CHAPTER 6

SIMULATION OF TEMPERATURE EFFECT AND THE ROLE OF FUNCTIONAL GROUP FOR TOUR WIRE

6.1 INTRODUCTION

Analyzing the temperature effects on electron transport is necessary to design the molecular device, since these effects are connected to understand the thermal broadening conductance phenomena [141].

In this section, we have studied the influence of functional groups NO$_2$ and NH$_2$ over a set of phenyl-ethylene-oligomers known as Tour wire at different temperature ranging from 0K to 600K. The purpose of this study is to manifest the roles such as the current-controlling behaviors are played by the functional groups. Also, the effect of temperature on the conductance behavior of the system is analyzed by varying the temperature of the electrodes and the central molecular region. It is demonstrated how the temperature dependence of the conductance and its fluctuations can be modified by an appropriate design of molecular device.

6.2 ROOM TEMPERATURE ELECTRON TRANSPORT ANALYSIS

We focus on the temperature effect of phenyl-ethylene oligomer, so-called “Tour wire”, comprised of phenyl rings separated by triplet-bonded carbon atoms that form a long rigid molecule with π-conjugated delocalized frontier orbitals [142,143]. Here the influence of functional groups NO$_2$ and NH$_2$ on the electrical properties of TW molecular system is investigated at room temperature. We consider these molecules because Tour wire is perhaps the best studied molecule for charge transport, while the effect of temperature on the tour wire molecules has been studied experimentally [144].
The molecular system was defined by adding two Au (111) electrodes to the Tour wire (TW) molecule considered as a central region through the end group. The adsorption geometry is such that the molecules are located symmetrically at the top site of Au (111) surface. For the left and right electrodes, 3×3 unit cell is used and it is large enough to avoid any interaction with molecules in the next supercell [135].

The structural optimization and the transport properties of these systems have been investigated using ATK [110]. In our calculations, only valence electrons are self-consistently calculated and the atomic cores are described by standard norm conserving pseudo potential [111]. The valence wave functions are expanded by localized numerical (pseudo) atomic orbitals [145]. According to Yang et al., [146] analysis, for Au (111) - phenyl-ethylene oligomers- Au (111) molecular junction the use of single zeta polarized basis set shows the incorrect situation of the Fermi energy being closer to the molecular orbital but for double and triple zeta polarization basis set leads the Fermi energy closer to the molecular orbital, therefore in our investigation we computed with the double zeta plus polarization basis set for Au atoms and the other atoms.

For convergence, the Brillion zone of the leads is sampled by 3×3×100 K points in the direction of x, y, and z, where z is the electron transport direction. The self-consistency was controlled by a numerical tolerance of $10^{-5}$eV [136]. The optimized structure of Tour wire with differential functional group is represented in Figure 6.1 - 6.3.

To study the effect of adding the side groups to the parent molecule, we compute the transmission coefficient. The transmission spectrum at zero bias for TW and the TW with NO$_2$ and NH$_2$ sides groups at room temperature are shown in Figure. 6.4. The zero energy corresponds to the Fermi energy of the electrodes. The general shapes of the zero transmission spectra for the three TW systems more or less resemble the same with the narrow transmission peak at either side of the Fermi level.
Figure 6.1  Optimized structure of the Tour wire device from the GGA/DZ in ATK; Color codes: C(gray), H(white), S(yellow), Au(gold)

Figure 6.2  Optimized structure of the Tour wire- NH$_2$ device from the GGA/DZ in ATK; Color codes: C(gray), H(white), N(blue), S(yellow), Au(gold)
Figure 6.3  Optimized structure of the Tour wire- NO₂ device from the GGA/DZ in ATK; Color codes: C(gray), H(white), N(blue), O(red), S(yellow), Au(gold)

Figure 6.4  Transmission as a function of energy for the Tour wires under zero bias
We observed that the HOMO and LUMO transmissions are dominated for the TW but in the case of TW-NO₂ and TW-NH₂ systems, the transmission will happen either through HOMO or LUMO. As electron-donating substituent replace the H atoms on the Tour wire ring, the energy of the HOMO orbital increases. Similarly, when electron-withdrawing substituent replaces H atoms, the energy of the HOMO is lowered as shown in Figure 6.4. Such behavior can be justified as a consequence of quantum interference of the molecular orbitals [147], where the variation of interference conditions is due to the presence of functional groups.

Table 6.1 Isosurface - transmission eigenchannel of HOMO and LUMO resonance for Tour wires

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Energy value for HOMO (eV)</th>
<th>Energy value for LUMO (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TW</td>
<td>-0.65</td>
<td>1.32</td>
</tr>
<tr>
<td>TW-NO₂</td>
<td>-0.7</td>
<td>0.89</td>
</tr>
<tr>
<td>TW-NH₂</td>
<td>-0.54</td>
<td>0.73</td>
</tr>
</tbody>
</table>
Figure 6.5  K - dependent transmission for (a) TW  (b) TW-NO$_2$  (c) TW-NH$_2$
Table 6.1 gives the isosurface transmission eigen channel of HOMO and LUMO resonance. By calculating the eigenstates at the resonance energies ($E_{\text{HOMO}}$, $E_{\text{LUMO}}$), the orbital that are responsible for the current flow through the molecule can be analyzed. From Table 6.1 it is clear that the NH$_2$ side group participate in the HOMO resonance but not in LUMO resonance, while NO$_2$ group participate in LUMO resonance not in HOMO resonance, consisting with their respective donating/accepting characters.

It is, however clear from the isosurface of transmission eigenchannel analysis the molecular orbitals of the TW are delocalized entirely all over the molecule by providing a bath for better $\pi$ - electron cloud overlap. It can be seen that the HOMO are delocalized in the electron donating group such as NH$_2$ and the LUMO are delocalized in the electron accepting group that is NO$_2$.

The converging transmission results have been confirmed using the contour plot of $k$ - dependent transmission. The contour plot of $k$ - dependent transmission for Tour wire shows a pronounced peak at ($k_A$, $k_B$) = (0.07, 0.0) with the transmission coefficient of 0.304 as in Figure 6.5(a). This illustrates that the 3×3 dense enough $k$ - point sampling, makes the transmission underestimated, and produced converging results for the Tour wire system. Similarly, the converging results for TW-NO$_2$ and TW-NH$_2$ are confirmed with $k$ - dependent transmission contour plot as shown in Figure 6.5 (b) and 6.5(c). Contour plot peak at (0.05, 0.0) is obtained for TW-NO$_2$ and (0.04, 0.0) for TW-NH$_2$ with the transmission coefficient 0.74 and 0.99 respectively.

The transmission spectra of Tour wire and Tour wire with NO$_2$ functional group and NH$_2$ functional group under different bias voltage ranging from 0.5 V to 2V in steps of 0.5 V are presented in Figure 6.6-6.8. The magnitude of the transmission function changes greatly with an increase in the bias voltage, which leads saturation behavior of TW systems. But in TW-NO$_2$ and TW-NH$_2$ system at higher external bias the HOMO transmission regions are getting lesser than at the lower bias and no additional transmission region is being included, which leads to decrease in current than TW. We also observe that most of the HOMOs and LUMOs structure appear to move rigidly towards $E_F$ when the bias voltage is increased. This is because the delocalized nature of the $\pi$ - orbitals is increased due to the influence of bias voltage.
Figure 6.6 Bias dependent transmission spectra for TW

Figure 6.7 Bias dependent transmission spectra for TW-NO$_2$
Figure 6.8 Bias dependent transmission spectra for TW-NH$_2$

Figure 6.9 Current - voltage characteristics for TWs at room temperature
To analyze the current-voltage (I-V) characteristics at room temperature (300K), we carried out the self-consistent calculation for the biases in the range -4V to 4V in steps of 0.5V. The I-V spectra at T=300K, shown in Figure 6.5, are almost similar for all the three systems. At lower bias region the current increases gradually, while rapid increase around 1.0V is seen where the resonances come into alignment with the bias window. We also compared the I-V curve for the three TW molecular junctions; the current changes slightly over the whole range but limited variations are observed and these results are consistent with the experimental observations [148].

6.3 LOW AND HIGH TEMPERATURE EFFECT ON ELECTRON TRANSPORT

Apart from revealing the molecular signature, temperature dependent measurements can assist in understanding the transport mechanisms through Tour wire molecular junctions. The temperature dependent analysis suggested two important transport mechanisms:

(i) Thermionic emission, a temperature activated mechanism related to lower temperatures.

(ii) Thermal broadening of the lead properties and the thermal average over different geometrical configuration of the contacts.

In thermionic emission the conductance is determined by the hot electrons and the hot electrons are located in the energy range of the tails of the Fermi function. Thus, for an accurate determination of the conductance from thermionic emission, it is important that the energy range of the transmission spectrum is such that the tails of the Fermi functions are properly sampled.

For the temperature dependence conductance analysis, the linear conductance is calculated using the Landauer formalism as given by [149]
\[ G(T) = \frac{2e^2}{h} \int T(E) f \left( \frac{E - E_f}{k_B T} \right) \frac{1}{k_B T} dE \]  

(6.1)

where, \( T(E) \) is the transmission function as given as

\[ T(E) = \text{Tr}(\Gamma_1 G \Gamma_2 G^\dagger) \]  

(6.2)

We calculated the transmission function \( T(E) \) using the non equilibrium Green’s function formalism as represented in equation (2.84).

For zero temperature, equation 6.1 is reduced to

\[ G(T) = \frac{2e^2}{h} T(E_f) \]

For different temperature the energy window has been averaged to the order of \( k_B T \), as described by the derivative of the Fermi function \( f \left( \frac{E - E_F}{k_B T} \right) \). This averaging account for the “electronic” or “lead-induced” thermal broadening [62]. It is to be distinguished from a room temperature effect and it is arises from the derivatives of Fermi function, these fluctuations further modify the conductance [150,151].

In order to analyze the temperature dependent conductance properties for Tour wire and Tour wire with functional group NO\(_2\) and NH\(_2\) molecular junctions, we have computed the transmission \( T(E) \) of these systems and the transmission curves are plotted in Figure 6.10 and 6.11. With the increase of temperature, the energy levels of the isolated molecules are get broaden and determine the transport capacity. The most important observation to be made from Figure 6.10 and 6.11 is the large reduction in transmission at lower temperature than the higher temperature range, i.e., roughly around one orders of magnitude. This clearly reveals the involvement of thermionic emission for the charge transport in Tour wire molecular systems.
Figure 6.10  Transmission as a function of energy for TWs at low temperature (100 K)

Figure 6.11  Transmission as a function of energy for high temperature (600 K)
Figure 6.12  Current - voltage characteristics for TWs at low temperature (100 K)

Figure 6.13  Current - voltage characteristics for TWs at high temperature (600 K)
From the analysis of current-voltage characteristics of Tour wire molecular systems, we observed negative differential resistance behavior of TW-NO$_2$ at 100K reported in Figure 6.12. This can be understood by studying the coupling between the molecular orbitals and the incident state in the electrode under various biases and also at different temperatures. From Figure 6.12, the NDR-like peaks occur at the bias voltage varying from 2.5V to 3.8V. These results are comparable with the experimental observation [148,152]. The appearance of NDR peak in both positive and negative bias voltage is due to the breakdown of the molecular junction at the molecule-electrode interface. In this system, the NDR like effect is associated with the reduction of electro active nitro functional group rather than the reduction of Au-S bond.

The temperature dependent conductance G (T) is plotted in Figure 6.14 for the three TWs by varying the temperature of the molecular device in the range of 0K-600K. The average G (T) shows qualitative differences for the three TW molecular systems. TW and TW-NH$_2$ exhibit a rather linear increasing conductance G (T) with increasing temperature. In contrast, weak temperature dependence is found for TW-NO$_2$.

At different temperatures, the conductance depends upon two important temperature induced transport mechanism. One comes from the thermal broadening of the lead properties but the other one comes from the thermal average over the different geometric configurations of the central region. For the TW and TW-NH$_2$ molecules, to increase their conductance at higher temperature the lead induced temperature dependence contributions are not much supported.

Therefore, the configurational thermal broadening gives accessibility to increase the conductance values, resulting steady increase in G (T). For TW-NO$_2$ molecule, elevated temperatures give accessibility to both higher and lower conductance; as a result of which G (T) exhibits no clear trend. This is because; the lead-induced and the configurational thermal broadening play equal role for the elevation of temperature dependence conductance.
Figure 6.14  Conductance as a function of electron temperature for the central region of TWs

Figure 6.15  Conductance as a function of electron temperature for the left and right electrode
The temperature dependent conductance for the TW systems by varying the temperature of the left and the right electrode is shown in Figure 6.15. The lead induced conductance has the strongest effect on the longer junction systems and the conductance will increase as a function of temperature.

In our system, when the temperature varies from 0K to 450K the conductance decreases. This is because at this temperature range the lead-induced conductance is suppressed by large tunneling near the Fermi level. As we exceed 450K, the energy levels of the central region come closer to the Fermi energy of the electrode and larger conductance due to thermionic emission is visualized.