

BALLISTIC CONDUCTANCE OF A SWNT WITH A POSITIVE CHARGE AT ITS SURFACE

Slava V. Rotkin*, Ilya Zharov

Beckman Institute, University of Illinois at Urbana-Champaign, 405 N.Mathews, Urbana,
IL 61801, USA

E-mail: rotkin@uiuc.edu

Ballistic conductance calculations for a semiconductor p-doped single-wall carbon nanotube have been performed using a combined multiscale approach. A modulation of the transport due to a charge placed near the surface of the nanotube was calculated. A selfconsistent potential obtained results in forming of a barrier for carriers. An example of nanotube-ammonium ion complex is studied in details.

I. INTRODUCTION

The use of carbon nanotubes for nanoelectronics has been recently demonstrated [1], [2]. The success in creating these field effect devices motivated further studies of electrochemical and chemical analogues [14,15]. In the present work we have simulated the modification of the conductance of a single-wall carbon nanotube (SWNT) by applying a local electric field of a charge placed near the surface of the nanotube. The difference between our calculations and what has been previously done is in performing *a full selfconsistent electrostatics calculation* for the SWNT electronic structure which allows to obtain a more precise band bending picture at the equilibrium in a continuum approximation.

This paper presents the calculations of a ballistic conductance for a zigzag SWNT whose valence band bends due to an external electrical potential created by a single charge near the SWNT surface. We considered the p-doped SWNT because this type of doping is widely observed experimentally. The external potential creates a barrier for the holes to penetrate on their way from one end of the nanotube device to the other. The hole transmission coefficient is calculated quantum mechanically taking into account the semiclassical tunneling. It is not possible to treat the whole problem with the same level of accuracy (at the same level of the theory complexity) because (a) the system size is too large to implement a full quantum mechanics description, (b) the system does not remain in the ground state and, therefore, it requires selfconsistent modeling, and (c) interactions between subsystems (which are the charge and the SWNT) are not necessarily weak, which prohibits the use of continuum modeling at every step. Thus, the problem must be solved within a multiscale approach: (i)

*On leave from Ioffe Institute, 26 Politekhnicheskaya st., St.Petersburg 194021, Russia

the geometry of the charged molecule - SWNT complex, its electronic structure and charge transfer are studied with *ab initio* methods, (ii) the electronic structure of the SWNT is calculated within a tight-binding approximation (TBA), (iii) the tunneling and transmission coefficients are computed within semiclassical WKB approximation and (iv) the response function of the nanotube is calculated selfconsistently within a continuum statistical model.

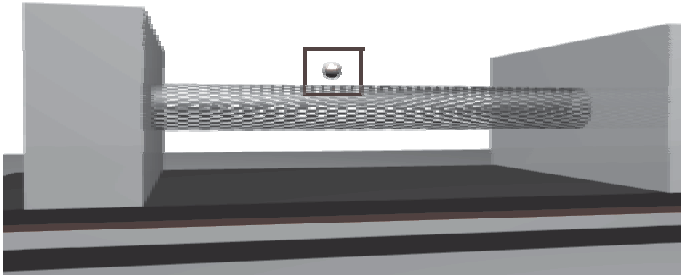


FIG. 1. Transport device discussed in the paper: a charged impurity is placed on the sidewall of a SWNT and may modify a current through the nanotube.

II. CHARGED COMPLEX MODELING

To obtain an accurate geometrical and electronic description of a charged molecule interacting with SWNT surface a high level of theory is desired. However, *ab initio* and DFT methods are presently too expensive to allow routine calculations of such large molecular systems as SWNTs. Therefore, we used the ONIOM approach [3,4], which consists of dividing a large molecular system into two or three levels, where a relatively small section essential for a SWNT property of interest is treated at a higher level of theory, while the remaining one or two serve mostly to constrain the general geometry and are described by a computationally less demanding method (molecular mechanics or semiempirical methods) [3,4]. Recently, the ONIOM approach was used to study the addition of hydrogen and fluorine atoms to zigzag [10,0] and armchair [4,4] SWNT side walls [5–7] and the amidation of terminal carboxylic groups of SWNTs [8]. In those works, the high level description of the reaction site was performed with the B3LYP DFT method in combination with 4-31G, 6-31G(d), or 6-311G(d) basis sets, and the low level was treated with the universal force field (UFF) [9] molecular mechanics method.

In the present work we studied the interaction of charged molecules with side-walls of zigzag SWNTs, using a two-level ONIOM approach [3,4] implemented in the Gaussian 98 suite of programs [10]. UFF was used for the low-level treatment, and the Becke’s three-parameter hybrid method [11] with the exchange functional of Lee, Yang, and Parr [12] (B3LYP) was used for the high-level description, conjunction with the 6-31G(d) basis set.

As a first model, we used a short fragment of a small diameter [10,0] zigzag SWNTs shown in Figure 2. The fragment contained 160 carbon atoms, and its

dangling bonds were saturated with 20 hydrogen atoms. We did not use free boundary conditions for the modeling to avoid any artificial effects. It is well known that hydrogen termination does not perturb neither the nanotube lattice nor the electronic structure. The average C–C bond length in the optimized tube was 1.41 Å. Twenty-four carbon atoms in the center of the tube were used for the high level treatment while the rest of the tube was treated at UFF level. Hydrogen atoms were used as boundary atoms in the ONIOM calculation. The high level fragment interacted with a single proton, also treated at B3LYP/6-31G* level.

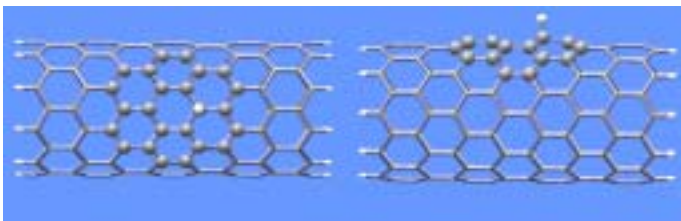


FIG. 2. Charge complex of a single proton and a [10,0] SWNT. The central part of the nanotube, shown as stick-and-ball lattice, and a charged impurity have been treated at *ab initio* level. The rest of the nanotube is treated with MM.

Minimization of the [10,0] zigzag SWNT fragment interacting with a proton led to the structure with the proton situated 1.1 Å from the surface of the tube above one of the carbon atoms, essentially forming a covalent C–H bond. The geometry shown in Figure 2 resulted regardless of the initial position of the proton over the tube surface. The interacting carbon atom is significantly distorted from the initial sp^2 geometry towards sp^3 geometry with the sum of valence angles of 319.1°. Similar results were reported recently for a hydrogen atom within a full *ab initio* calculation [16]. The Mulliken charge of the proton is only +0.38 e (where e is the elementary charge), showing a significant charge transfer from the tube to the proton.

This simplified model showed that the two-level ONIOM approach gives a reasonable description for the interaction between a charged molecule and SWNT. However, a small diameter of the nanotube used in this example may lead to additional effects. Therefore, next we considered a 1.3 nm wide zigzag [17,0] nanotube. The fragment we used contained 272 carbon atoms and was capped by 34 hydrogen atoms. Thirty carbon atoms were used for the high level treatment together with an ammonium (NH_4^+) ion. In this case the minimized structure consisted of the ammonium situated 3.2 Å from the surface of the tube. The tube geometry was not significantly distorted. The average C–C bond length in the tube was 1.41 Å, and its diameter was 13.3 Å. Both Mulliken and NBO [13] charges of the ammonium ion (+0.85 e and +0.91 e, respectively) show a strong charge transfer from the tube to the cation.

Based on the quantum mechanical calculations we conclude that the SWNT lattice may be left unperturbed by a sufficiently large charged molecule placed near the SWNT surface. *Ab initio* calculations provided an equilibrium distance between the SWNT and the charged molecule and the amount of charge transfer (and thus the

resulting positive charge creating the potential).

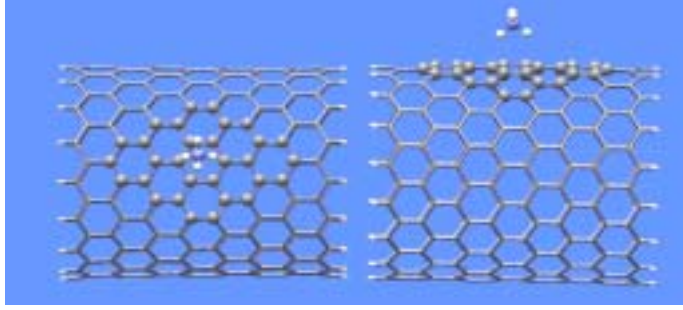


FIG. 3. The complex of ammonium ion and [17,0] SWNT. Notations are the same as in previous figure.

III. CALCULATION OF BAND BENDING

Neither the longitudinal nor the angular coordinate of the charged molecule in the complex is fixed, while the radial distance to the axis of the SWNT was calculated in the last section. We will prove later that the potential created in a typical charged complex has a short longitudinal length of several nanometers, and long weak tails, which decay as $1/z^3$. As long as the charge is at the distance of tens of nanometers from the side contacts, the influence of leads on the transport is negligible. Thus, we ignore all the contact phenomena which may appear at the leads and focus in this paper only on the change of the SWNT conductance due to the reflection of the electrons by the electrostatic potential created by the charged molecule (and its image charge in a substrate).

This potential on the surface of the nanotube reads as:

$$\frac{q}{\sqrt{(x - R \cos \alpha)^2 + (y - R \sin \alpha)^2 + z^2}} - \frac{q^*}{\sqrt{(x - R \cos \alpha)^2 + (y + 2h - R \sin \alpha)^2 + z^2}} \quad (1)$$

where R is the SWNT radius, x , y and z are the coordinates of the charged center if the coordinate origin is placed on the axis of the nanotube (of course, we impose the translational symmetry so the coordinate origin can be shifted along the axis arbitrarily). The angle α encompasses the SWNT circumference. $h = R + 3.4\text{\AA}$ is the distance from the axis of the nanotube to the substrate. We use notations q for the charge of the complex and q^* for its image charge. The latter is given by a simple relation:

$$q^* = q \frac{\varepsilon - 1}{\varepsilon + 1}, \quad (2)$$

where ε is the dielectric function of the substrate. For typical values of $\varepsilon \sim 12$ for Si, we can neglect the difference between the image charge and the original charge.

We consider now the band bending which is due to the subbands of the SWNT electronic structure being shifted by the electrical potential. The full quantum mechanical description of this mechanism is presented elsewhere [17]. Here we follow it briefly. We use the TBA to calculate the band shift. The electronic structure of the one-dimensional system is characterized by two quantum numbers k and m , which are the wavevector of the electron along the nanotube axis and its angular momentum. Each SWNT subband has its own discrete value of m , while k varies in each subband within the Brillouin zone.

To calculate the subband shift we use the first order "bubble" Feinman diagram (Fig.4) which will be extended later to the full sum of "bubbles" in RPA-E. In this approximation, no mixing between subbands is taken into account which means that the m quantum number is conserved and only the fully symmetrical component of the electric potential is required. This component is given by the integration of Eq.(1) over the angle α . After changing Cartesian to cylindrical coordinates, one obtains the potential as follows:

$$\phi^{xt}(z, \varphi; \rho, R) = \frac{q}{\sqrt{R^2 + \rho^2 + z^2}} - \frac{q^*}{\sqrt{R^2 + \rho^2 + 4h\rho \sin \varphi + 4h\rho^2 + z^2}}, \quad (3)$$

where ρ and φ are now the cylindrical coordinates of the charge. The one-dimensional potential $\phi^{xt}(z)$ depends on φ which varies nearly in the range $-\pi/2 < \varphi \leq \pi/2$ (where the left inequality is restricted because the complex is not assumed to penetrate *under* the SWNT). The potential depends also on the nanotube radius and the charge-SWNT separation $\rho - R \ll R$. Both of these parameters are known and fixed for a given nanotube and a given charged complex. For the ammonium, as it is shown in the last section, $\rho = R + 3.2\text{\AA}$.

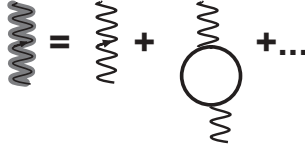


FIG. 4. Feinman diagram corresponding to the calculated depolarization of the electric field induced by a charged impurity.

IV. SELFCONSISTENT POTENTIAL OF THE CHARGE COMPLEX

So far, the potential was not selfconsistent. The selfconsistency, in the same sense as in RPA-E approximation, can be achieved by summing up all "bubble" diagrams. A simpler semiclassical description for the electrostatics of nanotubes has been developed in Ref. [18]. It was demonstrated that an induced charge density in the SWNT is linearly connected to the local external potential ϕ^{xt} . At the same time, the SWNT quantum capacitance [18] gives a relation between the charge and a full electrostatic potential ϕ^{act} , which we will call "an acting potential" hereafter. The proportionality

coefficient between the external and acting potentials can be rewritten in terms of a distributed atomistic capacitance. This capacitance has two contributions: a purely geometrical term and the quantum capacitance (a similar definition was proposed earlier for a quantum capacitance of a two-dimensional electron gas system in [19]).

We obtain the (selfconsistent) acting potential as the external potential divided by the SWNT depolarization factor which is much less than unity:

$$\phi^{act} = \frac{C_Q^{-1}}{C_g^{-1} + C_Q^{-1}} \phi^{xt} \simeq \phi^{xt} \frac{C_Q^{-1}}{C_g^{-1}} \quad (4)$$

here we used notations $C_g^{-1} = 2 \log \left(\frac{L}{R} \right)$ and $C_Q \sim 3.2$ [18] for the inverse capacitance (potential coefficient) of a metal cylinder and the quantum capacitance, respectively. The characteristic length L is given by the length of the SWNT device, calculated as the distance between the side electrodes. Because this length is placed under the logarithm sign, the resulting depolarization factor changes only slightly and is in the range of $0.02 - 0.04$ for almost any typical SWNT device.

Finally, the band bending as a function of the coordinate along the nanotube is given by the equation:

$$\frac{C_Q^{-1}}{C_g^{-1}} \left(\frac{q}{\sqrt{R^2 + \rho^2 + z^2}} - \frac{q^*}{\sqrt{R^2 + \rho^2 + 4h\rho \sin \varphi + 4h\rho^2 + z^2}} \right), \quad (5)$$

and is drawn in Fig.5 as a function of the distance from the charged complex for different angular positions of the complex. As the charge approaches the surface of the substrate, the potential decreases because the image charge potential cancels it. The typical length of the potential is several nanometers although weak dipole tails are present. At large distances from the complex, the potential decays as $2q(\varepsilon/2 + 1/2)h(\rho + h)C_Q^{-1}/z^3C_g^{-1}$. At small distances it can be approximated by a parabola.

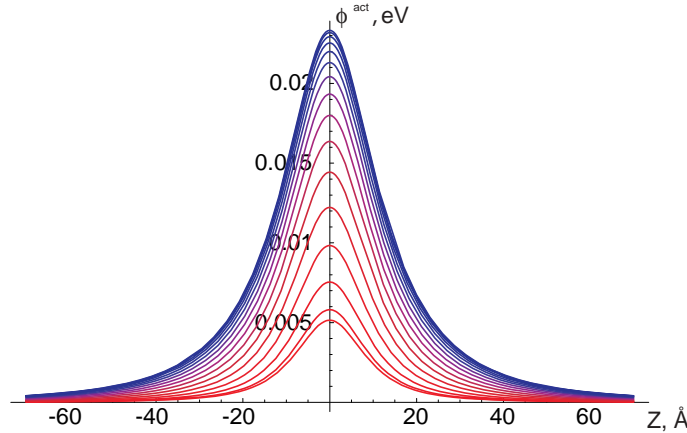


FIG. 5. Selfconsistent solution for the one-dimensional electric potential created by a charged impurity along the SWNT axis. Different curves correspond different angular positions of the charge: the maximum potential is for the charge on top of SWNT.

V. TRANSMISSION PROBABILITY

We model now the ballistic transport of holes through the potential barrier induced by the positively charged complex assuming that the nanotube is p-doped and the Fermi level is higher than the maximum of the barrier for the holes $|E_F| > |U_o|$. The latter assumption is reasonable because for the elementary charge placed at the distance from the surface of the SWNT $\sim 3.2\text{\AA}$ the maximum of the acting potential is about 24 meV. By expanding the acting potential near the maximum we obtain the harmonic potential barrier as follows:

$$U(z) \simeq U_o - \frac{z^2 C_Q^{-1}}{2 C_g^{-1}} \frac{eq}{(R^2 + \rho^2)^{3/2}} \left(1 - \frac{q^*}{q} \frac{(R^2 + \rho^2)^{3/2}}{(R^2 + \rho^2 + 4h\rho \sin \varphi + 4h\rho^2)^{3/2}} \right). \quad (6)$$

where U_o is the maximum value of the selfconsistent potential at $z = 0$ which reads as follows:

$$U_o = \frac{eq}{\sqrt{R^2 + \rho^2}} \left(1 - \frac{q^*}{q} \frac{\sqrt{R^2 + \rho^2}}{\sqrt{R^2 + \rho^2 + 4h\rho \sin \varphi + 4h\rho^2}} \right). \quad (7)$$

Using semiclassical probability for the reflection from the harmonic potential barrier [20] we obtain the transmission coefficient as follows:

$$\mathcal{T}(E) = \frac{1}{1 + \exp[-2\pi \frac{E-U_o}{\hbar} \sqrt{\frac{m^*}{\partial^2 U / \partial z^2}}]}, \quad (8)$$

where m^* is an effective mass which is about 0.06 of the free electron mass. The transmission coefficient is plotted in Fig. 6 as a function of the incoming electron energy for different angular position of the charged complex. The angular position controls the strength of the potential barrier and, hence, modulates the transmission.

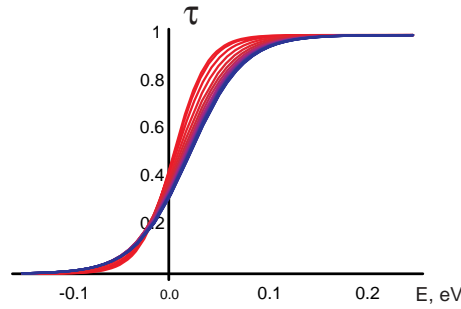


FIG. 6. Semiclassical transmission probability for a hole moving over the barrier described in the text as a function of the energy of incoming hole. Different curves represent different impurity potentials for different angular positions of the ion.

In a ballistic regime, the conductance of the zigzag SWNT is given by a simple relationship:

$$G = 2G_o\mathcal{T}(E_F) \quad (9)$$

here $G_o = e^2/h$ is the quantum of conductance. In Fig.7 we present the ballistic conductance of the SWNT as a function of the Fermi level and the angular position of the charged complex. An interesting fact is that for the charge, which is close to the elementary charge, $q \sim +|e|$ the conductance does not decrease to 0 even at the lowest Fermi energy $E_F = 0$. This is due to a large depolarization of the charge of the complex by the electrons of the nanotube, as described in the last section. This situation is similar to that in standard semiconductor devices when a remote impurity scattering is considered. The Coulomb potential is effectively cut at a moderate value and cannot completely block the transport through the nanotube channel.

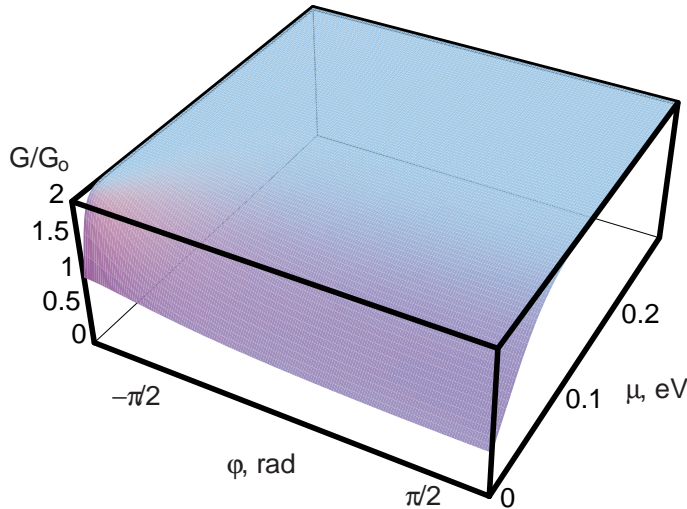


FIG. 7. The conductance of a [10,10] SWNT with a local gate, which is due to an ammonium ion, as a function of μ , a chemical potential of charge carriers, and φ , the angular position of the impurity charge.

CONCLUSIONS

In summary, we have developed a continuum theory for a ballistic transport in a single-wall nanotube, which is controlled by a local gating effect of a charged complex. An analytical expression for a conductance of the nanotube is presented. We have calculated a band profile in the gated nanotube device in a selfconsistent way. The quantum mechanical scattering from a barrier induced by the charged complex is computed based on *ab initio* calculated optimal geometry and charge of a charged complex. Our ultimate goal is to prepare a molecule capable of delivering a desired charge to the SWNT surface in a controlled manner. An example of such a molecule

is shown in Figure 8. This molecule could attach itself to the tube surface by van der Waals interactions, and its charge can be controlled by protonation/deprotonation of the terminal amino group.

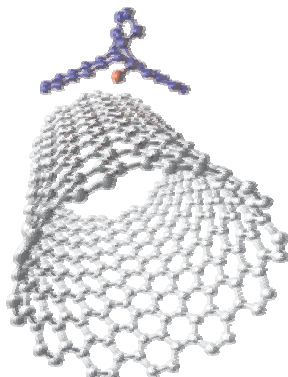


FIG. 8. A "rider"–molecule proposed to serve as a local electro–chemical gate to a SWNT.

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