Molecular Dynamics and Charge Transport in Organic Devices

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Abstract

In optimization of the device charge injection and electronic transport through the interface is very important. So, we can say that type of interface is very crucial for designing a device, especially at the molecular level. We have used DFT along with NEGF to study the interface between organic molecules and conductors. Koopman's theorem along with electronic coupling for holes, which results from the mixing of the frontier orbitals of the two nearest donors (or acceptor) molecules with the orbitals of the bridging acceptor (donor) molecule, is studied to compute the coupling integral. While calculating density matrix NEGF approach is suitable for open systems, however diagonals from Kohn-Sham Hamiltonian are used for closed or periodic systems. The distinct electronic structure of molecule and electrode, shifts the molecular levels dramatically which in consequence changes the HOMO-LUMO gap. So, coupling between the molecule and electrode is very crucial for designing a device at the molecular level.

Keywords: *Molecular junction, Non-Equilibrium Green Function (NEGF), Band Theory, Density functional theory (DFT), Benzene.*

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Introduction

Due to the continued downscaling of electronic devices, new challenges come into view at the molecular level. For next-generation devices one scale miniaturization at the nanometer level is required which causes quantum effects and materials which were suitable for the previous generation do not work properly for this generation [1-10]. So, we need new materials suitable for the next generation. Also, we need to change operation principles and geometries as per requirement. In our work, we focused on the electronic charge transportation for molecular wire within space between two electrodes. We have used repeating units of "Benzene" as a basic unit for understanding electronic transport properties. The molecular wire which is made by the repetition of the benzene ring allows analysis of both coherent and incoherent charge transport. The effect of other factors like tilt angle, the configuration of electrodes and interaction with molecular wire is also studied. Work done by others give additional understanding into the charge transport [11-19].

Computational methodology

We have taken Benzene molecular wire with two gold electrodes having orientation Au [111] and Au [100]. We have used constraining planarity to align and stabilize molecular wire in-plane with metallic electrodes. For easy understanding of the system, we have divided the system into two subspaces, electrodes and a central cluster (Fig. 1).

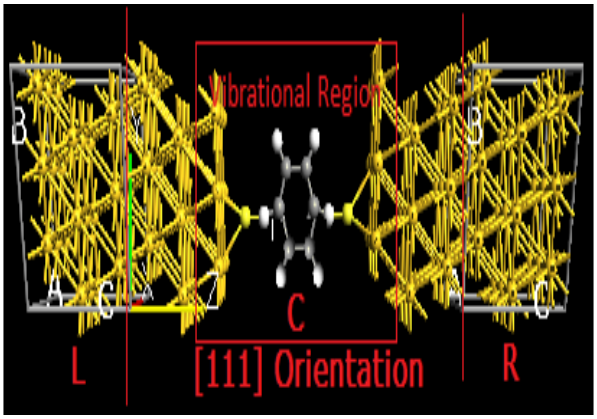

Fig-1. Benzene with 1 ring bridged between gold electrodes.

The central cluster is an extended part of molecular wire which consist of some layer of both right and left electrode along with the molecular wire.

Such arrangement helps us in:

- Study the molecule and metal in a self-consistent state
- inclusion of assumption for correction of the voltage drop across the molecule
- and reduction in the calculation time by use of the extended molecule concept.

For the calculation of charge transportation, we used the ab-initio density function theory along with the Non-equilibrium Green function (NEGF). We used geometry relaxation to get geometries of molecules that bonded to the gold surface. Periodic boundary conditions were applied to the atomic coordinates of molecular wire along with the surface of gold atoms as shown inthe vibrational region in fig-1. To calculate energy minima, we repeated geometry optimization for varying lengths and in perpendicular directions [20-28]. Electron-phonon coupling was assumed to be limited to subspace i.e. between the molecule and the first two layers of gold atoms. DFT-NEGF based upon a numerical basis set uses a density matrix as a key parameter in the self-consistent loop. We used, NEGF for the open system and diagonals from the Kohn-sham Hamiltonian for a closed system, for the calculation of the density matrix [29-40]. The trouble-Martins nonlocal pseudopotential is used for modeling of core electrons and expansion of valance electrons is done in SIESTA localize basis set. The method incorporates self-consistent field treatment of electrode-molecule-electrode junction for both zero bias and applied bias.

Results

We have taken molecular wires with varying benzene rings connected as shown in fig-2. We optimized the geometric structure using Gaussian-03 and then the HOMO-LUMO gap was calculated using SIESTA.

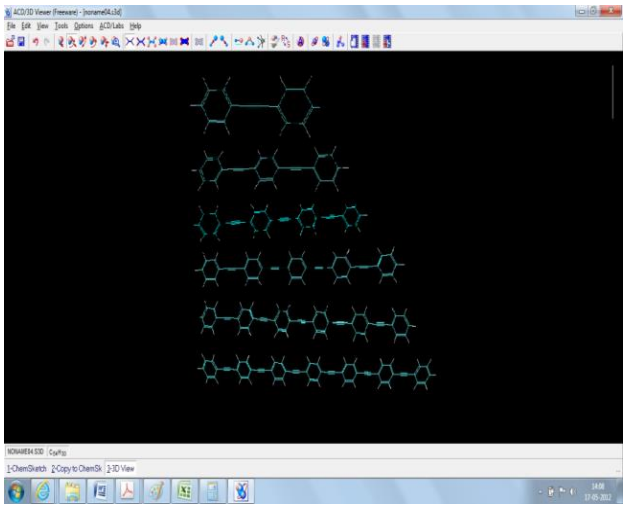

Fig-2. Different structures of benzene rings.

Coupling between benzene rings and gold electrodes at the interface shifts and expands molecular levels which results as change in the HUMO-LUMO gap. Due to coupling, discrete molecular levels are shifted to a continuous spectrum of the density matrix, which results in the enlargement of the HUMO-LUMO gap. This gap increase with the increase in the number of benzene rings. Due to an increase in benzene rings, the HOMO-LUMO gap increase and results in the overlapping of bands.

Table-1. Coupling parameter for molecular wires with varying benzene rings.

System	Distance	Coupling Parameter	System	Distance	Coupling Parameter
1 Ring	1.9	0.234	2 Ring	1.9	0.236
3 Ring	1.9	0.233	4 Ring	1.9	0.234
5 Ring	1.9	0.232	6 Ring	1.9	0.233
7 Ring	1.9	0.233	8 Ring	1.9	0.235

From table-1 we can conclude that overlapping of bands increases the transmission coefficient near Fermi level E_F which in consequence increases the coupling constant. This result remains valid with a change in orientation but

fails for a change in the electronic structure of the molecule.

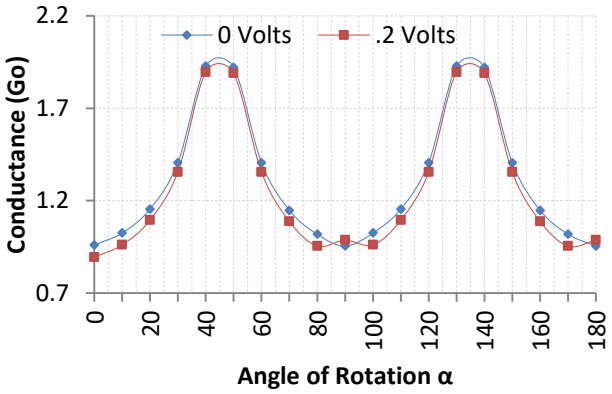

Fig-3. Conductance variation with rotation of molecular wire i. e. 0° to 180°.

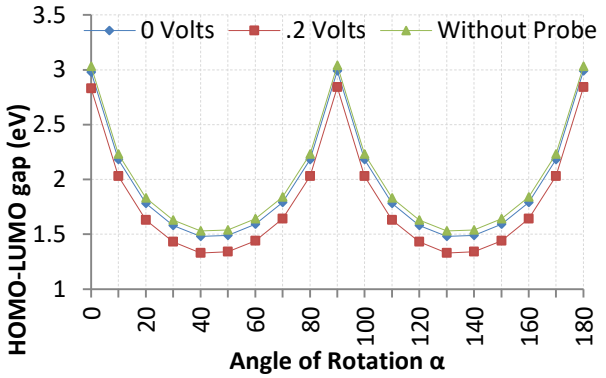

Fig-4. HOMO-LUMO gap variation with rotation of molecular wire i. e. 0° to 180°.

When we rotated the molecular wire around the bottom atoms, angle θ (angle between axis and surface perpendicular to it) changes and with change in θ, conductance changes. Results show that planar structure (benzene ring having angle 0° or 180°) exhibits better conductance as compared to twisted structure (benzene ring with angle about 90°)as shown in fig. 3 & 4. It is because of smaller band gap and superior orientation of orbital's for delocalization of electrons.

As shown in fig. 5 & 6, HOMO-LUMO gap initially increases and later on decreases with tilt in benzene wire it is because of the orientation of P and π orbital. As when the orientation remains perpendicular the conductance is maximum and as the angle changes it changes because of the change in coupling constant between electrodes and molecular wire.

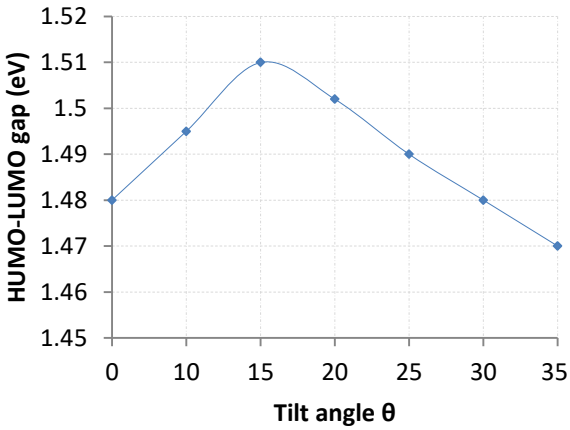

Fig-5. HOMO-LUMO gap variation with tilt (angle θ) of molecular wire.

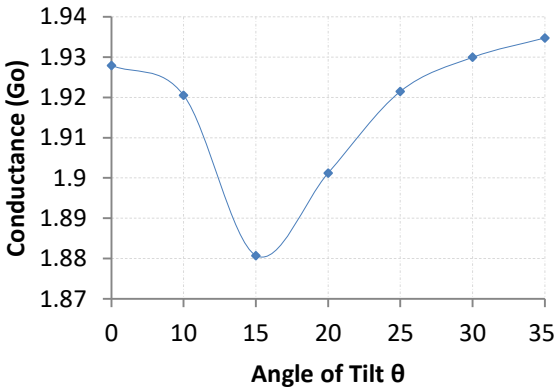

Fig-6. Conductance variation with tilt (angle θ) of molecular wire.

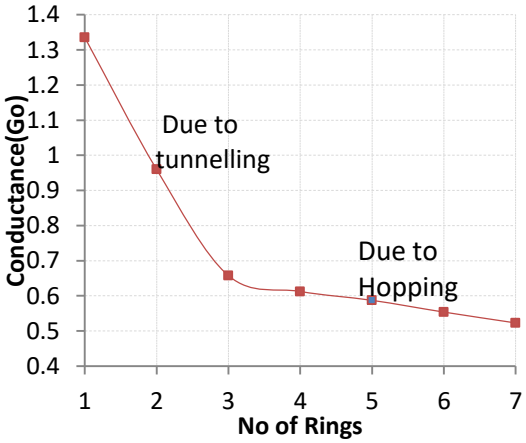

Fig-7. Variance in conductance with different benzene rings.

As shown in fig. 7 for small molecular wire conductance decreases exponentially but as we add more benzene rings decrease in conductance becomes linear, it is because of conductance behaviour that changes from tunneling to hopping. As tunneling is more dependent upon length as compared to hopping it explains this conductance behavior of molecular wire. Also, conductance varies for a system having an even or an odd number of benzene rings, it is due to distinct geometric symmetries of molecular wires. Because of the distinct geometric symmetries of molecular wires, their interfacial contact with electrodes is different from each other. A molecular wire with an even number of benzene rings has a higher coupling parameter as compared to a molecular wire with an odd number of benzene rings.

Discussion and conclusion

In this manuscript, the initiation of the field started with a single-molecule rectifier. For our system i.e. molecular wire sandwiched between gold electrodes, conductance decreases exponentially for short lengths and the decrease in conductance is linear for longer lengths. The reason for this is that initially charged transport takes place because of tunneling and later on for longer molecular wire it is due to hopping phenomena. For short lengths, results are highly length-dependent and temperature invariant and the case is opposite for the longer lengths. So, we can say that with an increase in benzene rings, conductance decreases but the tilting of molecular wire can help in achieving desired results. Rotation of molecular wire axially also results in an increase in conductance and a decrease in the HOMO-LUMO gap. Thus, rotation and angle of tilt play a crucial role to get desired results. Though, the effect of temperature on conductance at different angles cannot be subsided.

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