

A General Rule for Nanoelectronic Push–Pull Devices Based on Source- σ Bridge-Drain

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In this paper we show that, beyond the particular models, utilizing an hybrid equilibrium/nonequilibrium methodologies it is possible to create a general model for organics push–pull nano-scale devices within σ bonds in the backbone. It is shown by direct quantum-mechanic calculations under external electric field and a nonequilibrium calculation based on the ballistic Landauer-Büttiker equation that I – V curves are comparable to the equilibrium charge distribution results. These related models were successfully applied to the alkanethiol derivatives presenting a bi-directional rectification response with two operational regions and a very low commutation lost, thus revealing important applications for communication technologies. These results could provide novel insights to the emerging and fast growth field of molecular electronics.

Keywords: Landauer Formula, Push–Pull Device, Donor- σ Bridge-Acceptor, Coupled Quantum Mechanics/Green Function, Two-Terminal Device.

1. INTRODUCTION

Since the first work proposed by Aviram and Ratner¹ where a unitary molecular system with a donor (D) attached to an acceptor group (A) via a carbon bridge presenting a strong current rectification several works have been done. One example is the one of Marder and co-workers² where it was proposed a rule to increase the first hyperpolarizabilities for organic push–pull polyenes by taking into account the bond length conjugation.

In 1996, Martin and Sables³ made a comparison for donor-bridge-acceptor where the bridge could be composed by σ or π bonds type. The proposed explanation for conduction in σ bridges was interpreted in terms of a Poole conduction process between asymmetric Poole centres and non-centrosymmetric insulator. The process for π bridges was explained based on evidences that electrons are ‘pumped’ across the junction.⁴ The same molecular system with π bridge was investigated by Metzger et al.⁵ concluding that this particular system could be used as rectifier because it is governed by a competition between the *trans/cis* conformation and the zwitterionic forms.

Likewise, several theoretical works pointed out perspectives of molecular devices as logic gates,⁶ conformational rectifiers.⁷ Hliwa et al.⁶ designed logic gates as AND

and OR made by a single molecule raising two possible problems concerning more complex logic functions as XOR. A different work⁷ was done presenting rectification by changes in the molecule conformation (switch from *trans* to *cis* by applying external potential) and changing the conductivity. Also, phenomenological bipolar diode^{8,9} was addressed. In addition to this, experimental works pointed out perspectives concerning the stability,¹⁰ conductivity¹¹ push–pull devices as well as applications of three-terminal¹² and uni-directional¹³ transistors. In such works, it becomes clear the challenge to find out a general rule concerning the integration of nonlinear/linear transport phenomena obtained in nano and sub-nano scale.

In a previous work¹⁴ it was pointed out that a π -bridge system can operate as a molecular field effect transistor, and it was presented a new approach to investigate the electron charge flow in molecular structures. A complementary work by Wu et al.¹⁵ show that organic polar push–pull systems could be treated by hybrid time-dependent density functional theory. The results in their work suggest that zwitterionic state assumes full separation of charge carriers, thus activating possible optically forbidden states.

Recently, experimental results indicate that systems within σ bridges could lead to a rectification process up to a single electron regime.^{16–18} In the present work we propose an electronic transport rule for molecular devices composed by a push–pull system with Donor- σ

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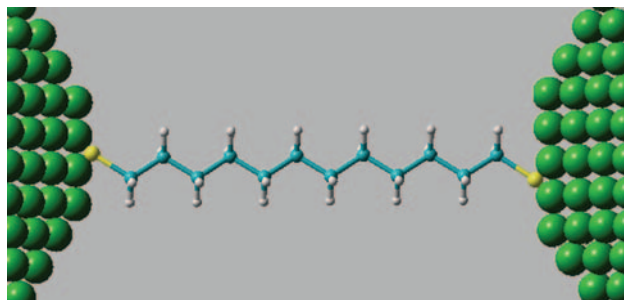


Fig. 1. Molecular structure investigated composed by a push–pull like system with saturated bonds in the bridge as Donor- σ Bridge-Acceptor.

Bridge-Acceptor [Fig. 1]. Using *ab initio* Hartree-Fock (HF) we determine the electron charge distribution along the structure as a function of an external voltage giving reliable information about the current versus voltage pattern of this device family. A general description based on the Landauer formula is also presented, that corroborates the *ab initio* calculations.

In the next two sections we present our methodology including our numerical results and conclusions, respectively.

2. METHODOLOGY AND RESULTS

We have applied the below methodology in the structures depicted in Figure 1 and we would like to stress that this is a general procedure for σ bridges structures, once it is always possible renormalize into a donor- σ bridge-acceptor chain.

HF approaches such as the ones contained in Gaussian package¹⁹ was employed. The standard 6-31G*, 6-31G**, and 6-311G*** basis sets were used for all calculations performing the same qualitative results. The geometries of the analyzed structures were fully optimized using Hartree-Fock methods including external electrical field in form of Roothaan-Hall matrix in a closed shell model:

$$FC = SCE \quad (1)$$

The Fock matrix F in the form of:

$$F_{\mu\nu} = \int dv \phi_{\mu} \left[-\frac{1}{2} \nabla_i^2 - \sum_{A=1}^M \frac{Z_A}{r_{iA}} \right] \phi_{\nu} + \sum_{\lambda=1}^K \sum_{\sigma=1}^K P_{\lambda\sigma} \left[(\mu\nu | \lambda\sigma) - \frac{1}{2} (\mu\lambda | \nu\sigma) \right] + V_{\mu\nu} \quad (2)$$

where in $F_{\mu\nu}$ the terms are core energy, Coulomb and exchange interaction energy, and influence of external fields energy, respectively. The $(\mu\nu | \lambda\sigma)$ and $(\mu\lambda | \nu\sigma)$ are 2 electrons integrals that may involve up to 4 different basis function as Φ_{μ} , Φ_{ν} , Φ_{λ} , Φ_{σ} .

Also, in Eq. (1), C , S and E are coefficient matrix in the linear combination of atomic orbitals, overlap integral matrix and orbital energy diagonal matrix, respectively.

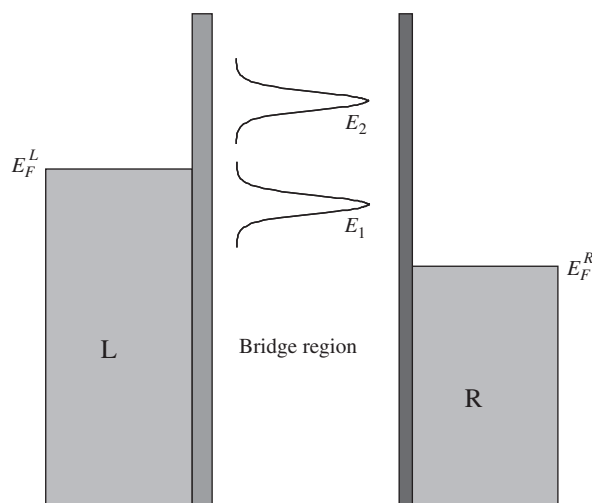


Fig. 2. Model adopted to describe the transport in the D- σ -A system. Localized levels are coupled to a source and a drain via asymmetric tunneling barriers. This coupling asymmetry generates a bi-directional step-rectification in the I - V curve.

To gain some more insight on the physical behavior of our system we propose a simple theoretical model that qualitatively reproduces the numerical findings. We consider a source and a drain of electrons coupled to each other via localized levels in between [Fig. 2]. In order to have a charge transport through the system a resonant condition is required, which means that at least one channel E_l should be below the left (E_F^L) or the right (E_F^R) Fermi energy. This condition can be achieved by applying an external bias voltage and/or a gate voltage. In general for increasing biases more levels attain resonance, thus enhancing the total current flowing in the system. The total current can be obtained from the Landauer formula (LF),²⁰ which is given by:

$$I = \frac{2e}{h} \int d\varepsilon [n_L(\varepsilon) - n_R(\varepsilon)] T(\varepsilon) \quad (3)$$

where e is the electron charge in modulus ($e > 0$), h is the Plank's constant, $n_{L/R}$ is the Fermi distribution function for the left (L) or the right (R) side of the molecular junction, and $T(\varepsilon)$ is the transmission coefficient through the sample. For a non-interacting system with many localized levels coupled to reservoirs we can show that the transmission coefficient is given by:

$$T(\varepsilon) = \sum_l \frac{\Gamma_0^L \Gamma_0^R}{(\varepsilon - E_l)^2 + \left(\frac{\Gamma_0^L + \Gamma_0^R}{2} \right)^2} \quad (4)$$

where $\Gamma_0^{L/R}$ is the electron tunneling rate between the left/right to the central region (the carbon bridge in the present case). The sum is taken over all the localized levels. One further assumption was made in the above transmission expression, i.e., the rates Γ_0^L and Γ_0^R are energy independent. To complete our description we need only to specify how the bias voltage drops along the system. The simplest assumption consists to take a drop as below

$$E_l = E_l^0 - xeV_{LR} \quad (5)$$

where E_l^0 is the level l without voltage, V_{LR} is the voltage between emitter and the collector and x gives some bias-drop asymmetry. In particular the parameter x is responsible for the rectification effects seen in some of the I - V curves.

To better fit the numerical results we take $\Gamma_0^L = \Gamma_0^R = 0.64$ meV. The values for E_l^0 and x can change depending on the number of carbon atoms in the bridge. In particular, we have applied our model to the alkanethiol families within 6, 8, 10, and 12 saturated carbons (so-called as Alk₆, Alk₈, and so on). For each family we optimize the values of E_l^0 and x . The option to apply for the alkanethiol derivatives rose up because of immense amount of experimental works (see, for example Refs. [18, 21–26]).

In Figures 3(a–d) we show the curves for the charge accumulation and for the current, obtained via *ab-initio* calculation (red lines + dots) and the Landauer formula (black lines). It is indeed curious how a simple theoretical *nonequilibrium* calculation for the current in a sort of a toy model can recover similar features of the full *ab initio* analyzes of the *equilibrium* charge accumulation. This suggests that the knowledge of an equilibrium quantity can provide some information about nonequilibrium

properties of the system. The parameters E_1^0 , E_2^0 and x are optimized for each alkanethiol families in order to better fit the *ab initio* data. In each panel we quote the values of E_l^0 and x adopted. In panel (a) we find only a qualitative agreement between both approaches. This is due to the strong asymmetries in the charge distribution that comes from the intricate *ab initio* calculation. In contrast, for larger bridges [Figs. 3(b–d)] we find a complete agreement between the two techniques up to a quantitative level.

Finally in Figure 4 we present in some more detail the resonance matches that give rise to the steps in the I - V curve. The meaning of resonance matches here is simple that $E_l = E_F^L$ or $E_l = E_F^R$, for positive or negative bias, respectively. In Figure 4(a) we just redraw the results seen in Figure 3(b). In Figure 4(b) we show the energies E_1 and E_2 (given by Eq. (5)) against bias voltage. The Fermi energies of the left and right side of the system are also presented. In particular, E_F^L is kept constant while E_F^R changes according to $E_F^R = E_F^L - eV$. For positive bias we observe that $E_1 = E_F^L$ and $E_2 = E_F^L$ around 1.2 V and 2.5 V, respectively. At these energies the charge accumulated and the current enhance as seen in Figure 4(a) (indicated by vertical arrows). The negative bias voltage counterpart shows similar behavior except by the matches that now take place between E_l and E_F^R .

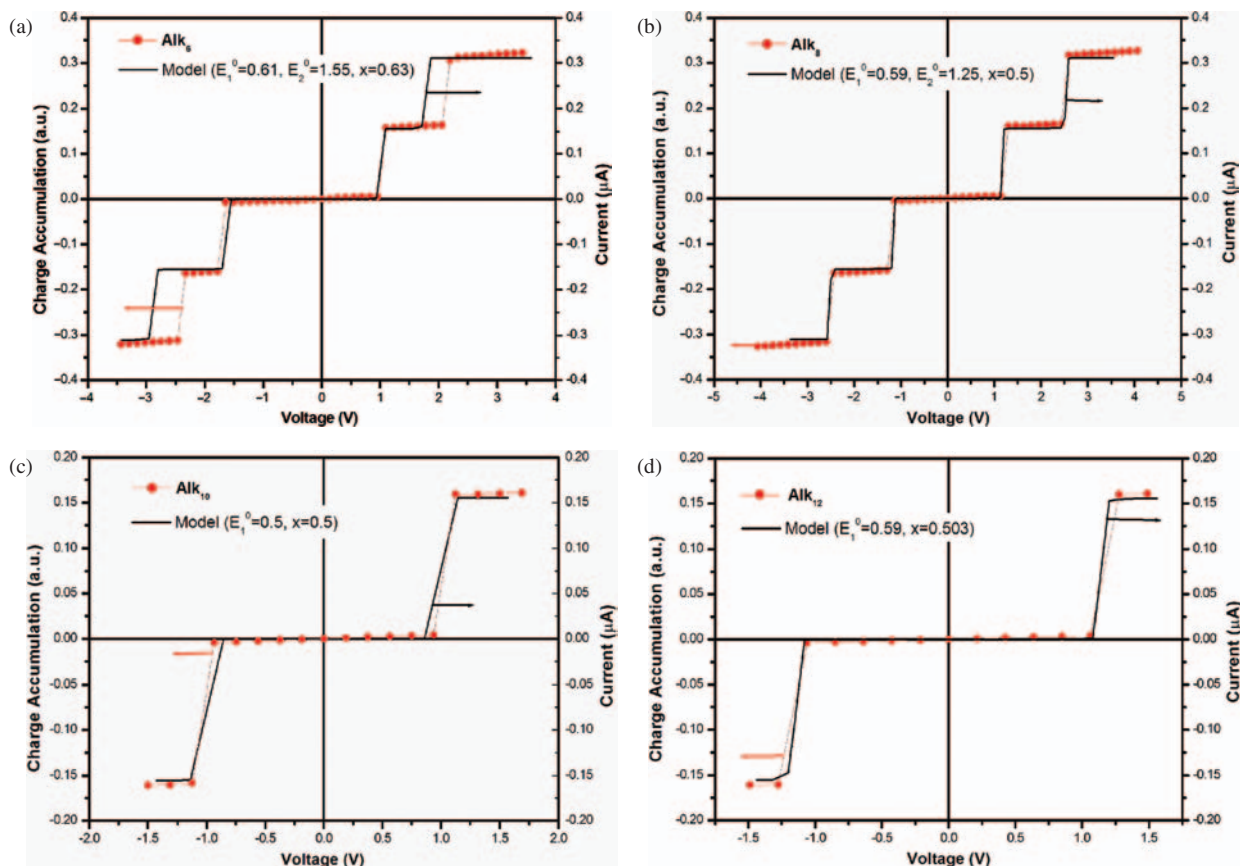


Fig. 3. Charge accumulated (Left axis) and current (right axis) as a function of the voltage for different saturated Carbons numbers in the alkanethiol derivative: (a) Alk₆, (b) Alk₈, (c) Alk₁₀, and (d) Alk₁₂. Both charge accumulated and current present resonant-tunneling behavior. The parameters E_1^0 , E_2^0 and x in the calculation of I are chosen in order to better fit the charge accumulation data.

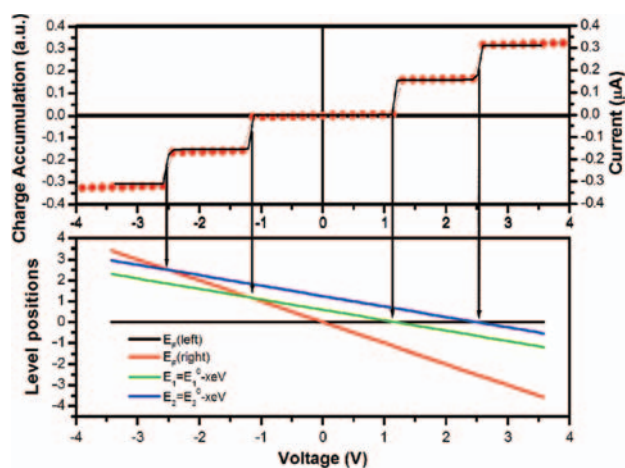


Fig. 4. (up) Charge accumulation, current and (down) level positions against external voltage. The results (up) present four resonances, around -2.52 V, -1.21 V, 1.20 V, and 2.51 V. These resonances (indicated by vertical arrows) take place when a state E_i of the bridge matches the left or the right Fermi energy E_F , depending on the sign of the voltage.

3. CONCLUSION

In this work were presented the electronic transport in a donor- σ spacer-acceptor in an alkanethiol derivative family. We simulate charge accumulation and depletion in the donor group as a function of an external voltage applied in the nanostructure backbone. By our results general rules were point out: (i) the rectification occurs for saturable bonds independent of the backbone size (beyond of previous *ab initio*²⁷ and semiempirical²⁸ prediction); (ii) the I - V and charge accumulation- V curves obtained by HF and LF calculations give us information about transport properties, presenting a simple picture in terms of a ballistic resonant model; (iii) Also, this system could be used as a bi-directional field effect transistor with two operation regions, in direct/reverse bias.

Overall, this paper is the second¹⁴ in push-pull devices, which indeed deserves further investigation. At this stage of the research it seems to be possible to separate molecular electronic devices in four general branches: (a) Donor_{bet}- π bridge-Acceptor_{bet},¹⁴ (b) Donor- σ bridge-Acceptor (presented here); (c) Donor_{bet}- σ bridge-Acceptor_{bet}, and (d) Donor- π bridge-Acceptor (Donor_{bet} and Acceptor_{bet} means donor and acceptor of betaine type, respectively). This speculation should be further studied and will be eventually reported elsewhere.

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Received: 27 July 2007. Accepted: 10 September 2007.