Molecular electronic device based on pH indicator by *ab initio* and non-equilibrium Green function methodology

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ABSTRACT

In the present work we simulate the transport properties and absorption spectra of the organic compound ethyl red. This is the first theoretical study of a specific pH indicator utilized as nano-device, based on first principle quantum mechanics calculations and a non-diffusive transport model. The charge distribution along the molecule is calculated via *ab initio* technique as a function of an external electric field. Based on a resonant multilevel model we also calculate the current against bias voltage. Both the charge accumulation and the current present similar behavior, like resonant type conduction and asymmetric charge–voltage and current–voltage curves. We also find an agreement between the theoretical absorption spectrum and experimental results for the zero-bias regime. Results for absorption spectra in several regimes under forward and reverse bias are analyzed. Our main results suggest that the present system could operate as a bi-directional molecular transistor.

1. Introduction

The use of molecular systems to control electronic transport between two independent terminals has been proposed showing that molecules with different attached groups should be carefully addressed due to the change in the molecular dipole moment provoking different pattern in the electrical characteristics [1].

Beside that, it has been investigated and proposed systems presenting ballistic molecular rectification for two-terminal nano-device with saturated and conjugated backbone [2–11]. In particular, for a complex helicoidal molecular structure it was found a nano-wire behavior due to the electronic coupling in a conjugated bridge [5]. Also, molecules with π bridges and octupolar termination groups have been synthesized and investigated with particular attention to the two-photon optical properties [6]. Henceforth, a *trans* to *cis* switching between different conformers [7], thin-film working as field-effect transistors [8], Schottky barrier diode of methyl red compound [9] and molecular π-bridge field-effect transistor [10,11] have been investigated.

Likewise, several experimental works pointed out perspectives presenting organic conjugated polymers used as device. For instance, LEDs [12], wire electrochemical transistor [13], diode [14] and solar cells [15]. But a technical problem with organic conjugated polymers is still open: There is a misalignment of the contact Fermi level with the molecular levels and symbiosis between them should be addressed [16].

In previous works [17–20] it was pointed out photonic applications of relatively small molecules coupled with sol–gel technique [17], where the non-linear effect of pH indicators was considered [18–20].

In the present work we propose specifically the electronic transport design for ethyl red molecular device [21] [Fig. 1]. Using *ab initio* Hartree–Fock derivative (HF) we simulate the electron charge distribution along the structure as a function of an external voltage. We compare this charge distribution to the current obtained via a phenomenological description based on a resonant tunneling model.

The paper is organized as follows. In Section 2 we present the methodology and the system investigated. In Section 3 we discuss the numerical results and in Section 4 we conclude.

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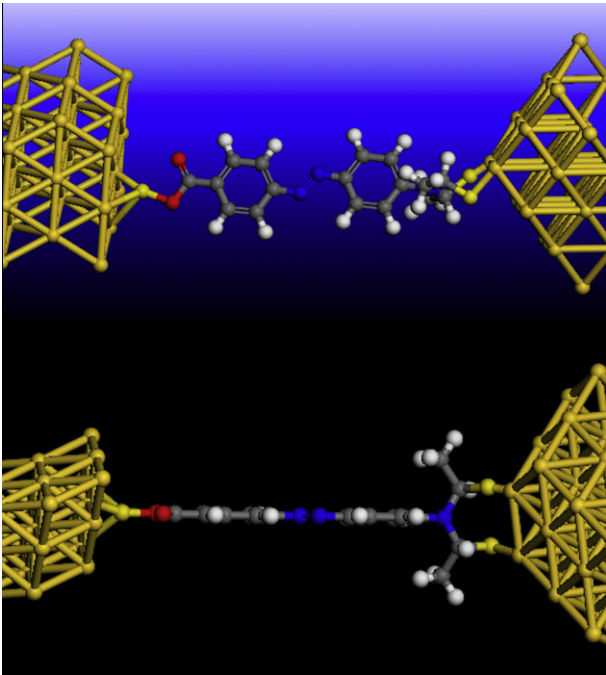
Fig. 1. (*up*) Side and (*bottom*) top view for pictogram of ethyl red structure investigated in this paper working as a push–pull type device with conjugated bonds represented by *azo* group.

2. Methodology

2.1. Ab initio calculation [10,11,22]

In the *ab initio* calculation we determine the charge accumulated in part of the molecule as a function of an external electric field. It has been employed state-of-art Hartree–Fock derivative methodology contained in Gaussian package [22]. Both the well-known 6-31G∗∗ and 6-311G∗∗ basis sets provide results with the same qualitative features. This demonstrates that both sets can be equally used in the present calculation. The geometric parameters of the analyzed structures were fully optimized in the presence of an external electrical field, using a closed shell model for the Roothaan–Hall matrix equation,

$$FC = SCE,$$

where S, C and E are overlap integral matrix, coefficient matrix in the linear combination of atomic orbitals, and orbital energy diagonal matrix, respectively. Also, the Fock matrix F is written as

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

where the three terms in $F_{\mu v}$ describe the core energy, the Coulomb and exchange interaction, and the external fields, respectively. The $(\mu v|\lambda\sigma)$ and $(\mu\lambda|v\sigma)$ are two electronic integrals that may involve up to four different gaussians basis function as ϕ_μ, ϕ_v, ϕ_λ, ϕ_σ.

From the Roothaan–Hall matrix we obtain the charge distribution through the molecular system.

2.2. Non-equilibrium calculation

In order to reproduce in the current the same behavior observed in the charge accumulation, we use a toy-model composed of many localized levels coupled to a left and a right electron reservoirs. For that we divide the molecular system in three parts as: (i) source; (ii) drain; and (iii) a central region that couples source and drain via localized tunneling channels.

We define the current leaving the donor or the acceptor side as $I_\eta = -e\langle \dot{N}_\eta \rangle$, where e is the electron charge ($e > 0$), $\langle \cdots \rangle$ is a thermodynamic average and $N_\eta = \sum_k c_{k\eta}^+ c_{k\eta}$ 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, $\dot{N}_\eta = \frac{i}{\hbar}[H, N_\eta]$, 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

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

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

$$H_M = \sum_n E_n d_n^+ d_n,$$

with E_n being the molecular levels and $d_n(d_n^+)$ 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

$$H_T = \sum_{kn\eta} \left[t c_{k\eta}^+ d_n + t d_n^+ c_{k\eta} \right],$$
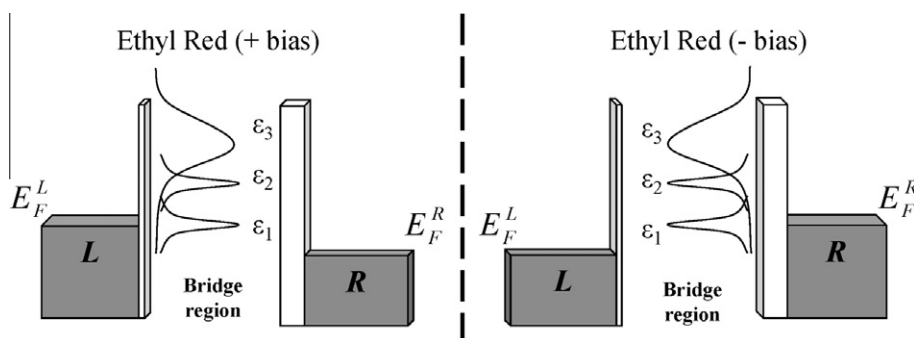
Fig. 2. Model utilized to describe the electronic transport in the source–drain system with positive and negative applied bias. Between the source and drain are the localized levels representing asymmetric tunneling barriers provoking a bi-directional rectification in the current–voltage pattern.
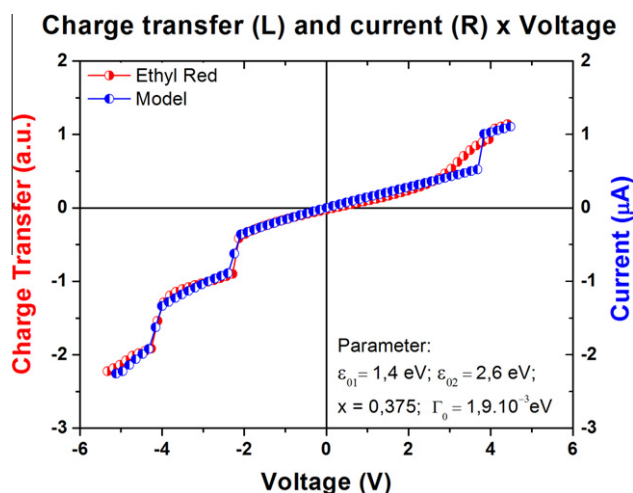
Fig. 3. Charge accumulated (*left axis*) and current (*right axis*) as a function of the voltage for ethyl red nano-device. Both, charge accumulated and current present resonant-tunneling behavior. For the non-equilibrium calculation were chosen parameters in order to better fit the *ab initio* data performed by Hartree–Fock derivative methodology.

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

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

which is valid for the noninteracting model assumed. The quantities Γ_i^D, Γ_i^A, and E_i will be taken as phenomenological parameters. In particular, the level E_i will change with the bias voltage following the linear relation

$$E_n = E_n^0 - x \text{ eV}$$

where V is the bias voltage, e ($e > 0$) the electron charge and x a phenomenological parameter that accounts for asymmetric drop of the bias voltage along the system. The donor and acceptor chemical potentials are related to the bias voltage as

$$\mu_L = \mu_L^0 \text{ and } \mu_R = \mu_R^0 - \text{ eV},$$

where the "0" upper-index denote the quantities without bias voltage. This model was applied to a device belonging to a family of well-known pH indicators [21]. The option to apply for the ethyl red structure rose up because of recent experimental results [21].

3. Results and discussions

The ethyl Red is a well-known pH indicator presenting a strong dipole moment and in the presence of external electric field could be considered as a push–pull device represented by a donor–π bridge–acceptor were the bridge is the azo group.

Fig. 3 presents the charge accumulation (*left axis*) vs. voltage and the current (*right axis*) vs. voltage for the ethyl red device. In between −2.3 V and 4.0 V the current and charge accumulation present an Ohmic (linear) behavior. In the present model this comes from the alignment between the emitter Fermi level and the tail of the broaden higher level (E_3 in Fig. 2). When the narrow level E_1 attains resonance around 3.5 V for positive and −2 V for negative bias, a step is seen in the current. Similar behavior can be observed in the charge accumulated, which is related to the match between the frontier molecular orbitals delocalized through all molecule.

For reverse bias one additional step (at −4.3 V) appears due to the second level E_2 that attains resonance with the right Fermi level. The asymmetry between positive and negative voltages comes from the difference in the right and the left part of molecular system. In our transport model this is taken into account via the parameter x, that gives an asymmetric bias voltage drop along the system. The voltage is assumed to drop fully at both contact-molecule contacts. It is important to mention that this is in sharp contrast to what occurs within a barrier model (Simmons model) of molecular transport, where the voltage drops evenly over the junction.

Note that Fig. 3 presents a qualitative agreement between non-equilibrium (*right axis*) and *ab initio* (*left axis*) approaches suggesting that the knowledge of an equilibrium quantity can provide some information about non-equilibrium properties of the system. The numerical parameters adjusted to best fit the I–V with the Q–V curves are the energy levels E_0, the coupling parameters $\Gamma_i^{D/A}(E)$, and x. Their values are shown in Fig. 3. Maiti has obtained similar results for the investigation of electronic transport feature through polycyclic hydrocarbon molecules attached with two metallic electrodes [23,24], phenalenyl molecules attached with two electrodes through thiol groups [25], and through molecular bridge systems [26].

Also, the feature presented in Fig. 3 shows that this molecular system has one resonance for $V > 0$ and two resonances for $V < 0$. This behavior is typical of bi-directional molecular transistor.

In Fig. 4 we present the shift in the electronic absorption spectra when the device are in operational regime (2.6 V for forward bias
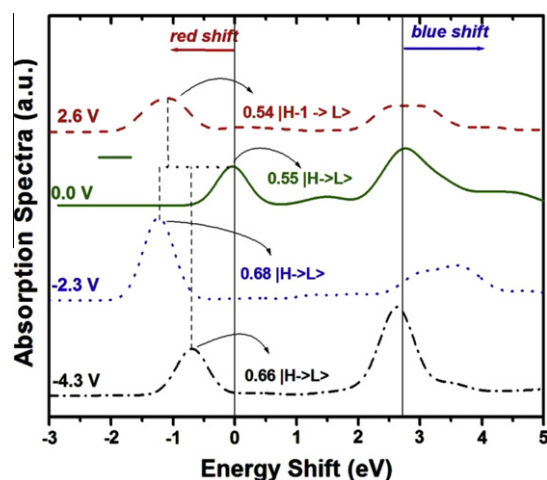
Fig. 4. Shifts in the theoretical absorption spectra of ethyl red device for *0.0* V, *2.6* V, *−2.3* V and *−4.3* V applied bias. The H and L means the highest occupied molecular orbital and the lowest unoccupied molecular orbital, respectively. The $A|H−x \rightarrow L>$ is a representation of a HOMO minus x to LUMO molecular transition weighted by the A coefficient of LCAO (linear combination of atomic orbitals) expansion.

and −2.3 V, −4.3 V for reverse bias). The HF methodology accounts for the configuration interaction to give the best description of the UV–Visible–IR optical transitions, including transitions between the first 12 unoccupied to the last 12 occupied molecular orbitals. Fig. 4 shows two main bands and they are centered at peak of the main HOMO to LUMO transition for comparison (centered in the 0.0 V, i.e., 0.55 $|H \rightarrow L>$).

A comparative analysis of Figs. 3 and 4 shows the following aspects: the behavior in the main transition occurs because in the ballistic regime the transport happens with energies *close to* the Fermi level or the HOMO–LUMO levels. It is interesting for systems that needs fast switching response and could be used as a device that works at low potency level with high operational frequencies as PHz, e.g., 10^{12} times higher than typical devices and demands high-speed static pulse signals.

The molecular device under forward [Fig. 4 (2.6 V)] and reverse [Fig. 4 (−2.3 V and −4.3 V)] bias shows a *prominent and unique* signature: for reverse bias (eV < 0) a strong red shift of $|H \rightarrow L>$ transitions appears equal to *1.25* eV (−2.3 V) and *0.68* eV (−4.3 V), thus resulting in a decrease of the HOMO–LUMO gap. This phenomenon could be well understood looking at the current for reverse bias (Fig. 3). (a) When the charge is removed from the ethyl molecular radical, it provokes an enhancement (in absolute values) of the current up to the resonance effect and then new operational region dominate; (b) when the voltage goes to the operational *forward* switch, a red shift (equal to *1.10* eV for 2.6 V) of the main transition also appears but with $|H - 1 \rightarrow L>$ transition. For completeness, the second transition centered in *2.77* eV suffers a blue shift for forward switch (2.6 V) and blue (−2.3 V) and red (−4.3 V) shift for reverse switch, respectively.

4. Conclusion

We studied charge distribution and absorption spectra of a well-known pH indicator, namely, the ethyl red molecular structure. Quantum-mechanic calculations were performed in the presence of an external electric field. The carrier rearrangement in the presence of an electric field can be understood considering the system as donor–π bridge (*azo* group)–acceptor junction. Based on that we developed a noninteracting tunneling model to describe current or carriers, which was calculated via the Landauer expression for the current. The simulations permit us point out a few rules: (a) the rectification appears associated with very specific capacitive effects showing a non-ohmic effect as example of ballistic conductors; (b) the accumulated charge–voltage and current–voltage characteristic obtained by Hartree–Fock and Landauer simulation permit us to reach a ballistic resonant model for organic nanodevices (also supported by previous *ab initio* calculations [27–29]); (c) a forward directional rectification response was established with operational regions starting at 2.6 V and a reverse double-rectification behavior was accomplished presenting two operational regions starting at −2.3 V and −4.3 V, respectively.

Acknowledgements

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