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Electronic transmission of three-terminal pyrene molecular bridge*

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This paper investigates theoretically the electronic transmission spectra of the three terminal pyrene molecular bridge and the quantum current distribution on each bond by the tight-binding model based on nonequilibrium Green's function and the quantum current density approach, in which one π molecular orbital is taken into account per carbon atom when the energy levels and HOMO-LUMO gap are obtained. The transmission spectra show that the electronic transmission of the three terminal pyrene molecular bridge depends obviously on the incident electronic energy and the pyrene eigenenergy. The symmetrical and oscillation properties of the transmission spectra are illustrated. A novel plus-minus energy switching function is found. The quantum current distribution shows that the loop currents inside the pyrene are induced, and some bond currents are much larger than the input and the output currents. The reasons why the loop currents and the larger bond currents are induced are the phase difference of the atomic orbits and the degeneracy of the molecular orbits. The calculations illustrate that the quantum current distributions are in good agreement with Kirchhoff quantum current conservation law.

Keywords: pyrene, three terminals, electronic transmission, current distribution
PACC: 0560, 6146, 7215

1. Introduction

Molecular electronic devices belong to the most promising candidates for future nanoelectronics since the electronic transmission through a single organic molecule was first proposed by Aviram *et al* in 1974.[1,2] Recently, many novel characteristics and unique functions of molecular devices have been widely investigated both theoretically and experimentally. These include electronic transmission of the single conjugated molecule,[3] pair tunnelling through a single molecule,[4] charge transport through individual molecule,[5] electronic transport properties of molecular junctions,[6] atomic wire[7] and molecular wire,[8] molecular memories,[9] switching,[10] molecular diodes[11] and transistors.[12,13] Among these topics, the electronic transport through molecular devices and the internal quantum current distributions inside molecular devices is one of the most basic scientific issues.[14−20]

For the electronic transmission property, prior work has focused mainly on two terminal molecular systems.[21−32] A measurement technique and a connection model have been developed based on the scanning tunnelling microscope (STM) and the atomic force microscope (AFM).[33] On the other hand, the electronic characteristics of multi-terminals molecular device has not been well studied. In this work, we present a three-electrode pyrene molecular bridge model. The electronic transmission and the internal quantum current distributions are investigated theoretically by tight-binding method based on nonequilibrium Green's function after proving its conductance. The pyrene molecule can be considered as a simplified system for the study of graphene film,[34,35] which is a very important new material for the development of nanoelectronic devices that can be patterned and positioned like conventional devices.[36] In addition, it is significant that the pyrene molecular bridge can be

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attached to the substrate conveniently since it is a planar film structure. Thus it can be connected easily to other nanoelectronic devices synthesized on the same substrate to realize nanoelectronic circuits.

2. Molecular device model

In this study, the pyrene molecular bridge model is composed of 4 aromatic rings with 16 carbon atoms and 3 atomic electrodes. The electrode connection of the molecular bridge is similar to a transistor structure. The optimized molecular bond length between adjacent carbon atoms is 0.14 nm. The geometric structure is represented by the D_{3h} symmetry group. The electrodes consist of long atomic chains that are connected to different carbon atoms as shown in Fig.1. The pyrene molecule is suitable for the electronic transmission since it has a small energy gap between the HOMO (highest occupied molecular orbital) and the LUMO (lowest unoccupied molecular orbital), as well as a relatively low lying LUMO and single occupied molecular orbital (SOMO) state. In addition, only one active π orbital electron in 4 valence electrons per carbon atom is also suitable for the electronic transmission.

For the three terminal pyrene molecular bridge in Fig.1, the electron transmission has three channels, namely, electronic transport from the electrode 1 to electrode 2, the electrode 1 to electrode 3, as well as from the electrode 2 to 3. In our model, the three electrodes are assumed to be semi-infinite length atomic chains to simplify the boundary conditions. Electron-phonon coupling effects are neglected which means that electron transmission is assumed to occur coherently and without inelastic scattering.

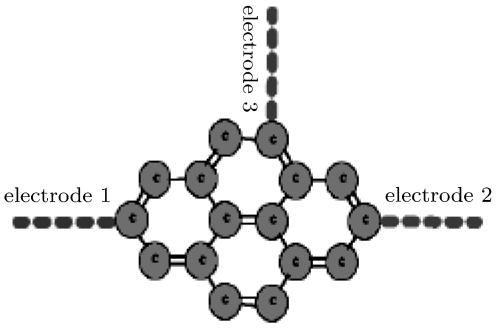


Fig.1. Three-terminal pyrene molecular bridge model.

3. Calculation method

For the three-electrode pyrene molecular bridge, its geometric structure is optimized and the energy level is calculated by the function $6-31G^*$ based on Gaussian computation. Then we adopt the tight-binding theory based on the nonequilibrium Green's function method, for simplicity, in which the SOMO localized in π state per carbon atom is taken into account. The transmission process is considered to involve electrons transmitting through the electrode 1, then the pyrene molecule, and output from the electrodes 2 and 3. In addition, reflection and scattering at the interfaces between the pyrene molecule and the electrodes are considered. Thus the electronic transmission function $T_{\rm SD}$ can be obtained in the framework of the Landauer–Buttiker theory based on the nonequilibrium Green's function,[37,38] which is written as

$$T_{\rm SD}(E) = {\rm Tr}[\Gamma_{\rm S} G^{\rm R}(E) \Gamma_{\rm D} G^{\rm A}(E)]. \tag{1}$$

where E denotes the electronic energy, $G^{\rm R(A)}$ denotes the retarded (advanced) Green's function of the whole system relating to the incident electron energy, which is defined by

$$G^{\rm R(A)} = \frac{1}{E - H_c - \Sigma_1^{\rm R(A)} - \Sigma_2^{\rm R(A)} - \Sigma_3^{\rm R(A)}}, \tag{2}$$

where H_c represents the Hamiltonian operator of the molecular part, the retarded (advanced) self-energy $\Sigma_q^{\rm R(A)}$ (q=1, 2, 3) represents an effective potential arising from the interaction between the pyrene molecule and each electrode. $\Gamma_{\rm S(D)}$ in Eq.(1) denotes the source (S) or the drain (D) interface couplings between the electrode and the carbon atom, which is described by

$$\Gamma_{\rm S(D)} = {\rm i}[\Sigma_{\rm S(D)}^{\rm R} - \Sigma_{\rm S(D)}^{\rm A}]. \tag{3}$$

The non-zero self-energy matrix elements corresponding to the carbon atoms attached to the source or the drain electrode are defined by

$$\Sigma_{\rm S(D)}^{\rm R(A)} = t'^2_{\rm S(D)} g_{\rm S(D)}^{\rm R(A)}, \tag{4}$$

where, $t'_{\rm S(D)}$ represents the coupling strength between the electrode and the pyrene molecule, and $g_{\rm S(D)}^{\rm R(A)}$ represents the Green's function for the three electrodes. The latter is defined as

$$g_q^{\rm R(A)} = \frac{E + {\rm i}\sqrt{4t_q^2 - E^2}}{2t_q^2}, \tag{5}$$

where q represents the nearest neighbouring atomic site, and t_q denotes a hopping integral between the nearest neighbouring atoms.

In order to apply the three-terminal molecular devices to a nanocircuit, it is necessary to clarify the internal current distributions, namely, the magnitude and the direction of the quantum current on each bond. By using the quantum current density theory,[39−41] the current density from site i to j is given by

$$I_{ij} = \frac{4e}{\hbar}\mathrm{Im}[\psi_i^* H_{ij}\psi_j], \tag{6}$$

where H_{ij} is ij-th element of the Hamiltonian operator, and $\psi_{i(j)}$ is the electronic wave function at the site $i(j)$. In our calculation, the wave function $\psi_{i(j)}$ is expanded in terms of the atomic orbital ϕ_n^ν, i.e.,

$$\psi_n = \sum_\nu a_\nu \phi_n^\nu, \tag{7}$$

where a_ν is the expanding factor. Finally, by using the above formulas, we obtain the electronic transmission spectra of the three terminal pyrene molecular bridge, and simulate the quantum current distribution inside the pyrene molecule at the energy point where the electronic transmission spectrum peaks.

4. Results

By density functional theory based on B3LYP functional and $6-31G^*$ base set, the geometric structure of the pyrene molecule is optimized, and the stabilization is proved. By the energy level calculation based on Gaussian 98, the HOMO and LUMO are obtained as shown in Fig.2.

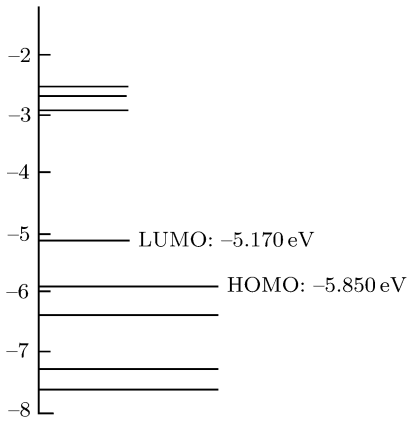


Fig.2. Energy level and energy gap of pyrene molecule.

The result illustrates that LUMO and HOMO are at –5.170 and –5.850 eV, respectively. The quite narrow energy gap (0.68 eV) between LUMO and HOMO demonstrates that electrons can transport easily through the pyrene molecule. According to this result, we found that the pyrene molecule may be formed into an electronic device. In the electronic transmission calculation, the hopping parameters t have a common value because of the elastic scattering inside the electrodes and the pyrene molecule. The coupling between the electrode and the pyrene molecule is taken as $t' = 0.6t$ because the coupling is weaker than one inside the electrode and inside the molecule. Then assume that the electronic transmission is also elastic process at each bond. In this case, the electronic transmission spectra from the electrode 1 to electrode 2, from the electrode 1 to electrode 3 and from the electrode 2 to electrode 3 are calculated by using Eq.(1), the results are shown in Figs.3(a), 3(b) and 3(c), respectively.

The results can be summarized as follows: (i) The transmission spectra are quite symmetrical in the energy interval, E=±2.0 eV due to the symmetric geometry composition of the pyrene molecule. (ii) The spectra peaks appear at the different energy values $E = \pm 1.02$ eV (Fig.3(a)); ± 1.16 eV (Fig.3(b)); ± 1.58 eV (Fig.3(a)) and ± 1.92 eV (Fig.3(c)) for the three channels, this means that electrons have a high probability to transmit from the input to the output terminal at these energies. On the contrary, the electrons hardly transmit through the pyrene molecular bridge at the other energy regions. In particular, in the energy region E=1.02–1.58 eV and E=-1.02 − -1.58 eV (Fig.3(a)), the total electrons almost transmit through the molecular bridge since the transmission probability approximates unit. (iii) From the electrode 1 to the electrodes 2 and 3, the transmission spectra have the minimum at E=0 eV. (iv) The oscillatory feature of the transmission spectra originates from the quantized energy levels of the molecular bridge because the molecular bridge is of nanometre size. (v) The switching function with the energy change is found in the three-terminal pyrene molecular bridge, this characteristic is presented obviously as shown in Fig.3(a). It is clear that the molecular bridge becomes a cut-off state in the energy region $E \approx \pm 0.5$ eV, and a conducting state in the energy region $E \approx \pm 1.0 - \pm 1.6$ eV. In addition, the switching functions are also found as shown in Fig.3(b) and 3(c), which means that the device conducts or blockages in different energy range. By the switching performance, we found that the three terminal pyrene molecular

bridge is similar to the biased semiconductor switching transistor. However, it is not necessary to add any bias voltage at the terminals. (vi) By comparison, it is found that more electrons transport from the electrode 1 to electrode 2, a small amount electrons transmit from the electrode 1 to electrode 3, as well as from the electrode 2 to electrode 3, which means that the electrons do not transport along the shorter path in such a molecular bridge. (vii) The electronic transmission spectra relate significantly to the electronic energy, and depend on the atomic sites connected to the electrodes, which means that the different functions can be achieved by changing the incident electron energy or the position of electrode connection.

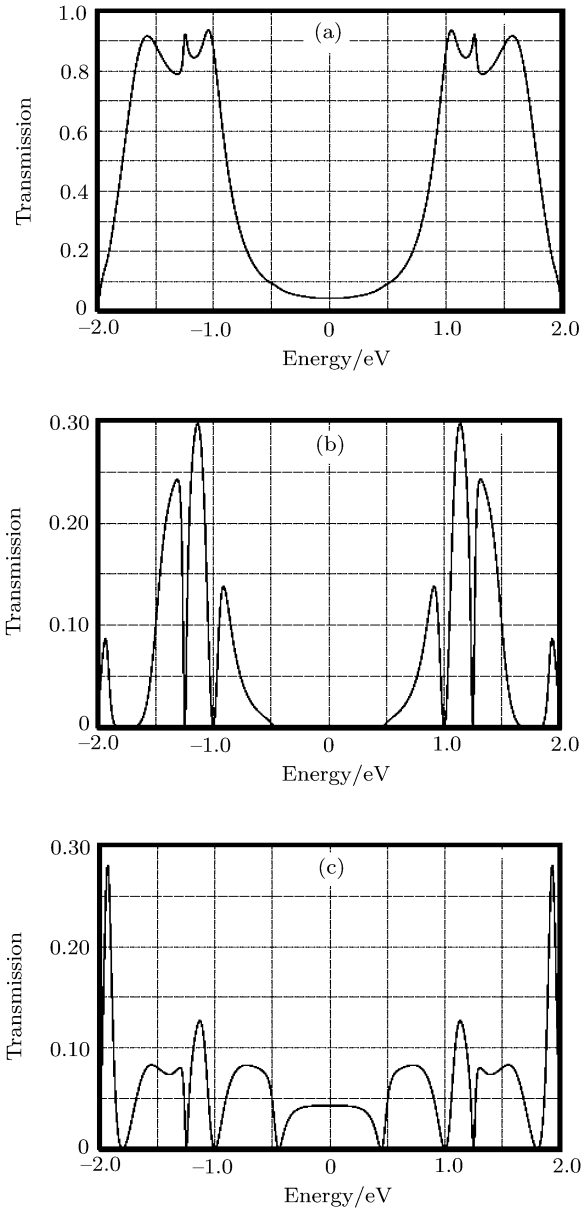


Fig.3. Quantum transmission spectra of 3-terminal pyrene molecular bridge: (a) from the electrode 1 to electrode 2; (b) from the electrode 1 to electrode 3; (c) from the electrode 2 to electrode 3.

By Eqs.(6) and (7), the quantum current on each bond is calculated numerically and simulated graphically at the energy points $E = \pm 1.58\,\mathrm{eV}$ where the electronic transmission spectra emerge the highest peaks. The total internal quantum current distributions are obtained as shown in Fig.4.

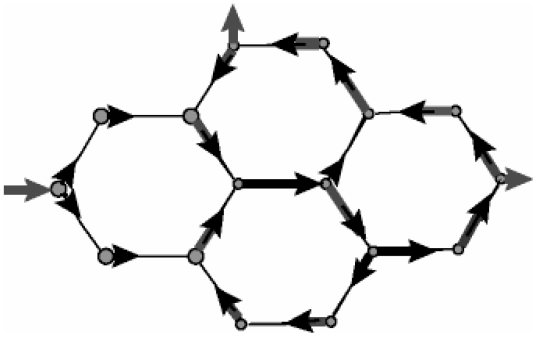


Fig.4. Quantum current distribution inside three-terminal pyrene molecular bridge at $E = \pm 1.58\,\mathrm{eV}$.

The current amplitudes and directions are expressed with vector arrows. The result shows that the incident electrons do not transmit uniformly through the pyrene molecular bridge. Some bond currents are weaker, and the others are stronger, even much larger than the input and the output currents. For the molecular devices, in addition, some loop currents are observed inside the hexagons of the pyrene molecule. One reason why the larger bond currents and the loop currents are induced is the phase difference of the expanded atomic orbits, this means that the larger bond currents are generated when the phase factors of the atomic wave functions are superposed positively. On the contrary, the smaller bond currents are induced by minus superposition of the phase factors. There is another reason that the enhancement of the internal quantum current originates from the degeneracy of the molecular orbits during the electronic transmission through the pyrene molecule. Finally, the calculation proves that the input currents equal the output currents at each atomic site, which agrees well with Kirchhoff quantum current conservation law.

5. Summary

In this work, we have investigated theoretically the electronic transmission properties of the pyrene

molecular bridge with the three atomic chain electrodes by the tight-binding theory based on the nonequilibrium Green's function method. We have calculated electronic transmission, and simulated the quantum current distributions inside the pyrene molecule. The result shows that the transmission spectra depend significantly on the electronic energy and on the connection between the electrode and the carbon atom site, and that the transmission spectra peak at the energy point where a resonance occurs between the electronic energy and the molecular eigen-level. The result also shows that three-electrode pyrene molecular bridge has the no-source plus-minus energy switching function. In addition, this theoretical result is useful to explain how the molecular devices are connected to the nano-electric circuit. The adopted theoretical approach in this research will help to understand, calculate, test and fabricate the graphene film device that is an important two-dimensional nano-material since the pyrene molecule is a basic unit of the graphene film.

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