

Quantum Transport through Na@C₆₀ Endohedral Complex

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ABSTRACT

We have investigated the electronic transport properties of molecular junctions constructed by Na@C₆₀ molecule by using non-equilibrium Green's function based on Landauer-Büttiker formula. For the systems under investigation, we study the effects of contact geometries and displacement of the central atom. Our results indicate that the electronic transport properties are obviously affected by the number of contact points between the device electrodes and the molecule. Also the movement of the central atom can play an important role in the electron conduction.

KEYWORDS: Endohedral fullerene, Electronic transport, Non-equilibrium Green's function, Contact geometries.

1. INTRODUCTION

Tremendous advances have been made in microelectronics technology during the past decades. Recently years, the progress in self-assembly techniques, such as chemical synthesis and scanning tunneling microscopy, have made it possible to design a single molecular device and control the electronic transport properties on molecular scale [1]. Endohedral fullerenes have attracted much attention in nanoscale science and technology because of their novel physical properties and potential for device applications [2-4]. Their formation occurs due to the geometrical confinement of atoms inside the fullerenes. It is known that non-metal atoms such as nitrogen and phosphorus can produce the endohedral structures M@C₆₀ with negligible effect upon the carbon cage [5,6], while the active metals (alkali, rare earth elements) interact much stronger with fullerenes such as C₆₀ [3,4,6,7].

Electronic transport through single molecules strongly depends on the nature and quality of the contacts with electrodes. Among many types of molecules, the fullerene C₆₀ is suitable for molecular bridge because its LUMO is situated at relatively lower energies in comparison with other organic molecules [8]. During the last decade, the electron conduction through C₆₀ molecule and endohedral fullerenes-carbon cages, encapsulating atomic or molecular species has been extensively investigated both experimentally [9-15] and theoretically [16-21].

Wu et al. showed that the coupling between the molecule and the two electrodes and the energy gap between the highest occupied molecular orbital and the lowest unoccupied molecular orbital of the molecule dominate the transport properties [22]. Joachim and co-workers found that the current-voltage characteristics present a linear behavior at low bias due to the absence of molecular orbitals around Fermi energy, and squeezing a C₆₀ molecule by applying a small force can result in a shift in the molecular orbital energy levels [9, 10].

Based on the Green's function method, it has been shown that a loop current emerges in a C₆₀ molecule by incorporating an extra atom at the center of the fullerene molecule [7, 23]. In this paper we study the transmission probability and current in the Na@C₆₀ molecule by using the non-equilibrium Green's function (NEGF) based on Landauer-Büttiker formula. Here we find it is possible to control the current by displacement of the Na ion. The central ion acts like a controlling element in the combined Na@C₆₀ molecular bridge so that it can act as some kind of functionality in the future nano-device applications. We also study the effect of contact geometry on the electron conduction through the molecule.

2. Model and Formalism

We consider a system consists of an endohedral complex Na@C₆₀ molecule attached to two 1D metallic electrodes. We extend the SSH Hamiltonian as:

$$H_C = \sum_i \varepsilon_i c_i^\dagger c_i + \sum_{\langle i,j \rangle} [-t_o + \alpha(y_{ij})](c_i^\dagger c_j + HC) + \frac{1}{2} \sum_{\langle i,j \rangle} K(y_{ij})^2 + V_{\alpha_i} \quad (1)$$

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Here y_{ij} is the change of the bond length between sites i and j , t_s is the hopping integral and α is the electron–phonon coupling constant, c_i^+ (c_i) is the creation (annihilation) operator of the electron at the site i , K is the spring constant, the sum is taken over nearest-neighbor pairs $\langle i, j \rangle$, ε_i is the orbital energy of π electrons that describes the additional Coulomb interactions between the inner metal ion and the cage.

$$\varepsilon_i = -\frac{e}{r_{oi}}, \quad (2)$$

Here $\frac{e}{r_{oi}}$ is the additional Coulomb interaction between the sodium ion and the π electrons on the cage

and r_{oi} is the distance between the sodium ion and carbon atoms of the cage.

The first two terms in the Hamiltonian describe the electronic interaction, and are expressed in second-quantized form and should be treated quantum mechanically. The last term in the Hamiltonian represents the interaction between the sodium ion and the carbon atoms on the cage. When a plane of graphite is rolled into a fullerene cage, a little electronic charge will be transferred from inside to outside the cage. This is due to the higher density of electrons inside and the repulsive interactions between them. Therefore, the C_{60} cage can be viewed as a spherical double layer with a slight positive charge inside and a negative charge outside. On the basis of such a physical picture, the interaction between the sodium ion and the carbon atoms on the cage is taken as:

$$V_{oi} = A \frac{e^{-\beta r_{oi}}}{r_{oi}^2}, \quad (3)$$

Here, A is a strength factor and β is a screening factor. These two parameters can be determined by other results of first-principle calculations or experiments [24, 25].

The Green's function of the system in the presence of the bias voltage can be given as:

$$G(\varepsilon, V_a) = [\varepsilon I - H_C - \Sigma_L(\varepsilon - eV_a/2) - \Sigma_R(\varepsilon + eV_a/2)]^{-1}, \quad (4)$$

H_C is the Hamiltonian of the central part and Σ_L and Σ_R describe the self-energy matrices which contain the information of the electronic structure of the electrodes and their coupling to the molecule. These can be expressed as:

$$\Sigma_{L,R}(\varepsilon) = \tau_{CL,R} g_{L,R}(\varepsilon) \tau_{CL,R}^+, \quad (5)$$

τ_C defines the coupling matrix between the surface atomic orbitals of the lead and the channel. Also, $g_{L,R}(\varepsilon)$ is the surface Green's function for the semi-infinite electrodes. Using the iterative method for the calculation of the transfer matrices based on the principal layers concept, the surface Green's function of the left and right leads can be obtained as [26]:

$$g(\varepsilon) = \left(-\frac{1}{t}\right) e^{ika}, \quad (6)$$

where k is the wave vector in the electrode.

We use the non-equilibrium Green's function (NEGF) method [27] to calculate the charge density due to the bias voltage V_a . The density matrix of the scattering region is calculated from the so-called lesser Green's function $G^<(\varepsilon)$ of the scattering region [27]. We solve self consistently the central part Hamiltonian by an iterative method [28]. Also, the Green's function and the charge density on each atom in the channel are iteratively calculated until a convergence of the change of the bond length is reached [29]. The current–voltage characteristic is calculated as:

$$I(V_a) = \frac{e}{h} \int_{-\infty}^{+\infty} T(\varepsilon, V_a) [f(\varepsilon - \mu_L) - f(\varepsilon - \mu_R)] d\varepsilon, \quad (7)$$

Where f is the Fermi distribution function, $\mu_{L,R} = E_f \pm \frac{1}{2} eV_a$ are the chemical potentials of the electrodes, and $T(\varepsilon, V_a) = Tr[\Gamma_L G^R \Gamma_R G^A]$ is the energy and voltage-dependent transmission function.

G^R , G^A are retarded and advanced Green's functions, and $\Gamma_{L,R}$ known as the broadening function, can be expressed as $\Gamma_{L,R} = -2\text{Im}(\Sigma_{L,R})$.

3. RESULTS AND DISCUSSION

Based on the formalism described in Section 2, we have investigated the electronic transmission spectrum and current of the Na@C₆₀ molecule attached to one-dimensional metallic electrodes. First, we adjust our parameters by results of first-principle calculations, such as the maximum and minimum bond lengths and off-centre position of metal atoms when all the carbon atoms are kept stable. In the numerical calculation, we used parameters from J. Liu paper [24].

$$t_0 = 2.50 \text{ eV}, \alpha = 3.99 \text{ eV/\AA}^\circ, K = 28.4 \text{ eV/\AA}^\circ, A = 196 \text{ eV/\AA}^\circ, 1/\beta = 0.44 \text{ \AA}^\circ$$

In the endohedral fullerene species such as Na@C₆₀, the encapsulated Na atom donates its valence electron to the C₆₀ cage due to the higher electron affinity of the cage. Therefore, in fact, it is a Na ion inside the cage, but now there is N + 1 π electron.

We kept all carbon atoms stable on the C₆₀ cage and moved the Na ion along the fivefold axis. In Fig 1, the I-V characteristics of Na@C₆₀ where one carbon atom in the C₆₀ is coupled to electrode, is indicated. When the sodium ion is at the centre of the cage, Na@C₆₀ endohedral has the same electronic structure as pristine C₆₀. Therefore one can expect its I-V characteristics be similar to pristine C₆₀. Our results are in accordance with the experimental results [11, 12]. At the center of the cage, the current has a maximum and when the ion moves from the center along the fivefold axis, the current decreases. At 1.6 \AA° from the center, the current reaches a local maximum and when the ion moves further towards the side of the cage, the current decreases again.

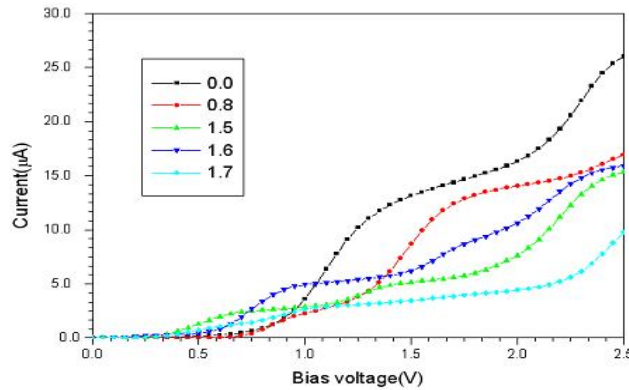


Figure 1. Current vs bias voltage characteristics for different positions of ion for one contact.

In Fig. 2 we have shown the transmission coefficient as a function of the energy of the electron which is emitted from the left electrode into the molecule, for $V_a = 2.5$ V. It is clear that the transmission functions have large values (peaks) near the molecular levels of Na@C₆₀.

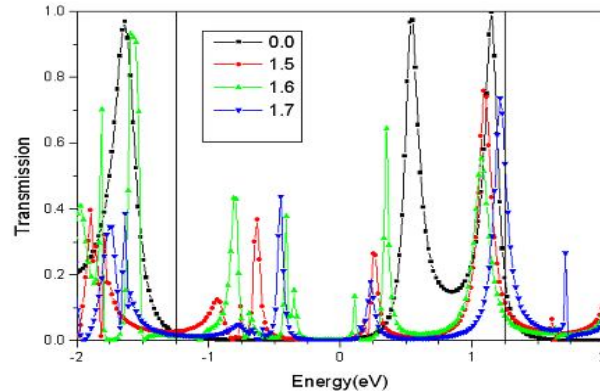


Figure 2. Current transmission probability as a function of energy for different positions of ion at $V_a = 2.5$ V when one carbon atom of C₆₀ is connected to the electrode. The regions between the vertical lines refer to the bias window.

In the coherent transport, the electron wave function is assumed to extend coherently across the whole system. Accordingly, when the electron energy nearly coincides with the molecular levels, the electron resonantly transmits through the molecule and a large transmission arises. From Eq. (6) it is seen that the current depends on two factors which are the transmission function and the Fermi function difference (FFD) between the left and right electrodes. The results indicate that only electrons with energies within the energy region, $[\mu_L, \mu_R]$, contribute to the total current integral, which is called the bias window or integral window [30]. Therefore, the integral area in the bias window determines the current. As a result, the total current is equal to the area under curve of transmission in the region of the bias window. The regions between the vertical lines of every transmission spectrum refer to the bias window.

Fig. 2 indicates that when the sodium ion is at the center of the cage, the area under the transmission curve in the bias window is largest and the current has a maximum. When the ion moves from center along the fivefold axis height of peaks decreases and therefore the current decreases. When the ion is at 1.6 \AA from the center, there are more peaks compared with two (1.5 \AA , 1.7 \AA) other curves. Therefore current has a local maximum.

Connecting the molecule to the electrodes broadens and shifts the discrete states of the molecule. This broadening of the states depends on the strength of the coupling to the contacts. Therefore, one can expect different behaviors for the transmission coefficient (TC) of the system in the cases of single and multiple contacts. We have also studied the effects of changing the number of contact points. The main difference between the single and multiple contacts is the interference effect. When the molecule is contacted through multiple carbon atoms to the electrodes, the electron waves in the molecule which come from the different contact points may suffer a phase shift. Thus, a constructive or destructive interference in the propagation process of the electron through the molecule can occur and hence the transmission curve can be change. As mentioned in Sec. 2, the effect of contacts is described by the self-energy matrices. Therefore, the Green's function (and hence the density of states) of the coupled molecule and the transmission spectrum vary with the number of contact points.

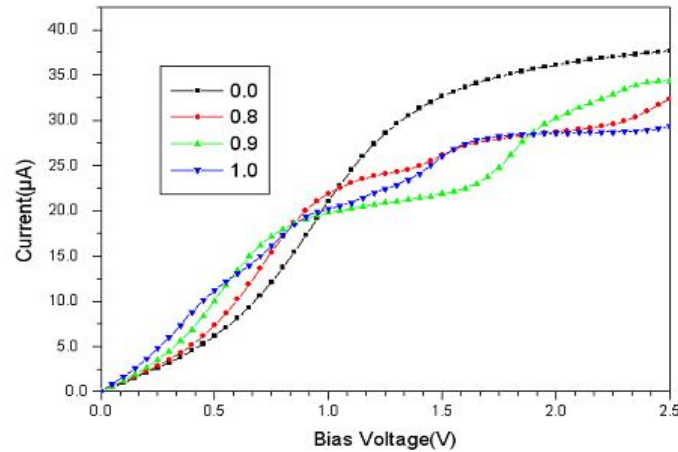


Figure 3. Current vs bias voltage characteristics for different positions of ion for five contacts.

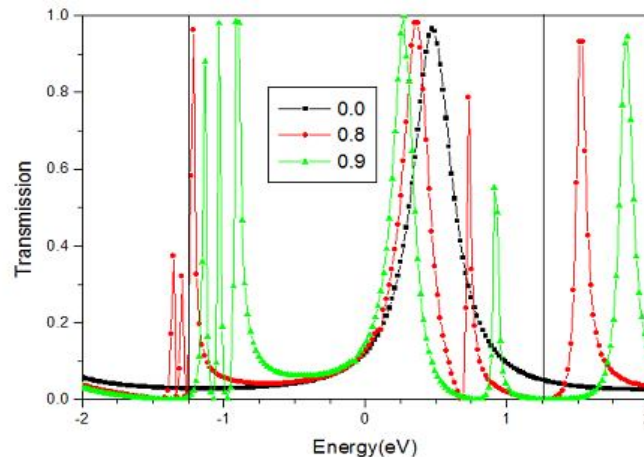


Figure 4. Current transmission probability as a function of energy for different positions of ion at $V_a = 2.5 \text{ V}$ when five carbon atoms of C_{60} is connected to the electrode. The regions between the vertical lines refer to the bias window.

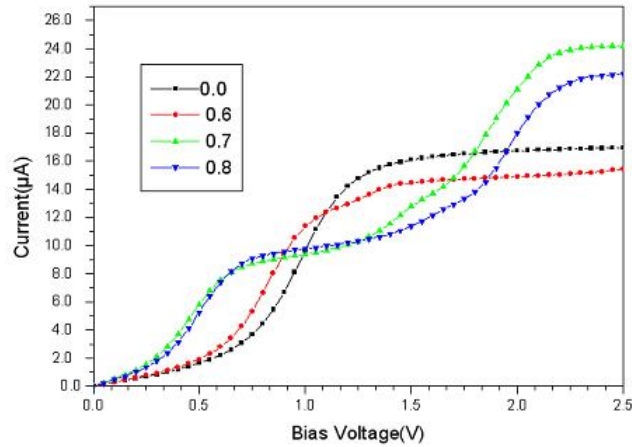


Figure 5. Current vs bias voltage characteristics for different positions of ion for six contacts.

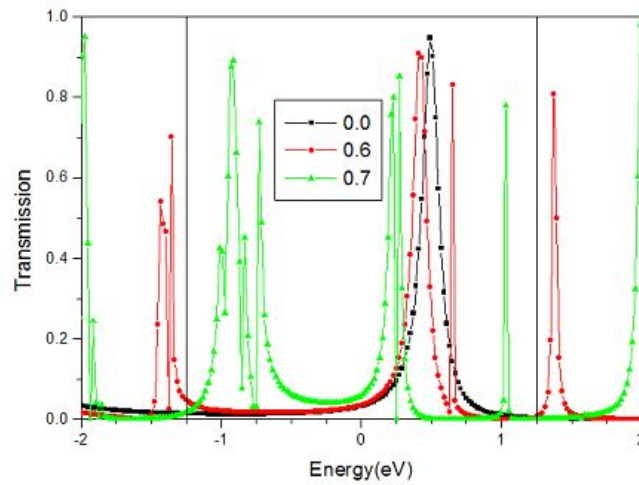


Figure 6. Current transmission probability as a function of energy for different positions of ion at $V_a=2.5$ V when six carbon atoms of C_{60} is connected to the electrode. The regions between the vertical lines refer to the bias window.

By comparing Figs. 3 and 5 with Fig. 1, and Fig. 4 and 6 with Fig. 2, one can easily observe the influence of interference effects on the electronic transport.

From Fig. 3, we can see that when the central ion is at the center of the cage, the current has a maximum and when the ion moves away from the center, the current decreases similar to the first case. At 0.9 \AA from the center, the current reaches a local maximum.

In the case of connection to one carbon atom, the value of TC at the Fermi energy is near zero, however, it is considerable in the case of five contacts. The area under curve of transmission in the case of connection to five carbon atoms is larger with respect to the two other cases therefore the current is largest. In Fig. 5 we have shown the current as a function of bias voltage where six carbon atoms in the C_{60} is coupled to the electrode. As similar as the two other cases the current decreases when the sodium ion moves from the center along the fivefold axis.

At 0.7 \AA from the center, the current reaches a maximum and when the ion moves further towards the side of the cage, the current decreases again. In spite of two other cases when the ion is at the center of the cage, the current is not a maximum. Fig. 6 indicates that the number of peaks when the sodium ion is at 0.7 \AA from the center is larger with respect to the two (0.0, 0.6) other curves and the current is a maximum.

4. Conclusions

We have studied the effects of different contact geometries and the movement of the central ion inside the cage on the electronic transport through $\text{Na}@C_{60}$ molecule sandwiched between two 1D

metallic electrodes by applying the nonequilibrium Green's function technique and the Landauer theory. The results indicate that the transmission curves and the I-V characteristics calculated at the single and multiple couplings to the electrodes can be completely different due to the interference effects. In addition, the displacement of sodium ion inside the C_{60} cage can completely change the I-V characteristics. Our results therefore indicate that the contact geometries, and displacement of the sodium ion play important roles and may change the physical picture of electron conduction in C_{60} -based endohedral devices. The model that we proposed could also be applied to other endohedral complexes which consist of different kinds of atoms or ions and different fullerenes.

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