

# Use of polarons and bipolarons in logical switches based on conjugated polymers

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Considering impurity molecules functioning as switches, the charge-transport process on a single conducting polymer chain is analyzed. The dynamics of polarons and bipolarons is studied with the time-dependent unrestricted Hartree-Fock approximation using a combination of the Su-Schrieffer-Heeger and extended Hubbard models, extended to include the potential due to the dopants. A Brazovskii-Kirova-type symmetry-breaking interaction is inserted in the Hamiltonian model. The polarons and bipolarons are put into motion by a spatially uniform external electric field introduced through a time-dependent vector potential. The process of charge transport through the sites with radicals that work like a switch is analyzed by the numerical resolution of the equations of motion. The use of polarons and bipolarons as information carriers is analyzed. The results show that the impurity molecule can work as a gate to the passage of charged polarons or bipolarons (i.e., it can control of charge transport). The polarons and/or bipolarons can be trapped by the impurity molecule or can pass through it, resulting in two configurations: closed and open logical switches. Such results show that polarons and bipolarons provide good candidates to logical switching in molecular circuits of conducting polymers. The energies involved are also discussed.

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## I. INTRODUCTION

The conjugated polymers have attracted much interest of the academic community. Possible technological applications of these materials show us a very promising field in the future. The applications of conjugated polymers in several areas, including electronic devices,<sup>1-3</sup> anticorrosion protection for metal,<sup>4</sup> electromagnetic shielding,<sup>5</sup> and others, have recently been realized. The basic properties of these systems are also of current interest, especially the issues concerning the microscopic mechanisms of charge and energy transport. The importance of these materials lies in the peculiar phenomena induced by the presence of the nonlinear excitations. These phenomena are associated with the prominent features of electric conductivity that can vary by many orders of magnitude with doping impurities.

Electronic devices have been fabricated<sup>6,7</sup> based upon conjugated polymers. Although performance is modest relative to similar devices based upon inorganic semiconductors, these devices provide a test bed for investigation of charge injection and transport phenomena.

Through different architecture, it would be possible to implement logical formal computation on molecular circuits as logical switches, binary decoders, and stack memories.<sup>8</sup> Special molecules functioning as artificial neurons could be linked in a net, with conducting polymers working as axons and dendrites. Such circuits of molecular dimensions have a real possibility of implementation considering the advances of the technique of tunneling microscopy.

Traditionally, polymer materials have been used for properties other than electronic and optoelectronic. Particularly advantageous properties of macromolecular materials include chemical inertness, electrical insulation, and especially ease of processing. Conducting polymers play an important role in the understanding of the conduction mechanisms. They are insulating materials that can be doped with the presence of strong oxidizing or reducing radicals that can

work as pinning centers and barriers to the passage of nonlinear excitations such as solitons,<sup>9,10</sup> allowing or denying the passage through a certain region of the chain.<sup>11</sup>

We consider the electron-electron interactions in the dynamical simulations. Nevertheless, there has been a relative lack of dynamical simulations,<sup>12-15</sup> even though there is a very strong link between the electronic part and the moving bond-order configurations.

A polaron has a spin  $\frac{1}{2}$  and an electric charge  $\pm e$ . In the case of bipolarons, they can be regarded as a confined pair comprising a charged soliton and a charged antisoliton. They are spinless with charge  $\pm 2e$ . A basic description of these excitations was given by the Brazovskii-Kirova (BK) model,<sup>16</sup> in which a symmetry-breaking term is added to lift the ground-state degeneracy in the Takayama-Lin-Liu model.<sup>17</sup>

The presence of trapped polarons in undoped poly(*p*-phenylene vinylene) was suggested by the electron-nuclear double-resonance measurements in a dark state.<sup>18,19</sup> Other experiments have been performed in some conjugated polymers describing the magnetic and optical properties.<sup>20-24</sup>

In the present work, our purpose is to establish the dynamical effects of radicals bonded to a linear chain to create molecular switches with the use of polarons and bipolarons moving along the chain. Doping radicals are introduced to alter the polymer-conduction characteristics, controlling the charge transfer throughout of the chain. To study the dynamics of polarons and bipolarons, a modified version of the Su-Schrieffer-Heeger (SSH) model<sup>25,26</sup> is used, which is extended to include the influence of an electric field, Coulombian interactions (extended Hubbard), and impurity potentials to represent the radicals bonded to the chain. The different configurations for a molecular device are determined by varying the parameters of the doping radicals.

The dynamics of charged polarons and bipolarons propagating on the conjugated polymers is studied numerically through the resolution of the coupled equations for electronic

wave functions and lattice displacements. The coupled equations are numerically integrated over real time. Since we consider a uniform electric field, the time-dependent vector potential is independent of the space coordinate, therefore periodic boundary conditions can be adopted to avoid edge effects. Here, the equations are solved in a self-consistent way without any previous assumption on the form of the nonlinear excitations.

In the following section, we present the formalism of the model and a brief discussion of the simulation method. Section III contains the results of the calculations. Finally, Sec. IV is destined to a summary of results and conclusions.

## II. MODEL AND METHOD OF SIMULATION

Our model polymer is defined by the Hamiltonian including impurities,

$$\begin{aligned}
 H(t) = & - \sum_{n,s} [(t_n - \alpha y_n) \{ \exp(i\gamma A_s) C_{n,s}^\dagger C_{n+1,s} + \text{H.c.} \}] \\
 & + U \sum_i (n_{i\uparrow} - \frac{1}{2})(n_{i\downarrow} - \frac{1}{2}) + V \sum_i (n_i - 1)(n_{i+1} - 1) \\
 & + \sum_n \frac{K}{2} y_n^2 + \sum_n \frac{M}{2} \dot{u}_n^2 + \sum_{p,s} V_p C_{p,s}^\dagger C_{p,s}, \quad (1)
 \end{aligned}$$

where  $y_n = u_{n+1,n} - u_n$  and  $t_n = t_0 + \delta_0(-1)^n$ . Here,  $t_0$  is the transfer integral between the nearest-neighbor sites in the undimerized system,  $\delta_0$  is the Brazovskii-Kirova symmetry-breaking term,  $\alpha$  is the electron-phonon coupling,  $u_n$  is the displacement of the  $n$ th CH unit from its equilibrium position in the undimerized phase,  $C_{n,s}^\dagger$  ( $C_{n,s}$ ) is the creation (annihilation) operator of a  $\pi$  electron with spin  $s$  on the  $n$ th site,  $K$  is the spring constant of a  $\sigma$  bond, and  $M$  is the mass of a CH unit.  $U$  and  $V$  are the on-site and nearest-neighbor Coulomb repulsion strengths, respectively.  $V_p$  is the strength of an impurity, which is located in the  $p$ th site. The parameter  $\gamma$  is defined by  $\gamma \equiv ea/(\hbar c)$ , where  $e$  is the absolute value of the electronic charge,  $a$  is the lattice constant, and  $c$  is the light velocity. The relation between the time-dependent vector potential  $\mathbf{A}$  and the uniform electric field  $\mathbf{E}$  is given by  $\mathbf{E} = -(1/c)\dot{\mathbf{A}}$ . In the Coulomb repulsion terms, we use the electron-hole symmetry, since we are interested mainly in nearly half-filled states.

First, we prepare a stationary state, which is fully self-consistent with regard to the degrees of freedom of both, the electrons and the lattice, as the initial conditions for the calculations.<sup>27</sup> Then, under the action of the electric field, the electronic and the lattice equations of motion are numerically integrated and the lattice equations of motion<sup>28</sup> are solved by discretizing the time variable with a step  $\Delta t$ . The time step  $\Delta t$  is chosen so that the changes of  $u_i(t)$  and  $A(t)$  are always very small in the electronic scale during this interval. The time-dependent Schrödinger equation is analytically integrated by introducing single-electron eigenstates at each moment. We have that

$$\Psi_k(t) = T \exp \left[ -i \int_0^t dt' \frac{\hat{h}(t')}{\hbar} \right] \Psi_k(0),$$

where  $\hat{h}(t')$  is the electronic part of the Hamiltonian  $H(t)$  at time  $t'$  and  $T$  is the time-ordering operator. Through the discretization of the time variable, this expression becomes

$$\Psi_k(t_{j+1}) = \exp \left[ -i \Delta t \frac{\hat{h}(t_j)}{\hbar} \right] \Psi_k(t_j).$$

Consider the expansion

$$\Psi_k(t_j) = \sum_l C_{lk} \phi_l(t_j),$$

where  $C_{lk} = \langle \phi_l | \Psi_k \rangle$  and  $\{\phi_l\}$  and  $\{\varepsilon_l\}$  are the eigenfunctions and the eigenvalues of the electronic part of the Hamiltonian  $H(t)$  at a given time  $t_j$ , respectively. The solution of the time-dependent Schrödinger equation can then be put into the form

$$\begin{aligned}
 \Psi_{k,s}(n, t_{j+1}) = & \sum_l \left[ \sum_m \phi_{l,s}^*(m, t_j) \Psi_{k,s}(m, t_j) \right] \\
 & \times e^{-i(\varepsilon_l \Delta t / \hbar)} \phi_{l,s}(n, t_j). \quad (2)
 \end{aligned}$$

The lattice equations of motion are written as

$$u_n(t_{j+1}) = u_n(t_j) + \dot{u}_n(t_j) \Delta t, \quad (3)$$

$$\dot{u}_n(t_{j+1}) = \dot{u}_n(t_j) + \frac{F_n(t_j)}{M} \Delta t, \quad (4)$$

where  $F_n(t_j)$  is the force in the  $n$ th site in the  $j$ th time step.<sup>27</sup> Thus, using Eqs. (2), (3), and (4), the electronic wave functions and the displacement coordinates at the  $(j+1)$ th time step are obtained from the  $j$ th time step.

We use the relevant parameters for simulation commonly accepted for conjugated polymers:<sup>15,25</sup>  $t_0 = 2.5$  eV,  $K = 21$  eV  $\text{\AA}^{-2}$ ,  $\alpha = 4.1$  eV  $\text{\AA}^{-1}$ ,  $U = 0.50$  eV,  $V = 0.25$  eV,  $a = 1.22$   $\text{\AA}$  and for the impurity potentials we take  $V_p$  ranging from  $0.04t_0$  to  $0.30t_0$  (bipolaron) and from  $2.10^{-3}t_0$  to  $0.20t_0$  (polaron). The bare optical-phonon energy is  $\hbar\omega_Q^{-1} = (4K/M)^{1/2} = 0.16$  eV. Such parameters yield a good qualitative description of the conjugated polymers of interest.<sup>16</sup> We accelerate the charged polaron and bipolaron by applying the electric field. The field is kept on from  $t = 0$  to  $t = t_{off}$ . The field strength  $E$  is fixed at  $0.025E_0$  for the bipolaron and  $E = 0.0050E_0$  for the polaron, where  $E_0$  is defined by  $E_0 = \hbar\omega_Q/ea = 1.3 \times 10^7$  V/m. This particular choice of electric field is based on the relative stability of polarons and bipolarons to applied external electric fields.<sup>27</sup> Periodic boundary conditions are assumed for the electronic wave functions  $\psi_{k,s}$  and for the lattice displacements  $u_n$ .

In this study, the total number of lattice points on the chain is  $N = 104$ . The total number of electrons is  $N_e = 102$  for the bipolaron and  $N_e = 103$  for the polaron. Hence, all the excitations are positively charged.

The excitation charge is given by the expression

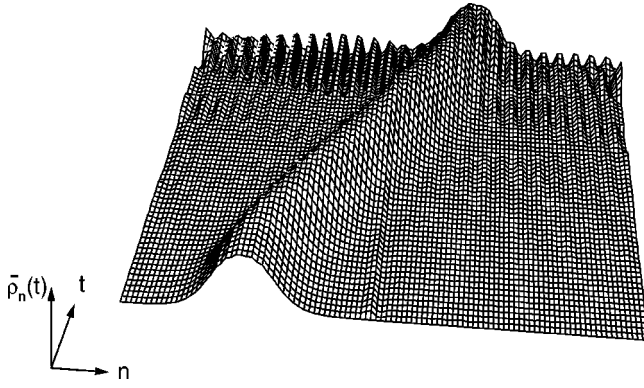


FIG. 1. Stereographic representation of the  $n$  and  $t$  dependences of the smoothed charged density  $\bar{\rho}_n$  in the case in which the radical intensity  $V_p = 0.225$  eV (bipolaron). The electric field is switched off at  $t_{off} = 60$  fs and the final time is 240 fs.

$$\rho(n, t) = 1 - \sum_{k, s} \psi_{k, s}^*(n, t) \psi_{k, s}(n, t). \quad (5)$$

To study the position and charge distribution of the polaron and bipolaron as a function of time, we introduce the smoothed excess-charge-density and bond-order variables expressed, respectively, by

$$\bar{\rho}_n = \frac{\rho_{n-1} + 2\rho_n + \rho_{n+1}}{4}, \quad (6)$$

$$\bar{y}_n = \frac{(-1)^n (y_{n-1} - 2y_n + y_{n+1})}{4}. \quad (7)$$

A time step of  $\Delta t = 0.001 \omega_Q^{-1} = 0.004$  fs is used. We follow the dynamics of the systems up to the 60 000th time step. Some simulations were carried out to 150 000 time steps; nevertheless, a trapped polaron or bipolaron only oscillates around the impurity position and the nontrapped ones continue to move freely. Therefore, there is no point in going beyond 60 000 time steps. Each simulation took 90 h of CPU time on the DEC Alpha-400 work station.

### III. SIMULATION RESULTS

We have performed simulations by systematically varying the impurity intensity of the radical.

First, we consider the case of one single positively charged bipolaron initially present around the 20th site. The electric field is applied on the chain. One radical molecule is bonded at the 50th site. Figure 1 shows the stereographic tridimensional representation of the smoothed charge density  $\bar{\rho}_n(t)$  for the case in which the radical strength has the value  $V_p = 0.225$  eV. From Fig. 1 it is observed that the bipolaron passes through the impurity. The defect passes through the region where the radical is present, i.e., the radical works as a switch on. The figure show us that there is a small charge spread in the instant of the collision of the bipolaron with the radical molecule. This spread is about 1%. The only consequence of the presence of the impurity is a small charge-density oscillation.

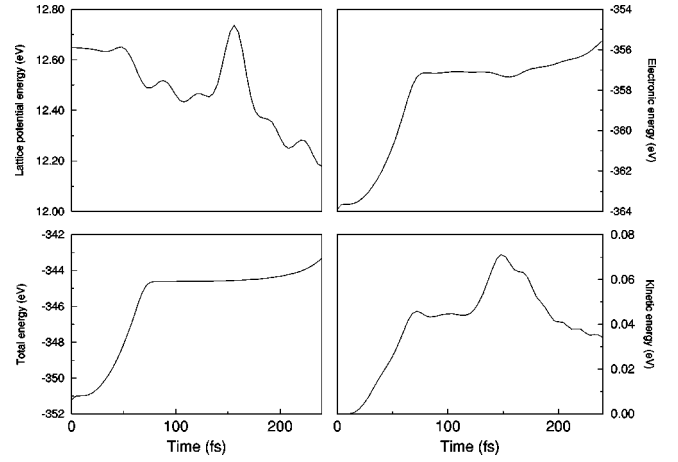


FIG. 2. Time evolution of the energies involved in the process (bipolaron): (a) lattice energy, (b) electronic energy, (c) total energy, (d) kinetic energy. The radical intensity is  $V_p = 0.225$  eV. The electric field is switched off at  $t_{off} = 60$  fs and the final time is 240 fs.

Figure 2 represents the energies involved in the process of collision in Fig. 1 with the same impurity strength. Figure 2(a) shows the lattice energy of the chain. In the dynamics of the collision, this energy has an oscillatory behavior.<sup>29</sup> Such an oscillation might be related with phonon modes. The electronic energy increases during the application of the electric field [see Fig. 2(b)]. The small variation that occurs around 156 fs is explained by the collision of the bipolaron with the radical linked to the chain.

The total energy increases rapidly during the application of the electric field, as should be expected [see Fig. 2(c)]. After the electric field is switched off, the total energy becomes constant. A small variation of the total energy is observed over the time; it is thought to come from the discretization of the time variable. Since this variation is small enough, it is verified that the mesh adopted for the time is quite good.

The charged bipolaron acquires a velocity close to its maximum possible value of around 75 fs.<sup>27</sup> The subsequent variations on the kinetic energy are thought to come from the interaction of the bipolaron with the net phonons present.

In the simulation considering the radical strength equivalent to  $V_p = 0.375$  eV the charged bipolaron is confined after the collision with the switching region around the molecule bonded to the chain. In this case, the system works as a switch off in the interacting region. The presence of lattice vibrations is evident here. In this study, such net perturbations occur with larger intensity when compared to the case of the switch on. A charge spread is observed among the charged bipolaron and the surrounding sites. The final charge of the bipolaron is about 98% of the original value.

The energies involved in this case showed the same basic characteristics the preceding case.

Summarizing the bipolaron position versus time, Fig. 3 presents the time evolution of the bipolaron in motion in the direction of a radical switch. Considering the situations in which the radical strength  $V_p$  is varied from 0.05 eV to 0.75 eV, we observed that when  $V_p$  is smaller than 0.3 eV the

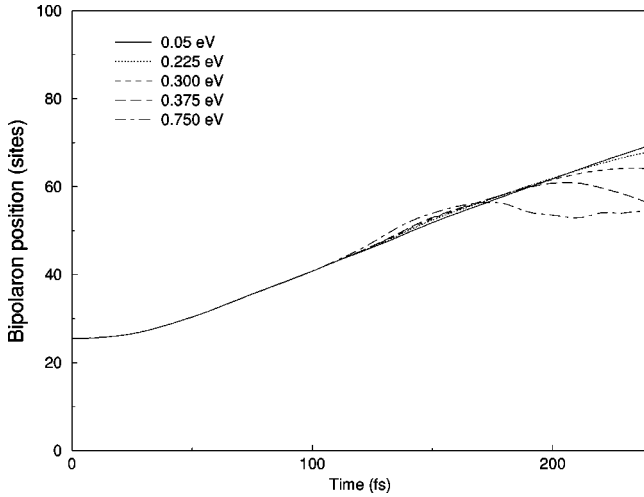


FIG. 3. Time evolution of the positively charged bipolaron position. The radical strength is varied from 0.05 eV to 0.75 eV. The electric-field switch off occurs in  $t_{off}=60$  fs.

bipolaron passes across the interaction region of the radical. When the impurity intensity is greater than 0.3 eV, the bipolaron is reflected or trapped by the impurity that forms a barrier to the passage of the bipolaron. The reflected bipolaron is led to collide repeatedly with the impurity if the external electric field is kept on the chain. Therefore, the threshold for trapping should be close to 0.3 eV.

Second, we perform the simulation of charged polarons initially located at the 25th site. The electric field is applied on the chain. The radical molecule is bonded at the 50th site and the radical strength is varied from 0.05 to 0.75 eV. Here, the polaron is accelerated and reaches a constant velocity, close to its maximum possible value.<sup>27</sup> Figure 4 shows the stereographic representation of the smoothed charge density  $\bar{\rho}_n$  for the case of radical strength  $V_p=0.05$  eV. Figure 5 represents the polaron-position evolution with time and radical intensities. Considering radicals with different intensities, the polaron collision with the radical leads to two possibilities: the excitation is trapped (or reflected) by the radical or it can pass through it. The polaron is trapped in the switching region when the impurity intensity is around or greater than 0.3 eV.

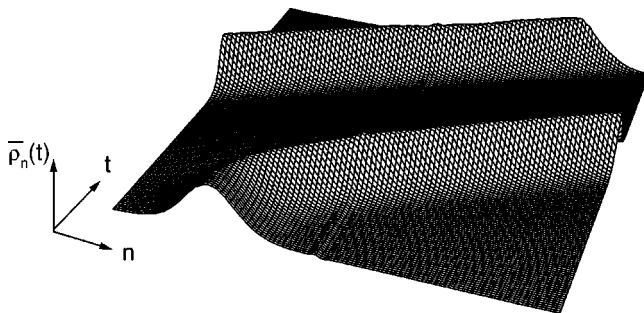


FIG. 4. Stereographic representation of the  $n$  and  $t$  dependences of smoothed charged density  $\bar{\rho}_n$  in the case when the radical intensity is  $V_p=0.05$  eV (polaron). The time of switch off for the electric field and the final time are, respectively,  $t_{off}=400$  fs and 400 fs.

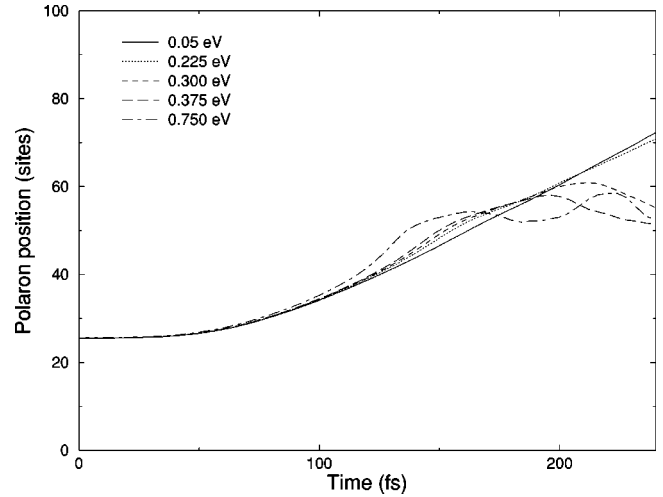


FIG. 5. Time evolution of the positively charged polaron position. The radical strength is varied from 0.05 to 0.75 eV.

Comparing the dynamics of polaron and bipolaron excitations, both of them show comparable sensitivity to radical parameter for the switching.

#### IV. DISCUSSION AND SUMMARY

We investigated the propagation of a moving charged polaron and bipolaron on a single polymer chain, where a radical molecule bonded to the chain works as a switch. This study was carried out through numerical calculations using a combined version of the extended Hubbard and SSH models. We have used an electric field to accelerate the charged excitations (polaron and bipolaron). The time-dependent Schrödinger equation and the equation of motion for the time-dependent lattice displacements form a coupled set that was numerically integrated over time in a self-consistent way.

The polaron and bipolaron passage or trapping on the switching site is investigated when the radical parameter is varied. Initially the charged polaron and bipolaron are accelerated through the application of an electric field until they reach a velocity close to their maximum possible velocities.<sup>27</sup>

If we consider greater values of electric fields than those adopted, stability effects should be considered.<sup>27</sup>

In some experiments,<sup>30</sup> the influence of radicals is very important to the process of switching, which permits the fabrication of electronically configurable molecular-based logic switches and gates.<sup>31</sup> In these cases, the flow current of the charge carriers is controlled through of the application of a bias voltage across the switching device, obtaining two configurations: closed and open states.

We have verified that the molecular switches on conjugated polymers are very sensitive to the radical parameter. As a consequence, it admits two configurations: closed and opened logical switches. In the first, the radical permits the passage of the polaron and/or bipolaron working as a molecular linear circuit, while in the second case, the radical blocks the motion of the excitation. Therefore, the external control of the radical effect on the chain (e.g., optical con-



trol) could lead to the implementation of molecular gates.

We have shown that the polaron and bipolaron excitations can be blocked up by controlling of impurity radicals in the chain that function as molecular switches. Therefore, polaron and bipolaron excitations can work as information carriers in the molecular scale.

Our results are certainly dependent on the numerical parameters used for the model. Changes in these parameters do change the physical parameters of the polaron and the bipolaron. It should be mentioned that our model is a simplified one and contains a phenomenological BK parameter  $\delta_0$ , which is rather difficult to relate to quantitative results and

the  $\sigma$ -backbone structure of each polymer. Nevertheless, we think that the qualitative results obtained here are very robust and valid for conjugated polymers, in general.

The inclusion of interchain interactions on the chain backbone and the influence of several switches with the use of magnetic field will be presented in a forthcoming paper.

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