Electronic transport through a C_{60} molecular bridge: The role of single and multiple contacts

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The effects of different contact geometries, bond dimerization, and gate voltage on quantum transport through a C_{60} molecule are studied by the Landauer-Büttiker formula based on the Green’s function technique. It is shown that the number of contact points between the device electrodes and the molecule can play an important role in the electron conduction. The transmission is due to the resonant tunneling when the electrodes are contacted to one carbon atom of the molecule. In the case of multiple contacts, the interference effects are responsible for the change of the transmission through the C_{60}. The bond dimerization and a gate voltage shift the molecular levels and by adjusting the related parameters the electron conduction can be controlled.

I. INTRODUCTION

Molecular electronics using single molecules as active elements is a promising technological concept with fast growing interest. Recent improvements in manipulation of individual or small numbers of molecules permit us to contact molecules to metallic electrodes and measure their electronic transport properties. Electronic transport through single molecules strongly depends on the nature and quality of the contacts with electrodes. If, e.g., a molecule is weakly coupled to the electrodes, the charge at the molecule becomes strongly localized and the transport takes place in the regime of Coulomb blockade. In the opposite case (strong coupling), we can expect to approach the ballistic regime.

The selection of a molecular bridge and the accurate control on its coupling to the electrodes are basic prerequisites for designing and manufacturing single molecule electronic devices. In such a structure, the energies of the molecular orbitals, in particular, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), are of crucial importance for the electronic transport through single organic molecules. Among many types of molecules, the fullerene C_{60} is suitable for molecular bridge because its HOMO is situated at relatively lower energies in comparison with the other organic molecules. The electronic structure of isolated C_{60} molecules shows a large gap (≈ 2 eV), which indicates that the molecules should behave like insulators at room temperature. However, when they are contacted by metallic electrodes, charge transfer occurs and they become conducting through the LUMO of the isolated molecules.

During the last decade, the electron conduction through a C_{60} molecule has been extensively investigated both experimentally and theoretically. Joachim and co-workers studied the conductance through a C_{60} molecule sandwiched between the Au(110) surface and a scanning tunneling microscopy (STM) tip at ambient temperature. The results showed that the current-voltage (I-V) characteristics of the molecule are linear at low voltages due to the absence of molecular orbitals around Fermi energy. Porath and co-workers deposited isolated C_{60} molecules onto a gold substrate, covered by a thin insulating layer. In this way, a double barrier tunnel junction configuration was realized in which a C_{60} molecule is coupled via two junctions to the gold substrate and the tip of a STM. The tunneling I-V spectra exhibited a nonvanishing gap in the curves around zero bias due to the single-electron tunneling effects, such as the Coulomb blockade and the Coulomb staircase. Park et al. studied contacts to a C_{60} molecule on Cu(100) and observed that the conductance rapidly increases in the transition region from tunneling to contact, with decreasing tip-molecule distance.

On the other hand, using the tight binding model, it was theoretically found that the strength of the metal/C_{60} interaction and the geometry of the contact between the tip and the molecule play an important role in the drastic increase in the conductance. Based on the Green’s function method and the Landauer-Büttiker formula, it has been shown that a loop current emerges in a C_{60} molecule when the electron energy approaches the energy levels of the molecule. The magnitude of the such loop currents can be much larger than that of the source-drain currents. By incorporating an extra atom at the center of the fullerene molecule, it is possible to control the currents in the loops and hence the procedure of transport. By using density functional theory, the electronic transport through a C_{60} molecule in between carbon nanotube leads and Al metallic electrodes has also been investigated.

The C_{60} molecule consists of 12 pentagons and 20
hexagons. Due to dimerization, the carbon-carbon bonds in the molecule have different lengths: $r_1 = 1.46$ Å for the single bonds (bonds on the pentagons) and $r_2 = 1.40$ Å for the double bonds (bonds on the hexagons that are not shared by a pentagon). We believe that the effect of bond dimerization on the electron transmission may considerably affect the $I$-$V$ characteristics, under suitable conditions. Furthermore, when two electrodes are connected to the molecule, the number of contact points will depend on the direction of the molecule; thus, single or multiple contacts may occur. Therefore, the effects of contact geometry in the presence of bond dimerization and a gate voltage on the electron conduction through the molecule should be studied. Such features have not been investigated in the above-mentioned studies. It is the purpose of this paper to study the role of bond dimerization, multiple contacts (see Fig. 1), and gate voltage in the coherent transport through a C$_{60}$ molecule, based on the tight-binding model and the nonequilibrium Green’s function technique.

The paper is organized as follows. The theoretical model and formalism are given in section II. In section III, we present the numerical results of the coherent transport through the C$_{60}$ molecular bridge with different electrode/molecule contacts in the presence of bias and gate voltages. A brief conclusion is given in section IV.

II. MODEL AND METHOD

We consider a system consists of a C$_{60}$ molecule attached to one-dimensional metallic electrodes. The Hamiltonian of the system is described within the tight-binding approximation with only one orbital per atom,

$$\hat{H} = \sum_i \epsilon_i c_i^\dagger c_i - \sum_{<ij>} t_{ij} c_i^\dagger c_j.$$  

(1)

Here, $\epsilon_i$ is the on-site energy and will be set to zero except in the gated region (C$_{60}$ molecule) where it is equal to $V_g$. $c_i^\dagger$ ($c_i$) is the creation (annihilation) operator for an electron at $i$th site and $t_{ij}$ is the hopping matrix element between nearest-neighboring sites $i$ and $j$. The hopping strength in C$_{60}$ molecule depends on the C-C bond length; thus, we assume different hopping matrix elements: $t_1$ for the single bonds and $t_2$ for the double bonds. In the case of bond dimerization, it is reasonable to use $t_2 \approx (r_1/r_2)^2 t_1$. The coupling between the nearest sites in the electrodes is taken to be $t = t_1$ and that between the molecule and the electrodes is taken to be $t'$. In this study, we assume that the electrons freely propagate and the only resistance arising from the contacts. This means that the transport is ballistic, therefore, we set $t' = t/2$ according to Ref. 2.

The Green’s function of the C$_{60}$ molecule coupled to the two metallic electrodes (source and drain) in the presence of the bias voltage is given as

$$\hat{G}_C(\epsilon, V_a) = [\epsilon \hat{1} - \hat{H}_C - \hat{\Sigma}_L(\epsilon - eV_a/2) - \hat{\Sigma}_R(\epsilon + eV_a/2)]^{-1},$$  

(2)

where $\hat{H}_C$ describes the Hamiltonian of the molecule in the absence of the electrodes and $\hat{\Sigma}_L$ and $\hat{\Sigma}_R$ 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

$$\hat{\Sigma}_{L,R}(\epsilon) = \tilde{\tau}_{C_{L,R}} \hat{g}_{L,R}(\epsilon) \tilde{\tau}_{L,R} C,$$  

(3)

where $\hat{g}_{L,R}$ are the surface Green’s functions of the uncoupled leads, i.e., the left and right semi-infinite leads. $\tilde{\tau}$ is a matrix that couples the molecule to the leads and is determined by the geometry of the molecule-lead bond. Note, that in the semi-infinite one-dimensional electrodes described by the single-band tight-binding model, only the first site is connected to the molecule. As a result, the surface Green’s function for the semi-infinite leads can be written as $g_{L,R} = -(1/t) e^{iE_{K_{L,R}}/2}$, where $k_{L,R}$ is the wave vector in the left (right) electrode 22.

When the molecule is brought close to an electrode, the bonding between them will depend on the molecule orientation. This orientation can be such that only one carbon atom, a pentagon or a hexagon, of the C$_{60}$ molecule be in contact with the leads. Therefore, one can expect different conduction through the molecule, which arises due to the interference effects, and will be discussed in detail in the next section. For this reason, we make use of the nonequilibrium Green’s function technique to obtain the current for a constant bias voltage $V_a$ between two electrodes. Since the total Hamiltonian [Eq. (1)] does not contain inelastic scatterings, the current is computed from the Landauer formula 25,26

$$I = \frac{2e}{h} \int_{-\infty}^{\infty} T(\epsilon, V_a) [f(\epsilon - eV_a/2) - f(\epsilon + eV_a/2)] d\epsilon,$$  

(4)

where $f$ is the Fermi function and $T(\epsilon, V_a)$ is the energy- and voltage-dependent transmission function given by

$$T(\epsilon, V_a) = \text{Tr}[\hat{\Gamma}_L(\epsilon - eV_a/2) \hat{G}_C(\epsilon, V_a) \hat{\Gamma}_R(\epsilon + eV_a/2) \hat{G}_C^\dagger(\epsilon, V_a)].$$  

(5)
FIG. 2: Transmission probability as a function of energy at $V_G = 0.0$ V and $V_a = 0.5$ V for different contacts in two cases: $t_2 = 1.1 t_1$ (solid curve) and $t_2 = t_1$ (dashed curve).

The coupling matrices $\hat{\Gamma}_{L,R}$, also known as the broadening functions, are related to the self-energies through

$$\hat{\Gamma}_{L,R} = i[\hat{\Sigma}_{L,R} - \hat{\Sigma}^\dagger_{L,R}].$$

Equations (4) and (5) form the basis for our analysis of the coherent transport through the molecular bridge. Our approach, as a real-space method, makes it possible to model arbitrary the number of contacts. In this regard, the core of the problem lies in the calculation of the self-energies $\hat{\Sigma}_{L,R}$. In the case of contact through a single carbon atom of the molecule, only one element of the self-energy matrices is non-zero. However, for the transport through opposite pentagons or hexagons, 25 or 36 elements of the self-energy matrices are nonzero, respectively.

FIG. 3: The same as Fig. 2 but for $V_G = 2.0$ V.

III. RESULTS AND DISCUSSION

The present formalism can be applied to the systems in which an arbitrary number of carbon atoms of the C$_{60}$ molecule can be coupled to the one-dimensional metallic electrodes. In this study, the coupling through one, five, and six carbon atoms to the electrodes will be considered (see Fig. 1). These cases were chosen as the most probable experimental orientations. In the numerical calculations we set $t_1 = 2.5$ eV, $t_2 = 1.1 t_1$, $E_F = 0.0$ eV, and $T = 300$ K.

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 as well as the wave function of the particular state. Therefore, one can expect different behaviors for the transmission coefficient (TC) of the system in the cases of single and multiple contacts. In order to investigate such a behavior, in Figs. 2 and 3 we have shown the TC as a function of the energy of the elec-
tron which is emitted from the left electrode into the molecule, for $V_a = 0.5\,\text{V}$ at $V_G = 0.0\,\text{V}$ and $V_G = 2.0\,\text{V}$, respectively. It is clear that the transmission functions have large values (peaks) near the molecular levels of C$_{60}$. 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 Fig. 3, it is evident that, a gate voltage shifts the states and, due to this effect, the transmission channels can significantly vary. Therefore, a gate potential can change the electron conduction through this device, producing field-induce molecular switching.

The number of peaks in the case of connection to five carbon atoms of the C$_{60}$ molecule is lower with respect to the other cases. 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. In both figures, the main factor for the difference between the single and multiple contacts is the interference effect. In fact, when the molecule is contacted through one carbon atom to the electrodes, the transmission through the molecule corresponds to the resonant tunneling effects. With increasing the number of contact points, the interference effects around these contact points become important, some resonances might completely disappear, and the transmission curve changes. By comparing the Figs. 2(b) and 2(c) with Fig. 2(a), and Fig. 3(b) and 3(c) with Fig. 3(a), one can easily observe the influence of interference effects on the electronic transport. The physical meaning of the interference effect is that 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. As mentioned in Sec. II, 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.

Note that in the quantum transport, the width of the transmission resonances depends on the electrode/molecule coupling strength. In one-dimensional electrodes, only one atom (end site) is coupled to the carbon atoms. Therefore, if we increase the number of atoms at the surface of electrodes, by choosing electrodes with finite cross sections, then the width of resonances becomes significantly broader for the cases of five and six atomic contacts. We have also studied the effects of changing the electrode/molecule coupling strength. The results for the case of single contact showed that the TC increases with increasing $t'$. For strong coupling, the peaks are broadened which indicate that the electronic transport can no longer be considered as resonance tunneling through eigenstates of the isolated C$_{60}$ molecule. In the case of multiple contacts, however, the broadening of peaks and the increase in TC are not noticeable.

This suggests that the interference effects play a dominant role in the transmission through the molecule, when we increase the number of contact points.

On the other hand, it is important to note that the presence of both single and double bonds causes a shift in the peaks of TC. Shift to the higher or lower energies depends on the peak positions. From the Figs. 2(a) and 2(c), it is clear that the difference in bond lengths gives rise to an extra peak in the TC curves due to the
FIG. 5: The same as Fig. 4 but for $V_G = 2.0$ V.

The gate voltage shifts the position of peak, as shown in Figs. 3(a) and 3(c). Therefore, the effect of bond dimerization (i.e., $t_2 = 1.1 t_1$) is that, the degeneracy of one of the molecular levels is lifted. By applying a suitable gate voltage, this effect may be important, if this level be nearly coincided with the Fermi energy of the metallic electrodes.

In order to provide a deep understanding of the electronic transport, we have shown the $I$-$V$ characteristics in Figs. 4 and 5, at $V_G = 0.0$ V and $V_G = 2.0$ V, respectively. Since our structure is symmetric, we obtained a symmetrical behavior in the $I$-$V$ curves with respect to $V_a = 0.0$ V. For this reason, we have not shown the results for negative applied voltages. At $V_G = 0.0$ V and in the case of one contact point, a threshold voltage is needed to generate current through the device which shows that, at low applied voltage the device is in its off state. For a certain gate voltage such as $V_G = 2.0$ V, the device is turned on and the current linearly increases for low applied voltages [see Fig. 5(a)]. For the case that $t_2 = 1.1 t_1$, the threshold voltage is nearly two times larger than that in the case of $t_2 = t_1$. When the number of carbon atoms which take part in coupling between the molecule and the electrodes increases, the $I$-$V$ characteristics show an Ohmic behavior at low applied voltages. Such a behavior is reasonable because in this situation, the hybridization with the electrodes is stronger and there are more paths for the electrons to pass from the metal to the molecule. The curves in all figures, particularly in Fig. 4, show a steplike behavior which indicates that a new channel is opened.

The present results for the $I$-$V$ characteristics of the cases of single and multiple contacts are qualitatively in agreement with the experimental results in Refs. 12, 13, and 10 respectively. In Ref. 8, the bond length difference has been ignored because they believed that the shift in the energy spectrum is less than 2%, and there is no significant difference in the electron conduction through the molecule. The present results, however, show that by adjusting the parameters, a considerable difference in the $I$-$V$ characteristics between the cases of $t_2 = t_1$ and $t_2 = 1.1 t_1$ may occur.

In Fig. 6, we have shown the current as a function of gate voltage. The results reveal that the electron conduction can be strongly dependent on the gate voltage. For the values of the gate voltages that the current becomes zero, the molecule behaves as a semiconductor and for the other values it acts as a metal. Such a behavior can be clearly seen in the cases that one or five carbon atoms of the molecule are contacted to the electrodes. Therefore, the results suggest that the C$_{60}$ molecule is an interesting...
candidate for operation of devices as a nanoscale current switch.

IV. CONCLUSIONS

Using the nonequilibrium Green’s function technique and the Landauer theory, we have investigated the effects of different contact geometries on the electronic transport through a C\textsubscript{60} molecule sandwiched between two metallic electrodes. It has been shown 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 influence of gate voltage on C\textsubscript{60} and the effect of different bond lengths in this molecule were observed as a shift in the transmission peaks. Our results therefore indicate that the contact geometries, bond dimerization, and charge-transfer doping with gate voltage play important roles and may change the physical picture of electron conduction in C\textsubscript{60}-based molecular devices.

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