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Scattering processes between bipolaron and exciton in conjugated polymers

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The scattering processes between a bipolaron and an exciton in a conjugated polymer chain are investigated by numerical simulations based on the model extended with an external electric field of Su *et al.* It is found that there are two channels for these scattering processes. In one channel, the exciton is annihilated and the bipolaron dissociates into a polaron and an excited polaron. In the other channel, the bipolaron and the exciton are converted into each other. Furthermore, the probabilities for these two channels are calculated, and we found that they depend sensitively on the strength of the electric field. Our results show that the interactions of bipolaron-exciton open a channel to enhance the quantum efficiency of electroluminescence due to radiative decay of the excited polaron.

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Since electroluminescence from poly(p-phenylene vinylene) (PPV) was first reported in 1990,[1] research in the use of conjugated polymers as the active semiconductors in light-emitting diodes (LEDs) has advanced rapidly.[2] Conjugated polymers are chains of carbon atoms and have itinerant electrons in the backbones. Many research works have suggested that conjugated polymers support quasiparticles with inner structures which have novel physics properties, such as charged excitations (singly charged as a polaron and doubly charged as a bipolaron) and neutral excitons (spin singlet or triplet), which imply that they have rich intrachain dynamics.[3,4] Many unusual properties of conjugated polymers have been considered to be associated with these excitations. The interactions among these excitations, such as polaron recombination, (bi)polaron-exciton interaction, and exciton-exciton annihilation, are of fundamental importance in understanding the properties of this class of materials.

Bipolaron, like polaron, is also a type of self-localized excitation, which can be formed from two like-charged polarons. A number of experimental and theoretical works have shown the existence of bipolaron especially in doped polymers.[5–7] Bipolarons might also be created in organic LEDs where injection results in a large concentration of polarons.[8,9] Therefore, it is interesting and necessary to investigate the collision and recombination between bipolarons and excitons.

Polarons can efficiently quench excitons, which is commonly observed in conjugated polymers.[10–14] Such quenching consequently reduces the electroluminescence quantum yield of LEDs. However, to date, much less is known about the bipolaron-exciton interaction. Moreover, the products for bipolaron-exciton interaction remain controversial. By calculating the depths of the intragap states and binding energies of a variety of nonlinear excitations in PPV and poly(diacetylene), Choi and Rice[15] suggested that the bipolaron-exciton interaction process leads to the creation of an excited polaron, a free carrier, and an exothermic energy. Swanson *et al.*[9] conjectured that the products of the bipolaron-exciton interaction are a bipolaron and phonons. Basically, all the results obtained by them are based on conjectures.

In this Rapid Communication, we present results from a numerical study of the dynamics of a bipolaron-exciton interaction in a polymer chain under the influence of an external electric field. The electron wave function is described by the time-dependent Schrödinger equation in which the transition between instantaneous eigenstates is allowed, while the polymer lattice is treated classically by a Newtonian equation of motion.

The material studied in this work is chosen for PPV, which is the first candidate for preparing a LED.[1] The results are expected to be qualitatively valid for other conjugated polymers. For the calculations we use an extended Su-Schrieffer-Heeger (SSH) model plus an electric field that is introduced through the vector potential A appearing in a complex phase factor in the transfer integral.[16] The Hamiltonian is given by

$$H = -\sum_{n,s} t_{n,n+1}\left(e^{i\gamma A} c^{\dagger}_{n,s} c_{n+1,s} + e^{-i\gamma A} c^{\dagger}_{n+1,s} c_{n,s}\right) + \frac{1}{2}K\sum_{n} (u_{n+1}-u_n)^2 + \frac{1}{2}M\sum_{n} \dot{u}_n^2, \tag{1}$$

where $t_{n,n+1}$ is the transfer integral. For a PPV molecule, by a renormalization treatment, $t_{n,n+1}$ can be written as[17]

$$t_{n,n+1} = t_0 - \alpha(u_{n+1}-u_n) - t_1 \, cos \, n\pi + t_2 \, cos\left(\frac{n+1}{3}\pi\right)\delta\left(\frac{n+1}{3},\mathrm{int}\right), \tag{2}$$

with $\delta(\frac{n+1}{3},\mathrm{int})=1$, if $\frac{n+1}{3}=\mathrm{int}$, and $\delta(\frac{n+1}{3},\mathrm{int})=0$, if $\frac{n+1}{3} \neq \mathrm{int}$. Here, "int" indicates an integer. t_0 is the transfer

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integral of π electrons in a regular lattice, t_1 and t_2 are the renormalized parameter, α is the electron-lattice coupling constant, and u_n is the lattice displacement of the nth site from its equidistant position. Operator $c^\dagger_{n,s}(c_{n,s})$ creates (annihilates) a π electron with spin s at the nth site. Vector potential $A(t)$ is introduced to describe a uniform external electric field along the chain at the periodic boundary condition; the relation between potential A and uniform electric field E is given by $E=-(1/c)\partial A/\partial t$, where $\gamma \equiv ea/\hbar c$ is a constant quantity, c is the light speed, e is the absolute value of the electronic charge, and a is the lattice constant. K is the elastic constant due to the σ bonds, and M is the mass of a CH group. For a PPV molecule, we set the parameters as $t_0=2.66$ eV, $t_1=0.02$ eV, $t_2=-0.2$ eV, $\alpha=10.29$ eV/Å, $a=1.22$ Å, $K=99.0$ eV/Å^2, and $M=1349.14$ eV fs^2/Å^2.

The evolution of the lattice configuration is determined by the equation of motion,

$$M\ddot{u}_n = F_n(t), \tag{3}$$

where

$$F_n(t) = -K(2u_n - u_{n+1} - u_{n-1}) + 2\alpha(\rho_{n,n+1} - \rho_{n,n-1}). \tag{4}$$

Here $\rho_{n,n'}(t) \equiv \Sigma_k \psi_k(n,t) f_k \psi^*_k(n',t)$. f_k is the time-independent distribution function determined by the initial electron occupation. Evolutional electronic wave function $\psi_k(n,t)$ is the solution to the time-dependent Schrödinger equation,

$$i\hbar\dot{\psi}_k(n,t) = -t_{n,n+1}e^{-i\gamma A}\psi_k(n+1,t) - t_{n-1,n}e^{i\gamma A}\psi_k(n-1,t). \tag{5}$$

Coupled differential Eqs. (3) and (5) could be numerically solved by discretizing the time with an interval $\Delta t=0.01$ fs which is chosen to be sufficiently small so that the change in the Hamiltonian during that interval may be negligibly small.

It is well known that removing or adding two electrons to conjugated polymers creates lattice distortion in the form of bipolarons.[4,18] Following the similar process of forming bipolaron, when an electron originally occupying the highest occupied molecular orbit (HOMO) is excited to the lowest unoccupied molecular orbit (LUMO), a neutral self-trapped exciton is formed. The formation of the bipolaron or exciton state not only induces lattice distortion but also lets the HOMO and LUMO enter the original energy gap and become the localized deep levels.[4]

In our simulations, a 200-site chain is considered, which is long enough to contain two independent excitations. Before the applied electric field turns on, a neutral exciton is located at the 60th site while a negatively charged bipolaron is located at the 155th site. They are well enough separated to ensure they are noninteracting at the beginning. Starting from the initial conditions, the scattering processes between them driven by the external electric field are investigated.

For the convenience of discussion, we introduce bond-structure parameter $r_n(t)$ and mean charge density $\bar{\rho}_n(t)$ as

$$r_n(t) = (-1)^n \frac{u_{n-1}(t) + u_{n+1}(t) - 2u_n(t)}{4},$$

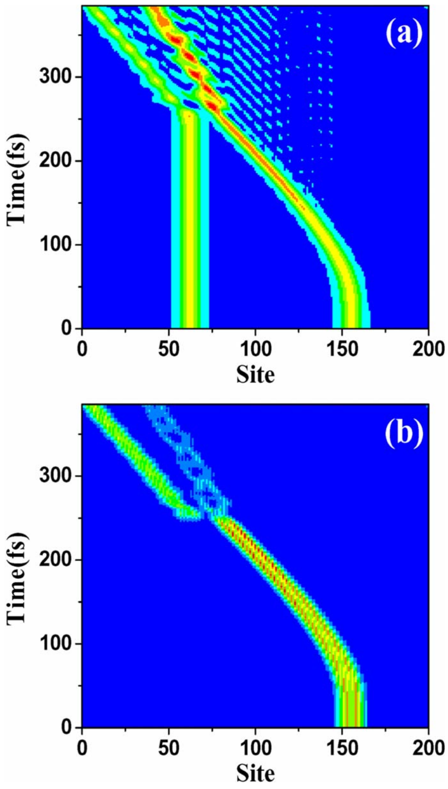

FIG. 1. (Color online) Time dependence of (a) r_n and (b) $\bar{\rho}_n$ for the bipolaron-exciton collision, $E=1.5$ mV/Å.

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

where $\rho_n(t)=\rho_{n,n}(t)$.

The external electric field is then applied, which will drive the charged bipolaron to move toward the neutral exciton. Figure 1 presents the temporal evolution of bond-structure parameter $r_n(t)$ and mean charge density $\bar{\rho}_n(t)$. From Fig. 1(a), one can find that at about 225 fs, the bipolaron meets the exciton and a collision between them will take place. It is found that charges transfer from the bipolaron to the exciton, as can be seen from Fig. 1(b). Charge transfer between the bipolaron and the exciton implies that they are no longer the original excitations.

To recognize the products after collision we draw the evolution of the energy levels inside and around the gap as shown in Fig. 2. There are four intragap levels caused by the bipolaron and the exciton: two of them come from the bipolaron and the others come from the exciton. Before the electric field is applied, the two bipolaron intragap levels and the two exciton intragap levels are degenerate. However, along with time evolution, the degeneracy is removed due to the effect of the electric field. On the other hand, when the bipolaron approaches the exciton, the interaction between them can also remove the degeneracy. Before collision, the bipolaron intragap levels $\varepsilon^u_{\mathrm{bp}}$ and $\varepsilon^d_{\mathrm{bp}}$ move a little toward midgap, while exciton intragap levels ε^u_n and ε^d_n remain at their initial positions. This is because the exciton is neutral and is not influenced by the electric field. After collision, it can be

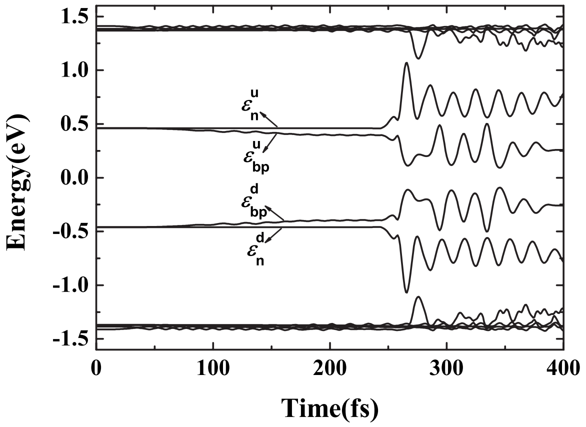

FIG. 2. Evolution of the energy levels inside and around the gap, $E=1.5$ mV/Å.

clearly seen that the four intragap levels all move a lot and oscillate. Level ε_n^u moves toward the conduction-band edge, while level ε_n^d moves toward the valence-band edge. Levels $\varepsilon_{\text{bp}}^u$ and $\varepsilon_{\text{bp}}^d$ move toward midgap. We note that the movement of the intragap levels after collision is related to the formation of new excitations which we have discussed above. We also note that the oscillation in the intragap levels is associated with the lattice oscillation caused by the bipolaron-exciton collision [see Fig. 1(a)].

Before the bipolaron collides with the exciton, two exciton intragap levels are occupied by one electron, respectively, while two bipolaron intragap levels are occupied by two electrons, respectively. The collision will result in electron transitions among these intragap levels as shown in Fig. 3. Figure 3(a) denotes no electron transition, Figs. 3(b) and 3(c) denote only one electron transition from the bipolaron intragap levels to the exciton intragap levels, and Fig. 3(d) denotes two electrons transition from the bipolaron intragap levels to the exciton intragap levels. It can be deduced from states (b) and (c) that the new excitations must be a polaron and an excited polaron. Certainly, the collision will also result in electron transitions from intragap levels to conduction-band levels and form other states besides the four states in Fig. 3. However, our results show that the yields of other states are very small and can be neglected.

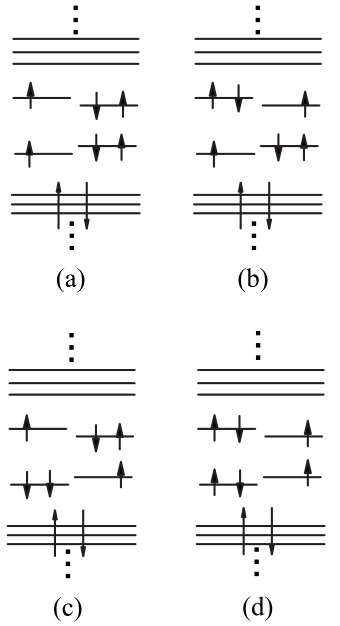

FIG. 3. The possible states corresponding to the electron transition from the bipolaron intragap levels to the exciton intragap levels.

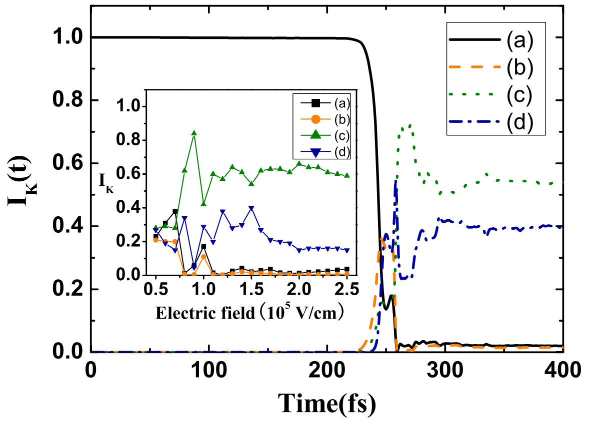

FIG. 4. (Color online) Time dependence of the yields are plotted for the four states (a)–(d) which are shown in Fig. 3, $E=1.5$ mV/Å. Curves (a)–(d) denote the yield of states (a)–(d) in Fig. 3, respectively. The average yields after collision versus electric fields for the four states are shown in the inset.

In the following, we will calculate the yields for the four states after the bipolaron-exciton collision. The evolved wave function of the whole system $|\Psi(t)\rangle$ can be constructed by the single electron evolutional wave function $\{\psi_k(n,t)\}$ as a Slater determinant. After each evolution step, the evolved state $|\Psi(t)\rangle$ is projected onto the space of eigenstates of the system. The relative yield $I_K(t)$ for a given eigenstate $|\Phi_K\rangle$ is then obtained from

$$I_K(t) = |\langle\Phi_K|\Psi(t)\rangle|^2. \tag{6}$$

In our cases, state $|\Phi_K\rangle$ can be any state of interest, for example, state Figs. 3(a)–3(d), etc.

In Fig. 4 we show the yields for the four states which are shown in Fig. 3. The yield of state (a) is 100% before 225 fs, which means that there are separated bipolaron and exciton before collision. When the bipolaron begins to collide with the exciton at 225 fs, the yield of state (a) sharply reduces to about 2%, which means that the original bipolaron and exciton do nearly no longer exist. At the same time, the yields of states (c) and (d) rapidly increase from zero to about 54% and 40%, respectively. The yield of state (b) sharply increases and then drops to about 2%. These results show that four new states appear after collision. It is important to note that only states (c) and (d) keep high yields after collision. We find that states (c) and (d) are related to the charge transfer from the bipolaron to the exciton. Thus, these results are quite consistent with the results in Fig. 1(b). We notice that the yield of state (b) is much smaller than state (c) after collision. This is because the energy of state (b) is higher than state (c) and because high energy state is not a favored state during a scattering process.

It should be mentioned that the yield is closely related to the external field or the velocity of the bipolaron before collision. The average yields after collision against electric fields for the four states are plotted in the inset of Fig. 4. In the low electric field, ranging from 0.5 to 0.7 mV/Å, the yields of the four states are nearly equal, about 25%. We know that the bipolaron intragap levels and the exciton intragap levels are nearly degenerate under a low electric field. This leads to almost equal energies of the four states. Thus, the yields of the four states should be equivalent. When the electric field gets high, the yield of state (c) oscillates and increases greatly, the yield of state (d) oscillates with the electric field and then lowers slightly, while the yields of the other two states reduce to nearly zero. The reduction in the yield of state (d) under a high field indicates that charge transfer between the bipolaron and the exciton also reduces. A high field makes a large value of level offset between the bipolaron and the exciton, which does not favor charge transfer. Moreover, a high field also induces the electrons in the gap states being excited to the conduction band with some probability. It also results in the reduction in the yield.

The results above suggest the following reaction:

$$\mathrm{Ex} + \mathrm{BP} \rightarrow P^{*} + P, \tag{7}$$

where Ex denotes an exciton, BP a bipolaron, P^{*} an excited polaron, and P a polaron. It is worth noting that an excited polaron can decay to a polaron state and emit a photon. During this process, an exciton is annihilated and bipolaron dissociates into two polarons. Therefore, it is expected that the bipolaron-exciton reaction can enhance the efficiency of electroluminescence in conjugated polymers.

From these scattering processes, we can also see that the annihilation of an exciton by a bipolaron will not be retarded by spin conservation because the bipolaron contains two electrons with opposite spin. It can always transfer an electron with an appropriate spin to the exciton without disobeying the Pauli's exclusion principle. In contrast, exciton annihilation by a polaron will be restricted by spin conservation because a polaron only contains one electron.[19] Therefore, bipolarons are more efficient in annihilating excitons than polarons.

The results above also suggest a channel in which a bipolaron is converted into an exciton while an exciton is converted into a bipolaron. In this channel there are no new excitations being created.

In summary, for a conjugated polymer, we studied the scattering processes of a bipolaron with an exciton and addressed the production for this reaction. We identified two channels for this reaction. In one channel, a polaron and an excited polaron are created. Finally, due to relaxation of the excited polaron, the exciton is annihilated and the bipolaron dissociates into two polarons. In the other channel, no new excitations are produced; the bipolaron and the exciton are converted into each other. The probabilities for these two channels are calculated by a projection method, which depend on the strength of the external electric field. The results for bipolaron-exciton scattering show a contribution to the efficiency of electroluminescence.

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