

## Rectifying and Negative Differential Resistance Behaviours Induced by Intermolecular Interaction in Molecular Device†

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By applying extended Huckel theory in combination with non equilibrium Greens function formalism, we investigate the transport properties of the molecular device with a donor-acceptor molecular complex sandwiched between two electrodes. In the benzene ring, OCH<sub>3</sub> and CN group have been substituted and used spacers such as CH<sub>2</sub>CH<sub>2</sub> between the donor and acceptor subunits to form an intramolecular donor spacer acceptor (D-S-A) rectifier. The molecule is attached to two gold leads (111). Calculated current-voltage curves show the pronounced rectification behaviour which is due to the asymmetric shift of the perturbed molecular energy levels under bias voltage. A molecule consisting of three aromatic phenyl rings in series exhibits the negative differential behaviour. The two hydrogen atoms of the middle ring are substituted by acceptor group NO<sub>2</sub> and donor group NH<sub>2</sub>, while the whole molecule is chemisorbed onto the contact surfaces of gold leads. Simulated results show that a negative differential resistance under applied bias is observed which is induced by the orbital match of molecule and electrodes as well as intermolecular charge transfer.

**Key Words:** Electron transport properties, Tunnel barrier, Molecular rectifier, Metallic electrodes.

### INTRODUCTION

The most effective way to make faster circuits is by scaling down *i.e.*, reducing the device size proportionally. The present day microelectronic techniques are limited by the incremental performance improvement offered by device scaling. To achieve an order of magnitude improvement in circuit performance, it is necessary to develop technologies that are not solely dependent on device scaling for performance enhancement.

Molecular electronics is envisioned as a promising candidate for the device miniaturization for the future. A complete theoretical study of electron transport in metal-molecule-metal interfaces is necessary in the development of molecular electronics. The molecule which consists of appropriate donor and acceptor, if placed between suitable electrode contacts, forms a rectifier structure. That is, electron flow through the structure should be strongly preferred only in one direction.

The resonant tunneling diode (RTD) has been widely studied because of its importance in the field of nanoelectronics and its potential applications in very high speed/functionality

devices<sup>1,2</sup> and circuits. The negative differential resistance<sup>3-5</sup> characteristic is observed in these devices, achieved due to resonant tunneling, is also ideally suited for the design of highly compact, self-latching logic circuits<sup>6</sup>.

In this study, we apply Extended Huckel Theory (EHT), a semi empirical approach coupled with the non-equilibrium Green's function (NEGF) formalism to investigate the working of our molecules as a rectifier and exhibiting NDR property.

#### Formalism and computational scheme

Aviram and Ratner<sup>7</sup> have suggested that electron donating constituents make conjugated molecular groups having a large electron density (N-type) and electron withdrawing constituents make conjugated molecular groups poor in electron density (P-type). According to them, a non-centrosymmetric molecule having appropriate donor and acceptor moieties linked with an s-bridge and connected with suitable electrodes will conduct current only in one direction-acting as a rectifier. They showed that in this molecule, the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) can be aligned in such a way that electronic conduction is possible only in one direction making it function like a molecular diode.

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Based on the above model we propose the diode structure consisting of two identical sections (S1, S2) separated by an insulating group R. Section S1 is doped by OCH<sub>3</sub> donating group (X) and section S2 is doped by CN electron withdrawing group (Y). The insulating group CH<sub>2</sub>CH<sub>2</sub> (R) is incorporated into the molecular wire, which acts like a spacer and provides a potential barrier for the electron transport from one end to another.

The single molecule ends are connected to the contact electrodes *e.g.*, gold. For current to flow electrons must overcome the potential barrier from electron acceptor doped section (S2) to electron donor doped section (S1) and this forms the basis for the formation of the mono-molecular rectifying diode.

The negative differential resistance is observed in ethynyl phenyl based organic molecules at room temperatures. We have used a molecule consisting of three aromatic phenyl rings in series. The two hydrogen atoms of the middle ring are substituted by acceptor group NO<sub>2</sub> and donor group NH<sub>2</sub>, while the whole molecule is chemisorbed onto the contact surfaces of gold leads.

An electron incident from the source with energy *E* has a probability *T* (*E*) of being transmitted through the molecule to the drain. By calculating this transmission probability for a range of energies around the Fermi function *E<sub>F</sub>* of the lead, current is calculated using the Landauer formula<sup>8</sup>.

$$I = \frac{2q}{h} \int_{-\infty}^{\infty} [\text{Tr}(\Gamma_1 G \Gamma_2 G^\dagger)] (f_1(E) - f_2(E)) dE \quad (1)$$

$$T(E) = \text{Tr}(\Gamma_1 G \Gamma_2 G^\dagger) \quad (2)$$

The self consistent potential is given by

$$U_{sc} = U(N - N_0) \quad (3)$$

where the number of electrons at equilibrium is approximated by  $N_0 = 2f_0(E_F)$  is the charging energy. Real nanoscale devices typically have multiple levels that often broaden and overlap. It is useful to rewrite the equations for the number of electrons *N* and the current *I* for a one-level model in terms of the Green's function<sup>9,10</sup> *G*(*E*) which is defined as follows:

$$G(E) = (ES - H - \Sigma_1 - \Sigma_2)^{-1} \quad (4)$$

The self energy functions  $\Sigma_{1,2}$  are used to describe the effect of contacts on the device.

The device is described by a Hamiltonian matrix *H* and overlap matrix *S*. Where *S* is the identity matrix of the same size as the other matrices and the broadening matrices  $\Gamma_{1,2}$  are defined as the imaginary (more correctly as the anti-Hermitian) parts of  $\Sigma_{1,2}$ :

$$\Gamma_{1,2} = i(\Sigma_{1,2} - \Sigma_{1,2}^\dagger) \quad (5)$$

## RESULTS AND DISCUSSION

Our calculations are based on the Huckel-IV<sup>11</sup> codes and it is assumed that the molecule under investigation forms symmetric contact with two semi-infinite gold<111> electrodes. The adsorption geometry is such that the molecule sits on-top of the triangular gold pad with an end nitrogen-gold surface distance of 1.9 Å. The geometry of the isolated molecule has been optimized using *ab initio*<sup>12</sup> DFT method (method:

B3PW91 and basis: 6-31G\*) as implemented in Gaussian 03 package.

Fig. 1 shows the calculated I-V and G-V characteristic curves, which show that the device acts as an effective molecular diode which acts as a rectifier.

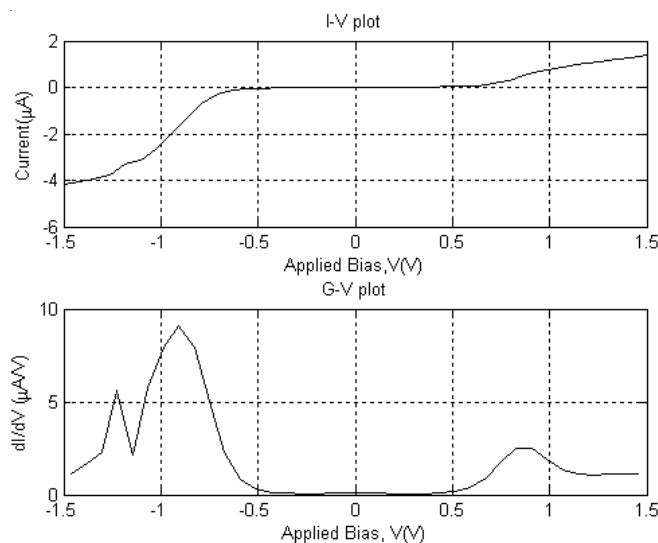


Fig. 1. Current-voltage (I-V) and conductance-voltage (G-V) characteristics of molecular rectifier

The molecular rectifier allows the electric current to pass through it when reverse bias is applied. During the forward bias it obstructs the electric current and it is mostly small. The molecule proposed here works as explained below.

The electron donating group X tends to place more electron density on the phenyl ring, which increases the mutual electronic repulsion on the ring. This pushes up the energy levels of the molecular orbitals on the donor side of the rectifier molecule. The acceptor side of the molecule works the opposite way: the electron withdrawing group Y tends to reduce the electron density on the ring, leading to reduced electronic repulsion on the acceptor side of the molecule, which in turn causes the energy levels on this side to be lowered. This causes an energy difference,  $\Delta E\text{-LUMO}$ , between the lowest unoccupied molecular orbital (LUMO) localized on the donor side and the LUMO localized on the acceptor side.

$$\Delta E\text{-LUMO} = E\text{-LUMO}(\text{donor}) - E\text{-LUMO}(\text{acceptor}) \quad (6)$$

The aliphatic spacer group ensures that the electron density on either side of the rectifier molecule does not equilibrate by establishing a tunnel barrier. There are also barriers on either side of the molecule at the contacts, which serve to maintain a degree of electrical isolation, while still allowing current flow under bias.

Fig. 2 shows the calculated transmission and density of states for various energies being plotted. It is seen that the density of states is asymmetric on forward and reverse bias region. In the bias region where the density of states is more and hence is transmission the conductance is high.

A resonant-tunneling diode is made by placing two insulating barriers in a molecule, creating between them an island or potential well where electrons can reside. Whenever electrons are confined between two such closely spaced barriers,

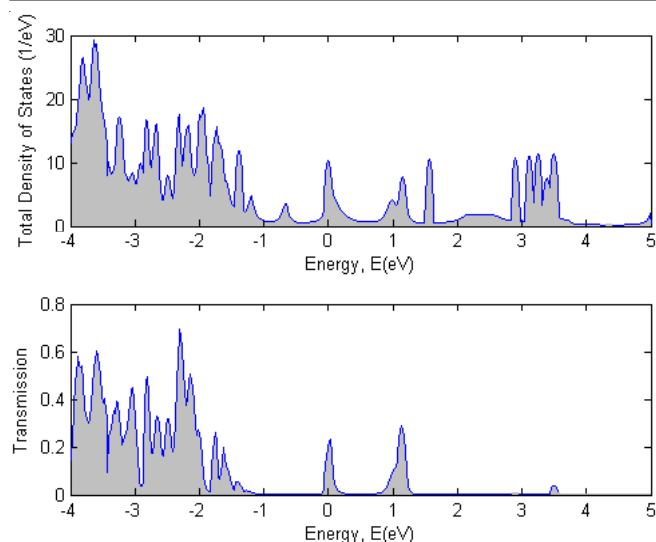


Fig. 2. Total density of states and transmission with respect to energy of molecular rectifier

quantum mechanics restricts their energies to one of a finite number of discrete 'quantized' levels. This energy quantization is the basis for the operation of the resonant-tunneling diode. The only way for electrons to pass through the device is to 'tunnel', quantum mechanically, through the two barriers. The probability that the electrons can tunnel is dependent on the energy of the incoming electrons compared to the energy levels on the island of the device. If the energy of the incoming electrons differs from the energy levels allowed inside the potential well on the island, then current does not flow.

However, when the energy of the incoming electrons aligns with that of one of the internal energy levels, the energy of the electrons outside the well said to be "in resonance" with the allowed energy inside the well. Then, maximum current flows through the device at this resonant voltage or peak voltage ( $V_p$ ) called the peak current ( $I_p$ ). As the voltage increases further the current through the device drops due to reduction in tunneling until the voltage reaches the valley voltage ( $V_v$ ).

The calculated I-V and G-V characteristics are shown in Fig. 3. The graph shows the negative differential resistance property with the maximum current and conductance at the peak voltage ( $V_p$ ) and minimum current and conductance at the valley voltage ( $V_v$ ).

The effectiveness of the operation of a particular RTD often is characterized by how well defined are the peak and valley in the current versus voltage plot. This is measured by the peak-to-valley current ratio. In Fig. 3, the measured peak-to-valley ratio is approximately 12:2.

## Conclusion

The molecular rectifier consists of a donor-spacer-acceptor combination. Current rectification is due to the presence

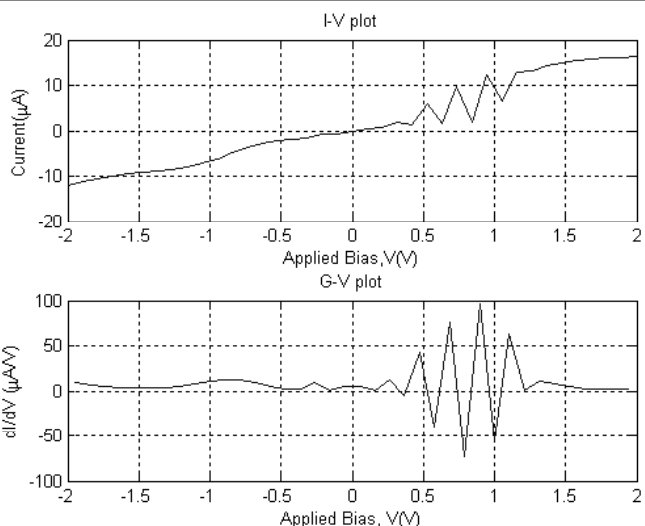


Fig. 3. Current-voltage (I-V) and conductance-voltage (G-V) characteristics showing negative differential resistance in a resonant tunneling diode

of chemical substituent groups and their influence. The I-V characteristics curve shows the current of 1.8  $\mu\text{A}$  in forward bias and 4.1  $\mu\text{A}$  in reverse bias of 1.5 V. So the diode conducts with the rectification ratio of 2.3.

A resonant-tunneling diode is made by placing two insulating barriers in a molecule, creating between them an island or potential well where electrons can reside. Maximum current flows through the device at peak voltage, when the energy of the incoming electrons aligns with that of one of the internal energy levels and as the voltage increases further the current through the device drops due to reduction in tunneling until the voltage reaches the valley voltage.

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