The effect of interface hopping on inelastic scattering of oppositely charged polarons in polymers*

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The inelastic scattering of oppositely charge polarons in polymer heterojunctions is believed to be of fundamental importance for the light-emitting and transport properties of conjugated polymers. Based on the tight-binding SSH model, and by using a nonadiabatic molecular dynamic method, we investigate the effects of interface hopping on inelastic scattering of oppositely charged polarons in a polymer heterojunction. It is found that the scattering processes of the charge and lattice defect depend sensitively on the hopping integrals at the polymer/polymer interface when the interface potential barrier and applied electric field strength are constant. In particular, at an intermediate electric field, when the interface hopping integral of the polymer/polymer heterojunction material is increased beyond a critical value, two polarons can combine to become a lattice deformation in one of the two polymer chains, with the electron and the hole bound together, i.e., a self-trapped polaron–exciton. The yield of excitons then increases to a peak value. These results show that interface hopping is of fundamental importance and facilitates the formation of polaron–excitons.

Keywords: polarons, electron–phonon interactions, exciton, polymers

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1. Introduction

Interest in the photophysics of conjugated polymers has been renewed by the discovery that these materials can be used as the emissive layer in polymer light-emitting diodes (PLEDs) to give efficient devices with a range of emission colors.[1–3] In these PLED devices, organic polymers are used as both the light-emitting and charge-transporting layers with the electrons and holes being injected into the organic layers from a cathode and an anode, respectively. Due to the strong electron–lattice interactions in conjugated polymers, these additional electrons or holes induce self-localized excitations such as solitons (only in *trans*-polyacetylene),[4,5] polarons,[6] and neutral polaron–excitons,[7] the stability of polaron and the effect of polaron on polarizability have been investigated.[8,9] Furthermore, the polaron as the major charge carrier moves under the influence of an external electric field in polymer.[10–15] When a positively charged polaron meets a negatively charged one, they collide and recombine to form a polaron–exciton state in which the electron and the hole are bound in a self-trapped lattice deformation.[16] Since the photoluminescent properties of PLEDs depend strongly on the yield of neutral excitons, the scattering processes of oppositely charged polarons and the quantum yield efficiency of excitons are of fundamental importance for understanding polymer based light-emitting diodes. Generally, if it is assumed that exciton combination in PLEDs is a spin-independent process, the maximum quantum efficiency of PLEDs is limited to 25.%.[17] It is observed experimentally, however, that the 25% limit is broken, and there has been much research, both theoretical and experimental, attempting to improve the quantum efficiency for electroluminescence to the 22%–60% range by finding additional channels,[18–24] and even to 75% as in some calculations.[25]

In order to balance the injection of holes and electrons, real PLEDs often have a multi-layer structure with a hole transporting layer (HTL) and an electron transporting layer (ETL) inserted into the PLED.[19,26,27] That is, the electroluminescent polymeric material is fabricated as a multi-layer structure, and the heterojunction is formed between dissimilar organic semiconductors. It has also been noted that the efficiency is higher in multi-layer materials. The reason may be related to the fact that polarons in a multi-layer conjugated polymer tend to pile up at the interface increasing the probability that they will interact. Transport studies of polarons in a system with a polymer/polymer interface and under the influence of an external field have been carried out in previous work of ours.[28] The results showed that the transport of a polaron through a heterojunction interface depends sensitively on the hopping integrals (t_h) at the interface, the interface potential barrier (Δ_e), and the applied electric field strength (E_0). These results also showed that the polaron can either migrate through the interface or be blocked at the interface due to the potential barrier, and that blocked polarons can meet and collide to form

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excitons at the interface. Furthermore, for triblock copolymer structures, the interface coupling between homopolymer segments is attributed to the hopping of π-electrons and the coupling of σ-bonds.[29] Therefore, in addition to the factors mentioned above, interface hopping will be another crucial factor for understanding the combination of oppositely charged polarons in real polymer heterojunction materials and the formation of exciton states.

Both the motion of polarons and the recombination of charged polaron pairs are dynamic processes involving both charge motion and lattice distortion. Thus, a real-time dynamical model revealing both charge motion and lattice evolution is appropriate for investigating the formation of excitons in PLEDs. Our previous work on inelastic scattering of polaron-pairs in conjugated polymers under the influence of various external electric fields also shows that the dynamic characteristics are important for understanding the physical phenomena in monolayer organic optoelectronic devices.[16,30] In this article, we employ a nonadiabatic molecular dynamic method, and focus on the effects of interface hopping and how it influences inelastic scattering of oppositely charged polarons in polymer heterojunctions.

2. Model and method

We consider a finite polymer/polymer heterojunction structure containing two polymers placed end-to-end. The Hamiltonian can be written as

$$H = H_{\rm SSH} + H_{\rm int} + H_{\rm ext}. \tag{1}$$

The first term is the Su–Schrieffer–Heeger (SSH) Hamiltonian with a Brazoskii–Kirova-type symmetry-breaking term describing each polymer chain,[6]

$$\begin{aligned} H_{\rm SSH} &= -\sum_{j,n} t_{j,n}\left(c^{\dagger}_{j,n+1}c_{j,n} + {\rm h.c.}\right) \\ &\quad + \frac{1}{2}K\sum_{j,n}(u_{j,n+1}-u_{j,n})^2 + \frac{1}{2}M\sum_{j,n}\dot{u}^2_{j,n} \\ &\quad + K'\sum_{j,n}(u_{j,n+1}-u_{j,n}). \end{aligned} \tag{2}$$

In this expression, $j = 1,2$ is the polymer chain index, and $t_{j,n}$ is the hopping integral between sites n and $n+1$ in the j-th polymer chain. That is, $t_{j,n} = t_0 - \alpha_j(u_{j,n+1}-u_{j,n}) + (-1)^n t_{\rm e}$, where t_0 is the hopping integral for zero displacement; $u_{j,n}$ is the monomer displacement of site n in the j-th polymer chain, and α_j describes the electron–lattice coupling between neighboring sites in the j-th polymer chain. The term $t_{\rm e}$ is the Brazovskii–Kirova symmetry-breaking term for describing nondegenerate polymers;[6] K is the elastic constant, and M the mass of a CH group. We use finite polymer chains with open ends, and the last term in the above expression with

$$K' = -\frac{2}{N}\sum_{j,n}\sum_{k}{}' \alpha_j \psi^*_k(j,n+1)\psi_k(j,n)$$

is included to avoid the chain collapsing.

The second term in Eq. (1) describes the interface hopping between the two polymer chains,[25]

$$H_{\rm int} = -t_{\rm h}\left(c^{\dagger}_{1,N}c_{2,1} + c^{\dagger}_{2,1}c_{1,N}\right), \tag{3}$$

where $t_{\rm h}$ is the hopping integral between the end site of the left polymer and the first site of the right polymer.

The third term in Eq. (1) describes a uniform electric field $E(t)$ along the $\hat{x}$ direction taken to be a half Gaussian/constant with an amplitude of E_0 centered at $T_{\rm C} = 75$ fs and with a width of $T_{\rm W} = 25$ fs. This gives the following contribution to the Hamiltonian:

$$H_{\rm ext} = |e|\sum_{j,n}(na + u_{j,n})\left(c^{\dagger}_{j,n}c_{j,n} - 1\right)E(t), \tag{4}$$

where, e is the electron charge, and a is the lattice constant. The model parameters used are those generally chosen for polyacetylene:[7] $t_0 = 2.5$ eV, $K = 21$ eV/Å^2, $M = 1349.14$ eV$\cdot$fs^2/Å^2, $a = 1.22$ Å (1 Å = 0.1 nm). The results are expected to be qualitatively valid for other conjugated polymers with a nondegenerate ground state. The term that removes the degeneracy is set here to be $t_{\rm e} = 0.05$ eV.

At $t = 0$, the polymer chains contain a hole polaron (P^+) at the left end of the left polymer and an electron polaron (P^-) at the right end of the right polymer. The lattice configuration at time $t(>0)$ can then be obtained using the equation of motion for the atomic displacements

$$\begin{aligned} M\ddot{u}_{j,n}(t) &= -K[2u_{j,n}(t) - u_{j,n+1}(t) - u_{j,n-1}(t)] \\ &\quad + 2\alpha_j[\rho_{jn,jn+1}(t) - \rho_{jn,jn-1}(t)] \\ &\quad + |e|E(t)[\rho_{jn,jn}(t) - 1], \end{aligned} \tag{5}$$

where

$$\rho_{jn,j'n'}(t) = \sum_k{}' \psi^*_k(j,n,t) f_k \psi_k(j',n',t),$$

and $f_k(=0,1,2)$ is the time-independent distribution function and is determined by the initial state. The electron wave functions are solutions of the time-dependent Schrödinger equation

$$i\hbar\dot{\psi}_k(j,n,t) = \sum_{j'n'} h_{jn,j'n'}\psi_k(j',n',t), \tag{6}$$

where $h_{jn,j'n'}$ accounts for both the electron terms and the contribution from the applied field. One can write the electron part of the Hamiltonian Eq. (6) in a matrix form, i.e.,

$$h_{jn,j'n'} = \begin{cases} -\left[t_0 - \alpha_j\left(u_{j',n'} - u_{j,n}\right)\right] + (-1)^n t_{\rm e}, & \\ \qquad\qquad\qquad\qquad \text{for } n' = n \pm 1,\ j' = j, & \\ -t_{\rm h}, \qquad\qquad \text{interface hopping}, & \\ |e|E(t)[\rho_{jn,j'n'}(t) - 1], \quad \text{for } n' = n,\ j' = j. & \end{cases}$$

The coupled differential Eqs. (5) and (6) are solved using the same technique as in Ref. [31] with a Runge–Kutta method of order 8 with step-size control.[32] This method has been shown to be an effective approach for investigating polaron dynamics in conjugated polymers.

3. Results and discussions

In the absence of external fields, the two polymer chains are dimerized in the half-filling case, and their energy bands have energy gaps as in an isolated polymer chain. In the presence of an external field, the energy bands have a incline opposite the electric field direction. In a multiple-layer PLED as shown in Fig. 1, the energy gap of the hole-transporting layer (HTL) is larger than that of electron-transporting layer (ETL), such as in a CN–PPV/PPV structure. It is known that the potential barrier Δ_e is determined by the dimensionless electron–phonon coupling parameter $\lambda \equiv 2\alpha^2/\pi K t_0$ and that the value of the energy-gap can be adjusted by changing λ.

To calculate the inelastic scattering processes of oppositely charged polarons, the two polarons are taken to lie initially in a finite degenerate polymer/polymer heterojunction structure arranged as: a left polymer composed of 150 CH-units labelled sites 1–150 and a right polymer labelled sites 151–300. The two chains are placed end-to-end with interface hopping between the end site of left polymer chain and the initial site of the right polymer chain. Before the applied electric field is turned on, a hole injected from the anode induces a hole polaron at the left end of the left polymer while an electron injected from the cathode is self-trapped to form an electron polaron at the right end of the right polymer. The two polarons are separated far enough from each other that they are independent.

It is now interesting to investigate the effects of varying the value of the hopping integral, t_h, on the inelastic scattering of oppositely charge polarons in the polymer heterojunction for fixed potential barriers (as an example $\Delta_e = 0.2$ eV) and electrical field ($E_0 = 0.5$ mV/Å). Simulations of the polaron dynamics have been carried out for a number of different hopping integrals, t_h, ranging from 0.1 eV to 2.0 eV. In all the cases, the polarons start to move along the polymer chains with constant speed shortly after the electric field is turned on. When the polarons reach the end of their respective polymer chains, however, the inelastic scattering of oppositely charged polarons show different behaviors depending on the values of the hopping integral as well as the barrier height and the external voltage.

For the weak coupling case, e.g., $t_h = 0.1$ eV, the polarons (both charge and lattice distortion) get stuck at the junction because of the small hopping probability, i.e., the wave functions of two polarons on opposite sides of the interface have only a small overlap. They therefore oscillate at the ends of their polymer chains respective, and there is electron accumulation at the interface. The staggered order parameter $\delta_n = (-1)^n(2u_{j,n} - u_{j,n+1} - u_{j,n-1})/4$ is shown in Fig. 2(a). In turn, charge transfer between the hole and electron polarons depends on the overlap of their wave functions and on the time they stay close together. As a result, when they rebound from each other, the amount of charge localized in the polarons is not decreased, and their signs are not changed. However, the two particles cannot become widely separated due to the presence of the external electric field. They therefore again approach each other driven by the external electric field.

With increasing hopping integral (e.g., $t_h = 1.0$ eV, in Fig. 2(b)), the wave functions of the two polarons have a greater overlap. In this case, only the amount of charge localized in the polarons is decreased, but their signs are not changed when they rebound from each other. When the hopping integral is increased to above a critical value ($t_h^c = 1.5$ eV;

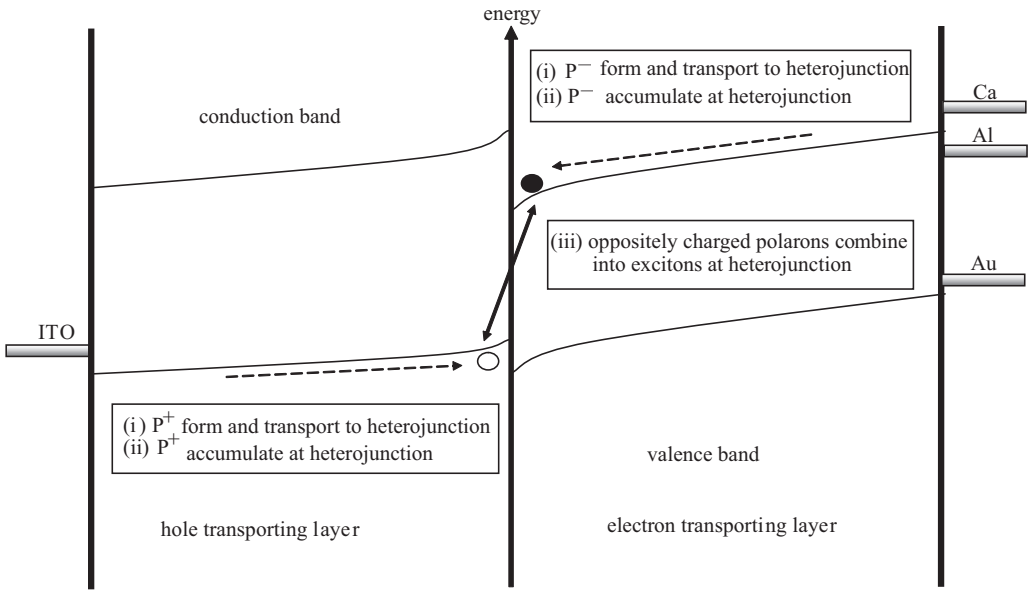


Fig. 1. Scheme for forming excitons by combination of oppositely charged polarons at an HTL/ETL heterojunction (a black dot denotes an electron; a white dot denotes a hole).

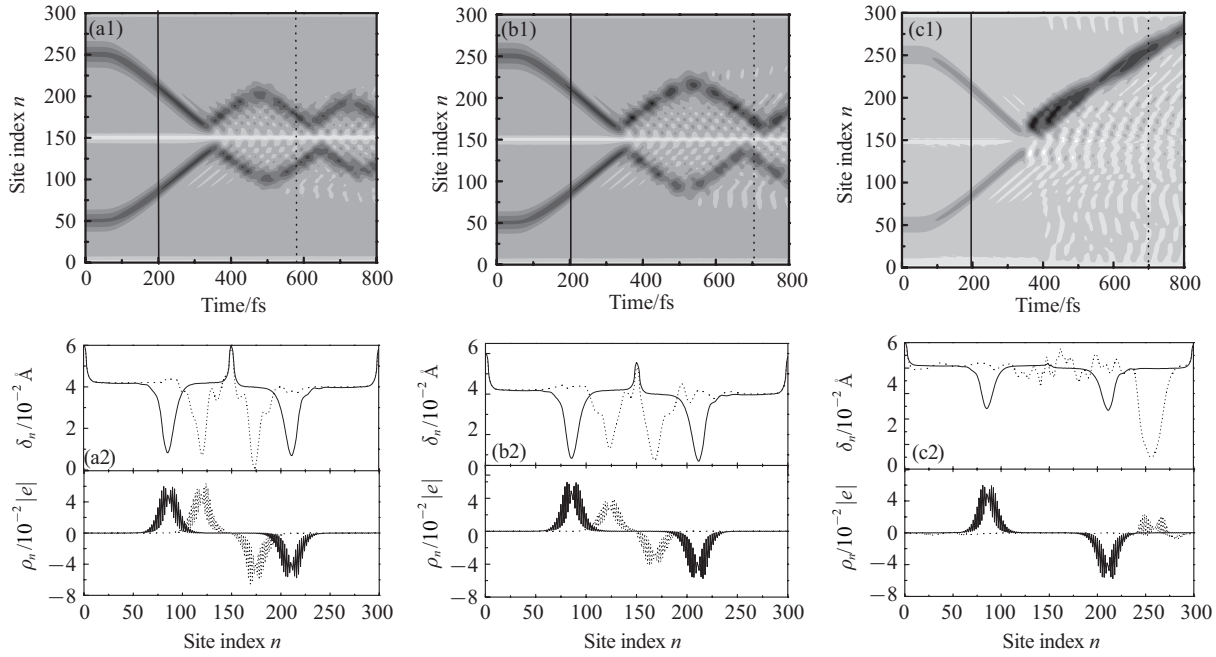


Fig. 2. Evolution of the staggered bond order parameter δ_n with time (upper row), and the staggered order parameter δ_n and the charge distribution ρ_n at two times shown by the solid and dotted vertical lines before and after the scattering (lower row) for different hopping integrals. (a) $t_h = 0.1$ eV (left column); (b) $t_h = 1.0$ eV (middle column); (c) $t_h = 2.0$ eV (right column).

e.g., $t_h = 2.0$ eV, as shown in Fig. 2(c)), the hole polaron has a high probability of jumping onto the other polymer chain, and the two polarons can combine together to become a lattice deformation with the electron and the hole bound together, i.e., a self-trapped polaron–exciton. However, a polaron–exciton is not stable in *trans*-polyacetylene because of the degenerate ground states. In this case, it therefore dissociates into a pair of solitons, as has been found in the photoexcitation process.[16,33] It should be stressed that a polaron–exciton can remain stable in a polymer with a nondegenerate ground state due to the confinement effect. See Fig. 3.

The electron characteristics of the different scattering processes are reflected in the eigen-energy levels and their occupied numbers. The evolution of the eigen-levels and their occupied numbers with time are plotted in Fig. 4. From Fig. 4(a), one can see that there are four energy levels in the energy gap, which are localized electron states corresponding to the two lattice defects. We denote by ε_l^u (ε_r^u) and ε_l^d (ε_r^d) the upper level and the lower level corresponding to the defect at the left (right) side, respectively. At the initial moment, ε_l^u and ε_r^u (ε_l^d and ε_r^d) are degenerate, because the two polarons are initially far apart. As time increases, the degeneracy is broken both by the electric field through the Stark effect (ε_r^u (ε_l^d) goes downwards and ε_l^u (ε_r^d) 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 of the oscillation of the lattice deformations. For the occupied number distribution functions, the results show that the charge localized in the polarons is decreased by only a small amount, and the signs of the charges are also not changed when they rebound from each other. With increasing t_h (see Fig. 4(b)), in the initial state, the energy levels in the valence band are doubly occupied except that ε_l^d is singly occupied, while the energy levels in the conduction band are empty except that ε_r^u

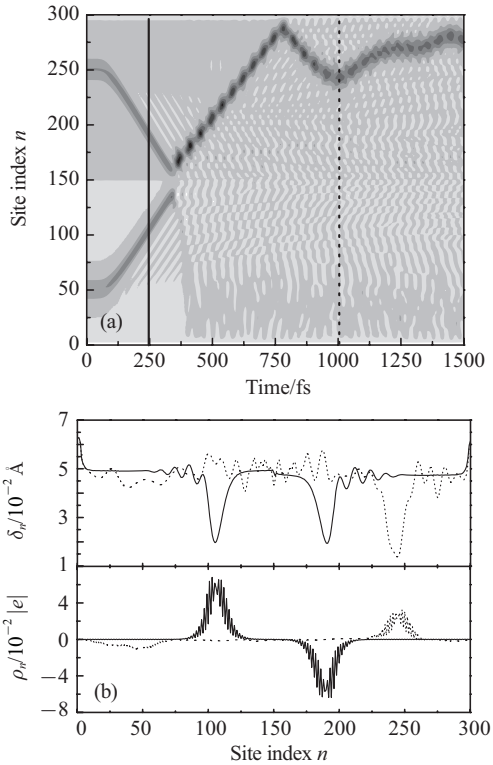


Fig. 3. Evolution of the staggered bond order parameter δ_n with time (a), and the staggered order parameter δ_n and the charge distribution ρ_n at two times shown by the solid and dotted vertical lines before and after the scattering (b) with the hopping integral $t_h = 2.0$ eV in a polymer with a nondegenerate ground state.

is singly occupied. This also indicates that a hole polaron is located on the left side of the left polymer and an electron polaron is on the right of right polymer side. The occupied numbers hardly change with time until the two polarons come into contact. After the inelastic scattering, the occupied numbers of $\varepsilon_{\rm r}^{\rm u}$ and $\varepsilon_{\rm r}^{\rm d}$ decrease while those of $\varepsilon_{\rm l}^{\rm u}$ and $\varepsilon_{\rm l}^{\rm d}$ increase. They remain constant (~ 1.2 for $\varepsilon_{\rm l}^{\rm d}$, and ~ 1.8 for $\varepsilon_{\rm r}^{\rm d}$), and remain at$\sim 0.2$ for $\varepsilon_{\rm l}^{\rm u}$ and ~ 0.8 for $\varepsilon_{\rm r}^{\rm u}$ when the two particles separate far enough. These results indicate that the oppositely charged polarons scatter into a pair of independent particles and each of them is a mix of polarons and excitons.

As shown in Fig. 4(c), when the hopping integral is increased to $t_{\rm h} = 2.0$ eV, there are only two energy levels in the energy gap after the scattering. These are localized electron states corresponding to the one lattice defect. The occupied numbers are ~ 2.0 for $\varepsilon_{\rm l}^{\rm d}$ and ~ 1.0 for $\varepsilon_{\rm r}^{\rm d}$, while they are ~ 0 for $\varepsilon_{\rm l}^{\rm u}$ and ~ 0.8 for $\varepsilon_{\rm r}^{\rm u}$. This indicates that the two polarons combine together to become predominantly a pair of soliton (or a self-trapped polaron–exciton in nondegenerate ground state polymers) lattice deformations in one of the two polymer chains. Simultaneously, another free charge is excited into the higher energy levels in the combination process. For even stronger hopping integrals, $t_{\rm h}$, the polarons are destroyed and free electrons are released by the stronger effect of interface hopping on the scattering (not shown in Fig. 4).

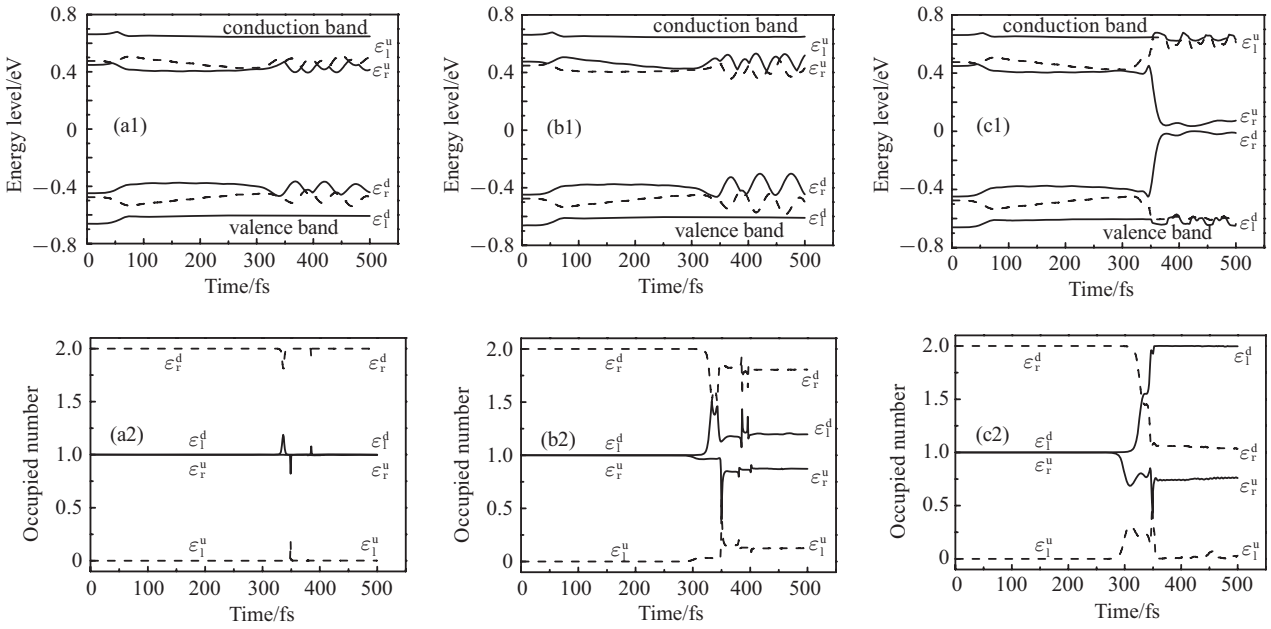


Fig. 4. Evolution of localized electron energy levels (upper row) and occupied numbers of localized energy levels (lower row) with time, corresponding to the scattering described in Fig. 2: (a) $t_{\rm h} = 0.1$ eV; (b) $t_{\rm h} = 1.0$ eV; (c) $t_{\rm h} = 2.0$ eV.

4. Summary

In summary, based on the one-dimensional tight-binding SSH model, the effect of interface hopping on the inelastic scattering of oppositely charged polarons in polymer/polymer heterojunctions has been investigated using a nonadiabatic molecular dynamic method. The results show that the formation of soliton pairs and/or an exciton at the interface depends sensitively on the hopping integrals between the two polymers, which effectively reduces the potential barrier at the interface, as well as on the electric field and the potential barrier. Generally, the quantum efficiency for electroluminescence in PLEDs is taken to be the ratio of the number of emitted photons to the number of emissive singlet excitons. For this reason, under intermediate electric fields, the yield of excitons can be increased by adjusting the hopping integral in CN–PPV/PPV multi-layer PLEDs for which the potential barrier is about 0.2 eV. Consequently, an increased understanding of interface hopping and how it affects the inelastic scattering of oppositely charged polarons will be helpful for designing a PLED structure with higher electroluminescent efficiency.

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