

## Effect of $\pi$ Orbital on $I/V$ Characteristics and Transmission in Molecular Diode Structures with Au Contacts

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The electronic transport properties of electrons in a molecules are observed by using Non equilibrium Green's function(NEGF). We present a extremely through and careful computational approach well ordered method to do a framework analysis of donor ( $\text{CH}_3$ ) and acceptor (CN) molecules connected between the Au(111) contacts, and also observed current progress through molecular devices depends on number of  $\pi$  bonds or not. Such observations implementation through not possible by standard quantum chemistry soft wares. The results shows  $I-V$  characteristics, Transport spectrum and Transport analysis can effectively tune the molecules works like a conventional semi-conductor based diodes, these results invoke to design the logic gates and logic circuits.

**Keywords:** HOMO, LUMO, Molecular orbital, Transmission spectrum.

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### 1. INTRODUCTION

Current computers made up of silicon material Integrated chips and down scaling according to Moore's law, same integrated chips are made up of molecules in the atomic scale arouse in the year 1959 lecture by famous physicist Richard Feynman [4, 19, 10] "I don't know how doing this on a small scale in a practical way, but I do know that computing machines are very large; they fill rooms. Why can't we make them very small, make them of little wires, little elements and by little, I mean little for instance, the wire should be 10 or 100 atoms in diameter, and the circuits should be a few thousand angstroms across... there is plenty of room to make them smaller. There is nothing that I can see in the physical laws that says the computer elements cannot be made enormously smaller than they are now. In fact, there may be certain advantages"

But in that time impossible to place an atom by atom and not been accredited. Later searching for molecule groups some of group of molecules donating electrons and some group accepting electrons similar to semi conductors. Technologically single molecule performs electronic functions to meet the device characteristic group of molecules considered. In that one of the group is Nitro group elements are donating electrons and amino group of elements accepting electrons [1].

One experiment on an organic system reported manifest for coulomb charging. We have performed transmission current in the configuration of a single molecule between gold metallic contacts. At room temperature one benzene 1, 4 dithiolate, nitro group and amino group molecules connected between stable proximal metallic gold contacts. This approach complements the previous approach by presenting statically stable contacts, and at the same time restrict the number of active molecules to as little ones. The Main theme of this work explains the implementation of mo-

lecular logic diode electrical characteristics and primary molecular computational behave does not require to execute with commercial available three terminal device. A few two terminal molecules sufficient to perform computational functions [5].

Molecules based logic structures or diodes occupy an area one million times smaller than silicon based devices presently they are enforced micron scale and limits of generating heat energy [13]. Electronic computer miniaturization possible systems design with molecular logic switches and logic gates in near future possible to fabricate ultra-small and ultra-dense circuits.

There are three types of molecular moxie 1) Poly phenylene chains 2) Carbon nanotubes 3) Bio molecules. Poly phenylene based molecules conduct small currents observed several groups theories, including Datta et al., Reimens et al.[7 ], explains the computational imminent. Further substituted poly phelenes and similar small organic molecules have observed experimentally have witching of Nano amperes currents. Poly phenylene chain molecular groups singly bonded aliphatic groups, doubly bonded ethenyle groups and triply bonded ethynyl or acetylenic groups act as a conducting wire or switch is a set of  $\pi$ -type orbitals that stay above and below the plane of the molecule when it is in a planar or near planar conformation[6].

### 2. THEORETICAL APPROACH & MODEL

The correlation and understanding the chemical and electrical attributes of different molecules, firstly developing the "bottom up" approach for understand and analyze the different molecules of their chemical & electrical properties [13]. Applying semi empirical formula the electrical properties explained quantitatively & qualitatively and also from first principle study [17] [18]. Typically the first principles methods are either computationally very valuable or neglect charging ef-

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fects by hiring non self-consistent forward yet exhaustive and self-consistent procedure for calculating transport characteristics while taking into account. With the quantum chemistry techniques can be applied to analyze the electronic structure of a limited size devices [2, 3].

The current calculation process consists of two steps that have to be repeat to obtain a self consistent solution.

1. Calculate the Fock matrix  $F$  for a given density matrix  $\rho$  using a specific scheme such as Hartree- Fock (HF) or density functional theory (DFT) to obtain the self consistent field.

2. Calculate the density matrix from a given self consistent fock matrix  $F$  and total number of electrons  $N$ , based on the locus of equilibrium stastical mechanics.

The Conductivity process in molecular junction under steady state (without bias voltage) observed entirely by the electron and orbital configuration in the terminal electrode-molecule-terminal electrode joint to be calculated by using number of existing methods [16]. The central electronic process can formed by charge transfer from terminal – molecule interface and potential alter in the molecular junction, which changes the charge dispersion of the molecular positions and adjust their energy levels proportional to the metal Fermi level. In conduction process, molecular states energies and nearer to the metal Fermi level (so called frontier molecular orbitals) and are suitable to the conduction process, usually highest occupied molecular orbital (HOMO) and the lowest unoccupied orbital (LUMO) key role to play charge transfer in the molecule, the energy gaps have estimated through the density of states (DOS) of molecular junction, including the total DOS and its projection onto individual molecular orbitals (PDOS).

The energy structure of the frontier orbitals by applying the bias and their extending towards conductance can be recognize qualitatively from calculation of LUMO and HOMO intermediated transport, which gives the transmission coefficient through the metal molecule metal junction as

$$T = \sum_{\substack{i=HOMO \\ LUMO}} \frac{\Gamma_{i,L}\Gamma_{i,R}}{(E_f - E_i)^2 + (\Gamma_{i,L} + \Gamma_{i,R})^2 / 4} \quad (1)$$

Where  $\Gamma$  denotes the broadening due to contact with the left (right) electrode respectively. The conductance is related to the transmission coefficient at energies around the Fermi level over a range found by the thermal broadening through the temperature dependence in the electrode Fermi distribution, and we can separate the tunneling and thermal activation contribution to the conductance as below.

$$G = \frac{2e^2}{h} \int_{-\infty}^{+\infty} T(E) \left[ -\frac{df}{dE}(E - E_f) \right] dE \quad (2)$$

The molecular junction conductance therefore is determined by both the lineup of the frontier molecular states relative to the metal Fermi level and strength of their coupling to the metal surface states[11, 12].

Both the energy level lineup and the conductance of the molecular junction can be examined from the equilibrium transmission  $Vs$  energy  $T(E)$  characteristics of the molecular junction. For the three phenyl dithiol molecules studies here we find that the metal Fermi level lines up closer to the HOMO than to the LUMO upon contact with two gold electrodes shown in the Fig. 3.

### 3. COMPUTATIONAL APPROACH

The circuit diagram of the two terminal molecular diode shown in Fig. 1. In the fig a shows two molecules  $CH_3$  and  $CN$  are act as a donor and acceptor, connected two ends of the benzene molecule and these two separated by one covalent bond and same structure molecules separated by two, three and four covalent bond shown in the successive figures b, c, d. each device connected between two Au (111)-(3 × 3) blocks. The geometry optimization and electrical behavior observations done ATK- SE Extend Huckel method, Current through the system getting from the Landauer-Buttiker formula

$$I = \frac{2e}{h} \int_{\mu_L}^{\mu_R} T(E, V) [f(E - \mu_L) - f(E - \mu_R)] dE \quad (3)$$

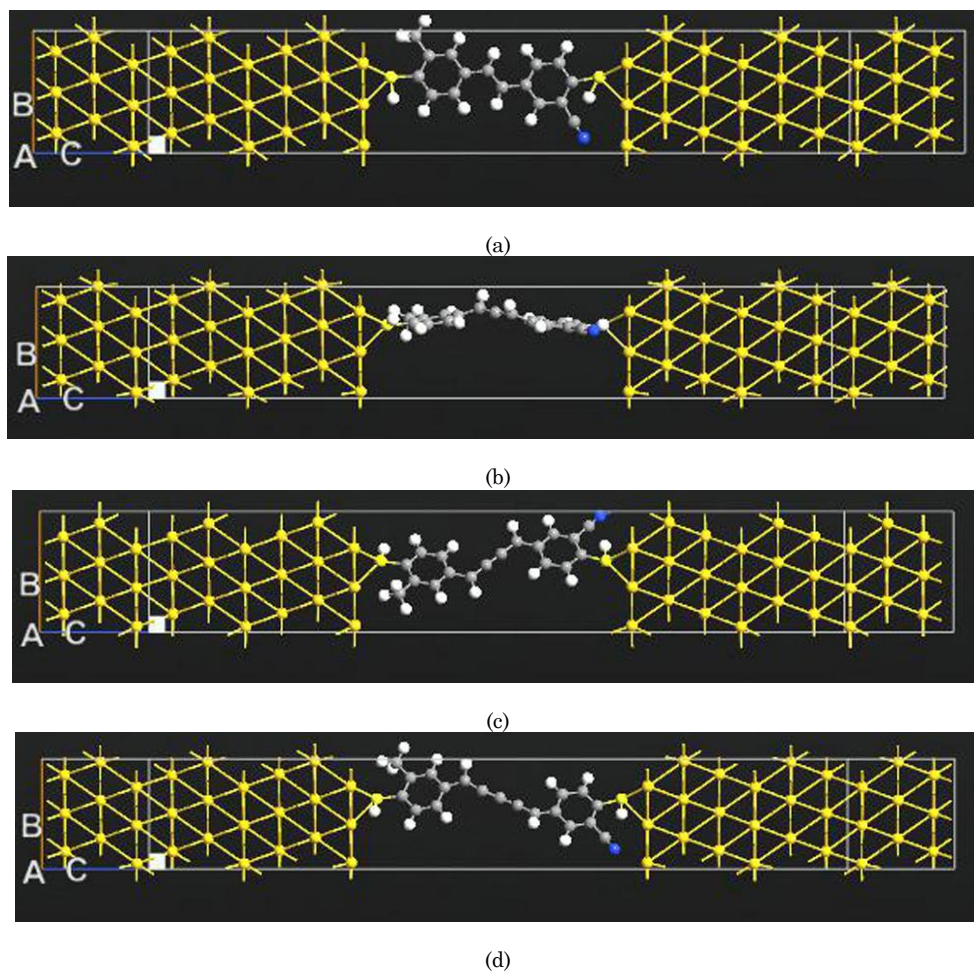
Where  $\mu_L(R)$  and  $f(E - \mu_L(R))$  are chemical potential and Fermi functions of left and right electrodes,  $T(E, V)$  is the transmission functions of the device at energy value  $E$  by applying the external voltage  $V$ . Calculated total energy listed in the Table 1,  $\mu_L, \mu_R$  proposed molecular diodes listed in the Table 2 with bias and without bias.

**Table 1** – Calculated Total energy of proposed molecular diode structures

| Molecular Structure Name | Total Energy (eV) |
|--------------------------|-------------------|
| Diode 1                  | – 19209.32 eV     |
| Diode 2                  | – 19271.47 eV     |
| Diode 3                  | – 19349.42 eV     |
| Diode 4                  | – 19417.80 eV     |

The current-Voltage relation in molecule is different from the self-consistent procedure following ways 1. A continuous density of states and variable number of electrons, rather than an isolated molecule with distinct levels and whole number of electrons. 2. Two to three volts of voltage sufficient to drive the electrons far from equilibrium. 3. Surface effects like chemical absorption and bonding with the contacts are expected to works a non-uniform role in transport. To find the current and voltage relation in the molecule which was connected between Au (111), DFT and non equilibrium Green's function is more desirable.

The origin of the transport of electrons in the molecule after applying the bias voltage to left and right electrodes can explained by transmission spectra  $T(E)$  and molecular projected orbital structures. Mainly HOMO (Highest Occupied Molecular Orbital), LUMO (Lowest Unoccupied Molecular Orbital), HOMO-1, LUMO+1 and LUMO+2 are participated in the current transportation. In Fig. 3 a(c) shows diode1&3 transmission spectrum, at energy 0 eV transmission coefficient  $T(E)$  value obtained 0.17(0.37) and by varying energy  $E$  both positive and negative sides transmissi



**Fig.1** – Schematic of Benzene with Donor ( $\text{CH}_3$ ) & Acceptor ( $\text{CN}$ ) connected to two Au contacts (a) Diode 1, Donor & Acceptor separated by 1  $\pi$  bond, (b) Diode 2, Donor & Acceptor separated by 2  $\pi$  bonds, (c) Diode 3, Donor & Acceptor separated by 3  $\pi$  bonds, (d) Diode 4, Donor & Acceptor separated by 4  $\pi$  bonds

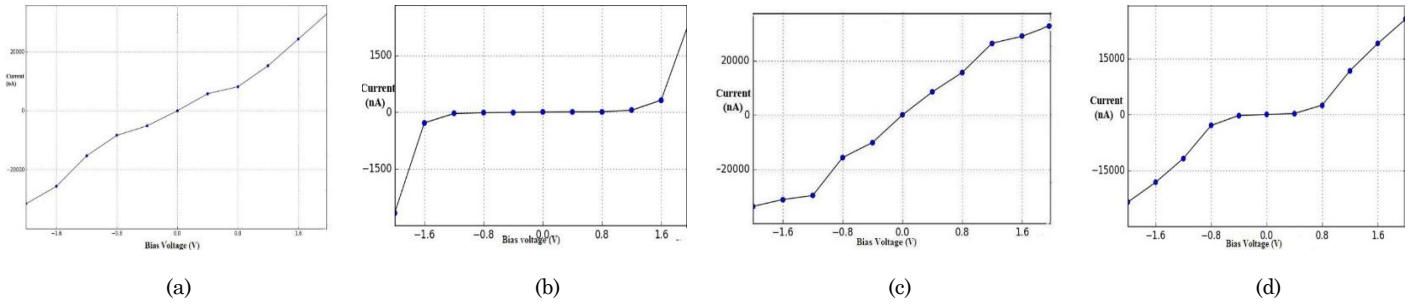
**Table 2** – Chemical potential ( $\mu_L, \mu_R$ ) calculated values on left and right electrodes with and without bias, observed that neutral condition both side electrodes maintain same chemical potential, under bias chemical potential increases in negative voltage electrode

| Name of the Diode | Bias Voltage = 0 V                     |   | Bias Voltage = - 2 V to 2 V            |   |
|-------------------|--|---|--|---|
|                   | Left electrode Chemical potential (eV) | Right electrode chemical potential (eV) | Left electrode Chemical potential (eV) | Right electrode chemical potential (eV) |
| Diode 1           | - 9.23                                 | - 9.23                                  | - 11.23                                | - 7.23                                  |
| Diode 2           | - 9.00                                 | - 9.00                                  | - 11.00                                | - 7.00                                  |
| Diode 3           | - 9.37                                 | - 9.37                                  | - 11.37                                | - 7.37                                  |
| Diode 4           | - 9.08                                 | - 9.08                                  | - 11.08                                | - 7.08                                  |

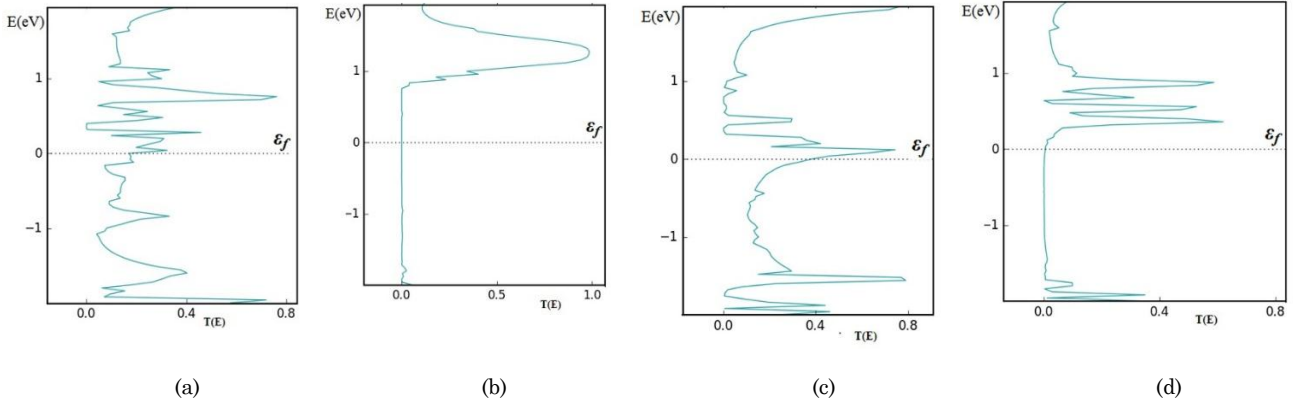
coefficients also varied, at energy for diode 1(3), 0.76 eV (0.12 eV) maximum first transmission coefficient 0.761(0.74) occurred in above Fermi level where as below Fermi level energy point -1.96 eV (-1.52 eV) transmission coefficients 0.71(0.77) obtained. Remaining proposed diodes 2(4) energy value 0 eV stage transmission coefficients also 0, and interesting observation is only positive energy time only transmission occurs whereas negative energy applied to diode structures no transmission says that diode 2(4) acts like a conventional semiconductor diode. It is notable that HOMO energy closer to the Fermi energy during positive bias and far away from Fermi energy in the negative bias applied [8, 9].

Beautiful phenomenon is the odd number of  $\pi$  bonds connects molecules simply act like a conducting wire even number of  $\pi$  bond connected molecules acts like diode, this one also observed in transmission spectrum of the diode 1,2,3 & 4 shown in Figure 4 (a, b, c, d). From the transmission spectra diode 1 & 3 -2v to 2v range current draws through the structure, diode 2 & 4 above 1.6v & 0.8v voltage only current draws.

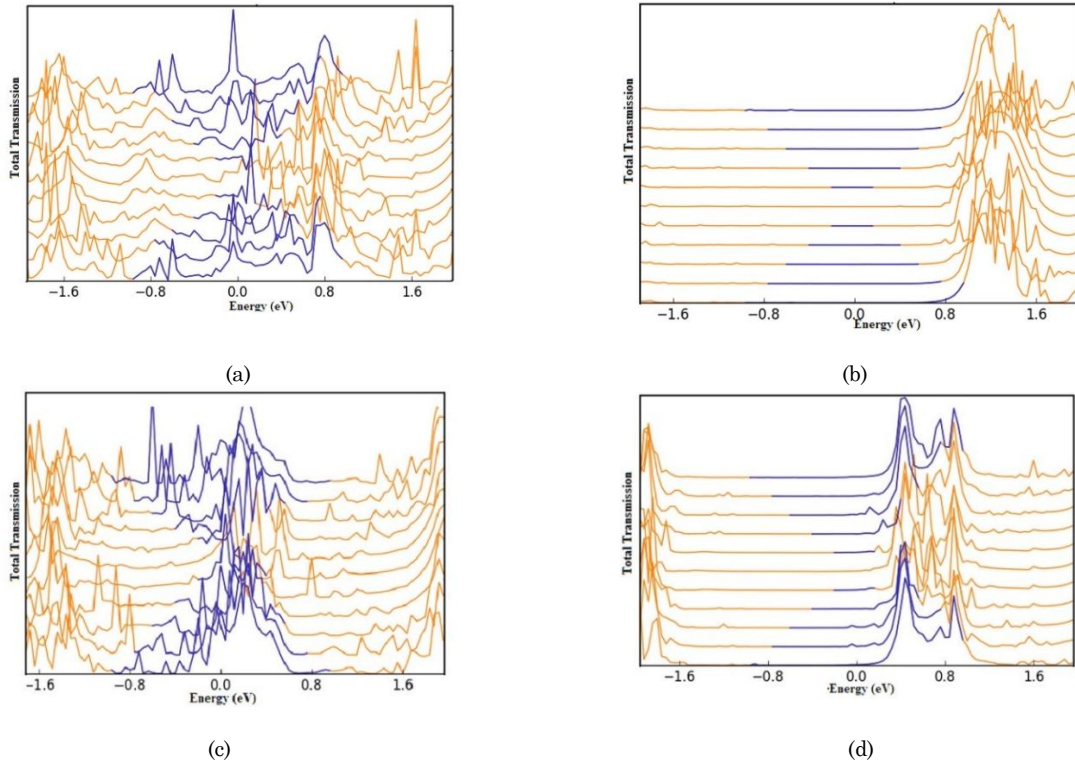
The self consistently calculated V-I characteristics of molecular diode with  $\text{CH}_3$  and  $\text{CN}$  donor and acceptor molecules shown in Fig. 2. We are applied -2.0v to 2.0v of voltage in steps 11 points observed for the diode 1, diode 2, diode 3 and diode 4. From the Fig. 2 (a) and Fig. 2(b) shows in the forward bias current linearly



**Fig. 2** – V-I Characteristics of (a) Diode 1, (b) Diode 2 , (c) Diode 3, (d) Diode 4



**Fig. 3** – Energy vs. Transport analysis of (a) Diode 1, (b) Diode 2, (c) Diode 3, (d) Diode 4 indicated with respect to fermi level.



**Fig. 4** – Comparison of Transport spectrum of (a) Diode 1, (b) Diode 2 , (c) Diode 3, (d) Diode 4

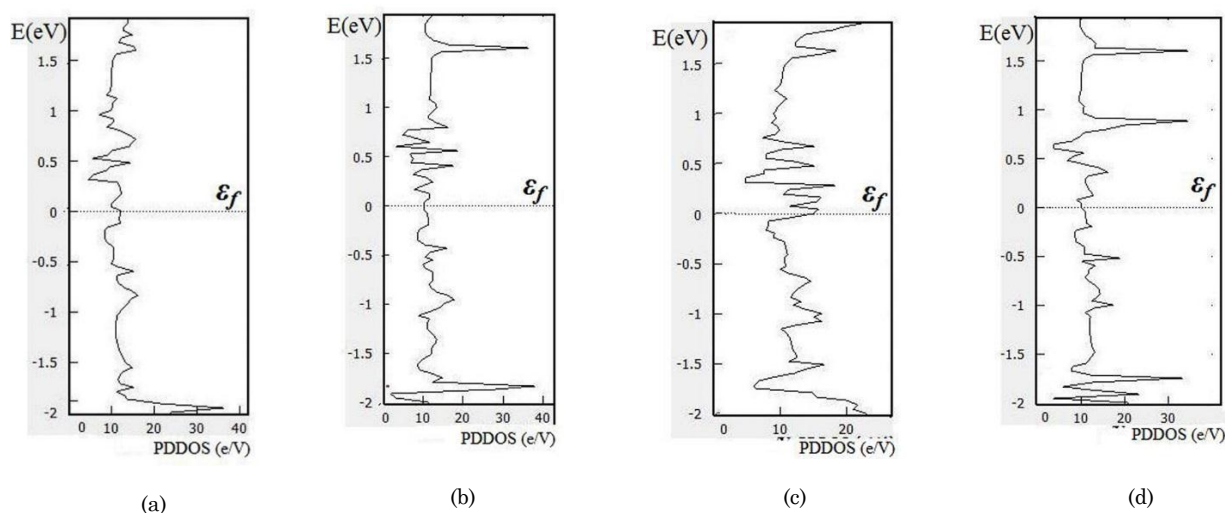


Fig. 5 – Charge Transfer and Self-Consistent band lineup coupling to gold contacts with changing  $\pi$  bonds

changing with respect to voltage and in the reverse bias also current linearly changing with respect to voltage. In these two diodes acceptor and donor molecules connected with odd number of covalent bonds and conclude that this structure act as a molecular wire. Whereas observe the figure 2 (b), diode 2, V-I characteristics 0v to 1.4v voltage, current passing through the diode zero later onwards current increases with increase in the voltage same diode in the reverse bias -2.0v to 0v applied insteps 5 points current linearly changes after -1.4v. In another diode 4, structure apply voltage range between -2.0v to 2.0v observed current starts at the 0.6v and observed current value is 266 nano amperes, at maximum 2.0v voltage current passing through diode is 25.5 micro amperes observed. These conclusions donor ( $\text{CH}_3$ ) and acceptor ( $\text{CN}$ ) molecules connected with odd number of chemical bonds, then that structure act as a conducting wire if donor and acceptor connected with even number of bonds it act as a molecular diode with increase in the number of bonds cut in voltage decreases.

#### 4. CONCLUSIONS

In this paper, we performed even or odd number of  $\pi$  orbital effect in the current transportation in the molecular diodes observed. The theoretical study and practical observations are relatively same observed,

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