Inelastic scattering of oppositely charged polarons in conjugated polymers

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Abstract. Within an one-dimensional tight-binding model, we investigate the inelastic scattering processes of oppositely charged polarons in conjugated polymers under the influence of an external electric field, by using a nonadiabatic evolution method. It is found that the polaron pair does not necessarily scatter into an entity(neutral exciton), but a mixed state composed of both polarons and excitons. The yield of the neutral exciton depends sensitively on the strength of applied fields. Additionally, effects of interchain coupling on the scattering processes are also discussed, which shows that the interchain coupling is of fundamental importance and facilitates the formation of the polaron-exciton.

PACS. 71.35.Aa Frenkel excitons and self-trapped excitons – 71.38.Ht Self-trapped or small polarons – 72.20.Jv Charge carriers: generation, recombination, lifetime, and trapping

1 Introduction

There have been considerable amounts of research works devoted to the study of nonlinear elementary excitations in conjugated polymers [1]. The motivation behind these works stems from the fact that these excitations play an important role in organic optoelectronic devices based on conjugated polymers, including light-emitting diodes, field-effect transistors, photocells and lasers [2].

In contrast to the conventional semiconductor, the conjugated polymer as a quasi-one-dimensional material has a novel property that its lattice structure can be distorted easily to form self-trapped elementary excitations by either charge injections or photoexcitations, such as soliton [3], polaron [4], and neutral polaron-exciton [5], due to strong electron-lattice interactions. In light-emitting diodes, it has been generally accepted that injected charge (electron and/or hole) from the metal electrodes deforms the polymer chain to form a polaron, the polaron as charge carrier transports under the influence of an external electric field [6–13]. Furthermore, when a positively charged polaron meets a negatively charged one, they will collide and recombine to form a polaron-exciton state, in which the electron and the hole are bounded in a self-trapped lattice deformation. The photon emission results from the radiative decay of the polaron-excitons. Therefore, the scattering process of oppositely charged polarons and the quantum yield of neutral excitons are believed to be of

fundamental importance for polymer based light-emitting diodes.

There have been extensive studies on the formation of excitons in polymer based light-emitting diodes [14–25]. Most of these works have devoted to understanding the generation mechanism of singlet and triplet excitons and their branch ratio since Cao et al. [14] reported a value of 50% for the ratio of quantum efficiencies of electroluminescence (EL) with respect to photoluminescence (PL) in a substituted PPV-based LED, which is much greater than the statistical limitation 25%. Despite many advances, many issues of great importance for the understanding and the improvement of polymer based devices, such as the dependence of exciton yield on applied electric fields, the interchain coupling effects on the formation of excitons, etc., remain unresolved. In this paper, we will focus on the dynamical formation of self-trapped excitons resulting from the inelastic collision of oppositely charged polarons in a single polymer chain and/or coupling chains.

Both the motion of polaron and the recombination of oppositely charged polaron pair are dynamic process accompanied by both charge and lattice distortion, thus, a real-time dynamical model revealing both charge motion and lattice evolution will be appropriate in order to investigate the formation of excitons in OLED's. Our previous work on the dynamics of photoexcitations in conjugated polymers also shows that the dynamic characteristics are essentially important to understand the physical phenomena in organic optoelectronic devices [6].

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The Su-Shrieffer-Heeger(SSH) model [26,27] and its extended versions have been predominantly used and have performed much progress in describing both the static electronic structure and dynamic properties of the elementary excitations in polymers. A great deal of effort has been devoted to the dynamics of a single polaron under the influence of external electric fields in the framework of the SSH model [6–13]. It has been known that the polaron moves as one entity consisting of both the charge and the lattice deformation with a constant velocity after being accelerated for a short time. A breather-like lattice oscillation is developed behind the polaron, which bears the increased energy due to the electric field acting on the polaron [8,9]. Furthermore, Stafström et al. examined the charge accompanying polaron defect transfers from one chain to another chain, and found that the polaron migration strongly depends on the strength of the electric field [13]. However, the collision of two oppositely charged polarons has attracted less attention in literatures.

In this paper, we will present the numerical results on the formation of the neutral polaron-exciton under the influence of an external electric field. Two cases have been considered here. First, the inelastic scattering of a pair of oppositely charged polarons initially presented on the same polymer chain is investigated. Then, the collision process is considered when the positively charged polaron lies on one of two coupling polymer chains and the negatively charged polaron lies on another chain. In our simulations, the lattice is described classically while the electrons are treated by solving the time-dependent Schrödinger equation where the transitions between instantaneous eigenstates are allowed. It should be stressed that the nonadiabatic effects are of crucial importance to describe the dynamic process of polaron in polymers [6–8].

2 Model and method

Our starting point is the Hamiltonian

$$H = H_0 + H_{ext} \qquad (1)$$

where

$$H_0 = -\sum_n t_n \left(c_n^\dagger c_{n+1} + c_{n+1}^\dagger c_n \right)$$
$$+ \frac{K}{2} \sum_n (u_{n+1} - u_n)^2 + \frac{M}{2} \sum_n \dot{u}_n^2, \qquad (2)$$

is the standard Su-Schrieffer-Heeger (SSH) model [26,27]. Here, $t_n = t_0 - \alpha(u_{n+1} - u_n)$ with t_0 being the transfer integral of π-electrons in a regular lattice, α the electron-lattice coupling constant, and u_n the lattice displacement of the nth site from its equidistant position. The operator $c_n^\dagger(c_n)$ creates (annihilates) a π-electron at the n-th site; K is the elastic constant due to the σ bonds, and M is the mass of a CH group.

The second term in equation (1)

$$H_{ext} = |e| \sum_n (na + u_n) \left(c_n^\dagger c_n - 1 \right) E(t) \qquad (3)$$

is the contribution from the applied field $E(t)$, where e is the electron charge, and a the lattice constant. In order to avoid the abrupt perturbation induced by the external field, we increase smoothly the field strength from 0 to E_0 according to a Gaussian function with a width $t_w = 25$ fs before $t_c = 75$ fs, and then keep the constant E_0,

$$E(t) = \begin{cases} E_0 \exp\left[-(t - T_c)^2/T_w^2\right], & t < t_c \\ E_0, & t \geq t_c. \end{cases} \qquad (4)$$

Initially, the polymer chain contains a hole polaron at the left side and an electron polaron at the right side. The initial bond configuration and the electronic structure can be obtained by solving the following self-consistent equations of the bond configuration $\{u_n\}$ and the electronic wave functions $\{\phi_\mu(n)\}$:

$$\varepsilon_\mu \phi_\mu(n) = -[t_0 - \alpha(u_{n+1} - u_n)]\phi_\mu(n+1)$$
$$- [t_0 - \alpha(u_n - u_{n-1})]\phi_\mu(n-1) \qquad (5)$$

$$u_{n+1} - u_n = -\frac{2\alpha}{K} \sum_\mu^{occ.} \phi_\mu(n)\phi_\mu(n+1)$$
$$+ \frac{2\alpha}{NK} \sum_{\mu,n}^{occ.} \phi_\mu(n)\phi_\mu(n+1), \qquad (6)$$

where ε_μ is the eigenvalue of μ-th energy level.

Once the initial lattice configuration $\{u_n\}$ and the electron distribution $\{\phi_\mu(n)\}$ are determined, the temporal evolution of the lattice configuration is determined by the equation of motion for the atom displacements

$$M \ddot{u}_n = -K(2u_n - u_{n+1} - u_{n-1})$$
$$+ 2\alpha[\rho_{n,n+1}(t) - \rho_{n,n-1}(t)]$$
$$+ |e|E(t)[\rho_{n,n}(t) - 1], \qquad (7)$$

where the density matrix ρ is defined as

$$\rho_{n,n'}(t) = \sum_k \Phi_{n,k}(t) f_k \Phi_{n',k}^*(t). \qquad (8)$$

The quantity f_k is the time-independent distribution function and is determined by the initial electron occupation, the electronic wave functions $\Phi_{n,k}(t)$ are the solutions of the time-dependent Schrödinger equation

$$i\hbar\dot{\Phi}_{n,k}(t) = -[t_0 - \alpha(u_{n+1} - u_n)]\Phi_{n+1,k}(t)$$
$$- [t_0 - \alpha(u_n - u_{n-1})]\Phi_{n-1,k}(t)$$
$$+ |e|E(t)(na + u_n)\Phi_{n,k}(t). \qquad (9)$$

The coupled differential equations (7) and (9) are solved with a Runge-Kutta method of order 8 with step-size control [28], which has been examined in photoexcitation dynamics [6] and polaron dynamics [7,8] of polymer chains. The parameters in the calculation are chosen as those for trans-polyacetylene [26]: $t_0 = 2.5$ eV, $\alpha = 4.1$ eV/Å, $K = 21$ eV/Å^2, $M = 1349.14$ eV fs^2/Å^2, and the lattice constant $a = 1.22$ Å. The fixed ends boundary condition has to be used because the applied electric field breaks the translational symmetry. The results are the same as that obtained by using open chain boundary condition keeping the chain length fixed.
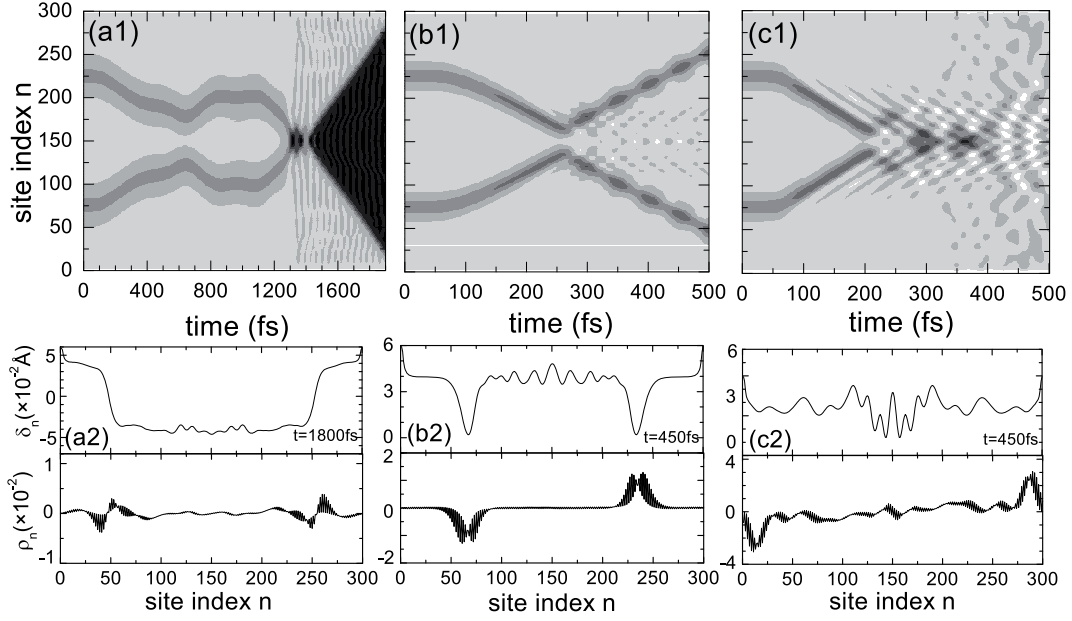
Fig. 1. Evolution of the staggered bond order parameter δ_n with time (upper row), and the staggered order parameter δ_n and the charge distribution ρ_n at a time after the scattering (lower row) for different electric field strengths: $E_0 = 0.1$ mV/Å (left column); $E_0 = 0.5$ mV/Å (middle column); and $E_0 = 2.0$ mV/Å (right column).

3 Results and discussions

3.1 The scattering of charged polarons in an isolated single polymer chain

Firstly, we describe the scattering processes of a pair of oppositely charged polarons initially presented in a single polymer chain. In our simulations, a polymer chain with total 300 sites is used, which is long enough to contain two independent polarons and to eliminate the chain-end effects. Before the applied electric field turns on, a hole injected from the anode induces a hole polaron at the 75th site of the chain while an electron injected from the cathode is self-trapped to form an electron polaron at the 225th site. The two polarons are separated far enough so that they are independent each other.

When the electric field (its direction is from the left to the right) turns on, The hole polaron at the left and the electron polaron at the right come close to each other and then collide driven by the applied electric field. Before their collision, the motion for both the electron polaron and the hole polaron is the same as that reported in references [9,13], that is, the polaron moves as one entity consisting of both charge and lattice defect with a constant velocity for a field strength less than about 4 mV/Å , above which the polaron will dissociate. The staggered order parameter, $\delta_n \equiv (-1)^n (2u_n - u_{n+1} - u_{n-1})/4$, at different electric strength, are depicted in Figure 1, in which, the medium gray regions represent perfect dimerization($\delta_n \sim$ 0.04 Å), and the darker gray regions indicate the center of the polaron(before collision) and/or exciton (after collision) ($\delta_n \sim 0.01$ Å), and the black regions show another perfectly dimerized phase($\delta_n \sim -0.04$ Å). One can find the velocities of the polaron before collision are about

0.15 Å/fs, 0.37 Å/fs and 0.5 Å/fs for 0.1 mV/Å, 0.5 mV/Å and 2.0 mV/Å, respectively, which are consistent with the results obtained in the single polaron case [9,13].

The collision occurs when the distance between the two polarons is less than about $60a$. The collisions of the polarons are different for the charge and the lattice deformation. For field strengths less than about 1.2 mV/Å, the polaron lattice deformations move close and then return back at the distance about $40a$, however, the charge transfer occurs between the two polarons, and they cancel each other when the two polaron lattice defects stay close. When the polaron lattice defect returns back, the charge localized in the lattice defect depends on the field strength. We identify basically three regions of the electric field strength.

(1) At a weak field ($E_0 < 0.2$ mV/Å), such as 0.1 mV/Å , the polaron has a smaller velocity before collision, see Figure 1(a1). The velocity of the two polarons decreases when they come close to each other at about 400 fs, because the potential energy increases due to the lattice interactions between the two polarons. They even need some waiting time to gain enough energy for further motion. Therefore, the two polarons can not move much close, and their wave functions have a less overlap. In turn, the charge transfer between them depends on the overlap of their wave functions and the time they stay close. As a result, only the amount of charge localized in the polarons is decreased, their signs are not changed when they rebound from each other. Thus, the two particles cannot separate far away due to the presence of external electric field. Then they come closer again driven by the external electric field, and finally they merge into an entity (polaron-exciton). The polaron-exciton is not stable in $trans$-polyacetylene because of the degenerated
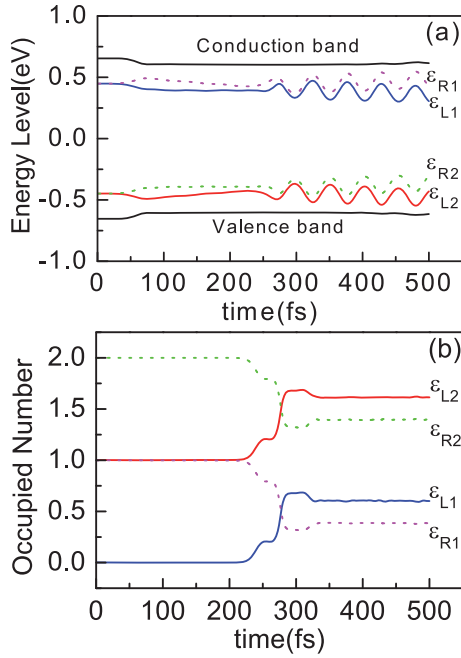
Fig. 2. Evolutions of the localized electronic energy levels (a) and their occupied numbers (b) with time. The electric field strength $E_0 = 0.5$ mV/Å.

ground states, which will be further dissociated as a pair of solitons, just like that found in the photoexcitation process [29]. It should be stressed that the polaron-exciton keeps stable due to the confinement effect in the polymers with nondegenerated ground state.

(2) At a mediate electric field ($0.2 < E_0 < 1.2$ mV/Å), the oppositely charged polarons will scatter into a pair of independent particles and each of them is a mix of polaron and exciton state. As an example, Figure 1(b1) shows the propagation of lattice deformation under an electric field of 0.5 mV/Å . One can find that the polarons start to move after about 75 fs due to the electric field, then keep a constant velocity about 0.37 Å/fs before collision. At about 260 fs, the two polarons reach their shortest distance, after that they return back. Different from the motion before collision, the amplitude of the lattice defects is found to exhibit an oscillation with a period about 40 fs. As pointed in the study on the width oscillation of moving soliton [30], this indicates that new phonon modes have been created in the collision process. In contrast to the case in weak field, not only does the amount of charge localized in the lattice deformations decrease, but also their signs have been changed after collision, as can be seen in Figure 1(b2). This can be easily understood as that the two polaron can move much more close than that in the weak field case, because they possess a faster velocity, i.e., higher kinetic energy before their collision. Therefore, their wave functions have a larger overlap, which makes charge transfer more easily. The separated two particles (including both electronic characteristic and lattice deformation) can go far and far away under the external electric field.

The electronic characteristics of the two new particles are reflected in the eigen energy levels and their occupied

numbers. The evolutions of the eigen levels and their occupied number with time are plotted in Figure 2. From Figure 2a, one can find that there are four energy levels in the energy gap, which are localized electronic states corresponding to the two lattice defects. We denote $\varepsilon_{L1}(\varepsilon_{R1})$ and $\varepsilon_{L2}(\varepsilon_{R2})$ to the upper level and the lower level corresponding to the defect at the left(right) side, respectively. At the start moment, the ε_{L1} and ε_{R1} (ε_{L2} and ε_{R2}) are degenerate, because the two polarons are far enough initially. As the time increases, the degeneration is broken both by the electric field due to the Stark effect ($\varepsilon_{L1}(\varepsilon_{L2})$ goes downwards and $\varepsilon_{R1}(\varepsilon_{R2})$ upwards), and by the coupling of the two polarons when they come close. After the collision, these energy levels also oscillate with time, corresponding to the amplitude oscillation of the lattice deformations. For the distributional functions, see Figure 2b, in the initial state, the energy levels in valence band are doubly occupied except that ε_{L2} is singly occupied, while the energy levels in conduction band are empty except that ε_{R1} is singly occupied. This indicates that a hole polaron is located at the left side of the chain and an electron polaron at the right side. The occupied numbers do not almost vary with time until the two polaron come into contact. The occupied numbers on ε_{R1} and ε_{R2} decrease while those on ε_{L1} and ε_{L2} increase in the collision process. They keep constant (~ 1.6 on ε_{L2}, and ~ 1.4 on ε_{R2}, while ~ 0.6 on ε_{L1} and ~ 0.4 on ε_{R1}) again when the two particles separate far enough.

Now, let's analyze the products after the scattering of the oppositely charged polarons. As indicated above, the two defects are independent each other because they are separated far enough, so we can obtain their eigenstates $\{\chi_L\}$ (for the left particle) and $\{\chi_R\}$ (for the right particle), separately. Then, we project the evolutional wavefunctions $\Phi_{n,k}(t)$ into these eigenstates to determine their species. We find that such a structure with two separated localized deformations in one polymer chain is a mixture of four possible states, which are shown in Figure 3 (only the gap states, $\varepsilon_{L1}, \varepsilon_{L2}, \varepsilon_{R1}$ and ε_{R2}, are shown). The oppositely charged polaron pair is indicated in Figure 3a and 3b, while the cases 3c and 3d contain a neutral polaron-exciton. The yield of exciton at different electric field strengths are depicted in Figure 4. One can find that the yield of the neutral exciton firstly increases with the external electric field strength, reaches its maximum value at about $E_0 = 0.6$ mV/Å, then decreases as the external electric field becomes larger. This indicates that the formation of the neutral exciton depends sensitively on the applied electric field. Furthermore, it should been pointed out that there are small amount of electron occupying on the higher levels after the collision, which results from the transitions between instantaneous eigenstates. They should be related to the phonon excitations which may be important in the scattering process.

We have also calculated the kinetic energy ($E_k \equiv \frac{1}{2} M \sum_n \dot{u}_n^2$), potential energy ($E_p$) which includes the electronic, lattice potential and electric field energies in every moment, and total energy ($E_T \equiv E_k + E_p$). We have subtracted its initial value from each energy to show only
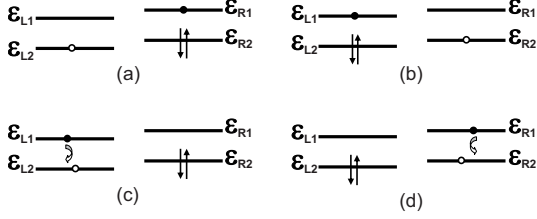
Fig. 3. The resultant states of the polaron scattering. (a) and (b) are still a pair of charged polarons, and (c) and (d) contain a polaron-exciton, respectively.
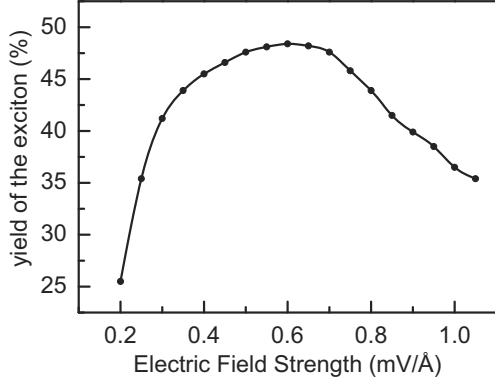

Fig. 4. Yield of the polaron-exciton vs. the strength of applied electric fields.

Fig. 5. Variation of the energy of the system, total energy (dash-dot line), the kinetic energy (dash line), and the potential energy (solid line), with time in the case of $E_0 = 0.5$ mV/Å.

No neutral excitation is found in this case. This indicates that it is unfavorable for the self-trapped exciton to be formed in the stronger electric field strength.

3.2 The scattering of charged polarons in two coupled polymer chains

In the above section, the scattering processes of oppositely charged polarons in an isolated single polymer chain have been discussed. The interchain interactions are completely ignored. In fact, although the interchain interactions between the polymer chains are weak in comparison with the intrachain interactions, it maybe play an important role in the recombination of oppositely charged polarons, as suggested in many previous works [19,20,31]. In this section, we will discuss the scattering processes of a pair of oppositely charged polarons in two coupled polymer chains, in order to investigate the interchain coupling effects. We will focus on the cases for the moderate electric field strengths, which are typical for polymer LED's.

In order to describe the two coupled polymer chains, we consider the interchain coupling Hamiltonain as [32,33],

$$H_{int} = -\sum_n [t_1 - (-1)^n t_2] \left(c_{1,n}^\dagger c_{2,n} + h.c. \right), \qquad (10)$$

where $t_1(t_2)$ denotes to the strength of the interchain interactions. Then, the initial lattice configurations, the electronic structures, and their dynamical evolution with time are treated by using the same method introduced in Section 2.

In the recombination of polarons in two coupled polymer chains, there are two cases need to be considered. One is that the two polarons lie initially on the same polymer chain, and the other case is that the two polarons lie initially on the different chains. For the former case, the two polymer chains are arranged as: one chain is composed of 400 CH-units labelled 1–400 (chain 1), while the other chain (chain 2) consist of 200 sites labelled 401–600, which is coupled with the middle part of chain 1, i.e., the 401th to the 600th sites are coupled with the 101th to the 300th

the change in energy, and have shown them in Figure 5. In the first 75 fs, the polarons move hardly, so the kinetic energy increases a little, while the potential energy, as well as the total energy increase with increasing the electric field strength. After the field keeps constant, the total energy does not change any longer, i.e. the energy conservation. With the polarons move close, the potential energy decreases while their kinetic energy increases. However, when they come into contact, the potential energy increases, and the kinetic energy decreases. The velocities of polarons become zero, and the kinetic energy gets to minimum when the two polarons stay most close. They have not enough kinetic energy to overcome the potential barrier, so that the two polarons do not form an entity. After the lattice deformations rebound each other, because the charge signs has changed, the potential energy oscillationally decreases.

(3) At a stronger electric field ($E_0 > 1.2$ mV/Å), the two oppositely charged polarons will break into irregular lattice vibrations after their collision. For example, the evolution of lattice order parameter with time is shown in Figure 1c, $E_0 = 2.0$ mV/Å. One can find that the two polarons can reach a higher velocity, about 0.5 Å/fs, i.e., much more kinetic energy before their collision. At about 200 fs (260 fs in the case of $E_0 = 0.5$ mV/Å), the two polarons reach their closest contact. After that, the two polarons dissociate, namely, the localized lattice deformations break into irregular lattice vibrations, at the same time, the electron/hole localized in the lattice defects become the free charge (the hole moves to the right side and the electron to the left side driven by the electric field).
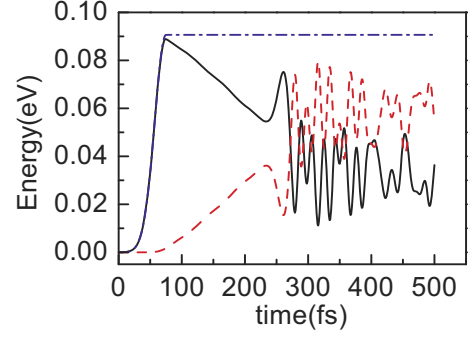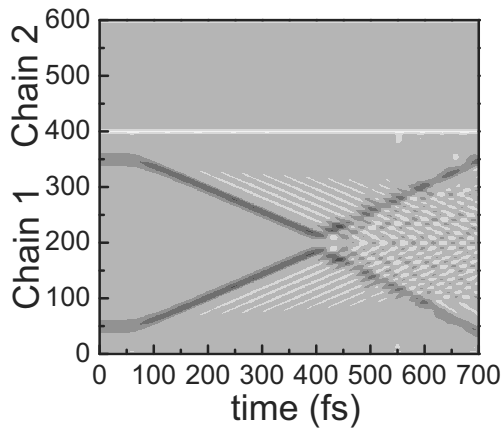
Fig. 6. Evolution of the staggered bond order parameter δ_n with time in the electric field $E_0 = 0.5$ mV/Å, when the two polarons lie initially on one of the two coupled polymer chains.
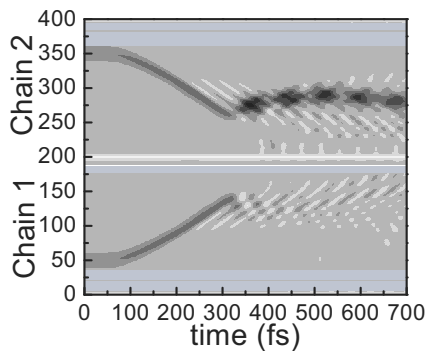

Fig. 7. Evolution of the staggered bond order parameter δ_n with time in the electric field $E_0 = 0.5$ mV/Å, when the two polarons lie initially on the different polymer chains.

sites, respectively. At the same time, there is a hole polaron at the 50th site, and an electron polaron at the 350th site of chain 1. As an example, the evolution of the lattice order parameter with time in the moderate electric field strength $E_0 = 0.5$ mV/Å, when the two polarons lie initially on the same polymer chain ($t_1 = 0.1$ eV and $t_2 = 0.15$ eV), is shown in Figure 6. When the polarons enter into the coupling area, their velocities increase slightly, but the collisional process of the two oppositely charged polarons is the same as that in the isolated single polymer chain case, as if the second chain do not exist at all. This means that interchain coupling effect on the inelastic scattering of oppositely charged polarons is not important in this case. In contrast to the static case [31], where the charge transfer occurs between the two coupled polymer chains, the electron and hole localized in the lattice defects can not transfer from one chain to the other. The reason is that the polarons are continuously moving along the polymer chain driven by the external electric field, before the charge transfer (accompanying by the lattice distortion) occurs, the electron (or hole) localized in the polaron has moved to the next sites along the chain, so that the charge has no chance to transfer from one chain to the other one.

Then, we discuss the inelastic scattering process of oppositely charged polarons which lie initially on the different chains. The two polymer chains are arranged as: each of them is composed of 200 CH-units (chain 1 is labelled 1–200, and chain 2 labelled 201–400), and they are placed beside each other and overlapping by 100 sites, i.e., the 101th to the 200th sites are coupled with the 201th to the 300th sites, respectively. Initially, there is a hole-polaron at the 50th site of chain 1, and an electron-polaron at the 350th site of chain 2. For an example, the evolution of the staggered bond parameter with time for this case ($E_0 = 0.5$ mV/Å, $t_1 = 0.1$ eV and $t_2 = 0.15$ eV) is shown in Figure 7. In contrast to the scattering processes of the two polarons on one chain, the two polarons combine together to become a lattice deformation in one of the two polymer chains, where the electron and the hole are bounded together, i.e., a self-trapped polaron-exciton, when they come close to each other. This recombination process is of importance for the formation of the neutral exciton, since it shows a higher quantum yield of exciton in comparison with that obtained in the scattering process of the oppositely charged polarons on one chain. Furthermore, it should be pointed out that a small amount of charge is excited into the higher energy levels in the recombination process.

4 Summary

In conclusion, we have simulated the inelastic scattering processes of a pair of oppositely charged polarons in a single polymer chain and two coupled polymer chains, in order to identify the generation mechanism of the self-trapped polaron-exciton, by using a nonadiabatic dynamical method. Our results show that it is a complicated dynamical process which depends on the electron-lattice interactions, the interchain interactions, and the applied electric field strength. For the scattering processes of the two polarons initially presented on a same polymer chain, we identify basically three regions of the applied electric field strength: (1) at a weak field strength, they finally scatter into an exciton state after a long and complicated process; (2) at a mediate electric field strength, the oppositely charged polarons scatter into a pair of independent particles and each of them is a mix of polarons and excitons. The yield of the neutral exciton depends sensitively on the the electric field strength; (3) at a stronger electric field strength, the two polarons break into irregular lattice vibrations after their collision. In contrast to the above case, the two polarons will combine together to form a self-trapped exciton in one of the two coupled polymer chains when they lie initially on the different polymer chains. Our results indicate that the interchain interaction is of fundamental importance and facilitates the formation of the polaron-exciton.

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