Quantum transport through polycyclic hydrocarbon molecules: Green’s function approach

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Abstract

Quantum transport properties through single polycyclic hydrocarbon molecules attached to two metallic electrodes are studied by the use of Green’s function technique. A parametric approach based on the tight-binding model is introduced to investigate the electronic transport through such molecular bridge systems. The transport properties are discussed in the aspects of (a) molecule-to-electrode coupling strength and (b) quantum interference effect.

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1 Introduction

Molecular electronics is an essential technological concept of fast-growing interest since molecules constitute promising building blocks for future generation of electronic devices where the electron transport is predominantly coherent \[1, 2\]. Understanding of the fundamental processes of electron conduction through individual molecules is a most important requirement for the purposeful design of molecules for electronic functionalities. Electronic transport through molecules was first studied theoretically in 1974 \[3\]. Following this pioneering work, numerous experiments \[4, 5, 6, 7, 8\] have been performed through molecules placed between two electrodes with few nanometer separation. It is very essential to control electron conduction through such molecular electronic devices and the present understanding about it is quite limited. For example, it is not very clear how the molecular transport is affected by the structure of the molecule itself or by the nature of its coupling to the electrodes. To design molecular electronic devices with specific properties, structure-conductance relationships are needed and in a very recent work Ernzerhof et al. \[9\] have presented a general design principle and performed several model calculations to demonstrate the concept. The operation of such two-terminal devices is due to an applied bias. Current passing across the junction is strongly nonlinear function of applied bias voltage and its detailed description is a very complex problem. The complete knowledge of the conduction mechanism in this scale is not well understood even today. Electronic transport through these systems are associated with some quantum effects, like as quantization of energy levels and quantum interference of electron waves \[10, 11, 12, 13, 14, 15, 16, 17\]. Here we focus on single molecular transport that are currently the subject of substantial experimental, theoretical and technological interest. These molecular systems can act as gates, switches, or transport elements, providing new molecular functions that need to be well characterized and understood.

In the present article, we reproduce an analytic approach based on the tight-binding framework to investigate the electron transport properties for the model of single polycyclic hydrocarbon molecules. Though several \textit{ab initio} methods are used for the calculation of conductance \[18, 19, 20, 21, 22, 23, 24, 25, 26\], yet simple parametric approaches \[22, 27, 28, 29, 30, 31, 32\] are still needed for this calculation. The parametric study is much more flexible than that of the \textit{ab initio} theories since the later theories are computationally very expensive and here we do attention only on the qualitative effects rather than the quantitative ones. This is why we restrict our calculations on the simple analytical formulation of the transport problem.

We organize the paper as follows. With a brief introduction (Section 1), in Section 2, we provide a theoretical description for the calculation of transmission probability and current through a finite size conducting system sandwiched between two metallic electrodes by the use of Green’s function technique. In Section 3, we investigate the behavior of conductance-energy and current-voltage characteristics for the model of single polycyclic hydrocarbon molecules and study the effects of molecule-to-electrode coupling strength and quantum interference on the above mentioned characteristics. These two factors i.e., the quantum interference and the coupling strength play crucial role on quantum transport through single molecular systems. Finally, we summarize our results in Section 4.

2 A glimpse onto the theoretical formulation

This section follows a brief theoretical description for the calculation of transmission probability \((T)\), conductance \((g)\) and current \((I)\) through a finite size conducting system attached to two semi-infinite one-dimensional (1D) metallic electrodes by the use of Green’s function formalism.

Let us first consider a one-dimensional conductor with \(N\) number of atomic sites (array of filled black circles) connected to two semi-infinite metallic electrodes, namely, source and drain, as shown in Fig. 1. The conducting system within the two electrodes can be an array of few quantum dots, or a single molecule, or an array of few molecules, etc. At much low temperatures and bias voltages, the
conductance $g$ of the conductor can be written by using the Landauer conductance formula,

$$ g = \frac{2e^2}{h} \tau $$

(1)

where, $\tau$ is the transmission probability of an electron through the conductor. It ($\tau$) can be expressed in terms of the Green’s function of the conductor and its coupling to the side attached electrodes through the expression,

$$ T = \text{Tr} \left[ \Gamma_S G^c_e G_D^c \right] $$

(2)

where, $G^c_e$ and $G^c_d$ are the retarded and advanced Green’s functions of the conductor, respectively. $\Gamma_S$ and $\Gamma_D$ are the coupling matrices due to the coupling of the conductor to the source and drain, respectively. For the complete system i.e., the conductor and two electrodes, the Green’s function is defined as,

$$ G = (E - H)^{-1} $$

(3)

where, $E$ is the injecting energy of the source electron. Evaluation of this Green’s function requires the inversion of an infinite matrix as the system consists of the finite size conductor and the two semi-infinite 1D electrodes, which is really a very difficult task. However, the entire system can be partitioned into sub-matrices corresponding to the individual sub-systems, and the Green’s function for the conductor can be effectively written as,

$$ G_c = (E - H_c - \Sigma_S - \Sigma_D)^{-1} $$

(4)

where, $H_c$ is the Hamiltonian of the conductor. With the non-interacting picture, the tight-binding Hamiltonian of the conductor can be expressed as,

$$ H_c = \sum_i \epsilon_i c^\dagger_i c_i + \sum_{<ij>} t \left( c^\dagger_i c_j + c^\dagger_j c_i \right) $$

(5)

where, $c^\dagger_i$ ($c_i$) is the creation (annihilation) operator of an electron at site $i$, $\epsilon_i$’s are the site energies and $t$ is the nearest-neighbor hopping integral. In Eq. 4 $\Sigma_S = h_{Sg} g_S h_{Sc}$ and $\Sigma_D = h_{Dg} g_D h_{Dc}$ are the self-energy operators due to the two electrodes, where $g_S$ and $g_D$ are the Green’s functions for the source and drain, respectively. $h_{Sc}$ and $h_{Dc}$ are the coupling matrices and they will be non-zero only for the adjacent points in the conductor, 1 and $N$ as shown in Fig. 1 and the electrodes respectively. The coupling terms $\Gamma_S$ and $\Gamma_D$ for the conductor can be calculated through the expression,

$$ \Gamma_{S,D} = i \left[ \Sigma_{S,D}^r - \Sigma_{S,D}^a \right] $$

(6)

where, $\Sigma_{S,D}^r$ and $\Sigma_{S,D}^a$ are the retarded and advanced self-energies, respectively, and they are conjugate to each other. Datta et al. [33] have shown that the self-energies can be expressed like,

$$ \Sigma_{S,D}^r = \Lambda_{S,D} - i \Delta_{S,D} $$

(7)

where, $\Lambda_{S,D}$ are the real parts of the self-energies which correspond to the shift of the energy eigenvalues of the conductor and the imaginary parts $\Delta_{S,D}$ of the self-energies represent the broadening of the energy levels. Since this broadening is much larger than the thermal broadening we restrict our all calculations only at absolute zero temperature.

The real and imaginary parts of the self-energies can be determined in terms of the hopping integral ($t_{s,d}$) between the boundary sites (1 and $N$) of the conductor and electrodes, energy ($E$) of the transmitting electron and hopping strength ($v$) between nearest-neighbor sites of the electrodes.

The coupling terms $\Gamma_S$ and $\Gamma_D$ can be written in terms of the retarded self-energy as,

$$ \Gamma_{S,D} = -2 \text{Im} \left[ \Sigma_{S,D}^r \right] $$

(8)

Here, all the information regarding the conductor to electrode coupling are included into the two self energies as stated above and are analyzed through the use of Newns-Anderson chemisorption theory[27, 28]. The detailed description of this theory is available in these two references.

Thus, by calculating the self-energies, the coupling terms $\Gamma_S$ and $\Gamma_D$ can be easily obtained and then the transmission probability ($T$) will be calculated from the expression as mentioned in Eq. 4.

Since the coupling matrices $h_{Sc}$ and $h_{Dc}$ are non-zero only for the adjacent points in the conductor, 1 and $N$ as shown in Fig. 1 the transmission probability becomes,

$$ T(E) = 4 \Delta^S_{11}(E) \Delta^D_{NN}(E) |G_{1N}(E)|^2 $$

(9)

where, $\Delta_{11} =< 1|\Delta|1 >$, $\Delta_{NN} =< N|\Delta|N >$ and $G_{1N} =< 1|G_c|N >$.

The current passing through the conductor is depicted as a single-electron scattering process between the two reservoirs of charge carriers. The current-voltage relation is evaluated from the following expression [33],

$$ I(V) = \frac{e}{\pi \hbar} \int_{E_F - eV/2}^{E_F + eV/2} T(E) \, dE $$

(10)

where, $E_F$ is the equilibrium Fermi energy. For the sake of simplicity, here we assume that the entire
Voltage is dropped across the conductor-electrode interfaces and it doesn’t greatly affect the qualitative aspects of the $I-V$ characteristics. This assumption is based on the fact that the electric field inside the conductor, especially for short conductors, seems to have a minimal effect on the conductance-voltage characteristics. On the other hand, for quite larger conductors and higher bias voltages, the electric field inside the conductor may play a more significant role depending on the internal structure of the conductor [33], though the effect becomes too small. Using the expression of $T(E)$ (Eq. 4), the final form of $I(V)$ will be,

$$I(V) = \frac{4e}{\pi \hbar} \int_{E_F - eV/2}^{E_F + eV/2} \Delta_{11}(E) \Delta_{NN}(E) \times |G_{1N}(E)|^2 dE$$  \hspace{1cm} (11)

Eqs. 4, 5 and 11 are the final working formulae for the calculation of conductance $g$, transmission probability $T$, and current $I$, respectively, through any finite size conductor sandwiched between two metallic electrodes.

In this article, we will study the behavior of conductance and current for some specific models of single polycyclic hydrocarbon molecules. Throughout our calculation, we use the units $c = \hbar = e = 1$.

3 Results and their interpretation

Here we describe conductance-energy and current-voltage characteristics of different single polycyclic hydrocarbon molecules and study the dependence of these characteristics on molecule-to-electrode coupling strength and quantum interference effects. The schematic representations of the different molecules taken into account are shown in Fig. 2. These molecules are: benzene (one ring), napthalene (two rings), anthracene (three rings) and tetracene (four rings). They are attached to the electrodes by thiol (S-H) groups. In actual experiments, gold (Au) electrodes are used and the molecules attached with them via thiol (S-H) groups in the chemisorption technique where hydrogen (H) atoms remove and sulfur (S) atoms reside. In order to reveal the quantum interference effects on electron transport, here we consider two different types of bridge configurations. For one type, the molecules are attached to the electrodes at $\alpha$-$\alpha$ sites (see the first column of Fig. 2), the so-called $cis$ configuration. In the other type, the molecules are coupled to the electrodes at $\beta$-$\beta$ sites (see the second column of Fig. 2), the so-called $trans$ configuration.

Here we shall describe all the essential features of electron transport for the two distinct regimes. One is $\tau_{S,D} \ll t$, called the weak-coupling limit and the other one is $\tau_{S,D} \sim t$, called the strong-coupling limit. $\tau_S$ and $\tau_D$ are the hopping strengths of the molecule to the source and drain, respectively. Throughout this work, the common set of values of the parameters used in our calculations for these two limiting cases are: $\tau_S = \tau_D = 0.5$, $t = 2.5$ (weak-coupling) and $\tau_S = \tau_D = 2$, $t = 2.5$ (strong-coupling). The hopping integral in the electrodes is taken as $v = 4$ and the equilibrium Fermi energy $E_F$ is fixed at 0.

In Fig. 3, we plot the conductance ($g$) as a function of the injecting electron energy ($E$) for the molecular bridge systems where the molecules are coupled to the electrodes in the $trans$ configuration. (a), (b), (c) and (d) correspond to the results for the benzene, napthalene, anthracene and tetracene molecules, respectively. The solid curves denote the results for the weak molecule-electrode coupling case and it is observed that the conduc-
tance shows sharp resonant peaks for some particular energy values, while it \( g \) drops to zero almost for all other energies. At resonance, the conductance approaches to 2 so that the transmission probability \( T \) becomes unity (from the Landauer conductance formula \( g = 2T \), see Eq. 1 with \( e = h = 1 \)). The resonant peaks in the conductance spectrum coincide with the eigenenergies of the single hydrocarbon molecules. Therefore, the conductance spectrum manifests itself the electronic structure of the molecules. On the other hand, in the strong-coupling limit the resonances get substantial widths, as shown by the dotted curves in Fig. 4, and it emphasizes that the electron conduction takes place almost for all energy values. This is due to the broadening of the molecular energy levels, where the contribution comes from the imaginary parts of the self-energies \( \Sigma_{S(D)} \) \(^{33} \), as mentioned earlier in the strong-coupling case.

To characterize the quantum interference effects on the electron transport, in Fig. 3 we plot the conductance-energy characteristics for the molecular bridge systems where the molecules are connected to the electrodes in the \( \text{cis} \) configuration. \( \text{(a), (b), (c) and (d) correspond to the results for the benzene, napthalene, anthracene and tetracene molecules, respectively, where the solid and dotted curves indicate the same meaning as in Fig. 3. These results show that some of the conductance peaks do not reach to unity anymore and get much reduced value. This behavior can be understood as follows. The electrons are carried from the source to drain through the molecules and thus the electron waves propagating along the two arms of the molecular ring(s) may suffer a phase shift between themselves, according to the result of quantum interference between the various pathways that the electron can take. Therefore, the probability amplitude of the electron across the molecules becomes strengthened or weakened. It emphasizes itself especially as transmittance cancellations and anti-resonances in the transmission (conductance) spectrum. Thus, it can be emphasized that the electron transmission
is strongly affected by the quantum interference effects, and hence, the molecule-to-electrode interface structures.

The scenario of electron transfer through the molecular junction is much more clearly observed from the current-voltage characteristics. Current through the molecular systems is computed by the integration procedure of the transmission function $T$ (see Eq. 11). The behavior of the transmission function is similar to that of the conductance spectrum since the equation $g = 2T$ is satisfied from the Landauer conductance formula. In Fig. 5, we plot the $I-V$ characteristics for the hydrocarbon molecules connected to the electrodes in the trans configuration. (a) and (b) correspond to the results for the weak and strong molecule-to-electrode coupling cases, respectively. The solid, dotted, dashed and dot-dashed lines represent the currents for the benzene, napthalene, anthracene and tetracene molecules, respectively.

Figure 5: $I-V$ characteristics for the polycyclic hydrocarbon molecules connected to the electrodes in the trans configuration. (a) and (b) correspond to the results for the weak and strong molecule-to-electrode coupling cases, respectively. The solid, dotted, dashed and dot-dashed lines represent the currents for the benzene, napthalene, anthracene and tetracene molecules, respectively.

The quantum interference effects on the electron transmission through the molecular bridge systems is much more clearly visible from Fig. 6, where we plot the $I-V$ characteristics of the hydrocarbon molecules connected to the electrodes in the cis configuration. (a) and (b) correspond to the results for the weak and strong molecule-to-electrode coupling cases, respectively. The solid, dotted, dashed and dot-dashed lines represent the identical meaning as in Fig. 5.

Figure 6: $I-V$ spectra for the polycyclic hydrocarbon molecules connected to the electrodes in the cis configuration. (a) and (b) correspond to the results for the weak and strong molecule-to-electrode coupling cases, respectively. The solid, dotted, dashed and dot-dashed lines represent the identical meaning as in Fig. 5.

steps depend on the width of the molecular resonances. With the increase of molecule-to-electrode coupling strength, the current varies almost continuously with the applied bias voltage and achieves much higher values, as shown in Fig. 6(b). This continuous variation of the current is due to the broadening of the conductance resonant peaks (see the dotted curves of Fig. 3) in the strong molecule-to-electrode coupling limit.

The quantum interference effects on the electron transmission through the molecular bridge systems is much more clearly visible from Fig. 6, where we plot the $I-V$ characteristics of the hydrocarbon molecules connected to the electrodes in the cis configuration. (a) and (b) correspond to the results for the weak and strong molecule-to-electrode coupling cases, respectively. The solid, dotted, dashed and dot-dashed lines represent the identical meaning as in Fig. 5.
configuration. (a) and (b) correspond to the currents in the two limiting cases, respectively. The solid, dotted, dashed and dot-dashed curves give the same meaning as in Fig. 4. These results predict that the current amplitudes get reduced enormously compared to the results predicted for the molecules connected to the electrodes in the trans configuration. This is solely due to the quantum interference effects between the different pathways that the electron can take. Therefore, we can predict that designing a molecular device is significantly influenced by the quantum interference effects i.e., the molecule-to-electrode interface structures.

4 Concluding remarks

To summarize, we have introduced a parametric approach based on the tight-binding model to investigate the electron transport properties of four different polycyclic hydrocarbon molecules sandwiched between two metallic electrodes. This technique can be used to study the electronic transport in any complicated molecular bridge system. Electronic conduction through the hydrocarbon molecules is strongly influenced by the molecule-to-electrode coupling strength and the quantum interference effects. Our study provides that designing a whole system that includes not only the molecule but also the molecule-to-electrode coupling and the interface structures are highly important in fabricating molecular electronic devices.

More studies are expected to take the Schottky effect, comes from the charge transfer across the metal-molecule interfaces, the static Stark effect, which is taken into account for the modification of the electronic structure of the molecular bridge due to the applied bias voltage (essential especially for higher voltages). However, all these effects can be included into our framework by a simple generalization of the presented formalism. Here, we have also neglected the effects of inelastic scattering processes and electron-electron correlation to characterize the electronic transport through such molecular bridges.

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