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Quantum Treatments of Electronic Characteristics of Carbon Nanotubes *via* the Density Functional Green's Function Method

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Density functional non-equilibrium green's function method is used to investigate the switching behaviour of various types of single walled carbon nanotubes (SWCNTs). Electron transport through both the defective and defect-free SWCNT molecular wires sandwiched between an Al (1 0 0) substrate and a monoatomic Al scanning tunneling microscope (STM) tip has been examined. Our first-principles calculations show that current intensity has the same values for all considered conformations for the defect-free SWCNTs and hence no significant difference in conductance was occurred by the STM tip displacement. However, when the tip moves laterally over the different configurations of the defective tube thus surprisingly, this simple molecular device switches between a strongly and a weakly conducting state. In addition, a realistic theory of its switching behaivour has been investigated by the projection of the density of states and transmission coefficients of the two-probe system.

Key Words: Molecular electronics, Density functional theory, Non-equilibrium Green's function, Single walled carbon nanotubes.

INTRODUCTION

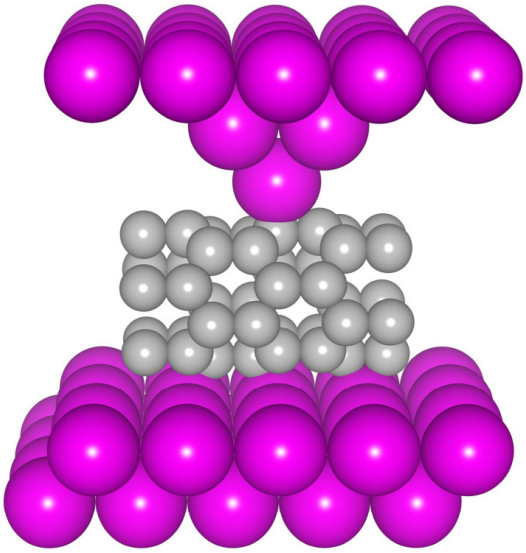
Since the discovery of carbon nanotubes[1] a tremendous experimental and theoretical investigations have been devoted for the manipulation and fabrication of these novel materials with the necessity of the understanding and interpretation of the obtained data, as well as their exploration of promising properties due to its rich electronic characteristics.

Particular attention has been given to the molecular electric (molectronics) switches[2,3] which are critical to the ability to store digital information and route signals in molectronic logic circuits[4]. Among these, single-molecule switches, in which the switching originates in the physical properties of individual molecules rather than molecular complexes or films, are especially valuable, since they allow the ultimate miniaturization of molectronic devices[4,5].

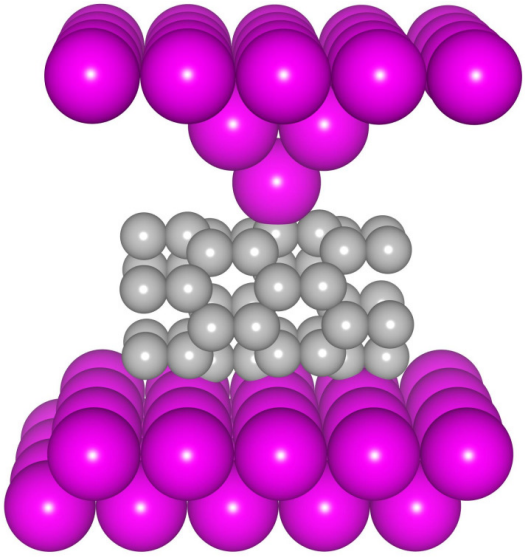
The transport properties of carbon nanotubes (CNTs), which are particularly intriguing due to their one-dimensional (1D) nature, have been attracted much attention because of their many unique properties, including very high conductance and possible applications for nanoelectronic devices[6-16]. Several theoretical[6-12] and experimental[13-16] studies have elucidated various aspects of electron transport through lead/CNTs/lead junctions aimed at utilizing the advanced materials properties including high carrier mobility, ballistic transport and non-volatile random access memory for molecular computing[17-24]. Despite intensive investigations, the possibility that wires of these types may be capable of switching is far from obvious a priori and has not been investigated until now. Motivated by these facts, we employ various types of the single walled carbon nanotube (SWCNT) and model the scanning tunnel microscope (STM) experiment, which enables us to simulate the switching behaivour of these novel materials. Thus, we intend to identify one of the simplest two-terminal molecular switches to date and reveal a new dimension of the physics of lead/CNTs/lead molecular wires by a theoretical simulation that combines both first-principles density functional theory (DFT) and non-equilibrium Green's function (NEGF) formalism.

COMPUTATIONAL METHODS

The aim of the *ab initio* study is to investigate the electron transport through the SWCNTs of different types. In order to treat the respective systems with high accuracy *ab initio* methods, we employed a supercell approach in all our calculations. The schematic representation of the molecular switch with two Al (1 0 0) electrodes is given in Fig. 1. For each electrode, four Au atomic layers are included into the extended molecule region to screen the perturbation effect from the



(a)



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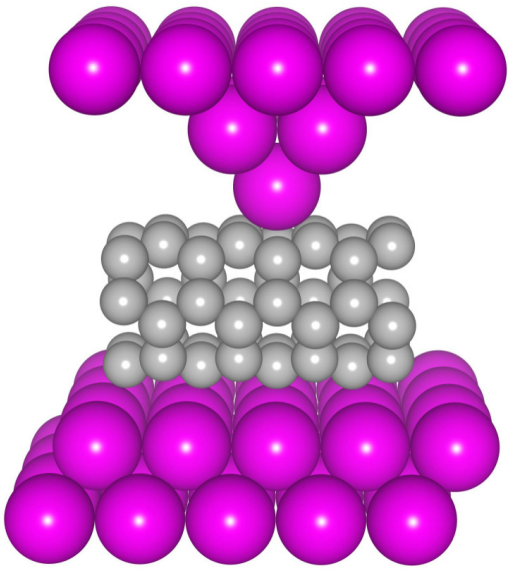

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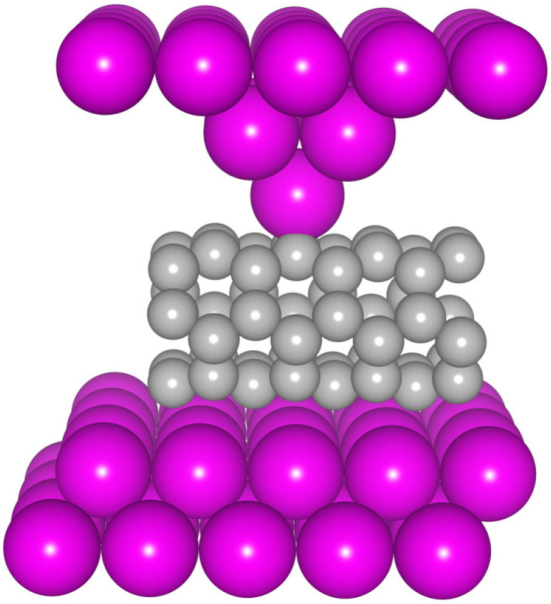

(d)

Fig. 1. A schematic of SWCNT molecular wires sandwiched between two Al (1 0 0) electrodes. (a) The top conformation and (b) hollow conformation of the (5, 0) carbon nanotube and (c) hollow and (d) bridge conformation of the (3, 3) carbon nanotube

central scattering region and they are denoted as surface-atomic layers. The electronic transport properties of the molecular switch are calculated by using the SMEAGOL package[25,26] which is based on the combination of DFT (as implemented in the well-tested SIESTA method[27]) with the NEGF technique[28,29]. SMEAGOL is capable of fully self consistently modeling the electrical properties of nano-scale devices that consist of an atomic scale system coupling with two semi-infinite electrodes. Further details of the method have been fully reviewed[26].

In our transport calculation, the local-density approximation (LDA) to the exchange-correlation potential[30] is used. Only valence electrons are considered in the calculation and the wave functions are expanded by localized numerical (pseudo) atom orbitals (PAO's)[31]. The atomic cores are described by norm-conserving pseudo potentials[32]. We use a DZP basis set for the carbon nanotube molecules and a SZP basis set for the Al atoms in the transport calculations. The k-grid sampling of $2 \times 2 \times 20$ for the Al electrodes and a $2 \times 2 \times 1$ k-grid sampling for the two-probe system, together with the mesh cutoff of 140 Ry for both of them, was implemented. In addition, to avoid the interaction between the molecule and its periodic images, a large supercell dimension in the plane perpendicular to the transport direction is used.

RESULTS AND DISCUSSION

By analyzing the recent studies[12,33-39] it is found that the overlap between the molecular orbitals and the states of the contacts is sensitive to the orientation of the molecule relative to the contacts, which implies a strong orientation-dependence of the molecular wire's conductance. Therefore, it is reasonable to expect them to result in a significant change in conductance when a lead/CNT/lead wire switches between various conformations and present investigations show this to be the case.

We first examine the electron transport phenomenon for the armchair (metallic) (3, 3) and zigzag (semiconducting) (5, 0) SWCNTs with similar diameters, *ca.* 4 Å. To evaluate the switching behaviour of the considered nanotubes, a number of distinct starting conformations were used to determine the current-voltage (I-V) characteristics. For this propose we consider two conformations for the attached wires to the Al electrodes. In the first conformation, the STM tip was placed above the carbon atom of the hexagon plane of the wall for the zigzag CNT and bridge situation of the C-C bond of the metallic CNT. In the second conformation, the Al tip atom was situated over the hollow site of the hexagon plane of the carbon atoms for both the selected CNTs. All the considered configurations are shown in Fig. 1(a-d).

Fig. 2 showed the calculated current of the considered SWCNTs in their ground state conformations for two respective positions of the STM tip along a linear trajectory over the plane of the tube. The calculated results show that the current intensity has the same values for all respective conformations and no significant difference in conductance was occurred by the STM tip displacement. It can be found that the lateral motion of the tip upon the tubes surface of the perfect SWCNTs may not lead to a significant ON/OFF ratio and therefore these nanotubes seem to be unsuitable materials for the molecular switches.

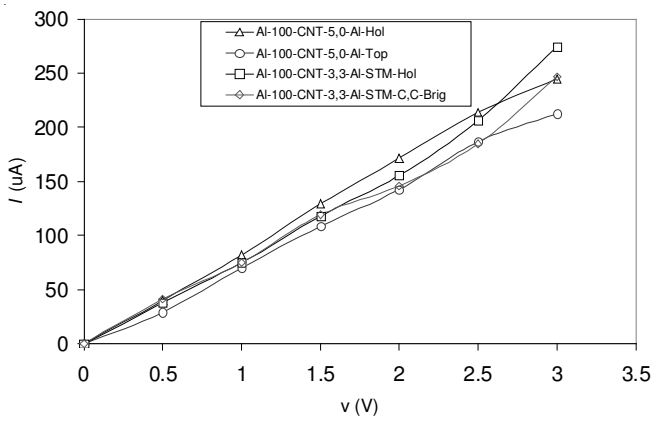

Fig. 2. Calculated current for ground state conformations at two STM tip positions for all the selected configurations of Fig. 1

To further investigate the potential capability of carbon based nanotubes for the molecular electronics devices we examine the electrical transport through the defective SWCNTs as an alternative candidate for the convenient molecular switch. In order to study the role of structural defects on electrical transport, we have introduced defects like pentagon and heptagon in the hexagonal structure of the (6, 0) SWCNT, as depicted in Fig. 3 and calculated I-V characteristics for different conformations with respect to the defect ring. Similar procedure has been performed for the Al tip situated above the respective nanotube surface. Fig. 4 shows the obtained current *versus* the various bias voltages for two considered conformation of the Al tip with respect to the heptagon defect of the tube. The calculated results show that for the defective CNT case when the tip is situated on the center of heptagon plane of the CNT, hollow conformation, the molecule has slightly lower current intensity at a source-drain bias around 3.0 V

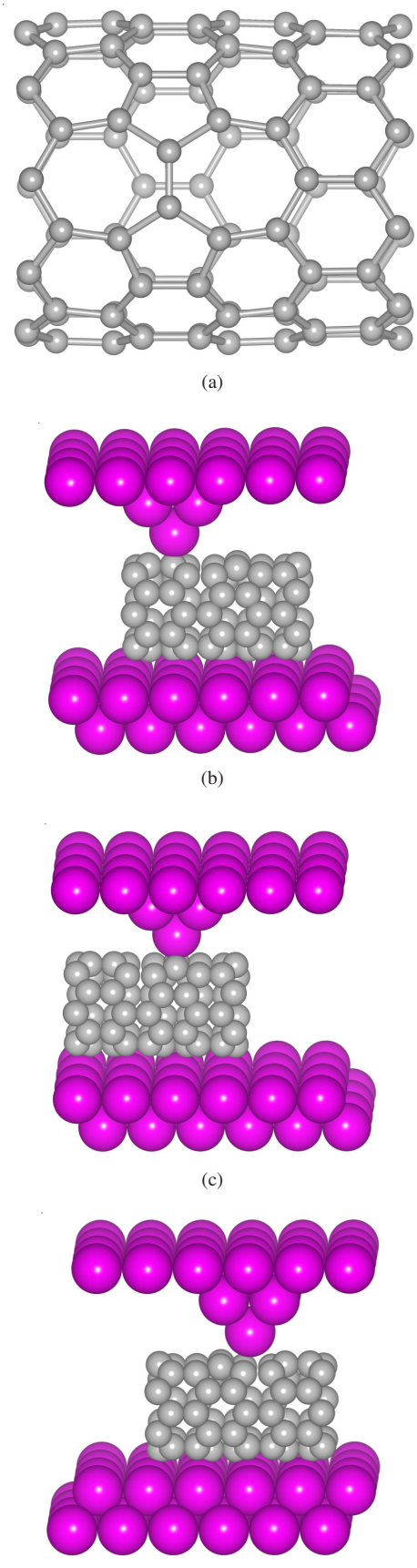

Fig. 3. Schematic representation of defective (6, 0) SWCNT molecular wires sandwiched between two Al (1 0 0) electrodes. (a) the pristine defected (6, 0) carbon nanotube, (b) top conformation, (c) bridge conformation and (d) hollow conformation

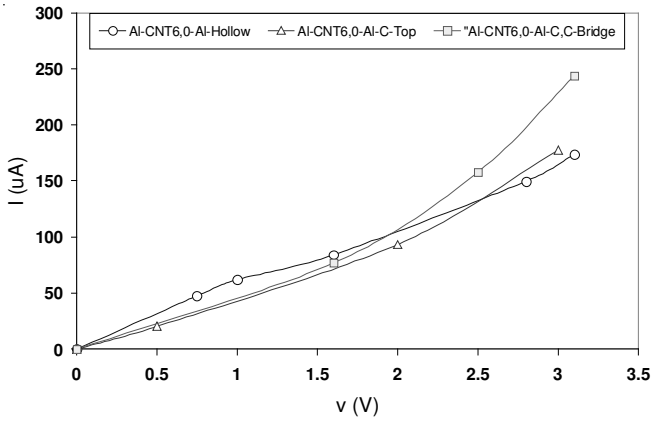

Fig. 4. Calculated current for ground state conformations at two STM tip positions for all the considered states of defected CNT (6, 0) of Fig. 3

(the ON/OFF ratio is about 1.5). When the tip moves towards the center of the heptagon the device switches to the bridge conformation, which is seen to be higher conducting in the same range of bias. Consequently, from the I-V characteristics of these conformations, it can be found that there exist slightly significant ON/OFF ratio to obtain a suitable switching behaviour. Therefore, whenever the defected CNT is made to flip from a hollow conformation to a bridge conformation, by displacing the STM tip, the tube is predicted to switch from a weakly conducting to a highly conducting state and *vice versa*. Therefore, it is predicted that a wire as simple as defective SWCNT can be made to switch through its interaction with a suitable STM tip. The ON state corresponds to the defective CNT oriented in such a way that the C-C bond of the ring faces the tip, whereas in the OFF state the hollow site of the tube linked to the tip. The switching can be induced by passing the tip over the CNT through the transition between Fig. 3(c-d).

This difference in current intensity between the considered conformations can be understood within Landauer theory[29] by considering the transmission coefficient probabilities, T, for electrons to scatter through the molecular wire in that the orientational effects were taken account[34,38].

The transmission spectra of the two considered conformations for all the considered systems at zero bias are shown in Fig. 5. It can be seen from the figure, there exists region of strong transmission at the Fermi energy for all the considered conformations where electrons incident from one of the electrodes can transmit across the CNT to the other electrode significantly.

In order to understand why incident states in these energy regions can transmit across the CNT significantly, we further calculated the projection of the density of states of the combined system onto all the CNT basis orbitals (PDOS), for the Al/CNT(5, 0)/Al system, as shown in Fig. 5(b). It's well recognized that the PDOS give us information on how much the basis orbitals in the CNT contribute to the eigenstate of the whole open system and how strongly the CNT couples with the electrodes at a certain energy E. Indeed, a strong coupling makes incident electrons at certain energy easily transmit across the CNT. This will give rise to a large transmission coefficient at this energy. This is clearly understood by

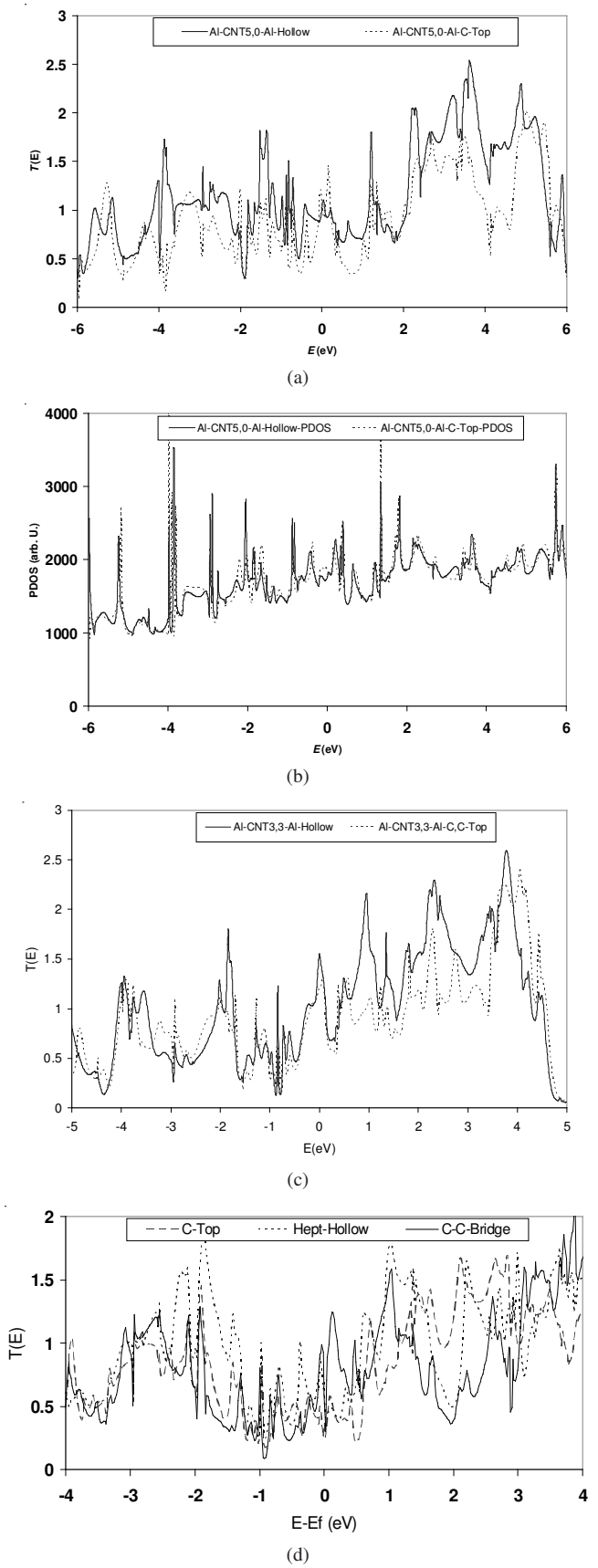

Fig. 5. (a), (c) and (d) transmission function under zero bias as function of the injection energy of electron of the CNTs coupled to the Al (1 0 0) electrodes of the considered configurations. (b) PDOS (arbitrary units) of the two probe system for defect-free (5, 0) CNT, around the Fermi energy. All energy is relative to the Fermi energy of the electrode

comparison of the PDOS spectra and transmission spectra. From the comparison of the transmission coefficient and PDOS curves one can find that, there exists a good correspondence between the position and width of the peaks in the transmission coefficient (Fig. 5(a)) and those in the PDOS (Fig. 5(b)) for the carbon nanotube.

Further insight can be gained by analyzing of the electronics structures of the two probe system. At zero bias voltage the HOMO is partly occupied and therefore pinned to the Fermi energy and hence due to the charge transfer from the tube to the Al the tube becomes slightly positively charged. Consequently there is a strong overlap between the first HOMO molecular orbital and the atomic orbitals of the Al atoms. This results in the strong transmission due to the first HOMO immediately below the Fermi energy in the figure and in the strong current peak seen for all conformations. However, in case of defective CNTs, for the bridge conformation, the molecular orbitals are oriented differently and their overlap with the orbitals on the Al surface atoms is stronger than that of the other considered conformations. As shown in Fig. 5(d), the Fermi energy lies also, nearest the HOMO but in contrast to the hollow and top conformations the transmission spectra is weaker due to the weak overlap between the first HOMO molecular orbital and the atomic orbitals of the Al atoms. This results in the weak transmission due to the first HOMO below the Fermi energy and in the weak current peak seen for the respective conformation (Fig. 4).

Conclusion

The DFT-NEGF method is applied to investigate the switching behaivour of a two-terminal molecular wire consisting of SWCNTs. We considered various types of SWCNTs molecular wire sandwiched between an Al (1 0 0) substrate and a monoatomic Al scanning tunneling microscope (STM) tip. The current-voltage (I-V) characteristics of two conformations of the Al-CNT-Al system: the top (bridge) and hollow conformations, has been investigated for the semiconducting and metallic SWCNTs.

Our first-principles results show that current intensity has the same values for all respective conformations for the defect-free SWCNTs and no significant difference in conductance was occurred by the STM tip displacement. Therefore, the lateral motion of the tip upon the tubes surface of the perfect SWCNTs may not lead to a significant ON/OFF ratio and therefore the defect-free nanotubes seem to be unsuitable materials for the molecular switches.

On the other hand, calculated I-V characteristics of the defective SWCNTs showed that these types of nanotubes can be made to switch through its interaction with a suitable STM tip. The OFF state corresponds to the nanotube oriented in such a way that the hollow site of the ring faces the tip, whereas in the ON state the C-C bond of the tube linked to the STM tip. The switching can be induced by passing the tip over the CNT through the transition between respective states. As a result one can conclude that the defective CNTs are suitable device for molecular electronics. Experiments with a conventional STM are proposed to test these predictions.

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