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Concentration Effects on Intrachain Polaron Recombination in Conjugated Polymers

Luiz Antonio Ribeiro Junior,[1, a)] Wiliam Ferreira da Cunha,[2, b)] Antonio Luciano de Almeida Fonseca,[2] Ricardo Gargano,[3] and Geraldo Magela e Silva[2]

[1)] *Department of Physics, Chemistry and Biology (IFM), Linköping University, SE-581 83 Linköping, Sweden*

[2)] *Institute of Physics, University of Brasilia, 70.919-970, Brasilia, Brazil*

[3)] *Department of Chemistry and Physics, University of Florida, Quantum Theory Project, Gainesville, Florida, 32611, USA* §

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The influence of different charge carrier concentrations on the recombination dynamics between oppositely charged polarons is numerically investigated using a modified version of the Su-Schrieffer-Heeger (SSH) model that includes an external electric field and electron-electron interactions. Our findings show that the external electric field can play the role of avoiding the formation of excited states (polaron-exciton and neutral excitation) leading the system to a dimerized lattice. Interestingly, depending on a suitable balance between the polaron concentration and the electric field strength, the recombination mechanism can form stable polaron-excitons or neutral excitations. These results may provide guidance to improve the electroluminescence efficiency in Polymer Light Emitting Diodes.

Keywords: Su-Schrieffer-Heeger Model, Recombination, Density, Exciton, Polaron, Conjugated Polymers.

[a)] Electronic mail: luiju@ifm.liu.se

[b)] Electronic mail: wiliam@fis.unb.br

I. INTRODUCTION

Polymeric materials are now the focus of intensive research in order to expand the current knowledge about the science and technology of some optoelectronic devices, such as Polymer Light Emitting Diodes[1] (PLEDs) and Organic Solar Cells[2] (OSCs). By presenting unique traits, these materials are favorable to the development of cheaper and more efficient devices than their inorganic counterparts. In fact, for PLEDs the polaron recombination mechanism forming excited species is recognized as one of the most important physical process to be fully understood in order to improve the electroluminescence yield in organic semiconductors. In this sense, relevant effort has been applied to provide guidelines to the understanding of this mechanism in polymer based materials.[3–12] Nonetheless, a detailed investigation about the impact of the polaronic concentration on the charge recombination process, albeit crucial, has not yet been performed and, therefore, requires further investigations.

Recently, Sun and Stafström used the Su-Schrieffer-Heeger (SSH) model to simulate the recombination process between an oppositely charged polaron pair in two coupled conjugated polymer chains.[13] Their results show that the spin-dependent recombination mechanism can form an exciton or a bound interchain polaron pair depending on the interchain coupling and the external electric field strength. An *et al.*[14] and Li *et al.*[15] have also investigated the polaron recombination mechanism in the scope of a tight-binging approach. In general, their findings show that the external electric field can play an important role on the polaron-exciton formation through the scattering of two oppositely charged polarons. For field strengths smaller than 0.2 mV/Å, the two polarons recombine directly in an neutral excited state. Considering field strengths that lie in the range of 0.2–1.2 mV/Å, the polarons scatter into a pair of two independent particles that are composed by a mixed state of polarons and excitons (polaron-excitons). Li and colleagues also briefly discuss the effect of electron-electron (e–e) interactions in the recombination dynamics between two oppositely charged polarons. They have reported that, for the products, a triplet exciton is much more energetically stable than a singlet one in the presence of on-site repulsions. Lei and collaborators have investigated the spin polarization effect on the formation of excited states via intrachain recombination of a polaron pair in conjugated polymers, using a version of the SSH model modified to include an external electric field and Coulomb interactions.[16] Their results have pointed out that, neglecting e–e interactions, the yield of total excitons is independent of the spin orientation of the polaron pair. Moreover, the presence of e–e interactions shows a depression on the yield of singlet excited states in cases where the spin configuration between the polaron pair is not spin-parallel. As reported by Lei and collaborators, the e–e interaction strength do not changes the content of the products formed from the recombination mechanism between two oppositely charged polarons, with spin-parallel or spin-antiparallel configuration, at all. Thus, in the present work, we can expect that relatively moderated variances in the e–e strength will not change the final products formed after the collision between the polarons. Very recently, our previous researches have shown that impurity levels[17] and temperature effects[18] can change dramatically the recombination dynamics between two oppositely charged polarons. When influenced by impurities, the polaron-exciton formation also occurs for weak electric field strengths. The impurity levels can significantly improve the excitation yield in order to facilitate the polaron-exciton formation. Regarding the temperature influence on the recombination process, the results show that there are two possible channels in which (1) a neutral excitation is directly formed for temperatures bellow a critical regime and (2) a dimerized lattice is the final product of the collisional process for temperatures higher than the critical value.

From the results of all aforementioned researches, one can see that further investigations of the polaron recombination mechanism, mainly considering the impact of the polaron concentration to the excited states formation are strongly desired. We can see that the previous work in the literature usually deal with the interaction of a single pair of quasiparticles. As features such as electron-electron interactions as well as impurities showed a major influence over the final products of the system, one can readily conclude that the effect of different carrier concentrations is also a crucial issue, particularly when it is desired to study the behavior of the system in a more realistic physical situation.

In this manuscript, the impact of the charge carrier concentration on the intrachain recombination dynamics between oppositely charged polarons in conjugated polymers is numerically investigated considering the influence of an external electric field and Coulomb interactions. In the scope of a one-dimensional tight-binding approach, an Ehrenfest Molecular Dynamics is carried out in order to combine the Extended Hubbard Model and a modified version of the SSH model. The present investigation is aimed to provide a more realistic physical picture about the products formed after the recombination process by considering the concentration effects on the formation of excited states, which may provide guidance to improve the internal quantum efficiency in PLDEs.

II. METHODOLOGY

The model Hamiltonian is given by $H = H_{SSH} + H_{ee}$. The first part in this equation is the SSH-type Hamiltonian[19,20] modified to include an external electric field and the Brazovskii-Kirova symmetry-breaking, in order to simulate a conjugated polymer chain with periodic boundary conditions. The SSH hamiltonian assumes the form

$$H_{SSH} = -\sum_{n,s}\left(t_{n,n+1}C^{\dagger}_{n+1,s}C_{n,s} + h.c.\right) + \sum_{n}\frac{K}{2}y_n^2 + \sum_{n}\frac{p_n^2}{2M}, \tag{1}$$

where n labels the chain sites. Here, $y_n \equiv u_{n+1} - u_n$ in which u_n is the lattice displacement of a particular site. p_n is the conjugated momentum to u_n, K is the harmonic constant for a σ bond and M is the mass of a CH group. The operator $C^{\dagger}_{n,s}$ ($C_{n,s}$) creates (annihilates) a π-electron with spin s at the nth site. $t_{n,n+1} = e^{-i\gamma A(t)}\left[(1 + (-1)^n\delta_0)\, t_0 - \alpha y_n\right]$ is the transfer integral, where t_0 is the transfer integral of a π-electron between neighboring sites in the undimerized chain, α is the electron-phonon coupling, and δ_0 is the Brazovskii-Kirova symmetry-breaking term.[21] $\gamma \equiv ea/(\hbar c)$, with a being the lattice parameter, e the absolute value of the electronic charge, and c is the speed of light. The external electric field is introduced in the model through the time-dependent vector potential, in which $\mathbf{E}= -(1/c)\dot{\mathbf{A}}$.[22] The last term in the model Hamiltonian denotes the contribution of the Coulomb interactions and can be written as

$$H_{ee} = U\sum_{i}\left(C^{\dagger}_{i,\uparrow}C_{i,\uparrow} - \frac{1}{2}\right)\left(C^{\dagger}_{i,\downarrow}C_{i,\downarrow} - \frac{1}{2}\right) + V\sum_{i}\left(n_i - 1\right)\left(n_{i+1} - 1\right), \tag{2}$$

where $n_i = C^{\dagger}_{i,\uparrow}C_{i,\uparrow} + C^{\dagger}_{i,\downarrow}C_{i,\downarrow}$ and U and V are the on-site and nearest-neighbor electron-electron repulsion strengths, respectively.[23] The parameters used here are recognized as standard and have the following values: $t_0 = 2.5\ eV$, $M = 1349.14\ eV \times fs^2/\text{Å}^2$, $K = 21\ eV\text{Å}^{-2}$, $\delta_0 = 0.05$, $\alpha = 4.1\ eV\text{Å}^{-1}$, and $a = 1.22$ Å. These values have been used successfully in previous simulations.[24–30]

The lattice backbone dynamics is described in a classical approach by a newtonian equation $M\ddot{u}_n = F_n(t)$. Where,

$$\begin{aligned} F_n(t) = M\ddot{u}_n(t) &= -K\left[2u_n(t) - u_{n+1}(t) - u_{n-1}(t)\right] \\ &\quad + \alpha\left[B_{n,n+1}(t) - B_{n-1,n}(t) + B_{n+1,n}(t) - B_{n,n-1}(t)\right]. \end{aligned} \tag{3}$$

$F_n(t)$ represents the force experienced by a particular site n. Here, $B_{n,n'}(t) = \sum_{k,s}{}'\psi^{*}_{k,s}(n,t)\,\psi_{k,s}(n',t)$ is the term that couples the electronic and lattice parts of the model Hamiltonian.[31] The primed summation represents a sum over occupied states. The equation (3) can be numerically integrated using the method

$$u_n(t_{j+1}) = u_n(t_j) + \dot{u}_n(t_j)\Delta t, \tag{4}$$

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

In its turn, the time evolution of the electronic part is performed by solving the time-dependent Schrödinger equation (TDSE). The wave functions are constructed by means of a linear combination of instantaneous eigenstates of the electronic Hamiltonian. In this way, the solutions of the TDSE can be put in the form

$$\psi_{k,s}\left(n, t_{j+1}\right) = \sum_l \left[\sum_m \phi^*_{l,s}\left(m, t_j\right)\psi_{k,s}\left(m, t_j\right)\right] \times e^{(-i\varepsilon_l \Delta t/\hbar)}\phi_{l,s}\left(n, t_j\right), \tag{6}$$

where $\{\phi_l(n)\}$ and $\{\varepsilon_l\}$ are the eigenfunctions and the eigenvalues of the electronic part for the Hamiltonian at a given time t_j, respectively.[32] At time t_j the wave functions $\{\psi_{k,s}(n, t_j)\}$ are expressed as an expansion of the eigenfunctions $\{\phi_{l,s}\}$: $\psi_{k,s}(n, t_j) = \sum_{l=1}^{N} C^s_{l,k}\phi_{l,s}(n)$, in which $C^s_{l,k}$ are the expansion coefficients. Thus, the occupation number for each eigenstate $\phi_{l,s}$ is $\eta_{l,s}(t_j) = \sum_k{}' |C^s_{l,k}(t_j)|^2$, which provides useful information about the redistribution of electrons among the energy levels.

III. RESULTS AND DISCUSSION

The main focus of the present work is to investigate the combined effects of different charge carrier concentrations and electric field values over the products of polarons scattering. In order to do so, we make use of polymer chain lengths of 200, 400, 600, 800, and 1000 sites, depending on the number of charge carriers initially present. Accordingly, we considered 2, 4, 6, 8, and 10 polarons as the initial state of the system and investigated the dynamics of these quasi-particles subjected to electric field strengths ranging from 0.1 to 2.0 mV/Å with an increment of 0.1 mV/Å. In order to better consider interaction between the quasi-particles we included electron-electron correlation through the extended Hubbard formalism with U = 1.0 eV and V = U/3, in accordance with values recently used in the literature.[33–39]

We begin our discussion by presenting schematic diagrams of the energy levels for the different initial configurations considered in our work. In Figure 1, "H" stands for the Highest Occupied Molecular Orbital (HOMO) level, "H-1" is the level immediately below it and so on. Analogously,

”L” represents the Lowest Unoccupied Molecular Orbital (LUMO) level, “L+1” the next one and so forth. Figures 1(a) to (e) show how 2, 4, 6, 8, and 10 polarons were created in each particular chain by placing the electrons (represented by arrows) in the corresponding levels. The dynamics is carried out through a time evolution starting from the initial state described by Figure 1. In all the cases we simulated initial carriers with opposite charges, so that collisions would take place when the electric field is turned on. From the experimental point of view, it is known that the generation dynamics of polarons from relaxed excited states in conjugated polymers may occurs through two different channels: (1) impurity induced in the absence of an external electric field and (2) electric field induced in a pristine lattice, where the photocarriers are charged polaron pairs created directly.[40] Moreover, it is well accepted that only a small part of the excited states generate free polarons in the absence of the electric field. On the other hand, when the influence of such effect is taken into account, a substantial amount of excitons may relax into polaronic states forming stable charge carriers, which are useful to generate electrical current. Thus, the charge carriers result from the field-induced dissociation of excitons, which are primarily formed by photoexcitations. In our simulations, the initial configuration for the charge carrier mimics

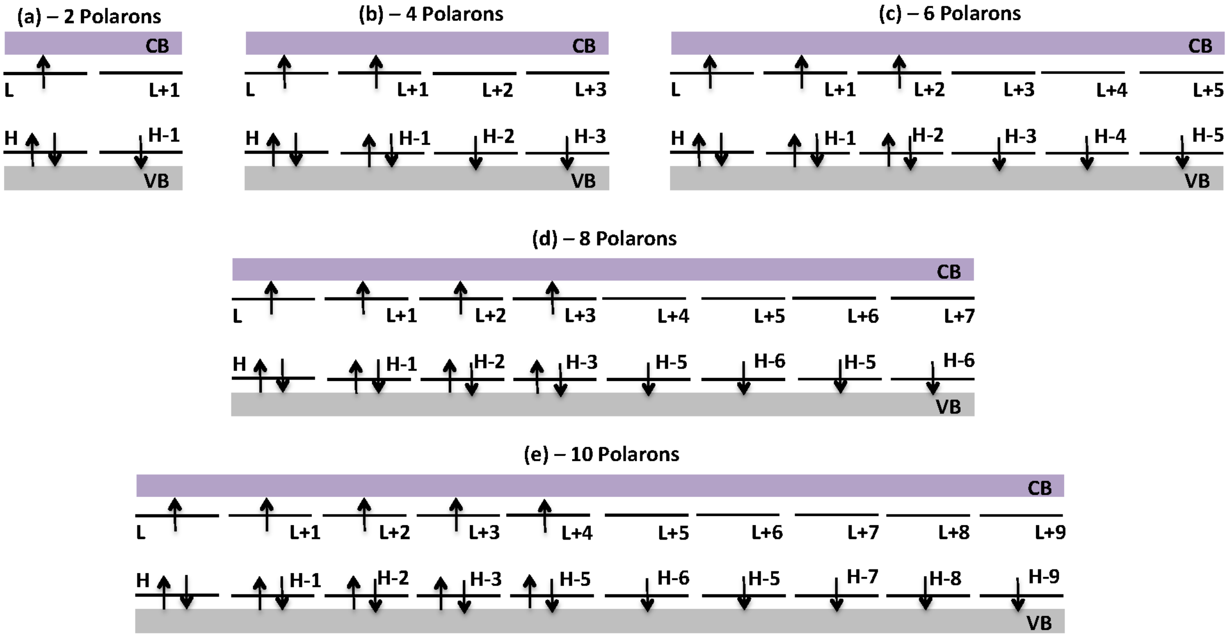

FIG. 1. Schematic representation of the energy levels for systems with different densities: (a) 2 polarons, (b) 4 polarons, (c) 6 polarons, (d) 8 polarons, and (e) 10 polarons. “CB” and “VB” stand for conduction and valence band, respectively.

a photoexcitation mechanism followed by exciton relaxation, in which a substantial ratio of the excited states is converted into polaronic states. In polyacetylene lattices, at a half-filling band, the electronic band gap is approximately 1.8 eV. It was shown that the most probable dipole-allowed transitions are those from ε_i^v to ε_i^c (i=1,2,3,), where ε_i^v and ε_i^c are the ith energy level in valence (from the top) and conduction (from the bottom), respectively. The transition dipole moments between ε_i^v and ε_i^c considering i raging from 1 to 4, for example, are 11.6, 11.1, 10.4, and 9.5 eÅ, and their transition energies are 1.76, 1.78, 1.81, and 1.85 eV, respectively.[29] Thereby, numerical procedure adopted here, to generate the initial configuration, can represent fairly well the photoexcitation mechanics and the subsequent exciton relaxation in order to generate free polarons.

Before we discuss the actual product nature of the polarons scattering, it is interesting to perform a general qualitative discussion on the influence of the carriers concentration to the product formation mechanism. In order to do so, we investigate the 0.5 mV/Å electric field induced dynamics of systems composed of the initial states presented in Figure 1. Figure 2 shows the staggered bond-length time evolution for this field strength, considering all different concentrations from 2 polarons in part (a) up to 10 polarons in part (e). The first feature that the lattice distortion patterns suggest is that the product formed after the collisional process is strictly dependent of the initial polaron concentration. This can be inferred from the different shapes and patterns of the structures that arise from the scattering of the initial quasi-particles. As it will be further discussed, these systems can present very different products even when the same initial carrier concentration is considered. Moreover, as the charge carrier density (N_{QP}/n), in which N_{QP} is the number of quasi-particles and n is the number of sites, is exactly the same, one can conclude that the products formed after the collisional process are concentration dependent instead of density dependent. In this work, the term "concentration" stands for a measure of the number of structures present in each chain, regardless of its length.

It is well known that two acoustic polarons with the same charge and antiparallel spins can recombine to form an acoustic bipolaron. These structures are spinless charge carriers and possess charge ±2e. Bipolaron can be created in organic–based materials when the charge injection or ptohexcitation mechanism result in a large concentration of polarons. Recently, Di *et al.* have investigated the combination and scattering of two polarons with same charges and or antiparallel spin in conjugated polymers in the framework of a tight-binding approach.[7] Their results shown that collisions between polarons with same charge and parallel spin are essentially elastic due

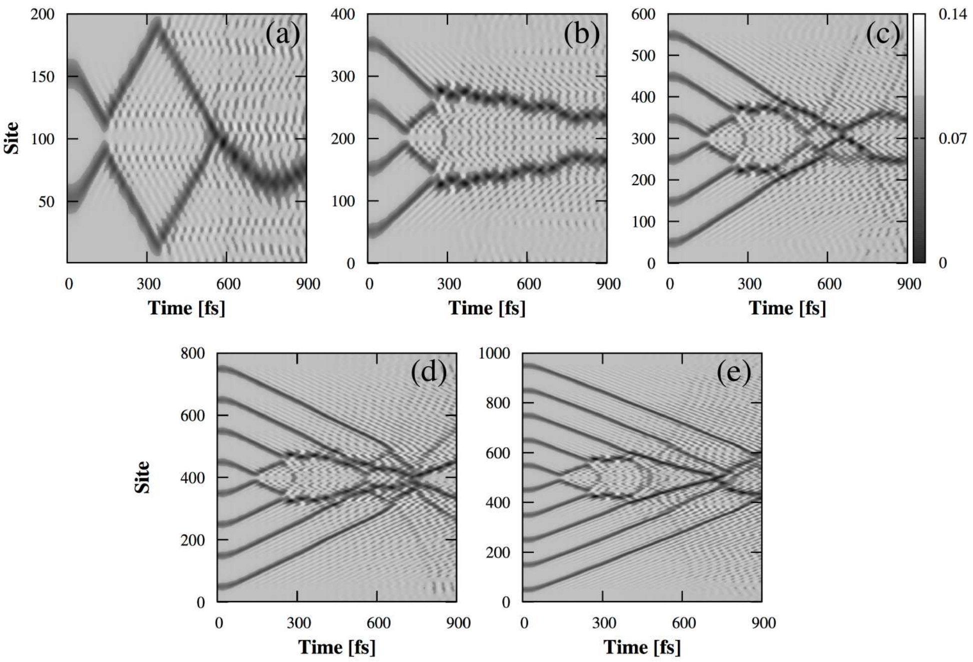

FIG. 2. Staggered bond-length time evolution for an electric field strength of 0.5 mV/Å for all the initial states in Figure 1.

to strong Pauli repulsion, whereas the combination between the polarons with same charge and antiparallel spin generates a singlet bipolaronic state. To enable the bipolaron formation, the charge carriers with same sign should accumulate in a certain region of the lattice. Thus, in the studies performed by Di *et al.*, a conjugated polymer lattice with fixed ends was used in order that the polarons were accumulated at one of the extremities of the polymer. Note that, in our simulations, due to the periodic boundary conditions and concentration of polarons with opposite charge, the accumulation of polarons with same charge in a certain region of the lattice is not favored. Moreover, the polarons with same charge signal has spin parallel configuration (Figure 1), which avoids the recombination between them to form new charged species. Therefore, we cannot expect the formation of bipolarons in the present work.

Figure 3 depicts the time evolution of the mean charge density related to the cases presented in Figure 2, where the figure labels are in connection with the cases just presented. By analyzing the mean charge density profile one can strictly assess the nature of the products. In Figure 3(a), in which two polarons are initially considered, we observe a pair of polaron-excitons arising after the first collision, but a quasi-neutral excited state is also observed as the final state after the second collision. In other words, this quasi-neutral state is the final product of the collision between oppositely charged polaron-excitons, that work as complex products. Figure 3(b) consists on the collision between four polarons, giving rise to neutral excitations and also to polaron-excitons. Note that the first collision between the two inner polarons give rises to a pair of polaron-excitons that subsequently collide with the two remainder outer polarons. After that, the collision between the polarons and the formed polaron-excitons forms two neutral excited states. This means that a recombination process between a charged state and a charged excited state tends to form only one neutral excited state. Interestingly, for the higher concentration regimes, Figures 3(d) and 3(e), mixed final states between polaron-excitons and neutral excitations are achieved. For higher concentrations, one can see that it is difficult to distinguish between the nature of the products, but a general pattern is to observe that collisions under higher concentrations tends to favor the formation of polaron-excitons over neutral excitations. This pattern is confirmed by observing that, whereas in Figure 3(a) the presence of neutral excitations is dominant, when the higher concentration cases of 3(d) and 3(e) are considered, one observes a higher ratio of polaron-excitons to neutral excitons. It should also be noted that the high degree of symmetry observed for small concentrations is lost for systems with higher number of initial carriers, as shown in Figures 3(c) to 3(e). This is mainly due to the higher amount of phonon states that is observed in these situations, and it is in close relation to the observed polarons. It is worth to mention here that the dissipative dynamics of polarons in conjugated polymers can be considered by including a damping term, a feature missing in the present work. Furthermore, the electric field is adiabatically turned on, reaching its full strength at bout 75 fs, and is not turned off in these simulations. Thus, the polaron can not lose its energy, at least before the collision process. Recently, the polaron dissociation in an organic molecule was theoretically investigated in the presence of dissipation.[41] It was shown that the polaron's velocity is inversely proportional to the damping, which means the relation between mobility and temperature is a power law. The damping term can suppresses the step-like behavior of the polaron's velocity regarding to electric fields. Moreover, it was obtained that, in the presence of a dissipative term, the threshold field that dissociates a polaron is reduced. As the main goal in this work is to figure out the possible products formed after the recombination mechanism between several oppositely charged polarons, we should ensure that these charge carriers might keep its integrity until the moment of the collision. So, the polaron dissipation mechanism is avoided in this work.

Another interesting manner to investigate the nature of the final states of the collisional process, as well as its evolution, is the study of its energy levels. It is well known that neutral excitations are

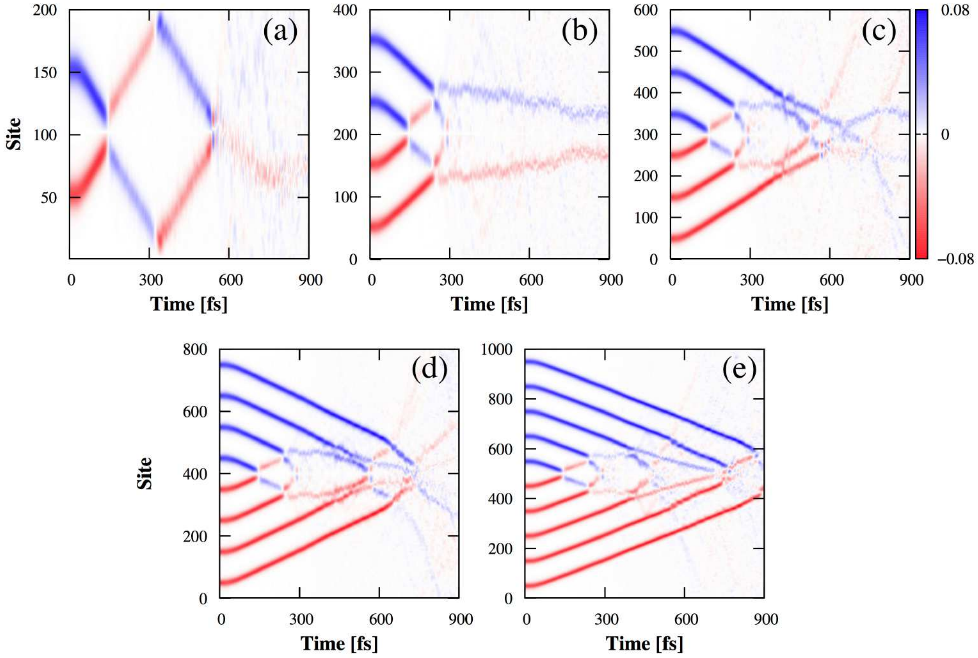

FIG. 3. Mean charge density time evolution for an electric field strength of 0.5 mV/Å for the cases shown in Figure 2.

more stable structures than the charged excitations. As a consequence, the energy levels related to the neutral excitations are positioned deeply inside the band gap, whereas the levels associated to the charged carriers and charged excitations lie in the band gap in regions closer to the valence and conduction bands.[13,17] In this way, Figure 4 confirms the previous discussion on the concentration dependence of the final products of the collision. The several levels inside the gap at the beginning of the simulation is a typical fingerprint of the presence of polarons. In this figure, the difference in creation time of the final structures is quite clear. Also, it is easily noted the presence of the neutral excitations for Figure 4(a) and both the neutral excitation and the polaron-exciton in Figure 4(b). For the other concentrations, the mixture between neutral excitation and polaron-exciton states is strongly presented by the entanglement of the energy levels in the final part of the simulation. However, the dominant presence of states near the conduction and valence band inside the energy gap is an indication that, for systems of higher densities, the polaron-exciton formation is stimulated.

After discussing the results of different products depending on the concentration of charge carriers, we now turn our attention to a particular collision between three negative and three positive polarons subjected to an electric field strength of 0.6 mV/Å in a 600 sites polymer chain. Figure

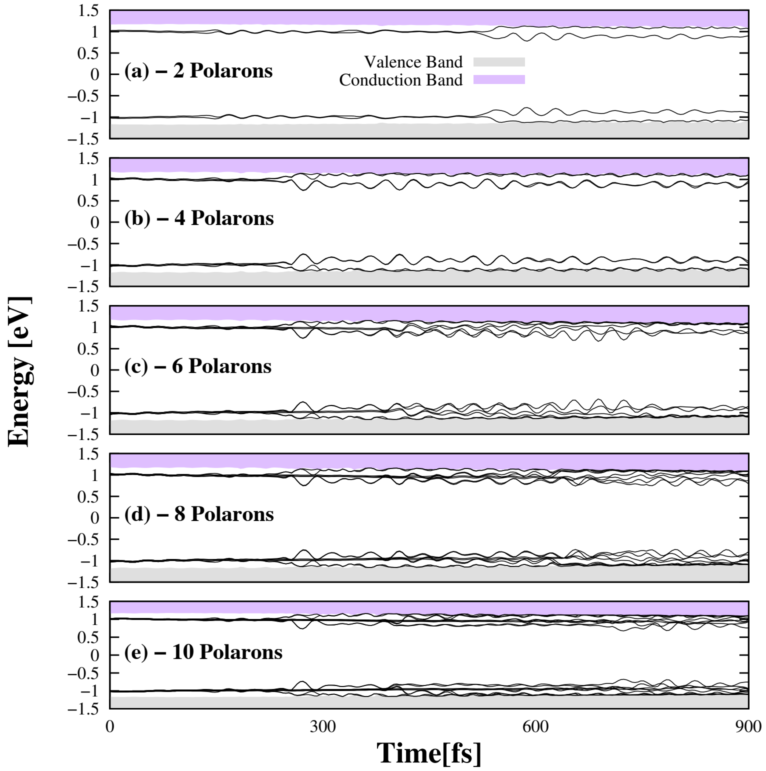

FIG. 4. Energy levels time evolution for the systems showed in Figure 2.

5(a) presents the bond-length and Figure 5(b) depicts the mean charge density time evolution of the system. Apart from the higher electric field applied, this situation is analogous to the simulation presented in Figure 2(c) and, nevertheless, one can see that the formed products are quite different. After several mutual collisions, the final state is composed of a polaron-exciton and neutral excitation states. This behavior is completely different to the results presented in Figure 3(c), in which the final state is dominated by neutral excitations. Therefore, one should conclude that, similar to higher concentrations, higher electric field values also plays the role of shifting the equilibrium towards the formation of more polaron-excitons rather than excitons.

Figure 6 presents the time evolution of the (a) HOMO and (b) LUMO levels relative to the systems presented in Figure 2. A quick glimpse to the figures allows one to observe the complementarity of the occupations between HOMO and LUMO levels. In other words, each HOMO level gains whatever fraction of electrons lost by the corresponding LUMO and vice versa. After around 150 fs of simulation, Figure 6(a) shows that the electron begins to leave HOMO towards other energy levels. A similar pattern is observed for the LUMO in Figure 6(b). As a general rule, it can be said that the simulations with higher concentrations present the lowest occupation

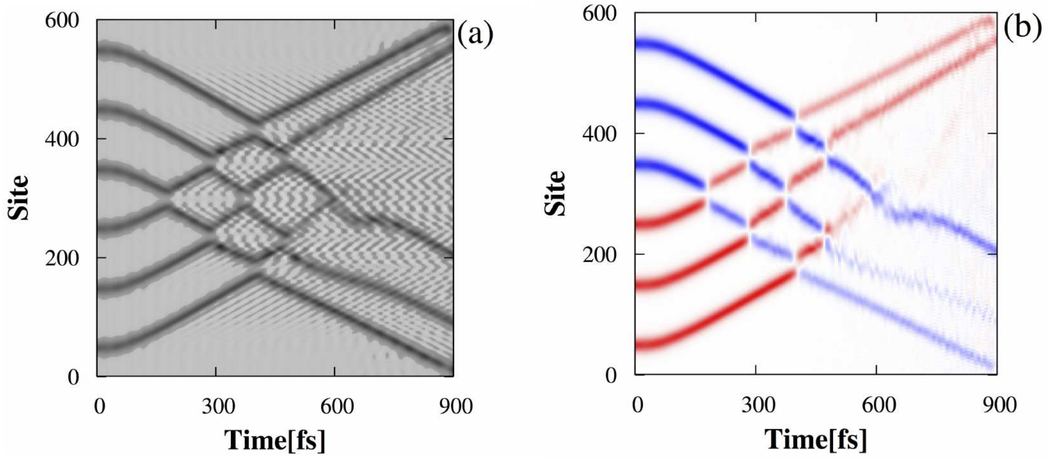

FIG. 5. (a) Staggered bond-length and (b) Mean charge density time evolution for an electric field strength of 0.6 mV/Å of a polymer chain in the presence of three polaron-pairs.

of LUMO and the highest occupation of HOMO. This is directly connected to the higher concentration of polaron-exciton that result from these collisional processes. As an practical example, if one follows the line correspondent to the initial 10 polarons case, it is clear that although the LUMO presents a relative small occupation, it is emptied in a slower pace when compared to cases with smaller concentrations. This happens because the large number of carriers causes a rather complex succession of collisions that yields a final stable state at a longer time. It is worth to mention here some important aspects regarding the final electronic occupation for the energy levels and the energy of the phonons after the collision process. In the relevant work performed by Sun and Stafström,[42] it was shown that the charge distribution in higher levels inside the conduction band is mostly due to the energy excess of the electron, provided by the energy level offset, in the exciton dissociation mechanism developed by them, *i. e.*, the charge may occupy the LUMO+8 even in the absence of an external electric field. Note that, for the results reported in present manuscript, there is no exciton dissociation mechanism, instead, a recombination mechanism between oppositely charge carriers, which may conduct to the formation of excited states. Considering now the energy released in the collision process and the subsequent generation of phonons, studies performed by An. *et al.* shown that, for electric field strengths higher than 1.2 mV/Å, the two oppositely charged polarons will break into irregular lattice vibrations after their collision. At the same time, the electron/hole localized in the lattice defects become free charges, where the electron and hole move for different sides of the lattice driven by the electric field. In this case, no neutral excitation is formed (as can be inferred from the results presented in Figure

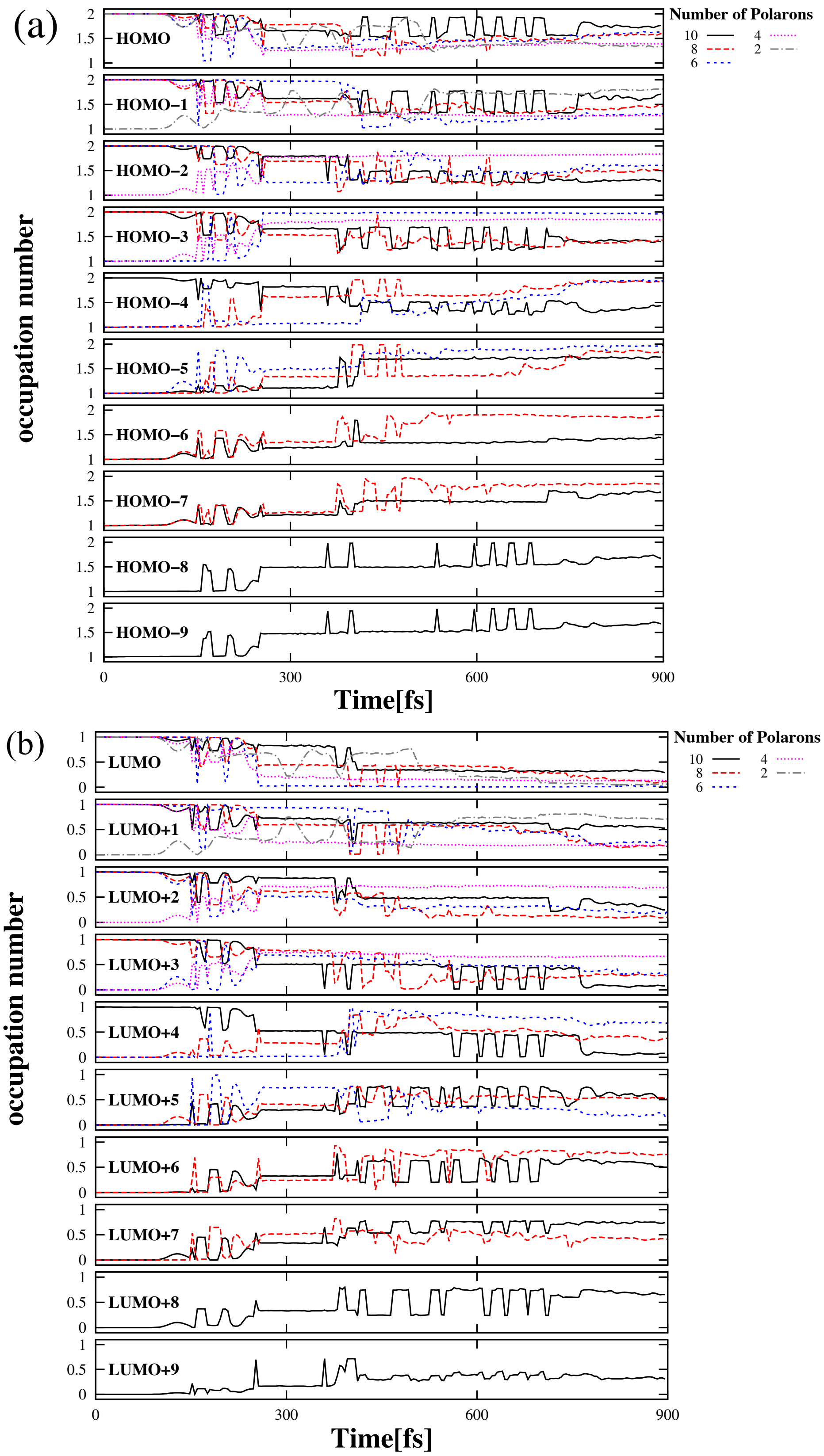

FIG. 6. Time evolution of (a) HOMO and (b) LUMO levels of the initial states presented in Figure 2.

5).

We finish our discussion by presenting the most important result of this work in Figure 7, which is an extension of the analysis performed in the previous figures for other values of electric field strengths. Figure 7(a) presents the sum of all the LUMO levels in the gap as a function of the applied electric field for all the simulated concentrations. Figure 7(b) is the equivalent figure for HOMO. Thus, Figure 7 consists of an useful tool to summarize our results besides providing new important results concerning the electric field dependence of the collision products. The first interesting feature of Figure 7 regards the definition of a critical electric field value of 1.0 mV/Å, above which, for all the simulated systems, a pristine lattice is obtained as the final state of the system. One can see that, for all values of electric fields greater than 1.0 mV/Å, all the LUMO levels are back to HOMO position, thus resulting in a lattice free of defects. In other words, for electric fields higher than this critical value, no exciton nor polaron-excitons are present as the final state of the system. This is a consequence of the high energy that these electric field strengths impose to the system. The amount of energy is enough to dimerize the chain, thus yielding the neutral final state. As already discussed, for electric field strengths between 0 and 1.0 mV/Å, a mixed final state between excitons and polaron-excitons is achieved. The relation between HOMO and LUMO also allows one to confirm the aforementioned hypothesis that with higher the concentrations, more polaron-excitons are formed compared to neutral excitations. This can be confirmed by the evaluation of total HOMO/LUMO ratio which shows that intermediate occupation are dominant for higher concentrations. This, again, is in accordance to the polaron-exciton presence picture. Therefore, the neutral excitation to polaron-exciton ratio depends directly on the final quantity of electrons in the LUMO (in relation to HOMO). This dependence, is observed to be a function of the initial charge carrier concentration. In the works by An *et al.*[14] and Lie *et al.*[16] the yield of the possible products formed from the recombination process between two oppositely charged polarons has been reported. An and coworkers have shown that the yield of the neutral excitation firstly increases with the electric field strength, reaching its maximum value (~47%) for 0.6 mV/.[14] For field strengths higher than this critical value, the yield for the neutral exciton decreases reaching (~35%) for 1.0 mV/Å. Lei and collaborators have reported that the total yield of excitons can reach at most 33.5% for an electric field strength of 0.5 mV/, which indicates that it is not a complete annihilation of the polaron pair.[16] Moreover, their results shown that, for a collision of spin antiparallel polarons, the yield of singlet excitons reaches the maximum. In such case, the yields of singlet and triplet excitons are the same, and each is about 16.75%. Just for the sake of information, very recently our previous research has shown that the presence of the temperature effects may increase the yield of neutral excitations to about 95%, considering a temperature regime ranging from 50 to 160 K for field a strength of 1.5 mV/Å.[18] These results give to us a good insight about the products formed after the recombination dynamics between a polaron pair for different concentrations of charge carriers. We can conclude that, for electric field strengths smaller than 0.6 mV/Å, the content of the products formed after the collision process is dominated by neutral excitations or quasi-neutral excitations. On the other hand, for electric field strengths ranging from 0.6 to 1.2 mV/Å, the content of the products is dominated by polaron-excitons. It is not difficult to conclude that for field strengths higher than 1.2 mV/Å, the yield for the ground state reaches its maximum value (~100%), once that all the electrons have returned to the valence band, as shown in Figure 7.

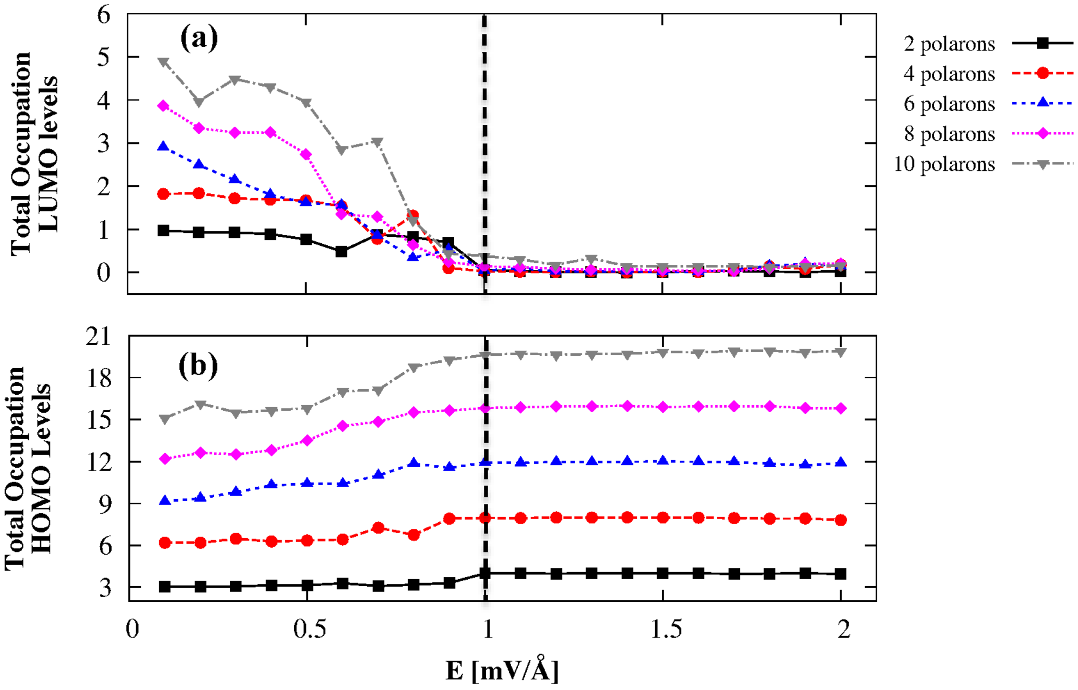

FIG. 7. Occupation numbers for the LUMO (a) and HOMO (b) levels for all the configurations of Figure 6 with different electric field strengths.

IV. CONCLUSIONS

In this work we investigated the influence of different charge carrier concentrations and electric field strengths on the recombination dynamics between oppositely charged polarons. We were able to determine different regimes in which polaron-excitons or neutral excitations were mainly formed from the collisional process of different numbers of polarons. These regimes were observed to be dependent on both the electric field strength and on the concentration of the initial charge carriers. Moreover, it was found that, the higher the concentration of charge carriers the more probable it is to the collisional process to yield polaron-excitons rather than excitons. Furthermore, higher values of electric field also favor the formation of polaron-excitons until the critical value of 1.0 mV/Å, above which a dimerized chain is achieved. As actual electronic devices present high concentration of charge carriers, this study is of fundamental importance to the understanding of the particular conditions in which the desired kind of quasi-particle is to be formed. Therefore this kind of knowledge is important to improve the performance of organic photovoltaic devices such as Polymer Light Emitting Diodes.

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REFERENCES

[1] Y.-H. Kim, T.-H. Han, H. Cho, S.-Y. Min, C.-L. Lee, and T.-W. Lee, "Polyethylene imine as an ideal interlayer for highly efficient inverted polymer light-emitting diodes," Adv. Func. Mat. **24**, 3808–3814 (2014).

[2] K. Vandewal, S. Albrecht, E. T. Hoke, K. R. Graham, J. Widmer, J. D. Douglas, M. Schubert, W. R. Mateker, J. T. Bloking, G. F. Burkhard, A. Sellinger, J. M. J. Frchet, A. Amassian, M. K. Riede, M. D. McGehee, D. Neher, and A. Salleo, "Efficient charge generation by relaxed charge-transfer states at organic interfaces," Nat. Mat. **13**, 63–68 (2014).

[3] Z. Sun, D. Liu, S. Stafström, and Z. An, "Scattering process between polaron and exciton in conjugated polymers," J. Chem. Phys. **134**, 044906–5 (2011).

[4] Z. Sun, Y. Li, K. Gao, D. S. Liu, Z. An, and S. J. Xie, "Dynamical study of polaron–bipolaron scattering in conjugated polymers," Org. Elec. **11**, 279–284 (2010).

[5] L. A. Ribeiro, P. H. O. Neto, W. F. da Cunha, L. F. Roncaratti, R. Gargano, D. A. da Silva Filho, and G. M. e Silva, "Exciton dissociation and charge carrier recombination processes in organic semiconductors," J. Chem. Phys. **135**, 224901–224906 (2011).

[6] L. A. Ribeiro, W. F. da Cunha, P. H. O. Neto, R. Gargano, and G. M. e Silva, "Dynamical study of impurity effects on bipolaron-bipolaron and bipolaron-polaron scattering in conjugated polymers," J. Phys. Chem. B. **117**, 11801–11811 (2013).

[7] B. Di, Y. Meng, Y. D. Wang, X. J. Liu, and Z. An, "Formation and evolution dynamics of bipolarons in conjugated polymers," J. Chem. Phys. B. **115**, 964–971 (2011).

[8] Y. Meng, B. Di, X. J. Liu, Z. An, and C. Q. Wu, "Interchain coupling effects on dynamics of photoexcitations in conjugated polymers," J. Chem. Phys. **128**, 184903–7 (2008).

[9] Y. Meng, X. J. Liu, B. Di, and Z. An, "Recombination of polaron and exciton in conjugated polymers," J. Chem. Phys. **131**, 244502–7 (2009).

[10] L. A. R. Junior, W. F. da Cunha, and G. M. e Silva, "Temperature effects on the scattering of polarons and bipolarons on organic conductors," J. Phys. Chem. A. **118** (2014), 10.1021/jp505590g.

[11] L. A. R. Junior, W. F. da Cunha, and G. M. e Silva, "Temperature effects on intrachain recombination of bipolarons in conjugated polymers," Chem. Phys. Lett. **614**, 151–155 (2014).

[12] W. F. da Cunha, L. A. R. Junior, A. L. de Almeida Fonseca, R. Gargano, and G. M. e Silva, "Reactive scattering between excitons and charge carriers in conjugated polymers," J. Phys. Chem. C. **118**, 23451?23458 (2014).

[13] Z. Sun and S. Stafström, "Spin-dependent polaron recombination in conjugated polymers," J. Chem. Phys. **136**, 244901–5 (2012).

[14] Z. An, B. Di, and C. Q. Wu, "Inelastic scattering of oppositely charged polarons in conjugated polymers," Eur. Phys. J. B. **63**, 71–77 (2008).

[15] Y. Li, K. Gao, Z. Sun, S. Yin, D.-S. Liu, and S.-J. Xie, "Intrachain polaron motion and geminate combination in donor-acceptor copolymers: Effects of level offset and interfacial coupling," Phys. Rev. B. **78**, 014304–13 (2008).

[16] J. Lei, Z. Sun, Y. Zhang, and S. Xie, "Effect of spin polarization on exciton formation in conjugated polymers," Org. Elec. **10**, 1489–1494 (2011).

[17] L. A. Ribeiro, W. F. da Cunha, P. H. O. Neto, R. Gargano, and G. M. e Silva, "Impurity effects on polaron–exciton formation in conjugated polymers," J. Chem. Phys. **139**, 174903–6 (2013).

[18] W. F. da Cunha, L. A. R. Junior, R. Gargano, and G. M. e Silva, "Critical temperature and products of intrachain polaron recombination in conjugated polymers," Phys. Chem. Chem. Phys. **16**,

17072–17080 (2014).

[19] W. P. Su, J. R. Schrieffer, and A. J. Heeger, "Solitons in polyacetylene," Phys. Rev. Lett. **42**, 1698–1701 (1979).

[20] W. P. Su, J. R. Schrieffer, and A. J. Heeger, "Solitons excitations in polyeacetylene," Phys. Rev. B. **22**, 2099–2111 (1980).

[21] S. Brazovskii and N. Kirova, "Physical theory of excitons in conducting polymers," Chem. Soc. Rev. **39**, 2453–2465 (2010).

[22] S. Stafström, "Electron localization and the transition from adiabatic to nonadiabatic charge transport in organic conductors," Chem. Soc. Rev. **39**, 2484–2499 (2010).

[23] Z. G. Yu, M. W. Wu, X. S. Rao, and A. R. Bishop, "Excitons in two coupled conjugated polymer chains," J. Phys. Condes. Matter **8**, 8847–8857 (1996).

[24] L. A. Ribeiro, W. F. da Cunha, P. H. O. Neto, R. Gargano, and G. M. e Silva, "Impurity effects and temperature influence on the exciton dissociation dynamics in conjugated polymers," Chem. Phys. Lett. **580**, 108–114 (2013).

[25] L. A. Ribeiro, W. F. da Cunha, P. H. O. Neto, R. Gargano, and G. M. e Silva, "Effects of temperature and electric field induced phase transitions on the dynamics of polarons and bipolarons," New J. Chem. **37**, 2829–2836 (2013).

[26] L. A. Ribeiro, W. F. da Cunha, P. H. O. Neto, and G. M. e Silva, "Dynamics of photogenerated polaron–excitons in organic semiconductors," Phys. Proc. **28**, 112–116 (2012).

[27] A. Johansson and S. Stafström, "Polaron dynamics in a system of coupled conjugated polymer chains," Phys. Rev. Lett. **86**, 3602–3605 (2001).

[28] A. Johansson and S. Stafström, "Nonadiabatic simulations of polaron dynamics," Phys. Rev. B. **69**, 235205–7 (2004).

[29] Z. An, C. Q. Wu, and X. Sun, "Dynamics of photogenerated polarons in conjugated polymers," Phys. Rev. Lett. **93**, 216407–4 (2004).

[30] L. A. Ribeiro, W. F. da Cunha, P. H. O. Neto, R. Gargano, and G. M. e Silva, "Predicting the equilibrium structure of organic semiconductors with genetic algorithms," Chem. Phys. Lett. **555**, 168–172 (2013).

[31] G. M. e Silva, "Electric–field effects on the competition between polarons and bipolarons in conjugated polymers," Phys. Rev. B. **61**, 10777–10781 (2000).

[32] M. P. Lima and G. M. e Silva, "Dynamical evolution of polaron to bipolaron in conjugated polymers," Phys. Rev. B. **74**, 224303–6 (2006).

[33] H. Zhao, Y.-G. Chen, X.-M. Zhang, Z. An, and C.-Q. Wu, "Correlation effects on the dynamics of bipolarons in nondegenerate conjugated polymers," J. Chem. Phys. **130**, 234908–5 (2009).

[34] Y. Meng, B. Di, X. J. Liu, Z. An, and C. Q. Wu, "Effects of e–e interactions on the dynamics of polarons in conjugated polymers," Eur. Phys. Lett. **79**, 17002–5 (2007).

[35] H. Ma and U. Schollwöck, "Dynamical simulations of charged soliton transport in conjugated polymers with the inclusion of electron–electron interactions," J. Chem. Phys. **129**, 244705–10 (2008).

[36] H. Ma and U. Schollwöck, "Effect of electron–electron interactions on the charge carrier transitions in trans-polyacetylene," J. Phys. Chem. A. **114**, 5439–5444 (2010).

[37] H. Ma and U. Schollwöck, "Dynamical simulations of polaron transport in conjugated polymers with the inclusion of electron–electron interactions," J. Phys. Chem. A. **113**, 1360–1367 (2009).

[38] Y. L. Zhang, X. J. Liu, Z. Sun, and Z. An, "Dynamics of exciton transfer in coupled polymer chains," J. Chem. Phys. **138**, 174906–6 (2013).

[39] Y. L. Zhang, X. J. Liu, Z. Sun, and Z. An, "Temperature effects on the dynamics of photoexcitations in conjugated polymers," J. Phys. Chem. C. **118**, 2963–2969 (2014).

[40] D. Moses, H. Okumoto, C. H. Lee, A. J. Heeger, T. Ohnishi, and T. Noguchi, "Mechanism of carrier generation in poly(phenylene vinylene): Transient photoconductivity and photoluminescence at high electric fields," Phys. Rev. B **54**, 4748–4754 (1996).

[41] Y. Yao, Y. Qiu, and C. Q. Wu, "Dissipative dynamics of charged polarons in organic molecules," J. Phys. Condens. Matter **23**, 305401 (2011).

[42] Z. Sun and S. Stafstöm, "Dynamics of exciton dissociation in donor-acceptor polymer heterojunctions," J. Chem. Phys. **138**, 164905–8 (2013).