Electron transport through molecular bridge systems

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Abstract

Electron transport characteristics are investigated through some molecular chains attached to two non-superconducting electrodes by the use of Green’s function method. Here we do parametric calculations based on the tight-binding formulation to characterize the electron transport through such bridge systems. The transport properties are significantly influenced by (a) the length of the molecular chain and (b) the molecule-to-electrodes coupling strength and here we focus are results in these aspects. In this context we also discuss the steady state current fluctuations, the so-called shot noise, which is a consequence of the quantization of charge and is not directly available through conductance measurements.

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1 Introduction

Recent progress in nanoscience and technology has allowed one to study the electron transport through molecules in a very controllable way. The prospect of individual devices based on single molecules is approaching realization since electronic components are getting smaller and smaller. Following experimental developments, theory can play a major role in understanding the new mechanisms of conductance. The single-molecule electronics plays a key role in the design of future nanoelectronic circuits, but, the goal of developing a reliable molecular-electronics technology is still over the horizon and many key problems, such as device stability, reproducibility and the control of single-molecule transport need to be solved. Electronic transport through molecules was first studied theoretically in 1974 [1]. Since then numerous experiments [2, 3, 4, 5, 6] have carried out on the electron transport through molecules placed between two metallic electrodes with few nanometer separation. It is very essential to control electron conduction through such quantum 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 with the electrodes. The electron conduction through such two-terminal devices can be controlled by some bias voltage. The current passing across the junction then becomes a strongly non-linear function of the applied voltage, and its understanding is a highly challenging problem. The knowledge of current fluctuations (quantum origin) provides a key idea for fabrication of efficient molecular devices. Blanter et al. [7] have described elaborately how the lowest possible noise power of the current fluctuations can be determined in a two-terminal conductor. The steady state current fluctuations, the so-called shot noise, is a consequence of the quantization of charge and it can be used to obtain information on a system which is not available through conductance measurements. The noise power of the current fluctuations provides an additional important information about the electron correlation by calculating the Fano factor \( \alpha \) which directly informs us whether the magnitude of the shot noise achieves the Poisson limit \( \alpha = 1 \) or the sub-Poisson \( \alpha < 1 \) limit.

In the present article we provide a simple analytical formulation of the transport problem through some molecular chains of different lengths by using the tight-binding formulation. There exist several ab initio methods for the calculation of the conductance [8, 9, 10, 11, 12, 13] as well as model calculations [14, 15, 16, 17, 18, 19, 20, 21, 22, 23]. The model calculations are motivated by the fact that the ab initio methods are computationally too expensive, while, the model calculations by using the tight-binding formulation are computationally very cheap and also provide a worth insight to the problem. In our present study attention is drawn on the qualitative behavior of the physical quantities rather than the quantitative ones. Not only that, the ab initio theories do not give any new qualitative behavior for this particular study in which we concentrate ourselves.

The article is specifically organized as follow. Following the introduction (Section 1), in Section 2 we describe very briefly the technique for the calculation of the transmission probability \( T \), current \( I \) and the noise power its current fluctuations \( S \) through a molecular chain sandwiched between two metallic electrodes by means of the Green’s function technique. In Section 3, we study the behavior of the conductance as a function of the injecting electron energy, the current and the noise power of its fluctuations as a function of the applied bias voltage for some molecular chains in the aspects of (a) the length of the chain and (b) the molecule-to-electrodes coupling strength. Finally, we draw our conclusions in Section 4.

2 The model and a brief description of the theoretical formulation

In this section we describe very briefly about the methodology for the calculation of the transmission probability \( T \), conductance \( g \), current \( I \) and the noise power of current fluctuations \( S \) for a molecular chain sandwiched between two metallic electrodes (schematically represented as in Fig. 1) by the use of Green’s function technique.

At low temperature and bias voltage the conductance \( g \) of the molecular chain is given by the Landauer conductance formula [24],

\[
g = \frac{2e^2}{h} T
\]

where the transmission probability \( T \) is expressed as [24],

\[
T = \text{Trace} \left[ \Gamma_S G_M^{\text{r}} \Gamma_D G_M^{\text{a}} \right]
\]

In this expression \( G_M^{\text{r}} \) and \( G_M^{\text{a}} \) are the retarded and advanced Green’s functions of the molecular chain.
and $\Gamma_S$ and $\Gamma_D$ describe its coupling with the source and the drain, respectively. The Green’s function of the molecular chain is written in this form,

$$G_M = (E - H_M - \Sigma_S - \Sigma_D)^{-1}$$  \hspace{1cm} (3)$$

where $E$ is the energy of the injecting electron and $H_M$ is the Hamiltonian of the chain. This Hamiltonian can be expressed in the tight-binding form within the non-interacting picture like,

$$H_M = \sum_i \epsilon_i |c_i|^2 + \sum_{<ij>} t \left( |c_i| |c_j|^2 + |c_i|^2 |c_j|^2 \right)$$  \hspace{1cm} (4)$$

where $\epsilon_i$’s are the site energies and $t$ is the nearest-neighbor hopping strength. In Eq. (3), $\Sigma_S$ and $\Sigma_D$ correspond to the self-energies due to the coupling

![Figure 1: (Color online). Schematic view of an array of benzene molecules attached to two metallic electrodes (made of gold in the actual experiment), the source and the drain, by thiol (sulfur-hydrogen i.e., S-H bond) groups (using the chemisorption technique).](image)

of the molecular chain with the two electrodes. Now all the information about the electrode-to-molecule coupling are included into these two self-energies through the use of Newns-Anderson chemisorption theory and the detailed descriptions of this theory can be found from the references [14, 15].

The current passing across the chain can be assumed as a single electron scattering process between the two reservoirs of charge carriers. The current-voltage relationship can be obtained from the expression [23],

$$I(V) = \frac{e}{\pi \hbar} \int_{-\infty}^{\infty} (f_S - f_D) T(E) \, dE$$  \hspace{1cm} (5)$$

where the Fermi distribution function $f_{S(D)} = f (E - \mu_{S(D)})$ with the electrochemical potentials $\mu_{S(D)} = E_F \pm eV/2$. For the sake of simplicity, here we assume that the entire voltage is dropped across the molecule-electrode interfaces and this assumption doesn’t significantly affect the qualitative aspects of the current-voltage characteristics. This assumption is based on the fact that the electric field inside the molecular chain especially for short chains, seems to have a minimal effect on the conductance-voltage characteristics. On the other hand for quite longer chains and higher bias voltage, the electric field inside the chain may play a more significant role depending on the internal structure of the chain [24], yet the effect is too small.

The noise power of the current fluctuations is calculated from the following expression [17],

$$S = \frac{2e^2}{\pi \hbar} \int_{-\infty}^{\infty} \left[ T(E) \{ f_S (1 - f_S) + f_D (1 - f_D) \} + T(E) \{ 1 - T(E) \} (f_S - f_D)^2 \right] \, dE$$  \hspace{1cm} (6)$$

where the first two terms of this equation correspond to the equilibrium noise contribution and the last term gives the non-equilibrium or shot noise contribution to the power spectrum. By calculating the noise power we can determine the Fano factor $F$, which is essential to predict whether the shot noise lies in the Poisson or the sub-Poisson limit, through the relation [17],

$$F = \frac{S}{2eI}$$  \hspace{1cm} (7)$$

The shot noise achieves the Poisson limit for $F = 1$ and in this case no electron correlation exists between the charge carriers. On the other hand for $F < 1$, the shot noise reaches the sub-Poisson limit and it provides the information about the electron correlation among the charge carriers.

Throughout this article we study our results only at absolute zero temperature, but the qualitative features of all the results are also invariant up to some finite temperature ($\sim 300$ K). For simplicity, here we take the unit $c = e = h = 1$ in our all calculations.

3 Results and their interpretation

Here we will study all the essential features of the electron transport characteristics for some molecular chains in the two distinct regimes. One is the so-called weak-coupling regime, which is defined as $\tau_{S(D)} << t$ and the other one is the so-called strong-coupling regime, denoted as $\tau_{S(D)} \sim t$. The symbols $\tau_S$ and $\tau_D$ correspond to the hopping strengths of the molecular chain to the source and drain, respectively. In our present calculations, the parameters for these two regimes are chosen as $\tau_S = \tau_D = 0.5$, $t = 3$ (weak-coupling) and $\tau_S = \tau_D = 2.5$, $t = 3$ (strong-coupling).

In Fig. 2 we plot the variation of the conductance $g$ as a function of the injecting electron energy $E$.
for the molecular chains in the weak-coupling limit. Figures 2(a), (b), (c) and (d) correspond to the results for the molecular chains with two, three, four and five benzene rings, respectively. The sharp resonant peaks are observed in the conductance spectra for some particular energy values, while for all other energies the peaks almost vanish. At these resonances the conductance $g$ approaches to 2 indicating that the transmission probability $T$ goes to unity (since we get the relation $g = 2T$ from the Landauer conductance formula, see Eq. (1) with $e = h = 1$ in our present formulation). These resonant peaks are associated with the molecular energy levels and their positions also change with the length of the molecular chain. Accordingly, we get more and more resonant peaks as we increase the length of the molecular chain. Thus it can be predicted that the conductance spectrum manifests itself the electronic structure of the molecular chain.

In the limit of strong molecular coupling, the resonant peaks in the conductance spectra get substantial widths as shown in Fig. 3 where Figs. 3(a), (b), (c) and (d) correspond to the bridges with two, three, four and five benzene rings as in Fig. 2. Such enhancement of the resonant widths is due to the broadening of the molecular energy levels caused by the coupling of the molecules to the side attached electrodes in this strong coupling limit, where the contribution comes from the imaginary parts of the two self-energies $\Sigma_S$ and $\Sigma_D$. From this figure (Fig. 3) two important features are observed those are: (I) the width and (II) the height of the resonant peak across the energy $E = 0$ gradually decrease with the increase of the length of the molecular chain. Such kind of features are not clearly visible in the limit of weak molecular coupling (see Fig. 2) since the widths of the resonant peaks are much narrow for this coupling case. Now try to explain these results. With the increase of the length of the molecular chain, the two energy levels across the zero energy value (associated with the two resonant peaks around the energy $E = 0$, those are observed from Fig. 2) become closer and closer. This is due to the existence of the molecular energy levels of the respective molecules at these energies and they become broadened with the increase of the molecular coupling. Since these two energy levels are very closely spaced they overlap with each other along with their widths.

![Figure 2](image1.png)

**Figure 2**: (Color online). Conductance $g$ as a function of the injecting electron energy $E$ for the molecular bridges in the limit of weak molecular coupling. (a), (b), (c) and (d) correspond to the bridges with two, three, four and five benzene rings, respectively.

![Figure 3](image2.png)

**Figure 3**: (Color online). Conductance $g$ as a function of the injecting electron energy $E$ for the molecular bridges in the limit of strong molecular coupling. (a), (b), (c) and (d) correspond to the bridges with two, three, four and five benzene rings, respectively.
other in some extent and produce a wide resonant peak across the energy \( E = 0 \), as shown in Fig. 3. The width of this resonant peak decreases gradually with the length of the chain which is due to the closeness of the two energy levels around the energy \( E = 0 \). Now the decrease of the height of the resonant peak across the energy \( E = 0 \) is due to the interference effect of the waves traversing through the different arms of the molecular rings. For the chains with smaller number of rings, the number of interfering paths are small, while for the longer chains we get several paths. As a result of this interference effect, the probability amplitude of getting the electron across the chain becomes strengthened or weakened (from the standard interpretation of the quantum mechanical theory). The anti-resonances in the transmission (conductance) spectra are due to the cancellation of the transmittances along the two paths. Therefore, the probability amplitude \( T \) becomes less than one and it gradually decreases with the increase of the length of the chain. Such anti-resonant states are specific to the interferometric nature of the scattering states and do not occur in the usual one-dimensional scattering problems involving potential barriers. From these results it can be emphasized that the electron transport characteristics significantly depend on the length of the molecular chain which provides a key idea for fabrication of molecular devices.

Now we describe the behavior of the current \( I \) and the noise power of its fluctuations \( S \) as a function of the applied bias voltage \( V \) for these molecular bridges, where both the current and the noise power are evaluated through the integration procedure of the transmission function \( T \) (see Eq. (5) and Eq. (6)). In Fig. 4 we plot the current and the noise power of its fluctuation for the molecular chains in the limit of weak-coupling, where Figs. (a), (b), (c) and (d) correspond to the results for the chains with two, three, four and five benzene rings, respectively. The red and blue curves correspond to the current and the noise power, respectively. It is observed that the current shows staircase-like structure with sharp steps as a function of the applied bias voltage. This is due to the existence of the sharp resonant peaks in the conductance spectra in the weak-coupling limit (Fig. 2). As the bias voltage increases, the electrochemical potentials on the electrodes are gradually shifted and eventually cross one of the molecular energy levels. Accordingly, a current channel is opened and a jump in the \( I-V \) curve appears. Another key observation is that for the bridge with two benzene rings we get the non-zero value of the current after some critical value of the applied bias voltage (see the red curve of Fig. 4), i.e., the conduction of electron through the bridge is started (on-state condition of the molecular bridge) beyond some critical value of the bias voltage. This

Figure 4: (Color online). Current \( I \) (red curve) and the noise power of its fluctuations \( S \) (blue curve) as a function of the applied bias voltage \( V \) for the molecular bridges in the weak molecule-to-electrodes coupling limit. (a), (b), (c) and (d) correspond to the bridges with two, three, four and five benzene rings, respectively.

The threshold voltage of the electron conduction gradually decreases with the increase of the length of the molecular chain. Thus in the limit of weak molecular coupling one can tune the threshold bias voltage for electron conduction quite significantly by changing the length of the molecular chain. It is also noted that the current amplitudes for all such bridges are almost invariant since the widths of the resonant peaks are nearly same for all these bridges (see Fig. 2) in this coupling limit.

In the study of the noise power of the current fluctuations for the weak-coupling limit (blue curves of Fig. 4) we see that for all these molecular wires the shot noise goes from the Poisson limit \( (F = 1) \) to the sub-Poisson limit \( (F < 1) \) as long as we cross the first step in the current-voltage \( (I-V) \) characteristics. Therefore, we can predict that the elec-
trons are correlated after the tunneling process has completed. Here the electrons are correlated only in the sense that one electron feels the existence of the other according to the Pauli exclusion principle (since we have neglected all other electron-electron interactions in our present formalism). Another significant observation is that the amplitudes of the noise power in the sub-Poisson regime for all such wires are almost invariant. These results emphasize that in the weak-coupling limit the noise power of the current fluctuations within the sub-Poisson limit remains in the same level independent of the length of the molecular chain.

The behavior of the current and the noise power is also very interesting in the strong-coupling regime and in the forthcoming part we will describe about

\[
\begin{align*}
I & = \frac{S}{2} \\
V & \in [-4, 2]
\end{align*}
\]

that. In Fig. 5 we display the results of the current and the noise power of its fluctuations in the strong-coupling limit for the molecular chains, where Figs. (a), (b), (c) and (d) correspond to the bridges with two, three, four and five benzene rings, respectively.

Figure 5: (Color online). Current $I$ (red curve) and the noise power of its fluctuations $S$ (blue curve) as a function of the applied bias voltage $V$ for the molecular bridges in the strong molecule-to-electrodes coupling limit. (a), (b), (c) and (d) correspond to the bridges with two, three, four and five benzene rings, respectively.

In conclusion of this article, we have introduced a parametric approach based on the tight-binding model to investigate the electron transport characteristics through some molecular chains attached to two metallic electrodes. All the results studied here provide several key ideas for fabrication of efficient molecular devices.
For the weak-coupling limit, the conductance shows very sharp resonant peaks (Fig. 2) associated with the molecular energy levels. The widths of these resonant peaks get broadened (Fig. 3) in the limit of strong molecular coupling, where the contribution comes from the imaginary parts of the two self-energies $\Sigma_S$ and $\Sigma_D$ [24].

In the calculation of the current we have seen that the current shows staircase-like behavior (red curves in Fig. 4) with sharp steps as a function of the applied bias voltage in the weak-coupling limit, while it gets continuous variation (red curves in Fig. 5) with the increase of the molecular coupling strength. For all such bridges the current amplitudes are comparable to each other in the weak molecular coupling, but the current amplitude decays substantially with the increase of the length of the chain in the limit of strong-coupling.

Finally, in the determination of the noise power of the current fluctuations, we have noted that in the weak-coupling regime the current fluctuations within the sub-Poisson limit are in the same level (blue curves in Fig. 4) independent of the length of the molecular chain. On the other hand, for the strong-coupling regime the noise power of the current fluctuations are less important for the longer chains than that of the shorter ones (blue curves in Fig. 5).

Throughout our study, we have ignored the effect of electron-electron interaction and the influence of all the inelastic processes. More studies are expected to take into account the Schottky effect which comes from the charge transfer across the metal-molecule interfaces, the static Stark effect resulting from the modification of the electronic structure of the molecular bridge in presence of the applied bias voltage (essential especially for higher voltages).

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