) SWCNT.

4. Conclusions

In the present paper, we have discussed some progress on the experimental and theoretical studies of carbon nanotubes doped with electron that never cease to cause excitement on the electronic properties of the system. Doped and undoped graphene, open ended (4,0) and (4,0) SWCNT with periodic boundary condition for those containing 320 carbon atoms in evaluation process from geometry to geometry is investigated within the framework of extended SSH model Hamiltonian. Effect of electron doping in (4,0) strongly relates to its electronic structure. Doping of electrons in carbon nanotubes appears to be exerted through different doping ratio. Hence, we first considered a weakly doped case for one and two electrons and then a significantly larger case consisting of three to six electrons. It should be mentioned that doping also results in narrowing the HOMO-LUMO gap. Behavior of electronic structure of (4,0) SWCNT from the energy gap point of view is not markedly different for the five and six electrons doping rate when the system is considered with periodic boundary conditions. No change in the type of electronic structure of (4,0) has been observed which still shows a semiconductor character. In

addition to this, there is a lack of detailed understanding of bond distortion of evaluation geometry of SWCNTs with and without electron doping for future work.

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