Modelling of Quantum Transport in Molecular Structure.

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We would like to thank our father, mother and all our family members for helping and supporting us.

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Researchers

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Contents

Abstract

We present the important properties of electron propagation in molecular modelling, such group velocity of the electron and the transmission-reflection coefficient as a function of energy using one-dimensional tight-binding model. The FORTRAN program have used to calculate these properties and to investigate quantum interference in single impurity on the one-dimensional crystal chain. We explained that the electron wave would pass directly without any obstacle on the perfect crystal. That means the transmission probability T(E) is 1 and the Reflection probability R(E) is zero, whereas if we place impurity in the middle of crystal chain on the site energy then we observed that the electron wave will be partially reflected and transmitted.

Introduction

Recent years have witnessed a significant increase in attention of studies, which related to electronic structure and great efforts to control on properties of single molecule by the researchers. These years of research in atoms have recently brought about the field of nanoscience, aiming at establishing control and making useful things at the atomic scale [1, 12]. The modification of the electronic properties of such systems has applications such as the quantum interference effect transistor (QuLET) and development of molecular switch [13]. In this report, we introduce the important properties of electron propagation in molecular systems, such as group velocity of the electron and the transmission-reflection coefficient as a function of energy. We also derive the transfer matrix that enables us to calculate the transmission-reflection of an electron through one-dimensional crystal system containing single impurity in the middle.

We use the tight binding model to study the single electron transport properties of a one dimensional (1-D) chain. Starting point to understand the electrical structure of one-dimensional crystalline chain.

Here we start with very simple one-dimensional crystalline system as shown in Figure (1.1). Furthermore we introduce the system in Figure 1.2, which involves single impurity on one-dimensional crystal chain that lead to be able to know the mechanism of transport in the materials.

Chapter 1

Electron transport theory

We start with a brief review to understand about electronic transport in nano-scale conductors, the transmission probability T(E) is an important expression for calculating electron transport, and the relation between T(E) and the conductance G(E) is given by the 'Landauer formula' which is represented by [7,8]:

$$G(E) = G_o T(E) \qquad (1.1)$$

Where G(E) is an electrical conductance as a function of energy, and $G_o = \frac{2e^2}{h}$ is quantum conductance value measured by 'Siemens unit which is the inverse of ohms, e = the electron charge value, h = Planck's constant, and T (E)= transmission coefficient as a function of energy.

We explain briefly the transport mechanism by physical and mathematical structures.

The transmission probability T(E) and the Reflection probability R(E) express the transport mechanism where:

$$|t|^2 + |r|^2 = 1 \quad \rightarrow T(E) + R(E) = 1$$

where t and r are amplitudes of transmission and reflection respectively.

1.1 One dimensional (1-D) linear crystalline chain

We consider simple tight-binding approach to get qualitative understanding of electronic structure calculation in periodic systems, as shown in figure (1).

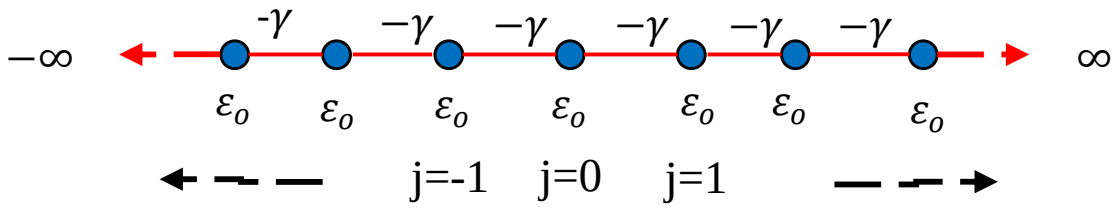


Figure 1.1. One dimension (1-D) linear crystalline chain. [14]

Where ε_o and γ are the site and hopping energies respectively.

For perfect crystal in Figure (1.1), we can imagine sending the finite wave packet along this crystal with group velocity v which is given by [5]:

$$v = \frac{1}{\hbar}\frac{dE}{dK} \qquad (1.2)$$

1.2 Transport for single impurity on the crystal chain:

One dimensional crystalline linear chain with single impurity is placed in the middle of chain as a defects as shown in figure (1.1), and analytical formula has been found to calculate the transmission and reflection probabilities, which are (1.3) and (1.4) equations.

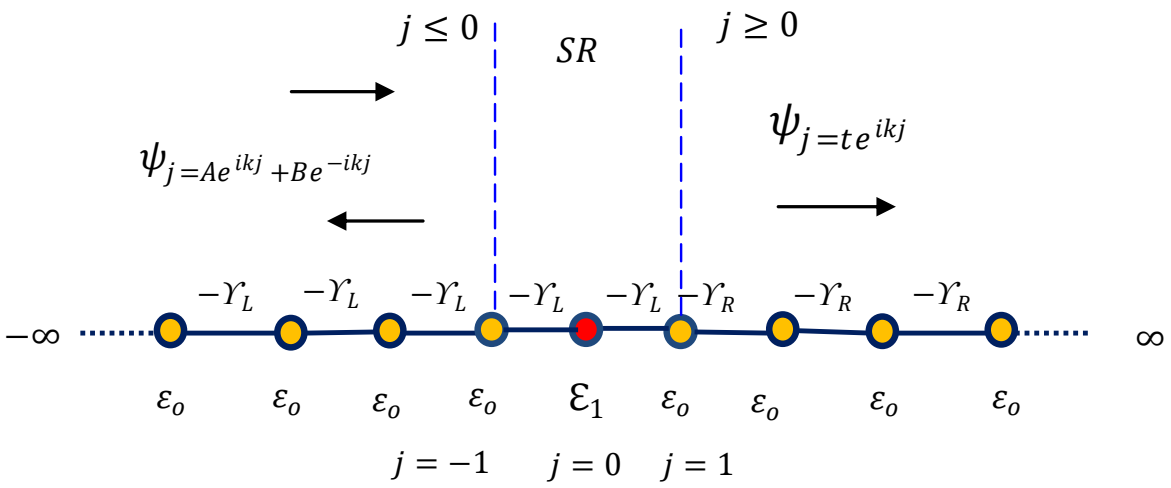


Figure 1.2. illustrates transport for scattering region that involves a single impurity which is coupled to the two symmetric leads.

The Hamiltonian based on tight-binding model has given for this system by:

$$H = \begin{bmatrix} \varepsilon_o & -\gamma & 0 \\ -\gamma & \mathcal{E}_1 & -\gamma \\ 0 & -\gamma & \varepsilon_o \end{bmatrix}$$

Schrodinger equation has applied to derive these formulas, which given by:

$$\mathcal{E}_1\psi_o - \gamma\psi_{-1} - \gamma\psi_1 = E\psi_o$$

It has been considered that $A=1$ and $B= r$ and then the analytical formula to calculate the transmission coefficient as a fu $where\ \alpha = \frac{\varepsilon_1 - \varepsilon_0}{\hbar v}$ for single impurity is given by: $k = \cos^{-1}(\frac{\varepsilon_o - E}{2\gamma})$

$$t = \frac{1}{i\alpha + 1} \rightarrow \quad |t|^2 = T(E) = \frac{1}{\alpha^2 + 1} \qquad (1.3)$$

$$r = \frac{-i\alpha}{i\alpha+1} \rightarrow |r|^2 = R(E) = \frac{\alpha^2}{\alpha^2+1} \qquad (1.4)$$

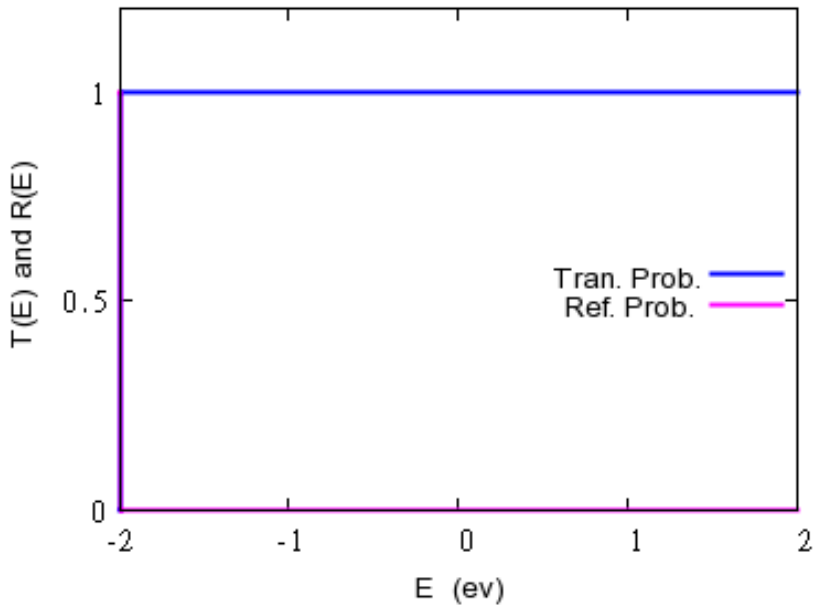
Chapter 2

Calculations and Results

Fortran95 programs have written in this study to compute transmission coefficient for single impurity chain. The results summarized in the following points:

2.1 Transport for single impurity on the crystal chain:

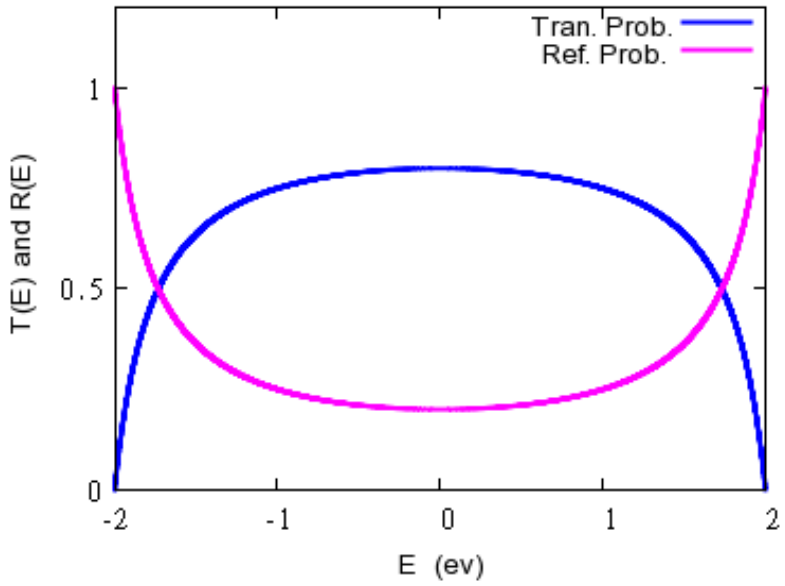
Using FORTRAN program we calculated the transmission coefficient as a function of energy for single impurity on the one dimensional crystal chain. The calculations show the properties of this impurity. This single impurity in this system explain the behaviour of scattering region and how to work as barrier or wall and shows the basic concepts for Quantum Interference QI.



Figures 2.1. shows the transmission coefficient and reflection coefficient as a function of energy for single impurity in figure (1.2) at parameters are $a)\ \varepsilon_o = 0\ ,\ \varepsilon_1 = 0\ ,\ \gamma = 1.$

Figure 1 shows the transmission coefficient as a function of energy for single impurity which is shown in figure 1.2. We consider the site energy$\varepsilon_o = 0$, the hopping energy $\gamma = 1$ the impurity energy $\varepsilon_1 = 0$, we found the horizontal line in plot and this shows that the system possesses the continuous feature for wave function of electron, where the electron passes through the system without any obstacle. This show there is only transmission probability T(E) whereas reflection probability R(E) is zero.

Figure 2 shows the transmission coefficient as a function of energy for single impurity which is shown in figure 1.2. We consider the site energy$\varepsilon_o = 0$, the hopping energy $\gamma = 1$ the impurity energy $\varepsilon_1 = 1$, the calculations show that there is unique resonance due the impurity energy $\varepsilon_1 = 1$ (up peak-blue curve) and this shows the T(E), and (down peak-pink curve) and this shows the R(E).



Figures 2.2. show the transmission coefficient and reflection coefficient as a function of energy for single impurity in figure (1.2) at parameters are $a)\ \varepsilon_o = 0\ ,\ \varepsilon_1 = 0\ ,\ \gamma = 1$, and $b)\ \varepsilon_o = 0\ ,\ \varepsilon_1 = 1\ ,\ \gamma = 1$.

We note that in Figure 2.1 the wave will pass directly without any obstacle, because it is perfect crystal. That means the transmission probability T(E) is 1 and the Reflection probability R(E) is zero. But if we place impurity in the middle of crystal chain on the site number zero (j = 0) and by apply the formula (1.3 and 1.4) for single impurity then the result is as shown in Figure 2.2. It is due to for this change we observe that the wave will be partially reflected and transmitted.

Chapter 3

Electron transport in realistic nanomaterials

In this chapter, we discus an examples of some realistic nanomaterials and show the mechanism of quantum transport through a single molecule devices.

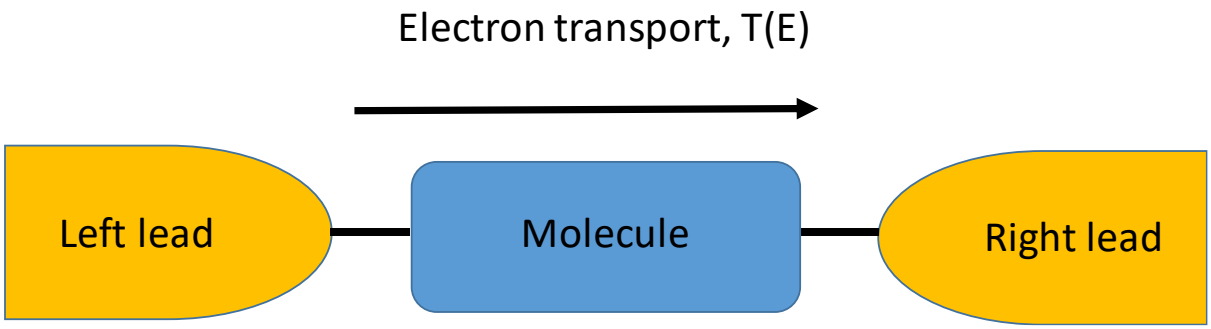


Diagram 1. Shows the mechanism of quantum transport through single molecule devices.

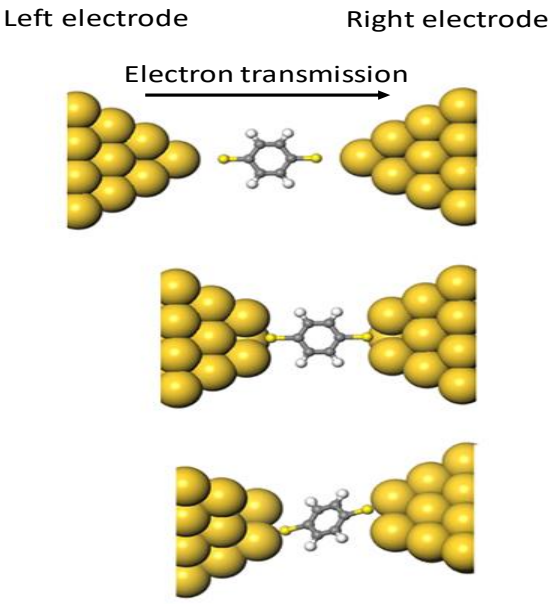


Figure 3.1. An example of single molecule junction.

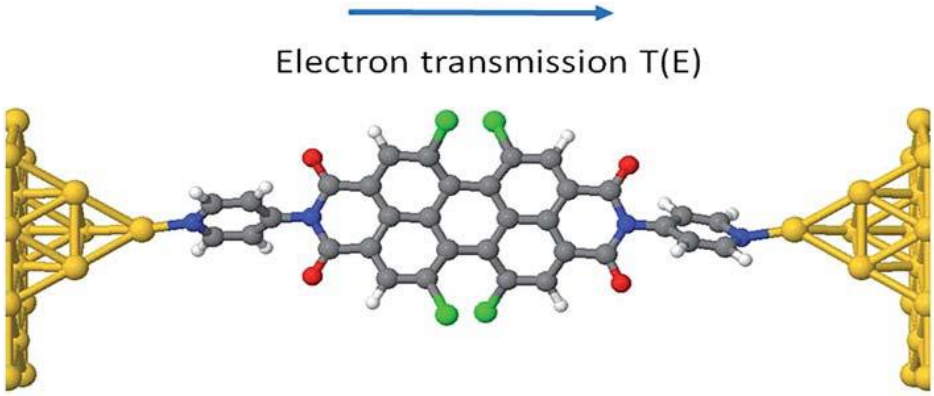


Figure 3.2. An example of an optimized configuration of the system containing single molecule (Cl-PBI) attached to two metallic leads. [1]

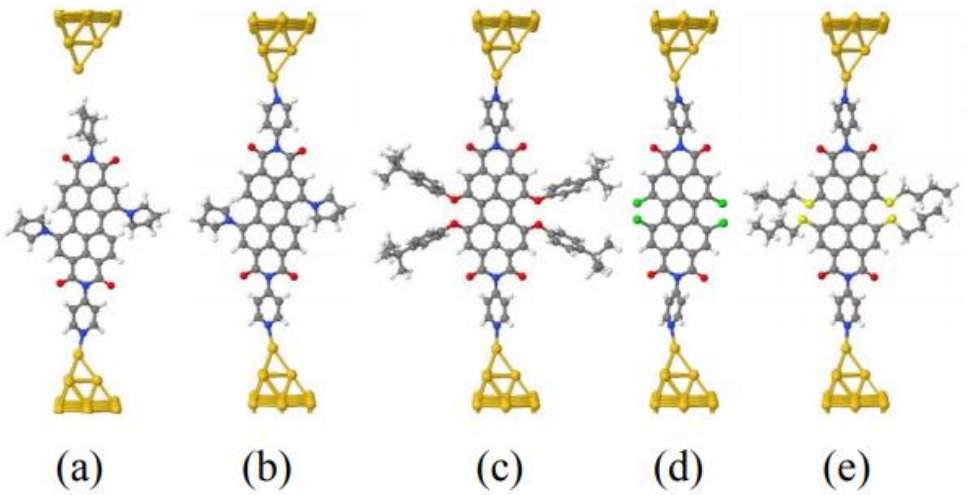


Figure 3.3. Optimised configurations of the single-molecules, perylene bisimides attached to two metallic electrodes.[1]

Figure 3.4. An example of an optimized junction configuration. To reduce the computational cost, we replace the electrically-inert alkyl group ($–C_8H_{17}$) with a methyl group ($–CH_3$).[2]

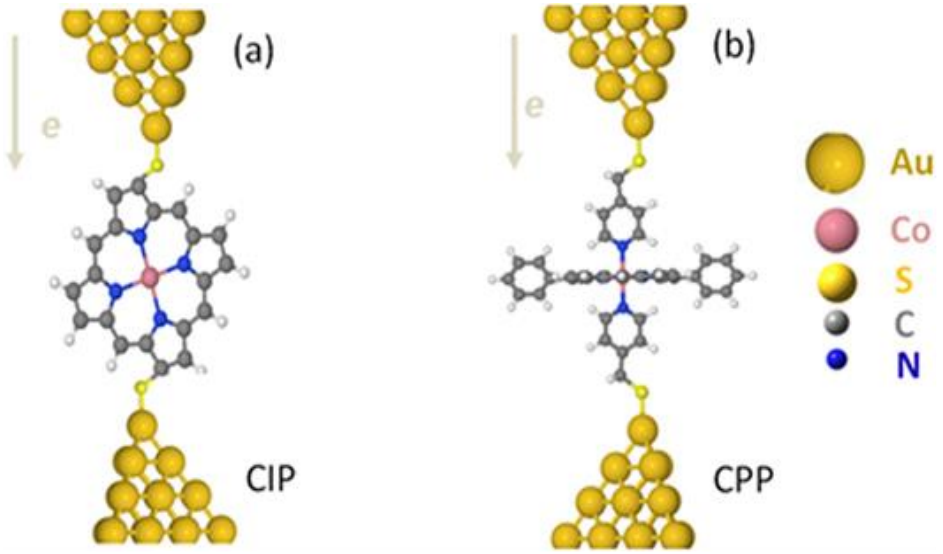


Figure 3.5. (a) Porphyrin skeleton aligned parallel to the direction of charge transport “current in plane” (CIP) up-right configuration and (**b**) the optimised sandwich configuration of DPP junction with the current perpendicular to the plane (CPP).[3]

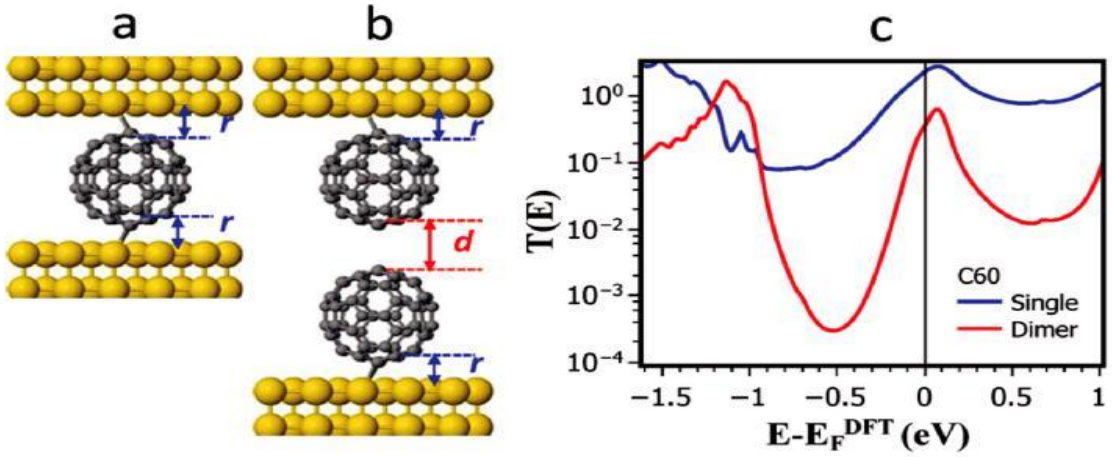


Figure 3.6. Left panel shows an example of an optimized junction configur-ation for the systems containing (a) single C_{60} and (b) a C_{60} dimer placed between two gold electrodes. Right panel, (c) shows a DFT calculation of their transmission coefficients T (E) as a function of energy E relative to the DFT-predicted Fermi energy $E^{DFT}_{F.}$ [4]

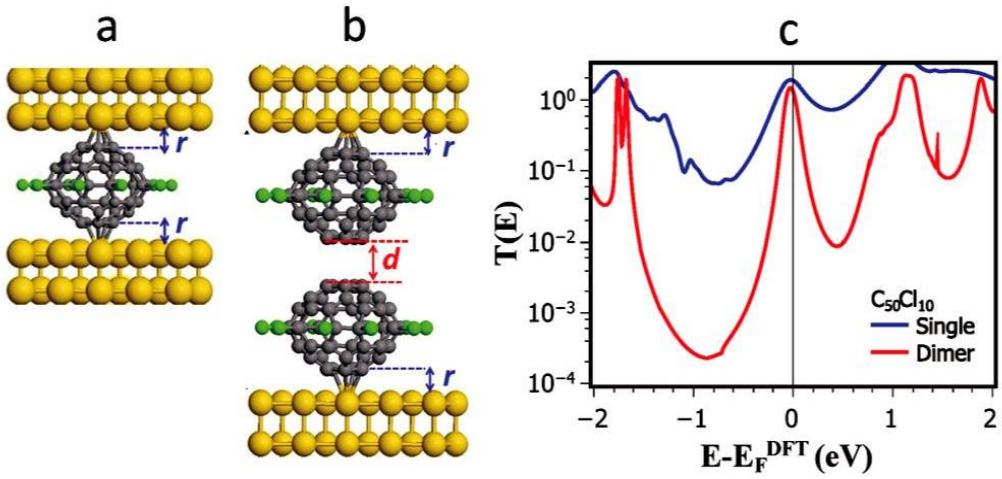


Figure 3.7. Left panel shows an example of an optimized junction configur-ation for the systems containing (a) single and (b) dimer fullerene-$C_{50}Cl_{10}$ placed between two gold electrodes. Right panel, (c) shows DFT calculation of transmission coefficient as a function of energy for the structures in Figure. 4a and b. [4]

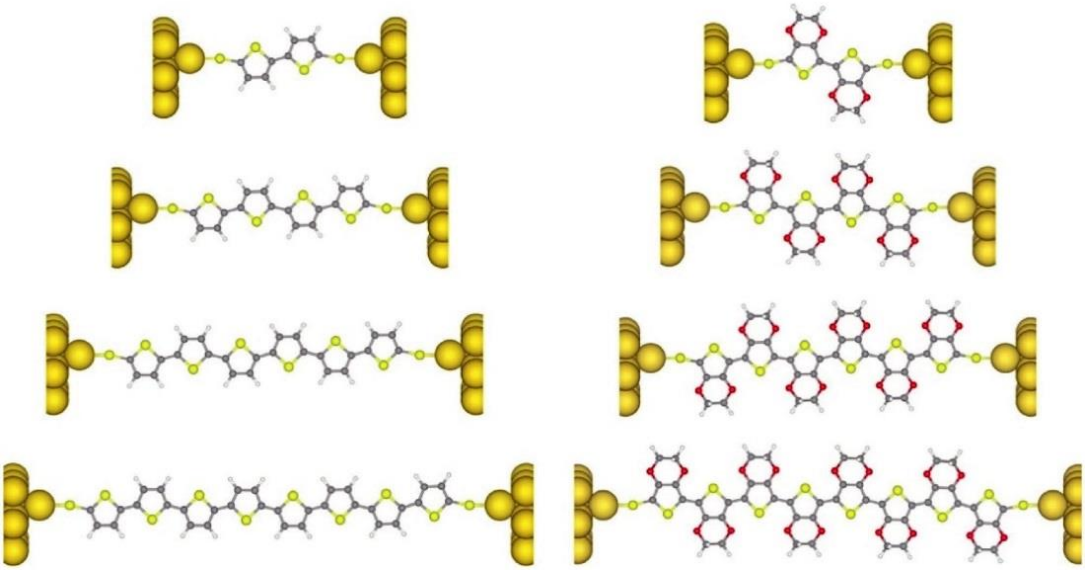


Figure 3.8. Optimized geometry of the thiophene series (left) and EDOT series (right) for *n* = 1–4 units contacted between gold electrodes. [5]

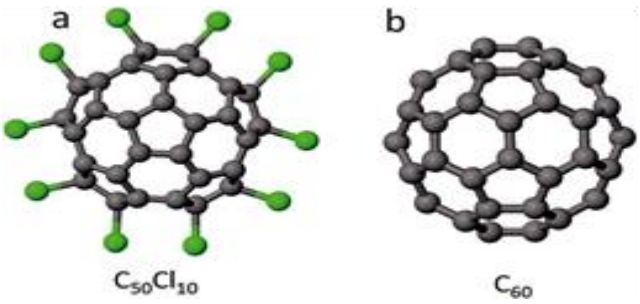


Figure 3.9. Optimized geometries for exohedral-fullerene ($C_{50}Cl_{10}$)[24,25] left and fullerene (C_{60}) right.[6]

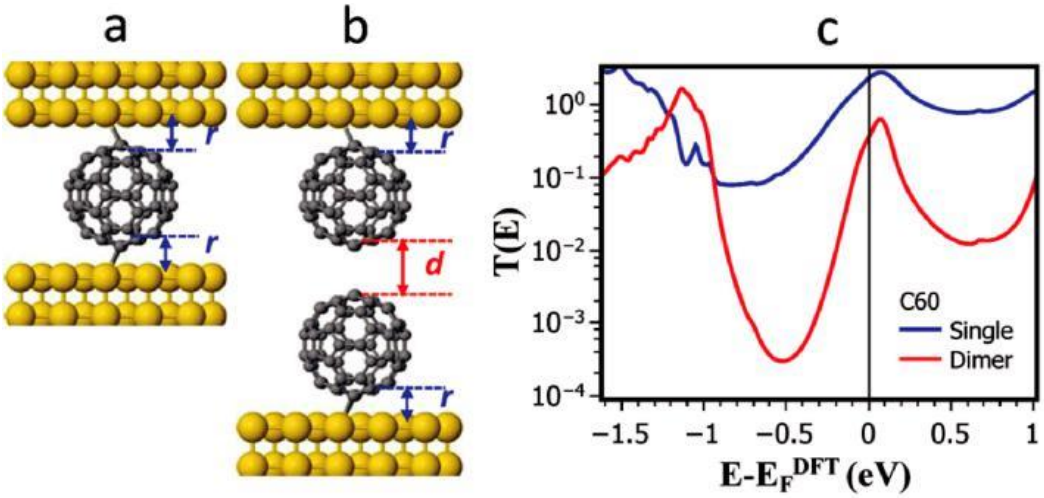


Figure 3.10. Left panel shows an example of an optimized junction configur-ation for the systems containing (a) single C_{60} and (b) a C_{60} dimer placed between two gold electrodes. Right panel, (c) shows a DFT cal-culation of their transmission coefficients T (E) as a function of energy E relative to the DFT-predicted Fermi energy $E^{DFT}{}_F$ [6]

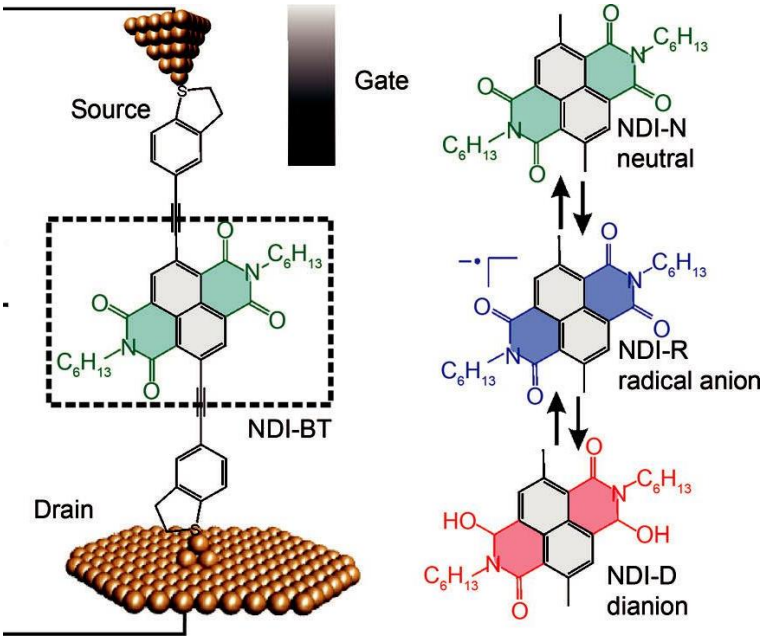


Figure 3.11. a) Schematic illustration of a single-molecule device with a central redox unit in the charge-transport pathway and a pendant redox unit. b) Schematic illustration of the electrochemically gated break junction experiment and molecular structure of NDI-BT in the neutral state (NDI-N), radical-anion state (NDI-R), and dianion state (NDI-D).[7]

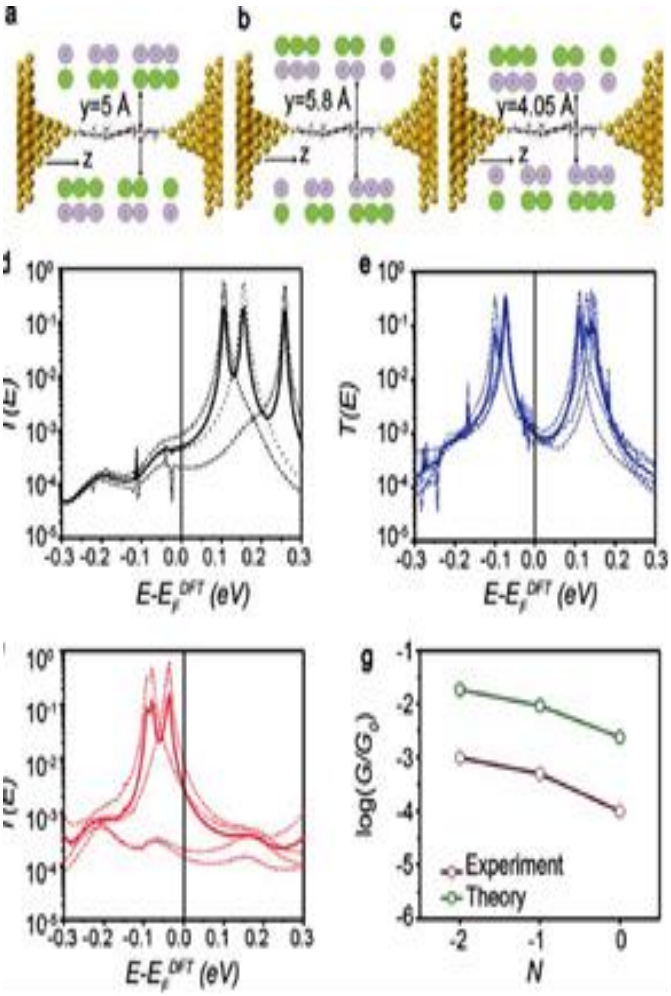


Figure 3.12. a–c) Junction geometries with charge double layers for the three states of electrochemical gating. a) The neutral state with negative-positive CDL that adjusts the molecular charge to zero. b,c) The radical anion and dianion states with positive-negative CDLs. d–f) Transmission curves for junction geometries with double layers located at distances y=5 , y=5.8 , and y=4.05

shown in (a)–(c), respectively. The continuous curves are the averaged transmission coefficients and the dotted curves show the transmission coefficients for different charge double layer arrangements. The color code refers to the three different states, NDI-N (black), NDI-R (blue), and NDI-D (red). g) Comparison of the measured and computed averaged conductance values. The computed conductance values were calculated from the averaged transmission coefficient using the finite temperature Landauer formula (Eq. (1) in the Supporting Information) with a temperature of 300 K.[7]

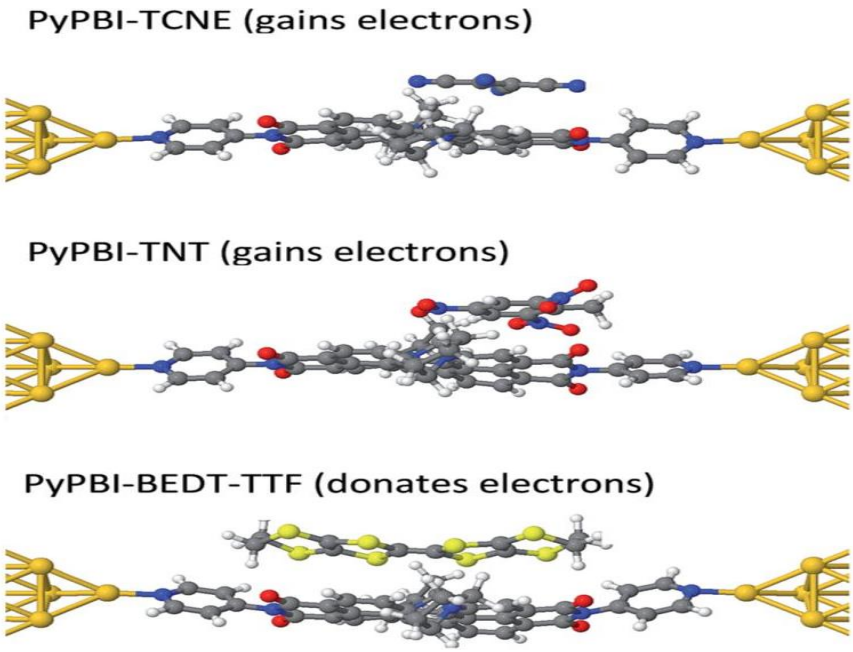


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Figure 3.13. Optimized configuration Py-PBI with (TCNE, TNT, and BEDT-TTF) which obtained from optimum configuration attached to two metallic electrodes. [8]

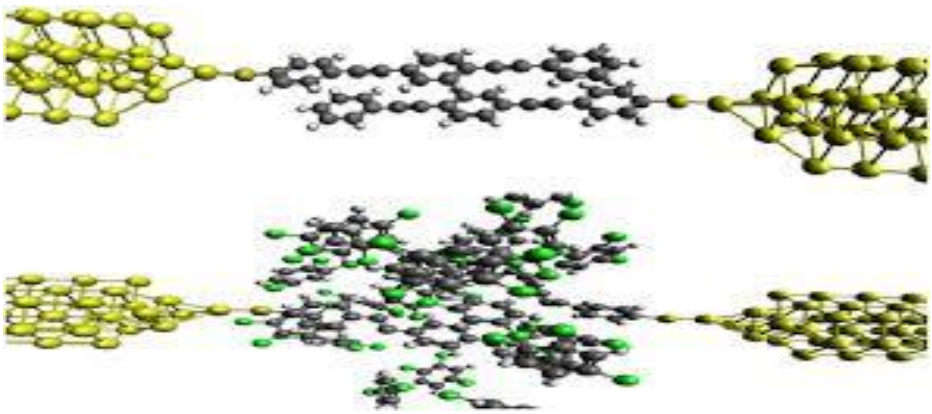

Figure 3.14. (Top) Geometry of a pi-stacked molecule connected to gold electrodes. (Bottom) Single snapshot of an MD calculation where the molecule is surrounded by TCB solvent molecules.[9]

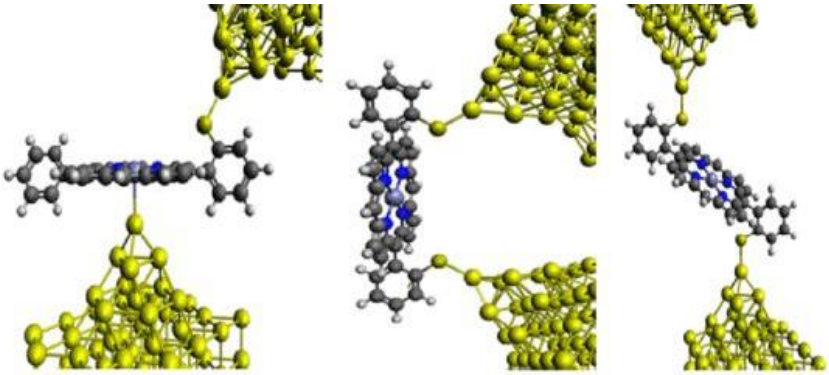

Figure 3.15. (Top) Contact geometries for the SAc series of molecules (left) G1, G2-cis (middle), and G2-trans (right). (Bottom) Zero-bias transmission coefficient T(E) vs electron energy for SAc anchor group (left) and SMe anchor group (right).[10]

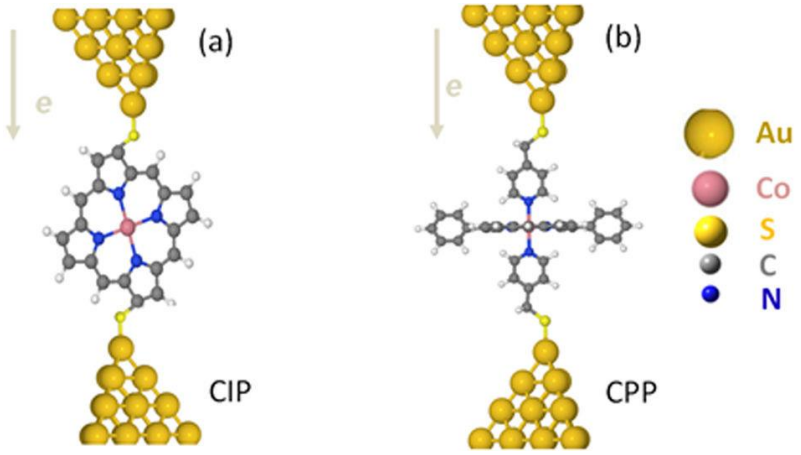

Figure 3.16 (a) Porphyrin skeleton aligned parallel to the direction of charge transport “current in plane” (CIP) up-right configuration and (b) the optimised sandwich configuration of DPP junction with the current perpendicular to the plane (CPP).[11]

Conclusions

We investigated the electronic transport through the system containing single impurity, which placed in the middle of one dimensional crystal chain. The FORTRAN program have used to calculate the transmission probability and reflection probability and to investigate quantum interference in this model. We explained that the electron wave would pass directly without any obstacle on the perfect crystal. That means the transmission probability T(E) is 1 and the Reflection probability R(E) is zero, whereas if we place impurity in the middle of crystal chain on the site energy then we observed that the electron wave will be partially reflected and transmitted.

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