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2009 J. Phys.: Condens. Matter 21 145502

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The size effects of electrodes in molecular devices: an *ab initio* study on the transport properties of C₆₀

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Received 15 July 2008, in final form 6 February 2009

Published 13 March 2009

Online at stacks.iop.org/JPhysCM/21/145502

Abstract

The role of electrodes in the transport properties of molecular devices is investigated by taking C₆₀ as an example and using gold nanowire and a gold atomic chain as the electrodes. The calculations are done by an *ab initio* method combined with the non-equilibrium Green function technique. We find that devices in which a single C₆₀ molecule is connected with different electrodes show completely different transport behavior. In the case of nanowire/C₆₀/nanowire the device shows a metallic behavior with a big equilibrium conductance (about 2.18G₀) and the current increases rapidly and almost linearly starting from zero. The transmission function shows wide peaks and platforms around the Fermi level. While in the atomic-chain/C₆₀/atomic-chain case, the device shows resonant tunneling behavior and the Fermi level lies between the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) transmission peaks. This results in a current that is one order of magnitude smaller than that in the nanowire/C₆₀/nanowire system and the current increases very slowly until the bias is big enough to include the LUMO peak in the bias window. The big difference in the conductance and the current arises from the different coupling between the electrodes and the C₆₀ and the different number of channels in the electrodes.

1. Introduction

One important starting point in developing molecular devices is to use the special properties of molecules in the electronic components. This makes it possible to control the electron transport properties on a molecular scale [1]. However, one big difference between molecular devices and traditional counterparts is that the transport properties of molecular devices are not always solely determined by the properties of the molecules themselves. In many cases, the atomistic details of the contact greatly affect the transport properties of the molecular devices. These factors include the distance between the molecule and the electrodes, the relative orientation of the molecule to the electrodes, the material that is used as the electrodes and the size of the electrodes, etc. These have been studied quite extensively [2–5]. In the study of size effects of the electrodes, two different models are generally used: nanowire electrodes and bulk electrodes. In nanowire electrodes, in the plane (*x*–*y*-plane) perpendicular to the transport direction (*z*-axis), the electrodes have a finite cross-section with a vacuum surrounding it. In bulk electrodes,

along the *x*–*y*-direction, the size is infinite and the system is periodic. Study shows that these two kinds of electrodes can lead to big differences in the transport properties of molecular devices [6].

Another goal of molecular devices is to decrease the size of the electronic components, since with the development of modern science and technology we hope to incorporate as many electronic elements as possible in integrated circuits with a small size. The smallest size can be a single atom or just an atomic chain. As the conductor part, the transport properties of single atoms or atomic chains have been studied quite extensively [7–17] and many interesting behaviors have been revealed, such as conductance oscillation with chain length, negative differential resistance, spin valve effect, etc. In these systems, the electrodes are much bigger than the conductor part. However, in an electronic circuit the size of the electrodes is generally much smaller than that of the conductor part. It will be very interesting if we can use electrodes with sizes as small as atomic chains in large scale integrated circuits. To achieve this, one possible choice is to use gold atomic chains. Now with the progress of nanofabrication

technology, gold chains can be formed by dragging the atoms out one by one from bulk gold using a STM tip [17–21]. Theoretical calculations even show that by inserting oxygen atoms as a glue between the gold atoms, the stability of the gold chains can be greatly strengthened [22]. This could provide possible candidate electrodes with the smallest size in molecular devices.

In this paper, the role of the electrodes is studied by taking a C_{60} cluster/molecule as the conductor part which is connected to two kinds of gold electrodes—one a gold atomic chain and the other a gold nanowire. It is found that these C_{60} -based devices with the C_{60} sandwiched between different kinds of gold electrodes show completely different transport behaviors. The transmission function in the nanowire/ C_{60} /nanowire case shows wide peaks and platforms around the Fermi level and the equilibrium conductance is as large as $2.18G_0$ ($G_0 = \frac{2e^2}{h}$: conductance quantum), while in the atomic-chain/ C_{60} /atomic-chain case, the transmission displays resonant peaks and the Fermi level lies between two peaks, resulting in a very small conductance of $0.027G_0$. Furthermore, the current in the nanowire/ C_{60} /nanowire case increases rapidly and almost linearly at a very low bias while it increases very slowly in the atomic-chain/ C_{60} /atomic-chain case. The current is one order of magnitude smaller in the atomic-chain/ C_{60} /atomic-chain case than in the nanowire/ C_{60} /nanowire case. Analyses show that the different coupling between the electrodes and the conductor part and different number of eigenchannels that the electrodes can provide are mainly responsible for these differences.

The rest of this paper is organized as follows. In section 2 we give a brief description of the geometric structure and the computational method. In section 3 the main results and discussions are presented. A short conclusion is given in section 4.

2. Geometric structure and computational method

The model structures we study are constructed as follows: in the nanowire/ C_{60} /nanowire case (see figure 1(a)), one C_{60} is sandwiched between two gold electrodes which are extracted from the bulk gold along the (100) direction and have a finite cross-section. The number of atoms in each atomic layer in the Au(100) electrode is periodically arranged as 5, 4, 5, 4 ... to simulate a nanowire electrode. In the atomic-chain/ C_{60} /atomic-chain case (see figure 1(b)), one C_{60} is sandwiched between two gold atomic chains. The C_{60} is connected to the electrodes by a C–C dimer in its structure and the C–C dimer is vertical to the z -direction. The equilibrium distance between the C_{60} and the electrodes is obtained by attaching the C_{60} molecule to one electrode and fully relaxing the C_{60} molecule while keeping the electrode atoms fixed. The Au–C bond length is found to be about 2.17 Å in both cases. The structure of the gold atomic chain is also fully relaxed and the bond length is 2.55 Å, which agrees very well with the literature [17, 23].

Calculations of the transport properties were performed using a first-principles package, the TranSIESTA-C method, which is based on the non-equilibrium Green function (NEGF) technique. TranSIESTA-C, as is implemented in the well tested

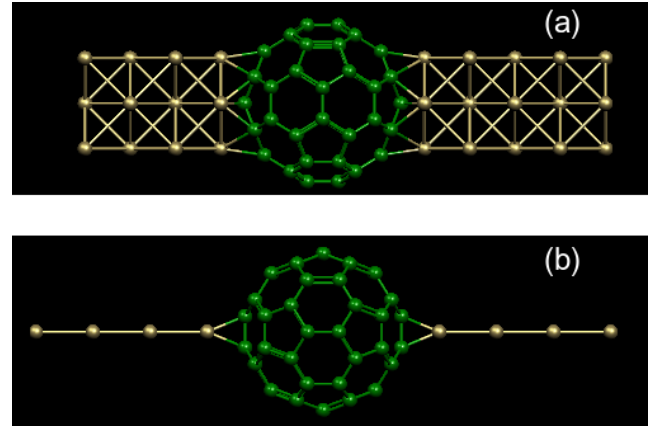


Figure 1. The geometric structure of the devices: (a) the nanowire/ C_{60} /nanowire structure; (b) the atomic-chain/ C_{60} /atomic-chain structure. Color: yellow for Au atoms and green for C atoms. (This figure is in colour only in the electronic version)

SIESTA method [24], is capable of fully self-consistently modeling the electrical properties of nanoscale devices that consist of an atomic scale system coupled with two semi-infinite electrodes. The potential in the semi-infinite electrodes provides natural real space boundary conditions for the Kohn–Sham potential of the scattering region, so the electronic structure of the two electrodes must be computed before the self-consistency procedure of the scattering region starts, but it will be calculated only once. The coupling of the scattering region with the electrodes is taken into account by self-energies. Details of the method and relevant references can be obtained elsewhere [25].

In the NEGF formalism, the transmission function is calculated by the following Landauer formula [26, 27]

$$T(E, V) = \text{Tr}(\Gamma_L(E, V)G^R(E)\Gamma_R(E, V)G^A(E)), \quad (1)$$

where $G^{R/A}$ are the retarded/advanced Green functions of the conductor part and $\Gamma_{L/R}$ are coupling functions to the left/right electrodes. The current through this system is calculated by integrating the transmission function over the bias window

$$I(V) = \frac{2e}{h} \int_{\mu_L}^{\mu_R} T(E, V)(f(E - \mu_L) - f(E - \mu_R)) dE, \quad (2)$$

where $f(E - \mu_{L/R})$ are the Fermi distribution functions of electrons in the electrodes and $\mu_L = E_f - V/2$ ($\mu_R = E_f + V/2$) are the chemical potentials of the left (right) electrode, with V the bias applied to the two sides and E_f the Fermi energy of the electrodes. The upper and lower limits in equation (2) are valid only for zero or very low temperature. Under finite temperature, the upper and lower limits are extended to $-\infty$ and $+\infty$, respectively.

3. Results and discussions

Figure 2 shows the I – V characteristics of the two systems in figure 1. In order to study the temperature effects, the currents at 0 and 300 K are calculated. Two

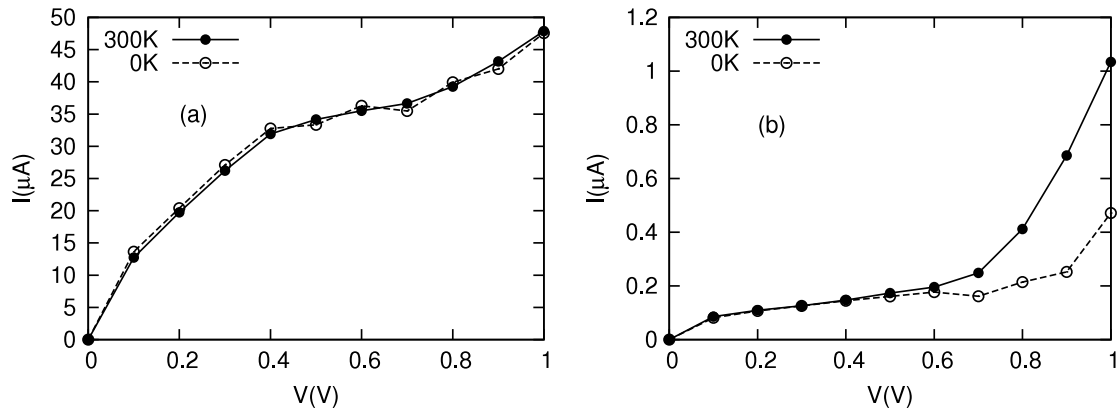


Figure 2. The I - V curve for (a) the nanowire/ C_{60} /nanowire system; (b) the atomic-chain/ C_{60} /atomic-chain system.

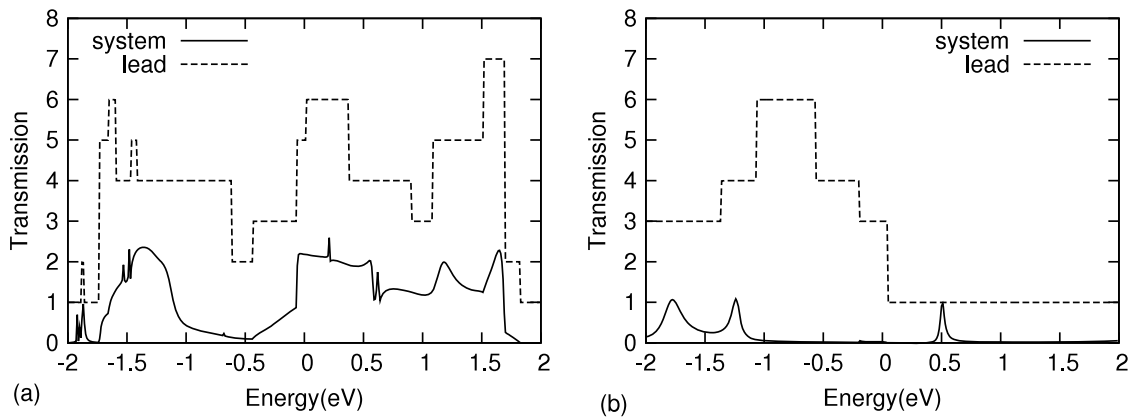


Figure 3. The transmission function for (a) the nanowire/ C_{60} /nanowire structure; (b) the atomic-chain/ C_{60} /atomic-chain structure. The solid line shows the transmission of the electrode/ C_{60} /electrode junction, while the dashed line shows the eigenchannels of the electrode.

big differences can be observed in these two systems: first, the current in the nanowire/ C_{60} /nanowire system is one or two orders of magnitude bigger than that in the atomic-chain/ C_{60} /atomic-chain system; second, the current in the nanowire/ C_{60} /nanowire system increases rapidly with bias while it increases very slowly at first and then increases faster with bias in the atomic-chain/ C_{60} /atomic-chain device. Meanwhile, the temperature effect in the nanowire/ C_{60} /nanowire system is very small at all biases, while in the atomic-chain/ C_{60} /atomic-chain system the temperature effect is very big when the bias is close to 1.0 V. Then we want to ask, what causes these differences? In order to understand them, the transmission functions of these two systems are plotted in figure 3.

From figure 3, we can find that the two systems show obviously different features in the transmission function in equilibrium cases. In a very big energy range around the Fermi level, the nanowire/ C_{60} /nanowire system shows very wide transmission peaks or platforms and we can get an equilibrium conductance of $2.18G_0$. However, in the atomic-chain/ C_{60} /atomic-chain system, the transmission function is composed of distinct and independent peaks. In fact, these peaks originate from the resonant tunneling of electrons through the molecular orbitals of the C_{60} . This can be clearly seen from the partial density of states (PDOS) contributed

by the C_{60} molecule in the device (see figure 4). There is good correspondence between the peaks in the transmission function and those in the PDOS. It is well known that C_{60} has a big HOMO-LUMO gap of about 1.70 eV [28], with a triple degeneracy for the LUMO and fivefold degeneracy for the HOMO. The peak at 0.50 eV is mediated by the LUMO while the peak at -1.30 eV arises from the HOMO. The origin of peaks in this system is different from other cases with 1D electrodes where sharp peaks are frequently observed at the band edges of the electrode and are due to the Van Hove singularities [29].

It is natural to ask where this big difference in the transmission functions for the two models comes from. Due to the large HOMO-LUMO gap of C_{60} , it is believed that it should have a poor conductance. Actually, the cluster solid made from C_{60} is an insulator [30]. However, when C_{60} is connected to two metal electrodes, electrons will be transferred from the electrodes to the cluster, so that the LUMO of the C_{60} is partially filled and electrons can transmit through C_{60} by the LUMO. This is why in the nanowire/ C_{60} /nanowire system we can observe a big conductance. This has also been observed in the system where the C_{60} is sandwiched between two Al electrodes [28]. Mulliken population analysis really shows that there is a charge transfer of 1.90 electrons from the electrodes to the cluster in the nanowire/ C_{60} /nanowire system

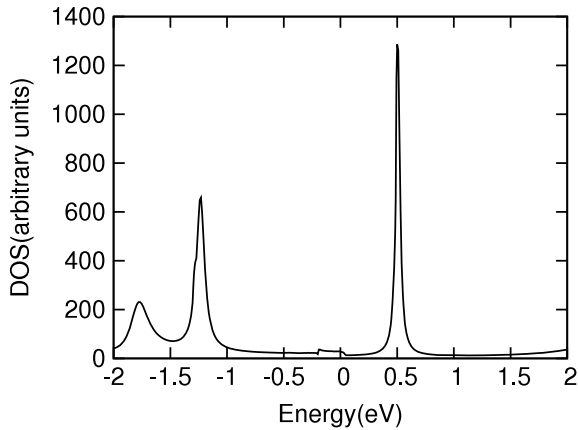


Figure 4. The PDOS contributed by the C_{60} molecule in the atomic-chain/ C_{60} /atomic-chain structure.

and the Fermi level crosses the LUMO of the C_{60} . However, in the atomic-chain/ C_{60} /atomic-chain structure, the electron transfer from the electrodes to the cluster is much less, indeed almost negligible (about 0.11 electrons), so that the Fermi level lies inside the HOMO–LUMO gap of the C_{60} . Thus, the transmission around the Fermi level is very small. Since the Fermi level is close to the LUMO, the transport under low bias in the atomic-chain/ C_{60} /atomic-chain system is determined by the LUMO peak at 0.50 eV shown in figure 3.

The big difference of charge transfer is a result of two factors: the electron donating ability of the electrodes and the contact geometry or bonding situation between the central molecule and electrodes. It is easy to understand that the nanowire electrode can provide more charge transfer due to its much larger number of atoms. Furthermore, due to the bigger size of the electrodes in the nanowire/ C_{60} /nanowire system, many more atoms in the electrodes and in the C_{60} molecule directly interact with each other. Especially, the C–C dimer at the interface is bonded to four Au atoms in the nanowire/ C_{60} /nanowire system while it is bonded to only one Au atom in the atomic-chain/ C_{60} /atomic-chain system. This gives rise to different electrode– C_{60} couplings and can be reflected by extra charge distribution on C atoms in the C_{60} molecule, as shown in figure 5. From this figure, we find that the C atoms on the C_{60} molecule in the nanowire/ C_{60} /nanowire system attract much more charge from the electrodes than those in the atomic-chain/ C_{60} /atomic-chain system. In the atomic-chain/ C_{60} /atomic-chain system, the extra charge on each C atom is almost zero except for the C–C dimer that is directly bonded to the end Au atom of the electrode on each side.

The different coupling strengths can also be indicated by comparing the binding energies of these systems. We study this by choosing the central region as an isolated unit, and the binding energy E_b is defined as follows:

$$E_b = (E_{C_{60}} + E_{\text{surface}}) - E_{\text{center}}, \quad (3)$$

where E_{center} is the total energy of the isolated unit, $E_{C_{60}}$ is the total energy of the C_{60} molecule and E_{surface} is the total energy of the isolated unit excluding the C_{60} molecule. The

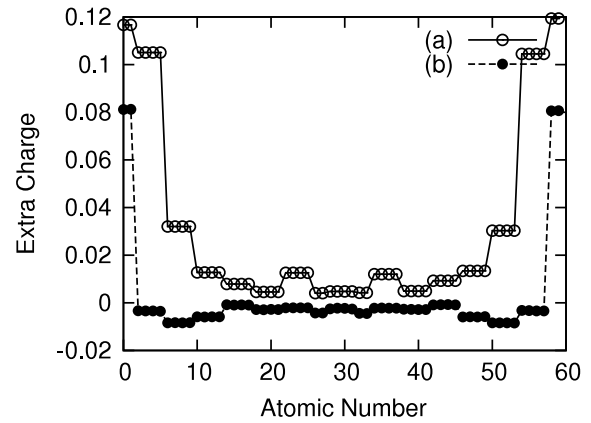


Figure 5. The extra charge on each atom in C_{60} for (a) the nanowire/ C_{60} /nanowire structure; (b) the atomic-chain/ C_{60} /atomic-chain structure. The atoms in the C_{60} are indexed from left to right.

binding energy is 3.95 eV for the atomic-chain/ C_{60} /atomic-chain system, while 5.10 eV for the nanowire/ C_{60} /nanowire system. This shows that the coupling strength is much stronger in the nanowire/ C_{60} /nanowire system than that in the atomic-chain/ C_{60} /atomic-chain system.

Due to the difference in the coupling strength, under the interaction of the electrodes the energy levels of the C_{60} molecule are differently affected. In the atomic-chain/ C_{60} /atomic-chain system, the energy levels of C_{60} change very little so that the transmission consists of sharp peaks, while in the nanowire/ C_{60} /nanowire system, the energy levels of C_{60} are strongly renormalized and broadened so that the transmission curve are composed of wide peaks or platforms.

Besides the completely different coupling strength between the electrodes and the cluster, the different number of eigenchannels that the electrodes can provide also play an important role in deciding the different transport behaviors in these two systems. Although we can get a big conductance of $2.18G_0$ at the Fermi level in the nanowire/ C_{60} /nanowire system, the triply degenerate LUMO in the C_{60} in the atomic-chain/ C_{60} /atomic-chain system only produces a transmission peak with a height less than $1G_0$ at 0.5 eV. This is because at this energy the electrodes can only provide one channel for the electrons in the atomic-chain/ C_{60} /atomic-chain system (shown in figure 3 by the dash line). This is an upper limit for the transmission through a molecular device. However, in the nanowire/ C_{60} /nanowire system, the upper limit set by the number of eigenchannels that the electrode can provide is much bigger. Thus a much bigger transmission is obtained in this device.

The features of the transmission functions can give us a clear explanation for why the current in the nanowire/ C_{60} /nanowire system starts to increase rapidly with bias while it starts to increase very slowly in the atomic-chain/ C_{60} /atomic-chain system. In the nanowire/ C_{60} /nanowire system, the transmission in the bias window is always very big so that it gives rise to a big current, while in the atomic-chain/ C_{60} /atomic-chain system, at the beginning, the

transmission is very small and almost close to zero. It starts to increase very slowly until the bias is big enough to reach the LUMO peak in the transmission function. Only then can a rapid increase of the current be observed.

Finally, it is easy to understand the difference in the temperature effects in these two systems. Finite temperature means that the transmission in a small energy range outside the bias window also contributes to the current, while the transmission in a small energy range very close to the chemical potentials μ_L and μ_R inside the bias window will make a lesser contribution to the current. Since the difference in the transmission at energies below and above μ_L and μ_R in the nanowire/ C_{60} /nanowire system is not big, no big difference is observed in the currents at 0 K and 300 K. However, it is a different story in the atomic-chain/ C_{60} /atomic-chain system. When the bias is close to 1.0 V, the chemical potential of the right electrode is close to 0.5 eV. This causes the upper limit of the integration to reach the LUMO peak at 0.5 eV in the transmission (see figure 3). Since the transmission above μ_R is much bigger than the transmission below μ_R , a big increase due to the finite temperature can be obtained.

4. Summary

We have studied the transport properties of the C_{60} molecule by using two different models of electrodes, one a gold nanowire and the other a gold atomic chain. Different transport behaviors are obtained. In the nanowire/ C_{60} /nanowire system, the device shows a metallic behavior with the transmission function composed of wide peaks and platforms due to the strong coupling between the electrodes and the cluster. The equilibrium conductance is as big as $2.18G_0$ and the current increases very quickly and almost linearly, starting from zero. While in the atomic-chain/ C_{60} /atomic-chain system, the transmission function is characterized by resonant tunneling peaks and these peaks are mediated by molecular levels of the C_{60} molecule. And since the Fermi level is a little far from the LUMO peak, the current increases very slowly at the beginning until the bias windows is big enough to include the LUMO peak. Two factors determine the different transport behavior of the two devices: one is the coupling strength between the molecule and the electrodes and the other is the number of eigenchannels the electrodes can provide.

Acknowledgments

The author (X H Zheng) is grateful to Dr W C Lu for helpful discussions. This work was supported by the National Science Foundation of China under grant nos 10774148, 10747161 and 10804110, the special Funds for Major State Basic Research

Project of China (973) under grant no. 141J00775601, 863 Project, Knowledge Innovation Program of Chinese Academy of Sciences, and Director Grants of CASHIPS, CUHK Direct grant no. 2160345. Part of the calculations were performed at the Center for Computational Science of CASHIPS and the Shanghai Supercomputer Center.

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