

Transport Model of Controlled Molecular Rectifier Showing Unusual Negative Differential Resistance Effect

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We investigate theoretically the charge accumulated Q in a three-terminal molecular device in the presence of an external electric field. Our approach is based on *ab initio* Hartree-Fock and density functional theory methodology contained in Gaussian package. Our main finding is a negative differential resistance (NDR) in the charge Q as a function of an external electric field. To explain this NDR effect we apply a phenomenological capacitive model based on a quite general system composed of many localized levels (that can be LUMOs of a molecule) coupled to source and drain. The capacitance accounts for charging effects that can result in Coulomb blockade (CB) in the transport. We show that this CB effect gives rise to a NDR for a suitable set of phenomenological parameters, like tunneling rates and charging energies. The NDR profile obtained in both *ab initio* and phenomenological methodologies are in close agreement.

Keywords: Landauer Formula, Coupled Quantum Mechanics/Green Function, Negative Differential Resistance.

1. INTRODUCTION

The field of molecular electronics has received growing attention in the last years due to its potential technological application in the design of novel devices with lower cost and higher performance.¹ On the other hand, a molecular device represents a unique system to study fundamental aspects of physics, like Coulomb blockade,² Kondo effect³ spin-dependent phenomena⁴ and so on. The main advantage of molecular electronics compared to the semiconductor technology (e.g., quantum dots) is the low cost and relative easy manufacture of the compounds. However, its stability and reproducibility remains a challenge that only recently starts to be overcome.⁵

The standard geometry of single-molecule devices is composed of two metallic electrodes sandwiching a molecule. For this setup a wealth of theoretical studies have emerged in the literature, that address, for instance, to the problems of conformational effects on the transport,⁶ rectification and the influence on transport of connecting groups between the molecule and the electrodes.⁷ More recently, novel geometries consider three electrodes

instead of only two. This additional electrode makes the system similar to a standard transistor geometry, with source, drain and gate. An extensive review related to molecular electronic device (MED) was organized by Cuniberti et al., where it was discussed perspectives in nanodevices with more than two-terminals.⁸ Also, a few prominent reviews considered this system.^{9,10}

In particular, recent works launch perspectives for organic conjugated backbone structures used as 3-terminals device.^{11–14} Two of them, experimentally made by Lieber and co-workers,^{11,12} present a complex nanowire structure with bipolar transistor behavior and nano-logic gates. In this context, conducting polymer covered with cyclodextrin molecules have been investigated using quantum mechanical simulations.¹³ It was found that the polymer chain can be stabilized inside the molecular structure, thus supporting the realization of MEDs. In spite of all this theoretical and experimental effort to better understand and implement MEDs, there is still a lack of understanding on how the symbiosis between the organic molecule and the metallic contact affects the electron conduction, resulting, for instance, in negative differential resistance (NRD).^{15–20}

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Recently, Pati et al.²¹ and Fan et al.²² have proposed two competitive new mechanisms to describe NDR effect in molecular system. In the first one, the authors explain the NDR as a result of the overlap between frontier molecular orbitals (FMO). In the second, *ab initio* calculations for planar devices with single, double and triple bonds were performed resulting in NDR for the last two structures. They justify the NDR as an alignment between the surface lead states with energies close to the Fermi level and the LUMO's of the molecule.

Previous works^{19,20} applying first principle quantum mechanic calculations, revealed that an organic three-terminal device with *molecular source, drain and gate* behaves as a controlled molecular rectifier (CMR), with three devices (*TRIAC, SCR and Schottky diode*) in one integrated circuit, depending on operational conditions. Henceforth, it could be used as bi-directional rectifier. Underlying the enormous functionality of this system, we find a sp^2 and sp^3 hybridization with large dihedral angle (no planar structure).

One final remark regarding the system discussed in Refs. [19, 20] is the strong capacitance response, which shows an enhancement for values lower and greater than a specific bias window. This turns into a powerful *on/off* current switcher with no depletion capacitance under reverse bias. Following this capacitance result, here we propose an alternative explanation for NDR effect based on a simple resistor-capacitor association that mimics the charging (Coulomb) effects of the molecule in the presence of bias voltages. A pictogram of the molecular system studied is illustrated in Figure 1. It is composed of three branches with conjugated rings attached with saturated Carbons. The main finding is a NDR like structure in the charge accumulated in the molecule as a function of a bias voltage applied between gate and T1 terminals. When a bias voltage is applied between T1 and T2 no NDR is found.

Interestingly, the NDR obtained can be regained in a general and standard nonequilibrium system, composed of many localized levels (e.g., LUMOs of a molecule) coupled to a source and a drain of electrons. To this aim, though, we need to take into account charging effects in a self-consistent way. Combining nonequilibrium Green function with a phenomenological capacitive model, we obtain a NDR which fits quite well the *ab initio* result for the charge accumulated Q . We believe that this alternative mechanism of NDR in terms of Coulomb effects allows to bridge the evident gap in the literature regarding NDR in molecules, thus being relevant for the emerging field of molecular electronics.

This work was divided as follows. In Section 2 we discuss the equilibrium and nonequilibrium methodologies. In Section 3 we present and discuss the numerical results, and in Section 4 we make the final remarks.

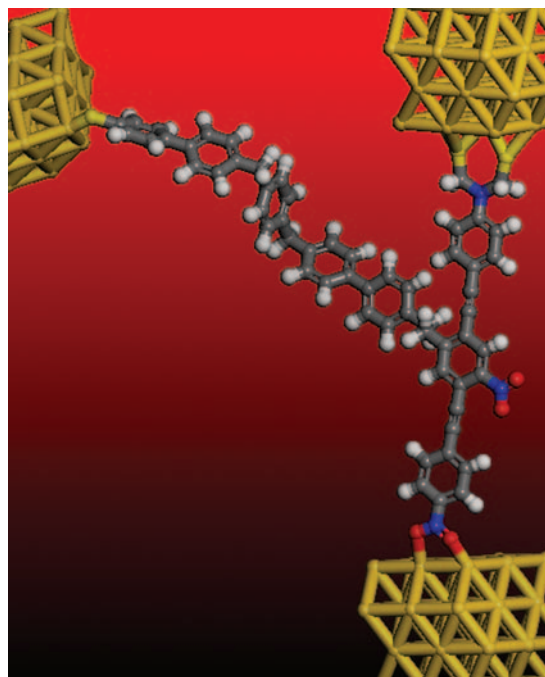


Fig. 1. Pictogram of the controlled molecular rectifier utilized in this work. The diagonal-left terminal is the gate terminal (T_{Gate}). *Top* and *Bottom* terminal are T_1 and T_2 terminals, respectively. Note that the structure is composed by heterogeneous electrons-type, i.e., conjugated rings attached with saturated carbons in the gate molecule (sp^3 and sp^2 electrons participating of conduction process) and conjugated rings attached with triple bonds carbons (sp bond) in the main molecule.

2. METHODOLOGY AND INVESTIGATED SYSTEM

2.1. Equilibrium Calculation

The equilibrium methodology is the same previous utilized based on *ab initio* Hartree-Fock and density functional theory methodology contained in Gaussian package²³ and geometric parameters of the analyzed structures were fully optimized including external electrical field in a closed shell model.^{19, 20, 24, 25}

2.2. Nonequilibrium Calculation

We define the current leaving the donor or the acceptor lead as $I_\eta = -e\langle \dot{N}_\eta \rangle$, where e is the electron charge ($e > 0$), $\langle \dots \rangle$ is a thermodynamic average and $N_\eta = \sum_k c_{k\eta}^\dagger c_{k\eta}$ is the total number operator for electrons in lead η [donor (D) or acceptor (A)]. The label k gives a set of quantum numbers for the electrons in the leads, like spin and wavevectors. To calculate the time derivative of the total number operator we use the Heisenberg equation of motion, $\dot{N}_\eta = (i/\hbar)[H, N_\eta]$, where H is the total Hamiltonian of the system, which is a sum of four terms,

$$H = H_D + H_A + H_M + H_T$$

The first and second terms describe the donor and acceptor parts of the system. These terms can be written as

$$H_{\eta} = \sum_k E_{k\eta} c_{k\eta}^{\dagger} c_{k\eta}$$

where $E_{k\eta}$ is the free-electron energy in lead η and $c_{k\eta}(c_{k\eta}^{\dagger})$ is the annihilation (creation) operator. The third term corresponds to the central molecular system, which in a simple model is given by

$$H_M = \sum_n E_n d_n^{\dagger} d_n$$

with E_n being the molecular levels and $d_n(d_n^{\dagger})$ the annihilation (creation) operator for electrons in the molecule. The last term accounts for tunneling of electrons from the donor or acceptor into the molecular orbitals. It is given by

$$H_T = \sum_{k\eta} [t c_{k\eta}^{\dagger} d_n + t d_n^{\dagger} c_{k\eta}]$$

with t being the coupling strength. Using the Hamiltonian inside the Heisenberg equation we find to the current the following result

$$I_{D/A} = \frac{2e}{h} \int dE T(E) [f_{D/A}(E) - f_{A/D}(E)]$$

where $T(E)$ is the transmission coefficient of the system and

$$f_{D/A}(E) = \frac{1}{1 + \exp[(E - \mu_{D/A})/k_B T]}$$

the Fermi distribution function, where $\mu_{D/A}$ is the donor/acceptor chemical potential, k_B the Boltzmann constant and T the reservoir temperature.

It is possible to show that $T(E)$ can be written as

$$T(E) = \sum_i \frac{\Gamma_i^D(E)\Gamma_i^A(E)}{\Gamma_i^D(E) + \Gamma_i^A(E)} A_i(E)$$

where $\Gamma_i^{D/A}(E)$ gives the tunneling rate between donor (D) or acceptor (A) and the molecule and $A_i(E)$ is the molecular spectral function. In what follows we assume that $\Gamma_i^{D/A}(E)$ is energy independent (wideband limit) and $A_i(E)$ is given by

$$A_i(E) = \frac{\Gamma_i^D + \Gamma_i^A}{(E - E_i)^2 + ((\Gamma_i^D + \Gamma_i^A)/2)^2}$$

The quantities Γ_i^D , Γ_i^A , and E_i will be taken as phenomenological parameters.

One additional ingredient in our formulation is the self-consistent calculation of the shifts of the levels E_i under external bias voltage (or equivalently electric field). For that we apply a capacitive model that accounts for charging effects on the molecule. This corresponds to a sort of mean-field treatment of the electron–electron repulsion inside the molecule. This repulsion is responsible to some

extent to a NDR observed in the present system. Figure 2 shows the equivalent circuit of a double-barrier tunneling device. The left and right capacitor–resistor associations correspond to the left and right barriers, respectively, with a molecule in between them. The capacitors account for charging effects in the system. To the charge in the molecule we write

$$Q_M = Q_D - Q_A$$

which gives

$$Q_M = C_D(V_M - V_D) - C_A(V_A - V_M)$$

where C_D and C_A are the donor and acceptor capacitances, V_M is the voltage drop in the molecule region, and V_D and V_A are the external voltages in the donor and the acceptor, respectively. While V_D and V_A are known external parameters, V_M is calculated self-consistently, using the following equation

$$V_M = \frac{Q_M + C_D V_D + C_A V_A}{C_D + C_A}$$

From V_M we determine the shifts of the levels E_i according to

$$E_i = E_i^0 + V_M$$

where E_i^0 is the position of the i -esimo level without bias voltage. To determine the charge accumulated in the molecule due to the electron transport we use the integral,

$$Q_M = e \int \frac{dE}{2\pi} \bar{f}_i(E) A_i(E) - Q_M^0$$

with Q_M^0 being the equilibrium molecular charge and

$$\bar{f}_i(E) = \frac{f_D(E)\Gamma_i^D + f_A(E)\Gamma_i^A}{\Gamma_i^D + \Gamma_i^A}$$

a generalized Fermi distribution function. It is valid to note that to determine Q_M we need the knowledge of $A_i(E)$, which itself depends on Q_M via the position of the level E_i . So a self-consistent procedure is performed till a converged spectral function and charge are found. In what follows we present the results of the present formulation, comparing to those found via *ab initio* calculation.

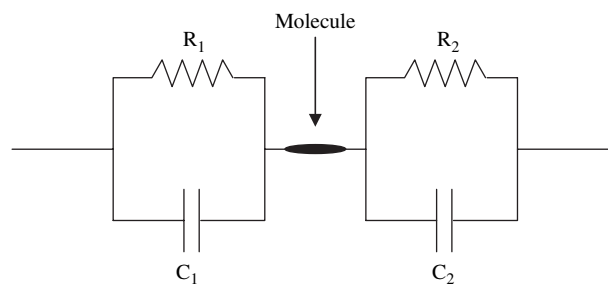


Fig. 2. Capacitive model describing the double barrier structure with a molecule in between. The capacitors account for charge accumulation and depletion around the barriers. The molecule represented here could be $T_{\text{GATE}}-T_2$ or T_1-T_2 . It depends which two terminals are in on state. The differences in the electrical behaviors are weight by R_1 , R_2 , C_1 and C_2 to reproduce the *ab initio* findings.

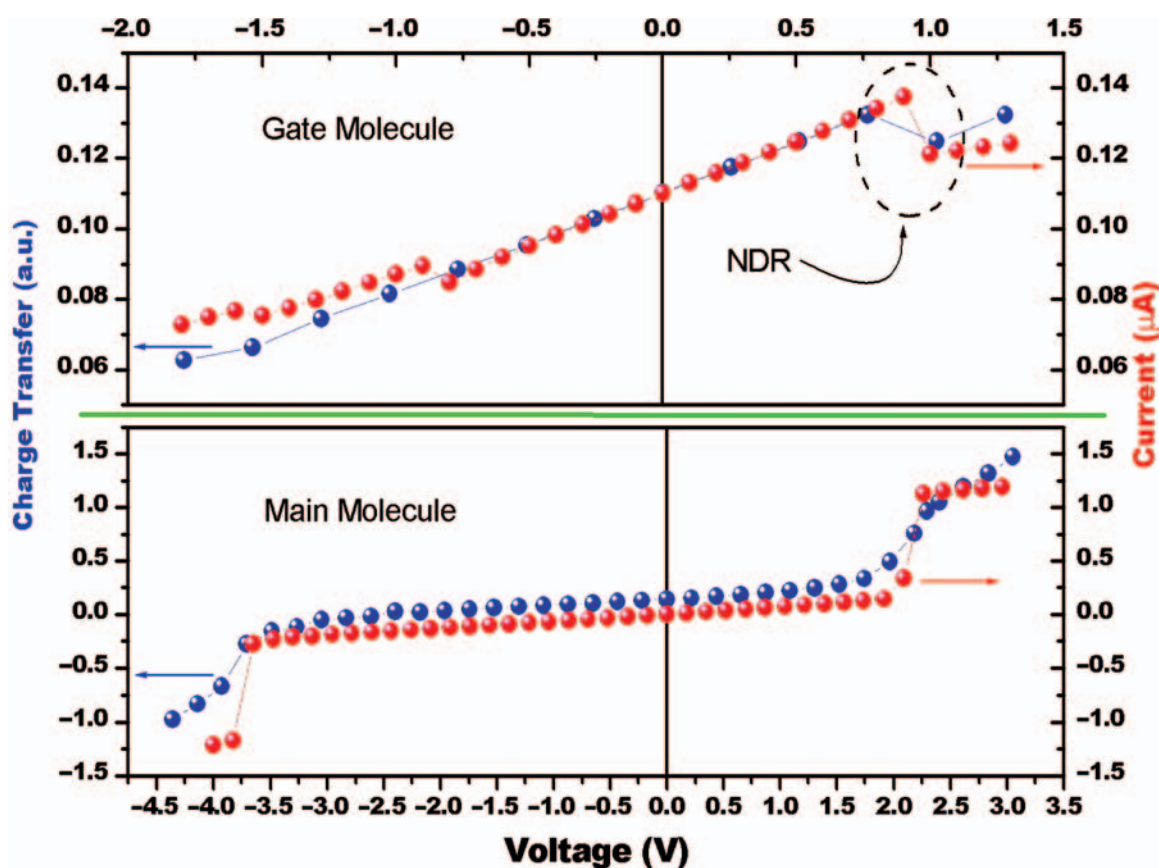


Fig. 3. Charge accumulated (dark gray or blue line) versus bias voltage for the system illustrated in Figure 1. For comparison we plot the current (light gray or red line) for a resonant tunnel junction within (top) a capacitive model and (bottom) asymmetric tunneling barriers. (top) Around $V = 1$ volt we observe a negative differential resistance (NDR) effect. This NDR in the $I-V$ curve is related to the Coulomb blockade in the molecule, which suppresses the current for some particular bias voltage range and (bottom) an asymmetric rectification behavior between the T_1 - T_2 terminals.

3. RESULTS AND DISCUSSION

Figure 3 (top [bottom]) shows the charge accumulated-voltage as well as the current-voltage for the $T_{\text{GATE}}-T_2$ [T_1-T_2] molecular structure. In order to better understand the equilibrium *ab initio* results, we apply the transport nonequilibrium calculation derived in the previous section. The adjustable parameters C_D , C_A , Γ_i^D , Γ_i^A , and E_i^0 are set to better fit the *ab initio* results. For positive bias voltages (Fig. 3 (top)) the current increases linearly with V until $V = 1$ volt, where it is rapidly suppressed and then it keeps increasing with V . This suppression of the current with increasing bias voltages characterizes the NDR effect.^{21,22} In our capacitive model this is clearly understood in terms of the charging energy of the molecule. Before $V = 1$ volt, all the molecular levels are above the emitter chemical potential, thus the molecule has its equilibrium charge Q_M^0 . When a bias voltage is applied, all the levels E_i are pushed down due to the external voltage value V_M around the molecule. For sufficiently high voltages, the first level E_1 attains resonance with the donor chemical potential, thus allowing electrons to resonantly tunnel into the molecule. As the electrons start to flow into the molecule, additional electrons trying to hop into

it experience a Coulomb repulsion to those that already lay in the molecule. This turns into a suppression (NDR) of the current till the bias voltage is high enough to provide additional energy to further electrons jump into the molecule.

Also (Fig. 3 (top)), for negative bias, a very fine NDR is observed around $V = -1$ volt. This is related to the inequality $\Gamma_1^D \gg \Gamma_1^A$ adopted in the simulation. Physically,

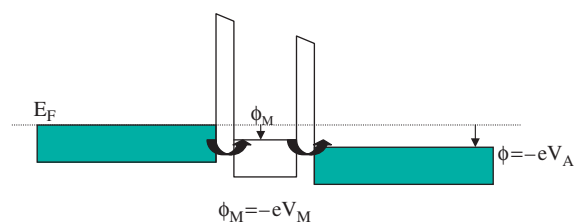


Fig. 4. Energy diagram of the system considered. When a bias voltage V_A is applied the Fermi level of the right side is shifted, giving rise to a nonequilibrium regime where a tunneling current flows. The shift ϕ_M of the molecular levels is calculated self-consistently taken into account charging effects via a capacitive model utilized to describe the electronic transport in the T_1 - T_2 terminals. Between the T_1 and T_2 are the localized levels representing asymmetric tunneling barriers provoking a bi-directional rectification.

$\Gamma_1^D \gg \Gamma_1^A$ means that the molecule is stronger coupled to the donor than to the acceptor group. For this particular inequality the electrons coming from the acceptor side ($V < 0$) tends to tunnel out the molecule (into the donor group) much faster than the corresponding $V > 0$ situation. This makes the Coulomb suppression of the current much less efficient for the reverse bias. Even though the present model recover the NDR observed in the *ab initio* results for $V > 0$, and provide a reasonable physical explanation for that, a full agreement between the phenomenological model and the full *ab initio* calculation is still desirable. It is indeed a formidable task to have a complete

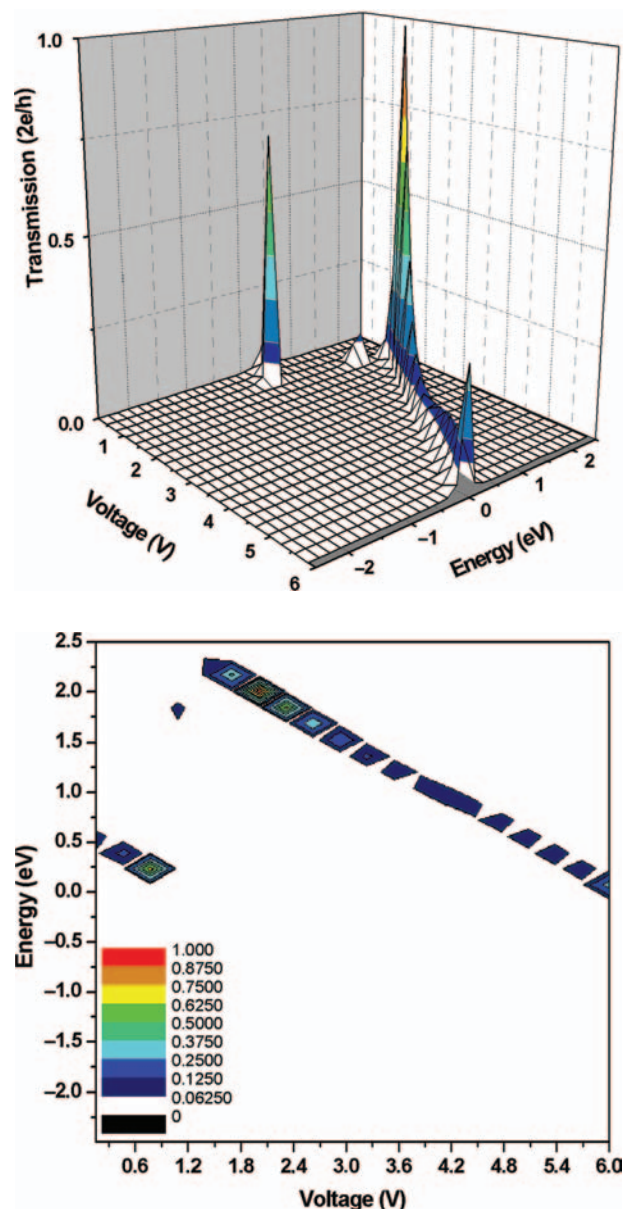


Fig. 5. (Top) 3D chart of transmission spectra $T(E, V)$ as a function of energy and bias voltage. (Bottom) bar code of $T(E, V)$ showing in perspective the NDR effect happens around 1.0V due the Coulomb repulsion.

agreement between these two approaches since the *ab initio* procedure accounts for many strongly correlated effects, not included in the transport model adopted here. However, the simple capacitive model can better guide the interpretation of the effects observed and provide physical insights.

In Figure 3 (bottom) no NDR effect is found and when T_1 - T_2 terminals is on under reverse and forward bias occurs electronic rectification presenting asymmetric bi-directional majority carrier flux.^{19,20} Also in Figure 4 is presented the energy diagram for the both considered systems.

For completeness, Figure 5 presents the transmission spectra as a function of energy and applied voltage ($T(E, V)$). There are two lines of main peaks. Their heights and locations are different from each other. The first peak above the average electrode Fermi energy when the system doesn't present NDR effect, and after the resonance. Also the shift in the bias direction is sensitive within NDR, clear rectification was observed for them.

4. CONCLUSION

We have showed a three-terminal molecular rectifier designed with sp^3 , sp^2 and sp hybridization type of electrons. For T_1 - T_2 applied voltage we found a asymmetric bi-directional rectification behavior. Interestingly, when is turned on the T_{GATE} - T_2 terminals presenting conduction channels with NDR effect. This can be explained with a capacitive model with double barrier. Note that a complementary paper²² shows different result when sp^3 hybridization participates of the conduction. Our unexpected behavior could be related with the no-planar structure and the overlap of σ and π orbitals. This possibility was not previously investigated and, of course, this new feature of charge transfer highly depends of molecular resonances and it is in agreement with previous review²⁶ and reference therein.

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