First Principle Study of Electron Transport in Single-Walled Carbon Nanotubes of 2 to 22 nm in Length

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An elongation method based on ab initio quantum chemistry approaches is presented. It allows to study electronic structures and coherent electron transportation properties of single-walled carbon nanotubes (SWCNTs) up to 22nm in length using the hybrid density functional theory. The 22nm long SWCNT, consisting of more than ten thousands electrons, is the largest carbon nanotube that has ever been studied at such a sophisticated all-electron level. Interesting oscillating behaviour of the energy gap with respect to the length of the nanotube is revealed. The calculated current-voltage characteristics of SWCNTs are in excellent agreement with recent experimental results. It confirms the experimental observation that a 15nm long SWCNT is still largely a ballistic transport device. The proposed elongation method opens up a new door for the first principle study of nano- and bio-electronics.

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Carbon nanotubes (CNTs) are probably the most studied nanomaterials in the last decade, owing to their great physical and chemical properties. Among many exciting applications, CNTs are believed to play an important role in the future electronics. This view is further enforced by an exciting recent development, namely the utilization of 10 to 50 nm long single-walled carbon nanotubes (SWCNTs) to study electronic structures and coherent electron transportation properties of single-walled carbon nanotubes (SWCNTs) to study electronic structures and coherent electron transportation properties of single-walled carbon nanotubes (SWCNTs). It has been demonstrated that the electron transport in SWNTs with finite length less than 15nm immunes from the optical phonon scattering and thereby exhibits nearly ballistic behaviour at high biases. However, the finite-length SWNTs present a great challenge for the first principle theoretical modelling because of the involvement of vast number of electrons. Over the years, different approaches, such as semi-empirical, ab initio tight-binding, and "integrated" methods, have been developed to describe the nano-sized systems, but all suffer from a relative low level of accuracy. For such large systems, the most accurate yet feasible approach is probably the density functional theory (DFT). In this letter, we present a straightforward elongation method in conjunction with the modern quantum chemical density functional theory calculations that allows to effectively treat very large nano-scale periodical systems without losing the accuracy. This method has applied for studying the electronic structures and the coherent electron transportation properties of SWCNTs of different lengths. The largest SWCNT reported here is about 22 nm long in length which consists of ten thousands of electrons and is described by fifteen thousands gaussian basis functions.

Our elongation method is based on a simple fact that for a large enough finite periodic system, the interaction between different units in the middle of the system should be converged, and consequently those units in the middle become identical. It is thus possible to elongate the initial system by adding the identical units in the middle of the system continuously. This can be easily done when the Hamiltonian of the system is in the site-representation. Obviously, the precondition for using the elongation method is to obtain an initial Hamiltonian in the site-representation with identical middle parts. Fortunately this condition can be achieved routinely with the modern quantum chemistry programs. The elongation method should be as accurate as the quantum chemistry method used for the initial system. We will use the (5,5) metallic SWCNTs to demonstrate the performance of the elongation method as implemented in the QCME code. With the same code, the coherent electron transport in the SWCNTs is also calculated using the generalized quantum chemical Green’s function method.

We first calculate two (5,5) metallic SWCNTs with 190 (19 units, CNT19) and 310 (31 units, CNT31) carbons, respectively, at the hybrid density functional theory B3LYP level with STO-6G basis set using GAUSSIAN03 program. The both ends of the finite-sized tubes are terminated by hydrogen atoms. The calculated Hamiltonian of the CNT19 is used as the base for the elongation method to construct a Hamiltonian of the CNT31. The calculated highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies from the elongation method are found to be -2.000 and -1.538 eV, respectively, in excellent agreement with the values of -2.070 and -1.598 eV, respectively, obtained from GAUSSIAN03 program. The derivation for the LUMO-HOMO gap $E_g$ from these two different approaches is as small as 0.009 eV. The calculated transition probability spectra above the Fermi level

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FIG. 1: (A) Transition probability (on a log scale) spectrum above the Fermi level, and (B) I-V characteristics of the CNT31 (310 carbons, 3.7nm in length) connected to two gold electrodes obtained from Gaussian03 (solid lines) and elongation (dashed lines) methods.

for the CNT31 connected to two gold electrodes, as well as the corresponding current-voltage curves, from both methods, agree very well as demonstrated in Figure 1. It should be mentioned that the coupling coefficients between electrodes and CNTs is approximated by a simple Au-C diatomic interaction. The coupling between electrodes and CNTs is a complicated issue and will be discussed elsewhere.

We are thus ready to explore the elongation method for even longer CNTs. To maintaining higher accuracy, we have used CNT21 (210 carbons, 2.6nm long) tube calculated at B3LYP/6-31G level with GAUSSIAN03 to construct a series of SWCNT systems with units of $n = 9 + 12 \times i$ ($i=2, 3, ..., 14$) whose length goes from 4.1 nm to 21.8 nm. In Figure 2(A), the molecular orbitals (MOs) around the energy gap are displayed. As expected the density of states (DOS) gets higher for longer SWCNT. The most interesting observation is that the energy gap ($E_g$) oscillates periodically with the increase of SWCNT length. For short SWCNTs, it is known that the $E_g$ should oscillate with a period of 3 units\[21, 22, 23\]. This behaviour is nicely reproduced by our calculations, see Figure 2(C). The trend given by the short SWCNTs seems to indicate that the gap should continuously decrease with the increase of the SWCNT length. However, our calculations present a very different picture. For instance, the energy gap of the CNT33 (0.598 eV) is already larger than that of the CNT21 (0.492 eV). This observation is further confirmed by Gaussian03 calculations with STO-6G basis set. The evolution of energy gap with respect to the tube length is clearly shown in Figure 2(B). It is noticed that the width of the oscillation peak covers 36 units from the CNT81 to the CNT117, while the one after it is about 60 units from the CNT117 to the CNT177. It seems to imply that the oscillation of the energy gap with respect to the length of the tube will be slowly faded out. Furthermore, discrete molecular orbital distribution is found for all the tubes under investigation, indicating that these tubes can be quantized electronic devices. One can at least conclude that a (5,5) SWCNT with length of 22 nm is still far from a real bulk material.

By using the QCME code, we are able to calculate the I-V characteristics of the tubes with different lengths. The electrode structure shown in Figure 3(A) is the same as that reported in the experimental work of Javey et al\[4\]. The I-V curves of short tubes up to the CNT45 (5.5nm) show stair-like profile in which each step represents an opening of a new conducting channel. These small devices are all semi-conductor-like, i.e. the elec-
FIG. 3: (A): Schematic draw of a SWCNT device with gold electrodes; (B) Calculated current-voltage characteristics for the CNT9 (1.1nm), the CNT21 (2.6nm), the CNT33 (4.1nm), and the CNT45 (5.5nm); (C) Calculated current-voltage characteristics for the CNT69 (8.5nm), the CNT93 (11.4nm), the CNT117 (14.4nm), and the CNT177 (21.8nm); and (D) Experimental I-V curve for a 15nm SWCNT.

FIG. 4: The conductance for SWCNTs with units $N = 8, 9, ..., 21$ biased at their first conduction state.

with $3n + 1$ units have the lowest conductance, while the tubes with $3n$ units give the smallest energy gap.

Another interesting quantum effect related to the SWCNT is the periodical distribution of its molecular orbitals along the tube axis. Venema et al. carried out the position-scanning I-V measurements for a finite-length metallic SWCNT. The experimental setup is schematically recaptured in Figure 5 together with the experimentally measured result. In this experiment, a STM tip scanned through the top of a 30nm metallic SWCNT deposited on a gold surface to measure the current at each positions. It was found that the conductance of this tube shows a periodic behaviour with a period of about 0.4 nm, roughly covering 3 layers. With the elongation method, we have simulated the STM experiment for two tubes, the CNT33(4.1nm) and the CNT117 (14.4nm) at external biases of 0.3V and 0.1 V respectively. The results are also shown in Figure 5. As one can see, the oscillating behaviour is well reproduced, which shows a period of 3 layers. It should be stressed that our calculations describe only the coherent electron transport, while for a 30nm long SWCNT phonon coupling can become important which might explain why the periodicity of the experimental result is less perfect.

Furthermore, there is a very interesting wave-packet-like behaviour in the position depended conductance of the CNT117. It seems to suggest that an electron standing-wave can emerge in SWCNT longer than 15 nm.

In summary, we have proposed an elongation method that is capable of calculating electronic structures and electron transportation properties of periodic nano-sized systems at the hybrid density functional theory level. With this method, we have studied the length dependence of the energy gap and the conductivity of the finite-length single-walled carbon nanotubes (SWCNTs) ranging from 1nm to 22nm. The calculated results agree
FIG. 5: Schematic draw of STM scanning experiment (A) and the corresponding conductance measurement B) for a 30nm SWCNT[24]. Calculated position dependent conductance for the CNT33 (4.1nm) at external bias 0.3V and for the CNT117 (14.4nm) at 0.1V.

very well with the full quantum chemical calculations and exiting experimental results. A new interesting oscillating behaviour for the energy gap of the finite-length SWCNTs is revealed. It is worth to mention that our elongation has also successfully applied to 50nm long poly(para-phenylene ethynylene)s and 60 pairs poly(G)-poly(C) DNA. The calculated I-V characteristics of these systems are also in very good agreement with the corresponding experiments. The details of these studies will be published elsewhere.

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