

The adsorption effect of C₆H₅ on density of states for double wall carbon nanotubes by tight binding model

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A theoretical approach based on a tight-binding model is developed to study the effects of the adsorption of finite concentrations of C₆H₅ gas molecules on double-walled carbon nanotube (DWCNT) electronic properties. To obtain proper hopping integrals and random on-site energies for the case of one molecule adsorption, the local density of states for various hopping integrals and random on-site energies are calculated. Since C₆H₅ molecule is a donor with respect to the carbon nanotubes and their states should appear near the conduction band of the system, effects of various hopping integral deviations and on-site energies for one molecule adsorption are considered to find proper hopping and on-site energies consistent with expected *n*-type semiconductor. We found that adsorption of C₆H₅ gas molecules could lead to a (8.0)@(20.0) DWCNT *n*-type semiconductor. The width of impurity adsorbed gas states in the density of states could be controlled by adsorbed gas concentration.

1. Introduction

Carbon nanotubes (CNTs) are cylindrical rolled hexagonal lattices of carbon atoms [1], where the synthesized CNTs show an unusual combination of a nanometer-size diameter and millimeter length. This topology, combined with absence of defects on a macroscopic scale, gives rise to uncommon electronic properties of individual single wall carbon nanotubes (SWCNTs) including nanoelectronic devices, energy storage, chemical probes and biosensors [2–4]. Gas adsorption of CNTs (for both SWCNTs and double-walled carbon nanotube (DWCNTs)) is an important subject for both fundamental research and technical application of nanotubes. The adsorption of chemical gas species is the main ingredient for many of these applications. For example, it has been found experimentally and theoretically that SWCNT transport properties changed upon exposure to O₂, H₂, NO₂, NH₃, COOH and to some benzene compounds [5–10]. Upon exposure to these gases, the electrical conductance of the semiconducting tubes are changed. The sensitivity of SWCNTs to these materials combined with their inherent characteristics such as their small size, good electrical and mechanical properties and also high interacting SWCNTs surface with gas molecule have led to envision their application in the nano sensors and in the immobilization of biological substances, and in their use as functionalized materials [11–16]. Adsorption effects of these gas molecules on electronic properties of SWCNTs are relatively weak. Theoretically it is shown that the O₂ adsorption has significant effects on the electronic properties of small semiconducting nanotubes, for example the electrical conductivity increases [17]. But adsorption of gas molecules by DWCNTs is not yet investigated based on

tight binding model. In this paper, by using the tight binding model we have investigated effects of gas adsorption on the electronic properties of DWCNTs.

The paper organized as following. In Sec. 2 model and method of calculation is introduced. In Sec. 3 we discuss our results and finally last section is conclusion.

2. Model and formalism

Let us consider the Hamiltonian as a general random tight-binding model [18],

$$H = - \sum_{ij\alpha\beta} t_{ij}^{\alpha\beta} c_i^{\alpha\dagger} c_j^{\beta} + \sum_{i\alpha} (\epsilon_i^{\alpha} - \mu) \hat{n}_i^{\alpha}. \quad (1)$$

where α and β refer to the A_1, A_2, \dots, A_{12} or B_1, B_2, \dots, B_{12} subsites inside of the unit cell.

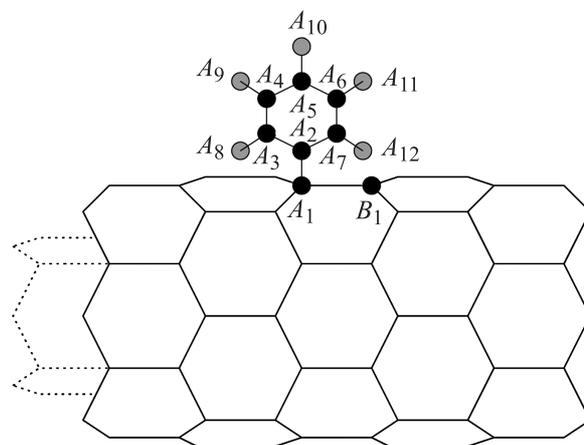


Figure 1. General form of the C₆H₅ molecule gas adsorption by outer layer of DWCNT.

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The A₁ and B₁ refer to 2 nonequivalent carbon subsites of outer wall of DWCNT. The A₂, . . . , A₁₂ or B₂, . . . , B₁₂ refer to carbon and hydrogen atoms of C₆H₅ adsorbed molecule on subsites A or B. Fig. 1 illustrate adsorbed one molecule C₆H₅ on a (5.0)@(10.0) DWCNT. C_i^{α†} (c_i^α) is the creation (annihilation) operator of an π-electron on Bravais lattice site i, and n̂_i^α = c_i^{α†} c_i^α is the electron number operator. t_{ij}^{αβ} are the hopping integrals between π orbital's of sites i and j. μ is the chemical potential, ε_i^α is the random on-site energy. An SWCNT can be constructing by role up a 2-dimensional (2d) graphene sheet in some specified directions with the periodic boundary condition along the circumference direction [19–20]. Following this, rolling up chiral vector **L** has been fixed on the x-axes of the 2d graphene sheet, hence the CNT axes is coincident on the y-axes. Therefore the real lattice primitive vectors **a**₁ and **a**₂ and their corresponding reciprocal lattice primitive vectors **b**₁ and **b**₂ for a zigzag SWCNT are,

$$\begin{aligned} \mathbf{a}_1 &= a\mathbf{i}, & \mathbf{a}_2 &= \frac{a}{2}(-\mathbf{i} + \sqrt{3}\mathbf{j}), \\ \mathbf{b}_1 &= \frac{2\pi}{a}\left(\mathbf{i} + \frac{\mathbf{j}}{\sqrt{3}}\right), & \mathbf{b}_2 &= \frac{2\mathbf{j}}{\sqrt{3}}\frac{2\pi}{a} \end{aligned} \quad (2)$$

where **i** and **j** are the unit vectors of the x–y graphene plane and a = |**a**₁|. The periodic boundary condition in the x direction imply that,

$$\exp(ik_x L) = 1, \quad (3)$$

where L is the length of the chiral vector, L = |**L**|. For a zigzag SWCNT L = na and for an armchair is L = √3na. So the periodicity condition Eq. 3 imply that the x component of the wave vectors, k_x, is restricted to,

$$k_x = \frac{2\pi m}{L}. \quad (4)$$

where m is an integer number. The equation of motion for electrons with the above Hamiltonian (Eq. 1) in terms of the Green function is,

$$\sum_i ((E\mathbf{I} - \varepsilon_i + \mathbf{I}\mu_i)\delta_{il} + \mathbf{t}_{ij})\hat{\mathbf{G}}(l, j; E) = \mathbf{I}\delta_{ij}, \quad (5)$$

where $\hat{\mathbf{G}}(i, j; E)$ is the random Green's function matrix. For adsorption of C₆H₅ gas molecule, Green's function is defined as

$$\mathbf{G}(i, j; E) = \begin{pmatrix} G_{i11j11}^{A_1A_1} & G_{i11j11}^{A_1A_2} & \dots & G_{i11j22}^{A_1B_{12}} \\ \vdots & \ddots & \dots & \vdots \\ \vdots & \dots & \ddots & \vdots \\ G_{i22j11}^{B_{12}A_1} & G_{i22j11}^{B_{12}A_2} & \dots & G_{i22j22}^{B_{12}B_{12}} \end{pmatrix}_{72 \times 72}. \quad (6)$$

Let us take the chemical potential, μ = 0, which is corresponding to contribution of one electron per carbon atom

in carbon nanotube. Just nearest neighbors are allowed and neglected others, so the nonzero elements of hopping matrix are t_(ij)^{A₁B₁} = t_(ij)^{B₁A₁} = t.

Since in Eq. 5, the random Green function matrix. $\hat{\mathbf{G}}(i, j; E)$, could not be calculated exactly, hence the full random Green function matrix $\hat{\mathbf{G}}^0(i, j, E)$ should expanded in terms of clean Green function matrix $\hat{\mathbf{G}}^0(i, j, E)$ and random potential,

$$\hat{\mathbf{G}}(i, j; E) = \hat{\mathbf{G}}^0(i, l; E)\hat{\mathbf{V}}_{ls}\hat{\mathbf{G}}(s, j; E). \quad (7)$$

where $\hat{\mathbf{G}}_0(i, j; E)$ is given by,

$$\hat{\mathbf{G}}^0(i, j; E) = \frac{2}{N} \sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}_{ij}} (E\hat{\mathbf{I}} - \hat{\varepsilon}_{\mathbf{k}} + \mu\hat{\mathbf{I}})^{-1}. \quad (8)$$

where **r**_{ij}'s are three vectors that connect an A(B) site to its nearest neighbor B(A) site (Fig. 1), ε_k is the band structure of system and random potential matrix **V**_{ls} is defined by, $\hat{\mathbf{V}}_{ls} = \hat{\varepsilon}_l\delta_{ls} + \delta\hat{\varepsilon}_{ls}$, where δt_{ls} = t̂_{ls}t̂_{ls}⁰ is the hopping integral matrix deviation with respect to the clean system. For adsorption of C₆H₅ gas molecule. If in random potential matrix hopping to the nearest neighbors is allowed and if the molecule is adsorbed by A₁ subsites, the random potential matrix is given by,

$$\mathbf{V}_{ls} = \begin{pmatrix} (\mathbf{V}_1)_{24 \times 24} & (\mathbf{V}_2)_{24 \times 24} & (\mathbf{V}_3)_{24 \times 24} \\ (\mathbf{V}_4)_{24 \times 24} & (\mathbf{V}_5)_{24 \times 24} & (\mathbf{V}_6)_{24 \times 24} \\ (\mathbf{V}_7)_{24 \times 24} & (\mathbf{V}_8)_{24 \times 24} & (\mathbf{V}_9)_{24 \times 24} \end{pmatrix} \quad (9)$$

where **V**_{5ls} ≠ 0 and other arrays are zero. **V**_{5ls} is defined by,

$$\mathbf{V}_{5ls} = \begin{pmatrix} \mathbf{a} & \mathbf{b} \\ \mathbf{c} & \mathbf{d} \end{pmatrix}, \quad (10)$$

where **a** ≠ 0 and other arrays are zero. The random potential matrix **a** can be written as

$$\mathbf{a} = \begin{pmatrix} 0 & \delta_1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ \delta_1 & \varepsilon & \delta_2 & 0 & 0 & 0 & \delta_2 & 0 & 0 & 0 & 0 & 0 \\ 0 & \delta_2 & \varepsilon & \delta_2 & 0 & 0 & 0 & \delta_3 & 0 & 0 & 0 & 0 \\ 0 & 0 & \delta_2 & \varepsilon & \delta_2 & 0 & 0 & 0 & \delta_3 & 0 & 0 & 0 \\ 0 & 0 & 0 & \delta_2 & \varepsilon & \delta_2 & 0 & 0 & 0 & \delta_3 & 0 & 0 \\ 0 & \delta_2 & 0 & 0 & 0 & \delta_2 & \varepsilon & 0 & 0 & 0 & 0 & \delta_3 \\ 0 & 0 & \delta_3 & 0 & 0 & 0 & 0 & \varepsilon & \delta_4 & 0 & 0 & 0 \\ 0 & 0 & 0 & \delta_3 & 0 & 0 & 0 & \delta_4 & \varepsilon & \delta_4 & 0 & 0 \\ 0 & 0 & 0 & 0 & \delta_3 & 0 & 0 & 0 & \delta_4 & \varepsilon & \delta_4 & 0 \\ 0 & 0 & 0 & 0 & 0 & \delta_3 & 0 & 0 & 0 & \delta_4 & \varepsilon & \delta_4 \\ 0 & 0 & 0 & 0 & 0 & 0 & \delta_3 & 0 & 0 & 0 & \delta_4 & \varepsilon \end{pmatrix} \quad (11)$$

where

$$\begin{aligned} \delta_1 &= \delta t_{(ij)}^{A_1A_2} = \delta t_{(ij)}^{A_2A_1}, \\ \delta_2 &= \delta t_{(ij)}^{A_2A_3} = \delta t_{(ij)}^{A_3A_2} = \delta t_{(ij)}^{A_3A_4} = \delta t_{(ij)}^{A_4A_3} = \delta t_{(ij)}^{A_4A_5} = \delta t_{(ij)}^{A_5A_4} \\ &= \delta t_{(ij)}^{A_5A_6} = \delta t_{(ij)}^{A_6A_5} = \delta t_{(ij)}^{A_6A_7} = \delta t_{(ij)}^{A_7A_6} = \delta t_{(ij)}^{A_7A_2} = \delta t_{(ij)}^{A_2A_7} =, \end{aligned}$$

$$\begin{aligned}\delta_3 &= \delta t_{(ij)}^{A_3A_8} = \delta t_{(ij)}^{A_8A_3} = \delta t_{(ij)}^{A_4A_9} = \delta t_{(ij)}^{A_9A_4} = \delta t_{(ij)}^{A_5A_{10}} = \delta t_{(ij)}^{A_{10}A_5} \\ &= \delta t_{(ij)}^{A_6A_{11}} = \delta t_{(ij)}^{A_{11}A_6} = \delta t_{(ij)}^{A_7A_{12}} = \delta t_{(ij)}^{A_{12}A_7}\end{aligned}$$

and

$$\begin{aligned}\delta_4 &= \delta t_{(ij)}^{A_8A_9} = \delta t_{(ij)}^{A_9A_8} = \delta t_{(ij)}^{A_9A_{10}} = \delta t_{(ij)}^{A_{10}A_9} = \delta t_{(ij)}^{A_{10}A_{11}} = \delta t_{(ij)}^{A_{11}A_{10}} \\ &= \delta t_{(ij)}^{A_{11}A_{12}} = \delta t_{(ij)}^{A_{12}A_{11}}.\end{aligned}$$

Also ϵ is difference between on-site energies of host carbon and adsorbed gas molecules.

The Green function $\hat{G}(i, j; E)$ could be expanded in terms of clean system Green function $\hat{G}^0(i, j; E)$ as,

$$\hat{G}(i, j; E) = \hat{G}^0(i, j; E) + \hat{G}^0(i, 0; E)\hat{V}_{00}\hat{G}(0, j; E). \quad (12)$$

Eqs (8) and (12) should be solved to obtain the Green function $\hat{G}(i, j; E)$, hence density of states at adsorbed site and host sites could be obtained by $N_1(E) = -\frac{1}{\pi} \text{Im} G^{A_1A_1}(i, i; E)$ and $N_2(E) = -\frac{1}{\pi} \text{Im} G^{B_1B_1}(i, i; E)$ respectively.

3. Results and discussion

As we mentioned in the previous sections, the gas molecules are adsorbed randomly by the DWCNT atoms, so Green's function should be calculated in the configurational average method. By calculation of the average Green's function in the tight-binding model (Eq. 1). The effects of finite C_6H_5 gas molecule adsorption on the electronic properties of (8,0)@(20,0) DWCNT is studied. To compare our conclusions with some theoretical and experimental results, we vary the hopping integral deviations and on-site energies. Also we set hopping integral deviations and on-site energies for C_6H_5 gas molecule as charge donors. Then using these parameters we investigate the effects of finite gas molecule adsorption on the electronic properties of (8,0)@(20,0) DWCNT. Fig. 2 illustrates the comparison of the local density of states of pure (8,0)@(20,0) DWCNT, with the case that A_1 subsite adsorbed one C_6H_5 molecule. Since the C_6H_5 molecule is a donor with respect to the CNTs and their states should appear near the conduction band of the system, so various hopping deviations and on-site energies are examined and we found just for two following cases the system became a n -type semiconductor, first case, $\delta_1 = -0.1t$, $\delta_2 = -0.1t$, $\delta_3 = 0.2t$, $\delta_4 = 0.2t$ and $\epsilon = 0.14t$, and the second case $\delta_2 = 0.2t$, $\delta_3 = -0.2t$, $\delta_4 = -0.2t$, and $\epsilon = 0.14t$.

4. Conclusions

By calculation of the local density of states in the tight binding model, effects of C_6H_5 gas molecule adsorption on the electronic properties of a (8,0)@(20,0) DWCNT. To find proper hopping and on-site energies consistent with expected n -type semiconductor, effects of various hopping integral deviations and on-site energies for one molecule

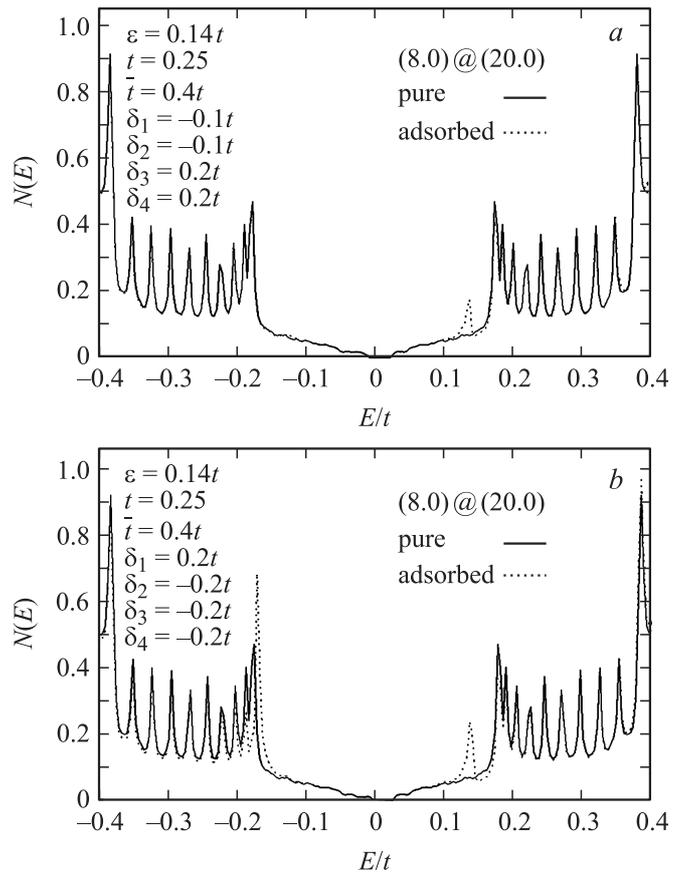


Figure 2. Comparison of the local density of states of a pure (8,0)@(20,0) DWCNT with respect to the local density of states of A_1 subsite, where a C_6H_5 gas molecule is adsorbed. The hopping deviation and on-site energy are chosen to be a — $\delta_1 = -0.1t$, $\delta_2 = -0.1t$, $\delta_3 = 0.2t$, $\delta_4 = 0.2t$, and $\epsilon = 0.14t$, b — $\delta_1 = 0.2t$, $\delta_2 = -0.2t$, $\delta_3 = -0.2t$, $\delta_4 = -0.2t$, and $\epsilon = 0.14t$, respectively. In this case, a n -type semiconducting DWCNT has been produced.

adsorption are considered. We found that the adsorption of C_6H_5 on the (8,0)@(20,0) could produce a n -type semiconductor.

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