Electric-field effects on the competition between polarons and bipolarons in conjugated polymers

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The charge transport on a single conducting polymer chain is investigated. The dynamics of polarons and bipolarons is numerically studied using the Su-Schrieffer-Heeger model combined with the Pariser-Parr-Pople model extended to include an external electric field and a Brazovskii-Kirova symmetry breaking interaction. The time-dependent unrestricted Hartree-Fock approximation is used. It is found that dynamical effects do not reverse the stability relation between polarons and bipolarons. On the other hand, as the electric field intensity gets stronger the moving polarons structure is blurred (destroyed) faster than the structure of moving bipolarons. This effect is reduced with increasing doping concentration. Therefore, it is shown within the present model that the applied external electric field as well as the doping concentration are fundamental in determining the relative prevalence of polarons or bipolarons.

I. INTRODUCTION

Polarons and bipolarons are charge carriers generated upon doping or photo-excitation in conjugated polymers with non-degenerated ground state. A polaron has spin $\frac{1}{2}$ and electric charge $\pm e$, whereas a bipolaron is spinless with charge $\pm 2e$. The polaron is accompanied by three sub-gap optical transitions associated with its localized levels in the band gap, while only two transitions are allowed in the case of a bipolaron. The difference comes from the occupancies of the localized levels.[1-3]

The prevalence of polarons or of bipolarons as charge carriers in these polymers is a very controversial subject. Magnetic and optical experiments have been conducted in a variety of non-degenerate conjugated polymers such as polypyrrole,[4,5] polyaniline,[6] polythiophene,[7,8] and poly(p-phenylene-vinylene).[9-11] The variation on the spin density with doping concentration suggests the existence of different regimes upon doping.[4,6,8] On the other hand, the basic theoretical description of these excitations given by the Brazovskii-Kirova (BK) model,[12] predicts that a bipolaron is always energetically more stable than two separate polarons. Despite this discrepancy, the BK bipolaron model is still widely used in interpreting experimental data.

The inclusion of electron-electron interactions on the theoretical treatment of conjugated polymers has rendered the polaron-bipolaron competition picture richer. It has been found that the relative stability of bipolarons and polarons should depend on the strength of electron-electron interactions.[13] Moreover, a possible doping-induced phase transition from a polaron lattice to a bipolaron lattice has been predicted.[14]

We have performed dynamical simulations considering electron-electron interactions and the strong link between the electronic part and the moving bond order configurations of conjugated polymers.[15-17]

The purpose of the present work is to establish the dynamical effects on the polaron-bipolaron competition. The effects of the excitations motion, applied electric field, and doping concentrations are determined. The dynamics of charged polarons and bipolarons propagating on the polymer chain is studied through numerical solution of the equations of motion for the electronic and lattice degrees of freedom of the system. The model Hamiltonians of Su-Schrieffer-Heeger (SSH) and of Pariser-Parr-Pople (PPP) are combined and extended to include an external electric field and a BK-type symmetry-breaking interaction. Actually, we determine the conditions for a moving charged carrier being stable as an electric field is applied and how the doping concentration alters the relative stability. We verify that single polarons are unstable when the system is subjected to stronger electric fields but their stability is enhanced with an increase on doping concentration. Bipolarons are very stable to strong electric fields and the increase on doping do not alter very much their stability. The saturation velocities of polarons and bipolarons is obtained. It is found that the saturation velocities are close to three times the sound velocity of the system.

In the next section, we present the model and a brief description of the simulation method. Section III contains the results of the calculations. The last section, Sec. IV, is devoted to a summary and concluding remarks.

II. MODEL AND FORMALISM

This presentation of the simulation method follows closely that of Ref. 17. We describe the electron-phonon system including the electron-electron interaction with the model Hamiltonian:

$$H(t) = -\sum_{i,s} (t_{i,i+1} C^{\dagger}_{i+1,s} C_{i,s} + \text{H.c.}) + U \sum_i \left(n_{i\downarrow} - \frac{1}{2} \right)$$

$$\times \left(n_{i\downarrow} - \frac{1}{2} \right) + V \sum_i (n_i - 1)(n_{i+1} - 1)$$

$$+ \sum_i \frac{K}{2} y_i^2 + \sum_i \frac{M}{2} u_i^2, \tag{1}$$

with $t_{i,i+1} = \exp(-i\gamma A)\{[1 + (-1)^n \delta_0] t_0 - \alpha y_i\}$, $y_n \equiv u_{n+1} - u_n$, $n_{i,s} \equiv C^{\dagger}_{i,s} C_{i,s}$, and $n_i \equiv \Sigma_s n_{i,s}$. Here, $H(t)$ is an SSH-PPP-type Hamiltonian, modified to include the electric field and the BK symmetry-breaking interaction. $C_{i,s}$ is the an-

nihilation operator of a π electron with spin s at the ith lattice site, u_i is the displacement coordinate of the ith CH group, t_0 is the transfer integral between the nearest neighbor sites in the undimerized chains, α is the electron-phonon coupling,[18] δ_0 is the BK symmetry-breaking parameter,[12] M is the mass of a CH group, K is the spring constant of a σ bond, U and V the on-site and nearest-neighbor Coulomb repulsion strengths, respectively. $\gamma \equiv ea/(\hbar c)$, e being the absolute value of the electronic charge, a the lattice constant, and c the light velocity. The relation between the time-dependent vector potential A and the uniform electric field E is given by $E = -1/c\dot{A}$. We use as parameters the commonly accepted values for conjugated polymers: $t_0 = 2.5$ eV, $K = 21$ eV Å^{-2}, $\alpha = 4.1$ eV Å^{-1}, $U = t_0/2$, $V = U/2$, $a = 1.22$ Å, and a bare optical phonon energy $\hbar\omega_Q = \sqrt{4K/M} = 0.16$ eV.

First, we prepare a stationary state, which is fully self consistent with respect to both degrees of freedom, of the electrons and phonons, as the initial conditions of the calculations.[19] Then, under the action of the electric field, the electronic and the lattice equations of motion are numerically integrated. Namely, the time-dependent Hartree-Fock equations for one-particle wave functions:

$$i\hbar \dot{\psi}_{k,s}(i,t) = -[t^*_{i,i+1} + V\tau_s(i,t)]\psi_{k,s}(i+1,t)$$
$$-[t_{i-1,i} + V\tau_s^*(i-1,t)]\psi_{k,s}(i-1,t)$$
$$+\left\{ U\left[\rho_{-s}(i,t) - \frac{1}{2}\right] + V\sum_{s'}\left[\rho_{s'}(i+1,t)\right.\right.$$
$$\left.\left. + \rho_{s'}(i-1,t) - 1\right]\right\}\psi_{k,s}(i,t),$$

with

$$\rho_s(i,t) = \sum_k{}' \psi_{k,s}^*(i,t)\psi_{k,s}(i,t)$$

$$\tau_s(i,t) = \sum_k{}' \psi_{k,s}^*(i+1,t)\psi_{k,s}(i,t)$$

and the Newtonian lattice equation of motion

$$M\ddot{u}_n = F_n(t), \tag{2}$$

where

$$F_n(t) = -K[2u_n(t) - u_{n+1}(t) - u_{n-1}(t)] + \alpha[e^{i\gamma A(t)}(B_{n,n+1}$$
$$- B_{n-1,n}) + e^{-i\gamma A(t)}(B_{n+1,n} - B_{n,n-1})].$$

Here $B_{n,n'} \equiv \Sigma'_{k,s}\Psi_{k,s}^*(n,t)\Psi_{k,s}(n',t)$. The prime on the summation means that the sum is taken over the occupied single-particle states in the initial stationary state. These equations of motion are solved by discretizing the time variable with a step Δt. The time step Δt is chosen so that the change of $u_i(t)$ and $A(t)$ during this interval is always very small in the electronic scale.[19]

The time-dependent Schrödinger equation is integrated by introducing single-electron eigenstates at each moment. The solution of the time-dependent Schrödinger equation can then be put in the form,

$$\Psi_{k,s}(n,t_{j+1}) = \sum_l\left[\sum_m \phi_{l,s}^*(m,t_j)\Psi_{k,s}(m,t_j)\right]$$
$$\times e^{-i\epsilon_l\Delta t/h}\phi_{l,s}(n,t_j), \tag{3}$$

where $\{\phi_l\}$ and $\{\epsilon_l\}$ are the eigenfunctions and the eigenvalues of the electronic part of the Hamiltonian $H(t)$ at a given time t_j.

The lattice equations are written as

$$u_i(t_{j+1}) = u_i(t_j) + \dot{u}_i(t_j)\Delta t \tag{4}$$

$$\dot{u}_i(t_{j+1}) = \dot{u}_i(t_j) + \frac{F(t_j)}{M}\Delta t. \tag{5}$$

Hence, the electronic wave functions and the displacement coordinates at the $j+1$th time step are obtained from the jth time step. Periodic boundary conditions are assumed for the electronic wave functions, $\Psi_{k,s}$, and the lattice displacements, u_i.

The total number of lattice points on the chain in all simulations is $N = 104$, thus allowing the presence of polarons and bipolarons on the chain. The total number of electrons on the chain (N_e) varies from $N_e = 98$ to $N_e = 103$, which means that in the initial condition we may have from a single polaron up to six polarons, and from one to three bipolarons on the chain. All the excitations are hence positively charged. The different results are obtained starting from appropriate initial conditions.

We study the positions of the polarons and bipolarons as a function of time introducing smoothed charge density and bond variable by

$$\bar{\rho}_i = \tfrac{1}{4}(\rho_{i-1} + 2\rho_i + \rho_{i+1}),$$

$$\bar{y}_i = \frac{(-1)^i}{4}(y_{i-1} - 2y_i + y_{i+1}).$$

We determine the polarons and bipolarons positions from $\bar{\rho}_i$ or $\bar{y}_i$ analogously to Ref. 16.

The position is observed at every 1000 time steps. A time step of $\Delta t = 0.004$ femtosecond is used. We follow the dynamics of the systems up to 600 femtoseconds.

III. RESULT OF SIMULATIONS

We have performed simulations systematically varying the doping concentration and the electric field intensity. We consider polymer chains with $N = 104$ sites in all simulations. The hole-doping concentration varies from 0.96% ($N_e = 103$) to 5.76% ($N_e = 98$).

As the initial state in all cases represents a stationary solution, we make the charged excitations start to move through the application of the electric field on the system. The electric field is applied during all the simulation, i.e., the electric field is not switched off. The electric field values varies from $|E| = 0.005E_0$ to $|E| = 0.1E_0$, with $E_0 = \hbar\omega_Q/(ea) = 1.3 \times 10^7$ V/m as the unit.

We calculate the electronic energy, the lattice potential energy, and the lattice kinetic energy along all the simulations.[15] The system total energy (the summation of all the energies) was a well-behaved function that increased as
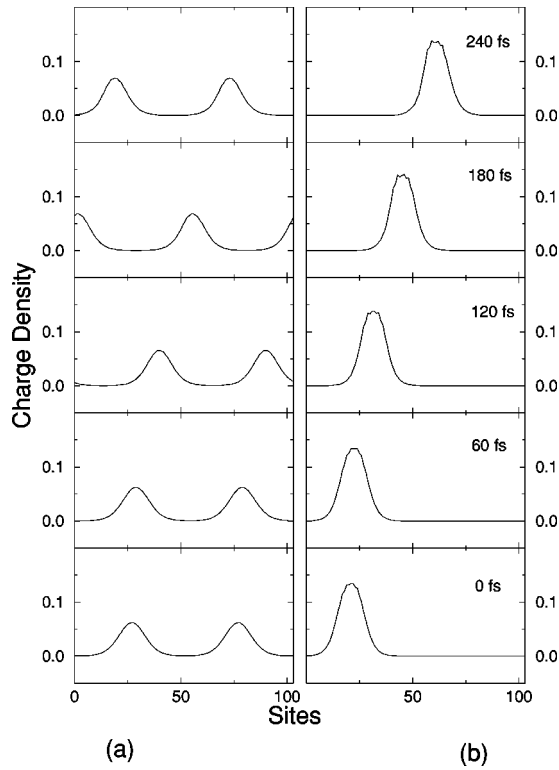
FIG. 1. Snapshots of the time evolution of the charge density. (a) Polaron pair, $|E|=0.005\,E_0$. (b) Bipolaron, $|E|=0.015\,E_0$.

the electric field is applied and that becomes constant if the electric field is switched off.[15,16]

In order to determine the saturation velocity of the excitations we followed the time evolution of single polarons and bipolarons. Figure 1 presents snapshots of their charge den-

Energies (t₀) – Double Polaron X Bipolaron
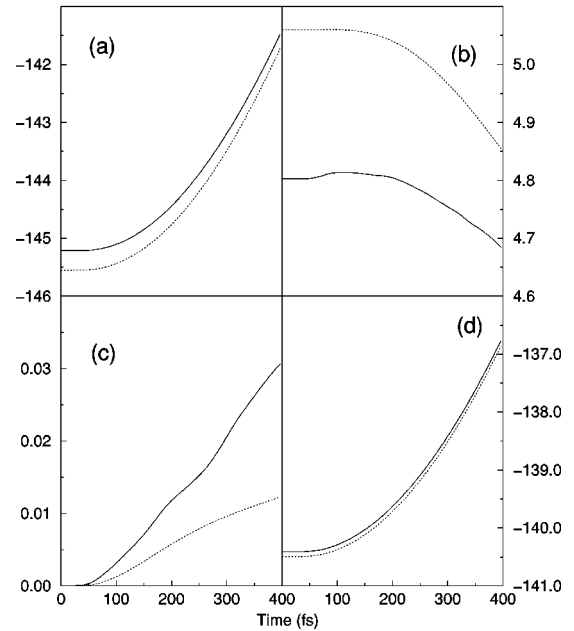
FIG. 3. Time dependence of the energies associated with the polaron pair (solid line) and bipolaron (dotted line). (a) Electronic energy. (b) Lattice potential energy. (c) Lattice kinetic energy. (d) Total energy.

sity time evolution. It is found that the saturation velocity value of polarons and bipolarons are of the same order, Fig. 2. The limiting factor on the velocity increase is the interaction of the moving excitations with lattice vibrations. The
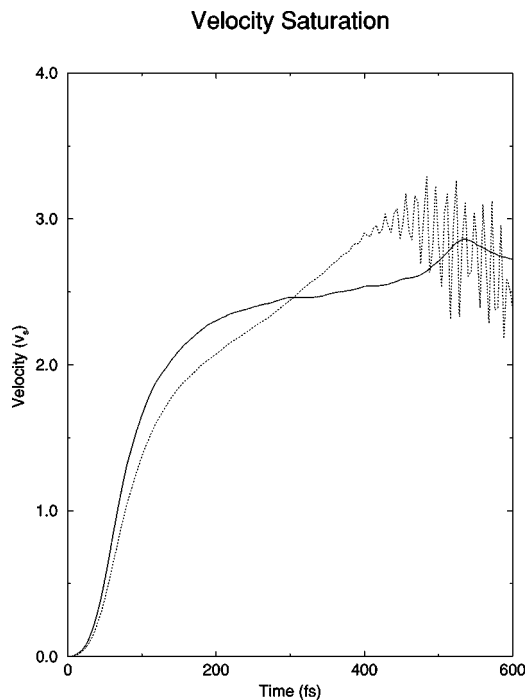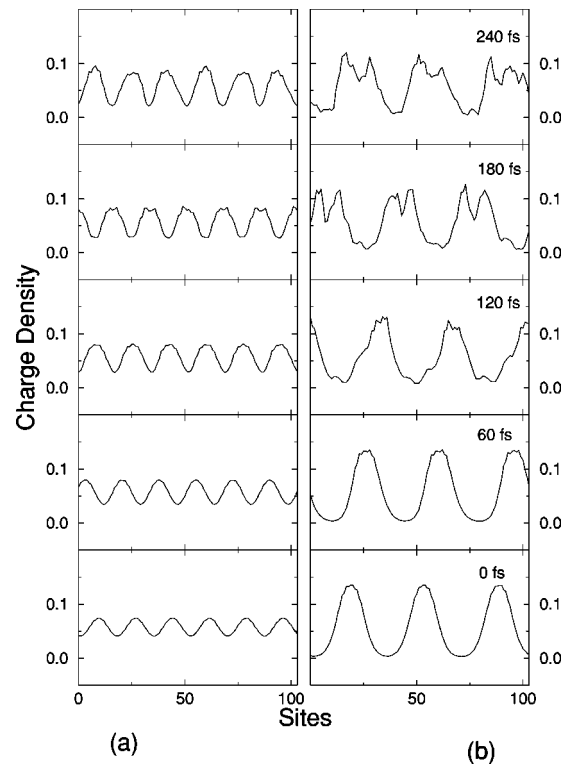
Velocity Saturation

FIG. 2. Time dependence of the polaron velocity (solid line) and bipolaron velocity (dotted line). The velocities are estimated from the spatial distribution of the excess charge.

FIG. 4. Time evolution of the charge density: (a) Polaron lattice, $|E|=0.05\,E_0$. (b) Bipolaron lattice, $|E|=0.1\,E_0$.
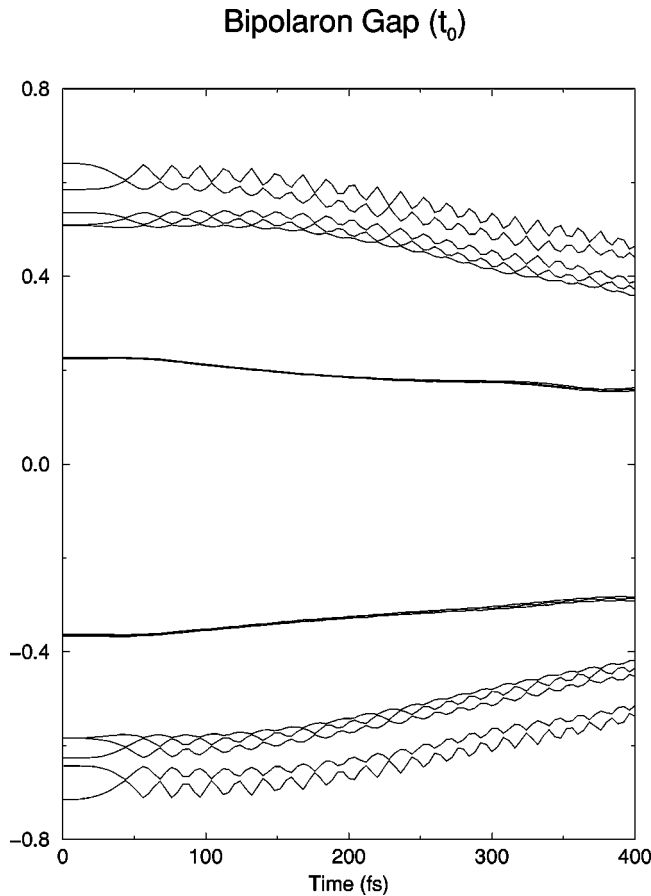
Bipolaron Gap (t$_0$)

FIG. 5. Time dependence of the bipolaron lattice gap. The mid-gap states, five higher energy states of the valence band and five lower energy states of the conduction band are depicted. ($|E| = 0.015\,E_0$).
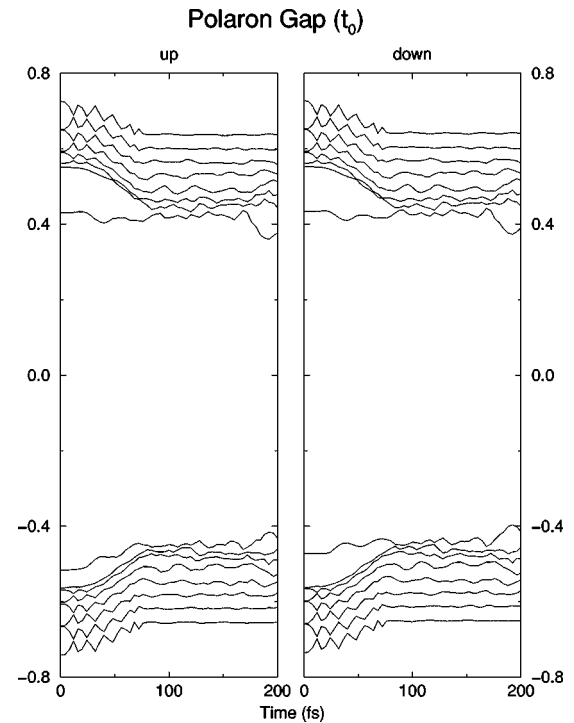
Polaron Gap (t$_0$)

FIG. 6. Vanishing of the single-polaron gap structure under the application of a strong electric field ($|E| = 0.05\,E_0$). Time evolution of thirty two state levels associated with the gap is shown.

lattice potential energy decreases in the relevant time interval [cf. Fig. 3(b)]. Nevertheless, it should be noted that the lattice energy is composed by the lattice potential energy [fourth term of Eq. (1)], the lattice kinetic energy [fifth term of Eq. (1)], and an effective electronic potential energy (the lattice and electronic degrees of freedom are coupled through the hopping term $t_{i,i+1}$). Therefore, the lattice energy effectively increases with the excitation of lattice vibrations.

We obtained that the dynamical effects do not change the polaron-bipolaron relative stability relation. Independently of doping concentration the bipolaron states are more stable with the present model at the initial stationary solution, i.e., the system total energy is smaller for bipolarons rather than polarons. When the electric field is applied the relative values of the total energies do not change, cf. Fig. 3.

With the higher doping concentration (cf. the time dependence of excess charge in Fig. 4), the energy behavior picture does not change compared to the low doping concentration.

Associated with the increase in the energy of the systems under the application of the external electric field a small closing of the gap is present. Figure 5 presents the gap time evolution of the bipolaron systems. The polaron systems show also a completely analogous small shrinking of the gap. The shrinking of the gap is due to the change in the shape of the polarons and bipolarons when they are moving. The dimerization parameter y_n decreases its mean value around the excitation region. The local decreasing in the

dimerization leads to the shrinking of the gap, in accordance with Peierls Theorem.

Finally, it is observed that the polaron and bipolaron excitations are unstable against intense electric fields. Their bond-order structure is completely blurred and their charge spreads out on the chain for electric field intensities above given values. Figure 6 shows the associated changing in the electronic levels of the polaron gap. Nevertheless, the bipolaron is much more stable than the polaron. The single bipolaron critical electric field is about 0.1 E_0 and the critical value for the polaron is $|E|\,0.01E_0$, i.e., they differ by one order of magnitude. The polaron-bipolaron stability against the electric field can be enhanced by increasing the doping concentration. For $N_e = 98$ (Fig. 4), the polaron and bipolaron lattices continued stable with electric field values one order of magnitude greater than the respective single excitation values.

IV. DISCUSSION AND SUMMARY

We have investigated the propagation of charged polarons and bipolarons on a single polymer chain. This study was carried out through numerical calculations using an improved version of the SSH model combined with the PPP model to accomplish an external electric field and a BK-type symmetry-breaking interaction. We have used the electric field to put the charged polarons and bipolarons in motion. The time-dependent unrestricted Hartree-Fock equation and the equation of motion for the time-dependent lattice displacements form a coupled set that was numerically integrated over the time in a self-consistent way.

Initially static charged polarons or bipolarons are accelerated through the application of electric fields. A saturation

velocity of about $3\,v_s$ is found for the two types of excitations. This value is close to the soliton saturation velocity in polyacetylene.[20] The deceleration is though to come from the interaction of the excitations with normal modes of vibration found in the chain.

Our results are certainly dependent on the numerical parameters used for the SSH and PPP models. Changes in these parameters do change the physical parameters of polarons and bipolarons, e.g., their width. Nevertheless, the used values, typical for conjugated polymers, are suitable for the study of the basic properties observed here.[14]

We have found that the polaron and bipolaron structures can be blurred by the application of strong electric fields. Nevertheless, bipolarons can stand electric field intensities about one order of magnitude greater than polarons before loosing their characteristics. The increase of doping concentration enhances the steadiness of the excitation structure and polaron (bipolaron) lattices can endure stronger fields than single excitations. In experiments devised to determine the polaron-bipolaron competition, the direct influence of electric fields on the excitations structure stability should be considered.

In going from the static picture of polaron and bipolaron systems to moving excitations the relative difference on the total energies of these systems do not change of sign. The relatively more stable bipolaron static system[12] continues to be more stable than the polaron system when dynamical effects are taken into account, i.e., when they are moving.

The indication of polaron lattices at high doping concentrations in polyaniline[6] and polythiophene[8] suggests that other effects cooperate with the greater electric field endurance of polaron lattices to determine their preponderance over bipolarons in these systems.

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