Effect of localizing groups on electron transport through single conjugated molecules

Santanu K. Maiti$^{1,2,*}$

$^1$Theoretical Condensed Matter Physics Division, Saha Institute of Nuclear Physics, 1/AF, Bidhannagar, Kolkata-700 064, India

$^2$Department of Physics, Narasinha Dutt College, 129, Belilious Road, Howrah-711 101, India

Abstract

Electron transport properties through single conjugated molecules sandwiched between two non-superconducting electrodes are studied by the use of Green’s function technique. Based on the tight-binding model, we do parametric calculations to characterize the electron transport through such molecular bridges. The electron transport properties are significantly influenced by (a) the existence of localizing groups in these conjugated molecules and (b) the molecule to electrode coupling strength, and, here we focus our results in these two aspects.

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1 Introduction

Molecular electronics and transport have attracted much more attention since molecules constitute promising building blocks for future generation of nanoelectronic devices. Following experimental developments, theory can play a major role in understanding the new mechanisms of conductance. The single-molecule electronics plays a significant role in designing and developing the 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]. Then lot of experiments [2, 3, 4, 5, 6] have been performed through molecules placed between two metallic electrodes with few nanometer separation. 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. In many molecular devices, electronic transport is dominated by conduction through broadened HOMO or LUMO states. In contrast here we find that the transport through single conjugated molecules can be controlled very sensitively by introducing the localizing groups in these molecules. This sensitivity opens up new possibilities for novel single-molecule sensors. Electron conduction through molecules strongly depends on (a) the delocalization of the molecular electronic orbitals and (b) their coupling strength to the two electrodes. In a very recent experiment, Tali Dadosh et al. [2] have measured conductance of single conjugated molecules and predicted that the existence of localizing groups in a conjugated molecule suppresses the electrical conduction through the molecule. These results motivate us to study the electron transport through such conjugated molecules.

The aim of the present paper is to reproduce an analytic approach based on the tight-binding model to investigate the electron transport properties for the model of single conjugated molecules taken in their experiment [2]. Several ab initio methods are used for the calculation of conductance [7, 8, 9, 10, 11, 12], yet it is needed the simple parametric approaches [13, 14, 15, 16, 17, 18, 19, 20, 21] for this calculation. The parametric study is motivated by the fact that it is much more flexible than that of the ab initio theories since the later theories are computationally very expensive and here we focus our attention 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.

The scheme of the paper is as follow. In Section 2, we give a very brief description for the calculation of transmission probability and current through a finite size conductor sandwiched between two one-dimensional (1D) metallic electrodes. Section 3 focuses the results of conductance-energy (\(g-E\)) and current-voltage (\(I-V\)) characteristics for the single conjugated molecules and study the effects of localizing groups in the above mentioned quantities. Finally, we summarize our results in Section 4.

2 A glimpse onto the theoretical formulation

Here we describe very briefly about the methodology for the calculation of transmission probability (\(T\)), conductance (\(g\)) and current (\(I\)) through a finite conductor sandwiched between two semi-infinite metallic electrodes by using the Green’s function technique.

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

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

Figure 1: Schematic view of a 1D conductor with \(N\) number of atomic sites (filled circles) connected to two semi-infinite electrodes, namely, source and drain, as presented in Fig. 1. The conducting system in between the two electrodes can be an array
in terms of the Green’s function of the conductor and the coupling of the conductor to the two electrodes by the expression,

\[ T = \text{Tr} \left[ \Gamma_S G_C^r \Gamma_D G_C^a \right] \tag{2} \]

where \( G_C^r \) and \( G_C^a \) are respectively the retarded and advanced Green’s function of the conductor. \( \Gamma_S \) and \( \Gamma_D \) are the coupling terms of the conductor due to the coupling to the source and drain, respectively. For the complete system, i.e., the conductor and the two electrodes, the Green’s function is defined as,

\[ G = (\epsilon - H)^{-1} \tag{3} \]

where \( \epsilon = E + i\eta \). \( E \) is the injecting energy of the source electron and \( \eta \) is a very small number which can be put as zero in the limiting approximation. The above Green’s function corresponds to the inversion of an infinite matrix which consists of the finite conductor and two semi-infinite electrodes. It can be partitioned into different sub-matrices those correspond to the individual sub-systems.

The effective Green’s function for the conductor can be written as,

\[ G_C = (\epsilon - H_C - \Sigma_S - \Sigma_D)^{-1} \tag{4} \]

where \( H_C \) is the Hamiltonian for the conductor sandwiched between the two electrodes. The single band tight-binding Hamiltonian for the conductor within the non-interacting picture can be written in the following form,

\[ H_C = \sum_i \epsilon_i c_i^\dagger c_i + \sum_{<ij>} t \left( c_i^\dagger c_j + c_j^\dagger c_i \right) \tag{5} \]

where \( c_i^\dagger \) (\( c_i \)) 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. Here \( \Sigma_S = h_{SC} g_S h_{SC} \) and \( \Sigma_D = h_{DC} g_D h_{DC} \) are the self-energies terms due to the two electrodes. \( g_S \) and \( g_D \) are respectively the Green’s function for the source and drain. \( h_{SC} \) 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,

\[ \Gamma_{\{S, D\}} = i \left[ \Sigma^r_{\{S, D\}} - \Sigma^a_{\{S, D\}} \right] \tag{6} \]

where \( \Sigma^r_{\{S, D\}} \) and \( \Sigma^a_{\{S, D\}} \) are the retarded and advanced self-energies, respectively, and they are conjugate to each other. Datta et al. \cite{22} have shown that the self-energies can be expressed like,

\[ \Sigma^r_{\{S, D\}} = \Lambda_{\{S, D\}} - i \Delta_{\{S, D\}} \tag{7} \]

where \( \Lambda_{\{S, D\}} \) are the real parts of the self-energies which correspond to the shift of the energy eigenstates of the conductor and the imaginary parts \( \Delta_{\{S, D\}} \) of the self-energies represent the broadening of these energy levels. This broadening is much larger than the thermal broadening and this is why we restrict our all calculations only at absolute zero temperature. By doing some simple algebra these real and imaginary parts of self-energies can also be determined in terms of coupling strength \( (\tau_{\{S, D\}}) \) between the conductor and two electrodes, injection energy \( (E) \) of the transmitting electron, site energy \( (\epsilon_0) \) of the electrodes and hopping strength \( (v) \) between nearest-neighbor sites in the electrodes. Thus the coupling terms \( \Gamma_S \) and \( \Gamma_D \) can be written in terms of the retarded self-energy as,

\[ \Gamma_{\{S, D\}} = -2\text{Im} \left[ \Sigma^r_{\{S, D\}} \right] \tag{8} \]

Now all the information regarding the conductor to electrode coupling is included into the two self-energies as stated above and is analyzed through the use of Newns-Anderson chemisorption theory \cite{23, 24}. The detailed description of this theory is obtained in these two references.

By calculating the self-energies, the coupling terms \( \Gamma_S \) and \( \Gamma_D \) can be easily obtained and then the transmission probability \( T \) can be computed from the expression as mentioned in Eq. 2.

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 and the electrodes respectively. The coupling terms \( \Gamma_S \) and \( \Gamma_D \) for the conductor can be calculated through the expression,

\[ T(E, V) = 4\Delta_{11}^S (E, V) \Delta_{NN}^D (E, V) |G_{1N}(E, V)|^2 \tag{9} \]

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 \cite{23},

\[ I(V) = \frac{e}{\pi h} \int_{E_F-eV/2}^{E_F+eV/2} T(E, V) dE \tag{10} \]

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 this assumption does not significantly change the qualitative behaviors of the \( I-V \) characteristics. Using the expression of \( T(E, V) \) as in
Eq. 9 the final form of $I(V)$ becomes,

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

Eq. 9, Eq. 10 and Eq. 11 are the final working formulae for the calculation of conductance $g$ and current-voltage characteristics, respectively, for any finite size conductor sandwiched between two electrodes.

With the help of the above formulation, we shall describe the electron transport properties through some conjugated molecules (Fig. 2). For the sake of simplicity throughout this article we use the unit $c = e = h = 1$.

### 3 Results and discussion

This section focuses the conductance-energy ($g$-$E$) and current-voltage ($I$-$V$) characteristics of three short single conjugated molecules. These molecules are specified as: 1,4-benzenedimethanethiol (BDMT), 4,4′-biphenyldithiol (BPD) and bis-(4-mercaptophenyl)-ether (BPE) those are attached to two electrodes by thiol (S-H) groups.

(BDMT), in which the molecular conjugation is broken near the contacts by a methylene group; 4,4′-biphenyldithiol (BPD), a fully conjugated molecule; and bis-(4-mercaptophenyl)-ether (BPE), where the molecular conjugation is broken by an oxygen atom at the center. The schematic representations of these three molecules, with thiol groups at the two extreme ends of each molecules, are shown in Fig. 2. These molecules are contacted to the two semi-infinite 1D electrodes by thiol (S-H) groups via single channels (same as shown schematically in Fig. 1). In actual experimental arrangement, two electrodes are constructed by using gold (Au) substance and molecule attached to the electrodes by thiol (S-H) groups in the chemisorption technique where hydrogen (H) atoms remove and sulfur (S) atoms reside. The electron transport through such conjugated molecules significantly influenced by the presence of localizing groups in the molecules and the molecule-to-electrode coupling strength. Here, we shall investigate our results in these aspects. Throughout the article, we discuss the results in two limiting regimes depending on the coupling strength of the molecule to the electrodes. One is defined as $\tau_{(S,D)} \ll t$, the so-called weak-coupling limit. The other one is $\tau_{(S,D)} \sim t$, the so-called strong-coupling limit. The parameters $\tau_S$ and $\tau_D$ correspond to the coupling of the molecules to the source and drain, respectively. The values of the different parameters used in
our calculations in these two limiting regimes are assigned as: \(\tau_S = \tau_D = 0.5; t = 2.5\) (weak coupling) and \(\tau_S = \tau_D = 2; t = 2.5\) (strong-coupling). For the side attached electrodes the on-site energy \((\epsilon_0)\) and the nearest-neighbor hopping strength \((v)\) are fixed to 0 and 4, respectively. The Fermi energy \(E_F\) is set at 0.

In Fig. 3 we display conductance \((g)\) as function of injecting electron energy \((E)\) for the three molecular bridge systems in the limit of weak molecular coupling. Figures 3(a), (b) and (c) correspond to the results for the bridges with BDMT, BPD and BPE molecules, respectively. Conductance shows very sharp resonant peaks for some particular energy values, while in almost all other cases it drops to zero. These resonant peaks are associated with the energy eigenstates of the individual molecules that bridges the two reservoirs. Therefore, the conductance spectrum manifests itself the electronic structure of the molecule. At resonances, the conductance \((g)\) achieves the value 2, and accordingly, the transmission probability \((T)\) goes to unity since we have the relation \(g = 2T\) from the Landauer conductance formula with \(e = h = 1\) in our present formulation. For the bridges with BDMT and BPD molecules, we see that the resonant peaks have very narrow widths, while for the bridge with BPE molecule the width of the peaks is almost zero. Thus, fine tuning in the energy scale is necessary to get the electron conduction through these bridges, specially in the case of BPE molecule for the weak-coupling limit. The most significant result is that, the BPD molecule conducts electron across the zero energy value, while the other two conduct beyond some critical energy values (see Fig. 3). Therefore, we can tune the electron conduction through the molecular bridge in a very controllable way.

In the strong molecular coupling limit, the resonant peaks in the conductance spectra get substantial widths as shown in Fig. 4. This enhancement of the resonant widths is due to the broadening of the molecular energy eigenstates caused by the coupling of the molecules to the side attached electrodes in the strong-coupling limit, where the contribution comes from the imaginary parts of the self-energies \([23]\). Though for the molecular bridges with BDMT and BPD molecules the resonant peaks get substantial widths, but, for the bridge with BPE molecule, the increment of the widths is very small. For this BPE molecule since the increment of the width of the resonant peak across the energy \(E = 2\) is comparatively higher than for the other energy values, we observe only one peak across this energy value \((E = 2, \text{Fig. 4(c)})\). Thus, for this molecular bridge electron conduction takes place across a particular energy value, while in all other energies no

![Figure 4: Conductance \(g\) as a function of the injecting electron energy \(E\) in the strong molecular-to-electrode coupling limit, where (a), (b) and (c) correspond to the results for the bridges with BDMT, BPD and BPE molecules.](image)

![Figure 5: Current \(I\) as a function of the applied bias voltage \(V\) in the weak molecule-to-electrode coupling, where the solid, dotted and dashed lines are respectively for the BPD, BDMT and BPE molecules.](image)
electron conduction takes place. This aspect may be used to describe switching action in an electronic circuit.

Thus we see that the electron conduction strongly depends on the molecule itself and also on the strength of the molecular coupling to the side attached electrodes. The behavior of electron transfer through the molecular junction becomes much more clearly observed from the current-voltage characteristics. Current passing through the molecular system is computed from the integration procedure of the transmission function $T$. The nature of the transmission function is exactly similar to that of the conductance spectrum since $g = 2T$ (from the Landauer formula), differ only in magnitude by the factor 2. In Fig. 5, we plot the current-voltage characteristics of these three molecular bridges in the weak-coupling limit. The solid, dotted and dashed curves correspond to the results for the molecular bridges with BPD, BDMT and BPE molecules, respectively. The current shows staircase-like structure with fine steps as a function of the applied bias voltage. This is due to the discreteness of molecular resonances as shown in Fig. 3. With the increase of the bias voltage, the electrochemical potentials on the electrodes are shifted and eventually cross one of the molecular energy level. Accordingly, a current channel is opened and a jump in the $I-V$ curve appears. The significant observation is that, for the molecular bridge with BPD molecule (free from localizing group), the current amplitude is much higher (see solid curve of Fig. 5) compared two the other two bridges. This is due to the fact that the localizing groups (both in BDMT and BPE molecules) interfere with the conjugated aromatic systems and suppress the overall conductance through the molecules. On the other hand, the another important feature is that, in purely conjugate molecule (BPD) the electron conduction takes place as long as the bias voltage is applied, while for the other two molecules it appears beyond some finite values of $V$. This behavior gives a key idea in the fabrication of molecular devices.

The shape and height of these current steps depend on the width of the molecular resonances. With the increase of molecule-to-electrode coupling strength, current gets a continuous variation with the applied bias voltage and achieves much higher values (compared to the current amplitude in the weak coupling case), as plotted in Fig. 6 where the solid, dotted and dashed curves correspond to the same meaning as in Fig. 5. In this strong molecular coupling limit, the current amplitude for the molecular bridge with BPE molecule is negligibly small compared to the other two bridges and the other features are also similar to the case of weak molecular coupling limit.

4 Concluding remarks

In summary, we have studied electron transport, at absolute zero temperature, through three short single conjugated molecules based on the tight-binding framework. We have used parametric approach, since we are interested only on the qualitative behaviors instead of the quantitative ones, rather than the ab initio theories since the later theories are computationally too expensive. This technique can be used to study the electronic transport in any complicated molecular system.

Electronic transport is significantly affected by (a) the molecule itself and (b) molecule-to-electrode coupling strength and in this article we have studied our results in these aspects. In the weak-coupling limit conductance shows sharp resonant peaks, while these peaks get broadened in the limit of strong molecular coupling. These results predict that by tuning the molecular coupling strength one can control the electron conduction very sensitively through the molecular bridges. In the study of current we have seen that the current shows step-like behavior with sharp steps in the weak molecular coupling, while it becomes continuous in the strong-coupling limit as a function of applied bias voltage. Both for the two limiting cases our results have clearly described that the localizing groups suppress the current amplitude in large amount compared to
the current amplitude in case of purely conjugate molecule. Another significant observation is that the threshold bias voltage of electron conduction across a molecular bridge strongly depends on the molecule itself. These results provide key ideas for fabrication of different molecular devices, especially in the fabrication of molecular switches.

Some assumptions have been taken into account for this present study. More studies are expected to take the Schottky effect which comes from the charge transfer across the molecule-electrode interfaces, the static Stark effect, which is taken into account for the modification of the electronic structure of the bridge system 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. In this article we have also neglected the effects of inelastic scattering processes and electron-electron correlation to characterize the electron transport through such bridges.

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