Dynamical Process of Excitation Fusion in Polymers

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Due to the confinement effect in the nondegenerate polymers and the electron−lattice interaction, the electron−hole pair forms a self-trapped single excitation. It is shown that two single excitations in one chain can fuse into one double excitation, and the relaxation time of the fusion process is about 160 fs.

I. INTRODUCTION

Conjugated polymers with nondegenerate ground states, such as poly(paraphenylenevinylene) (PPV) and poly(phenylquinoxalines) (PPQ), are found to have excellent nonlinear optical properties, and they can be used as the active luminescent layer in new polymer-based electroluminescence light emitting diode (LED) devices.[1] The excitations in the conjugated polymers, such as electron−hole pairs, polarons, and excitons, play essential roles in these photophysics processes.[2]

The polymer chain is a quasi-one-dimensional system. Due to the electron−lattice interaction, the electron excitation must induce lattice distortion in the polymer chain, and the electron itself is trapped by the distorted lattice to form a bound state. This is a self-trapping effect.

Under the photoexcitation, an electron is excited from the valence band to the conduction band; then the electron−hole pair interacts with the lattice and evolves to a self-trapped excitation. In the polymers with degenerate ground states such as *trans*-polyacetylene, this self-trapped excitation is a soliton−antisoliton pair which can be separated at any distance. However, most polymers possess a nondegenerate ground state, where the soliton and antisoliton cannot be apart but are bound together, which is the so-called confinement effect. Then the electron−hole pair evolves to a neutral bipolaron.[3] So, even without the electron−electron interaction, the electron−hole pair in the nondegenerate ground-state polymers does not separate and relaxes into a single bound excitation. Such a self-trapped excitation possesses two electronic bound states ψ_u and ψ_d in the gap, each of which is occupied by one electron. Roughly speaking, in the electron−hole pair excitation, the electron−lattice interaction causes the lattice distortion and pushes the HOMO and LOMO levels into the gap. Obviously, both the self-trapping and the confinement effect are independent from the electron−electron interaction, and they can result from only the electron−lattice interaction. This means that, even in very weak electron−electron interactions, the electron−hole pair will still evolve to a single self-trapped excitation. If the electron−electron interaction is comparable to the electron−lattice interaction, this kind of self-trapped excitation is simply an exciton.[4]

In the case of electroluminescence, the injection of electrons on one side and holes on the other side of a polymer film also produces electron−hole pairs. The heavy injection or strong photoexcitation can generate many single self-trapped excitations, and two single excitations can come to one chain. When two single excitations approach each other, they will interact.

Recent experiments show that although the primary excitation in polymers is single excitation (exciton),[4] the double excitation (biexciton) is also stable in the polymer solution.[5] As mentioned above, the single excitation has one electron in the lower gap state ψ_d and another electron in the upper gap state ψ_u. If the electron in ψ_d is further excited to ψ_u, it becomes a double excitation, where two electrons with opposite spins sit in ψ_u while ψ_d is empty. Obviously the common way to produce the double excitation is reexcitation: the first excitation produces the single excitation (bipolaron or exciton), and the second excitation causes the single excitation to become the double excitation. Our study shows there is another channel to form the double excitation, which is the excitation fusion: when two single excitations occur on one chain, they attract each other and fuse into a double excitation.

In this paper, the evolution of the excitation fusion is simulated by calculating the dynamical process. It is found that the relaxation time of the fusion process is about 160 fs. As a first step, we consider only the electron−lattice interaction, so the dynamical process here is the bipolaron fusion. We will consider electron−electron interactions later, whereby our theory can then simulate the fusion from exciton to biexciton.

II. THEORETICAL METHOD

It is well-known that the conjugated polymers can be mainly described by the SSH (Su−Schrieffer−Heeger) Hamiltonian.[3] In order to specify the polymers with a nondegenerate ground state, the SSH Hamiltonian is modified by adding a confinement term t_e (Brazovskii and Kirova[6]),

so that the Hamiltonian describing the nondegenerate ground-state polymers reads as

$$H = H_e + \frac{K}{2}\sum_n (u_{n+1} - u_n)^2 \quad (1)$$

$$H_e = \sum_n [t_0 - \alpha(u_{n+1} - u_n) + (-1)^n t_e] (a_{n+1,s}^+ a_{n,s} + hc) \quad (2)$$

where t_0 is the hopping constant, α is the electron−lattice coupling, u_n is the displacement of atom sitting at site n, $a_{n,s}^+$ and $a_{n,s}$ are the creation and annihilation operators of an electron at site n with spin s, and K is the elastic constant. The polymer chain consists of N atoms ($n = 1, 2, ..., N$) and N electrons. So, the second term in eq 1 is the elastic energy of the lattice distortion, the second term in eq 2 is the electron−lattice interaction, and the third term in eq 2 is the confinement for the nondegenerate ground-state polymers. For different polymers, the parameters vary over certain ranges:

$$t_0 = 2.2-3.0 \text{ eV}, \quad t_e = 0.04-0.07 \text{ eV},$$
$$a = 35-50 \text{ eV/nm}, \quad K = (1.5-2.5) \times 10^3 \text{ eV/nm}^2$$

In this paper, the parameters take the average values in these ranges.

For any lattice configuration $\{u_n\}$, the Hamiltonian H_e can be diagonalized numerically to get the electronic energy spectrum $\epsilon_i(\{u_i\})$ and the corresponding wave function $|\psi_i\rangle$,

$$H_e|\psi_i\rangle = \epsilon_i|\psi_i\rangle \quad (3)$$

Both ϵ_i and $|\psi_i\rangle$ are the functionals of the lattice configuration $\{u_n\}$. Then the total energy of this electron−lattice system is

$$E(\{u_n\}) = \sum_i^{occu} \epsilon_i + \frac{K}{2}\sum_n (u_{n+1} - u_n)^2 \quad (4)$$

where the first summation is only over the occupied states.

Since the atom is much heavier than the electron, the adiabatic approximation can be used to determine the electron state, and the atom dynamics is described by Newton's equation.[7] The force exerting on the nth atom is

$$f_n = -\frac{\partial E(\{u_n\})}{\partial u_n} = \sum_i^{occu} \frac{\partial \epsilon(\{u_n\})}{\partial u_n} + K(2u_n - u_{n+1} - u_{n-1}) \quad (5)$$

and the atom's dynamical equation reads

$$M\frac{d^2 u_n}{dt^2} = -\frac{\partial E(\{u_n\})}{\partial u_n} \quad (6)$$

where M is the mass of the atom.

By using the Hellmann−Feynman theorem, we get

$$\frac{\partial \epsilon_i}{\partial u_n} = 2\alpha\langle n|\psi_i\rangle (\langle n+1|\psi_i\rangle - \langle n-1|\psi_i\rangle) \quad (7)$$

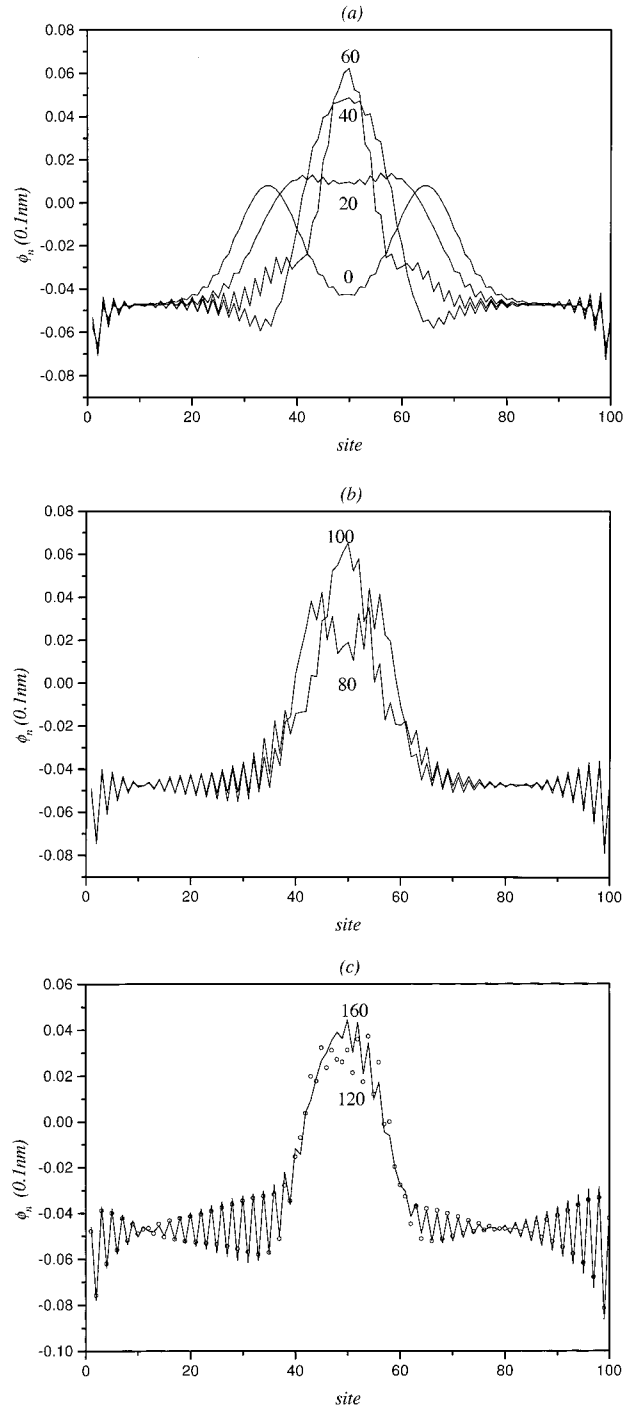With substitution of eq 7 into eq 5, the dynamic equation eq

Figure 1. Evolution of the lattice configuration: (a) from $t = 0$ to 60 fs; (b) from $t = 80$ to 100 fs; (c) from $t = 120$ fs to 160 fs, where the ordinate is $\phi_n = (-1)^n u_n$.

6 can be solved numerically step by step.[8,9] We can simulate the dynamic evolution of the bond structure. Since the period of lattice vibration τ_0 is about 4×10^{-14} s, the time step τ should be much shorter than τ_0, where we choose $\tau = 1$ fs(10^{-15} s). In the calculation, the final positions and velocities of the atoms at each step are taken as the initial condition for the next step. Then the evolution of the excitation fusion can be simulated.

III. RESULTS AND DISCUSSION

When two single excitations (bipolarons) occur on one chain whose length is 100 sites, their separation is about 40
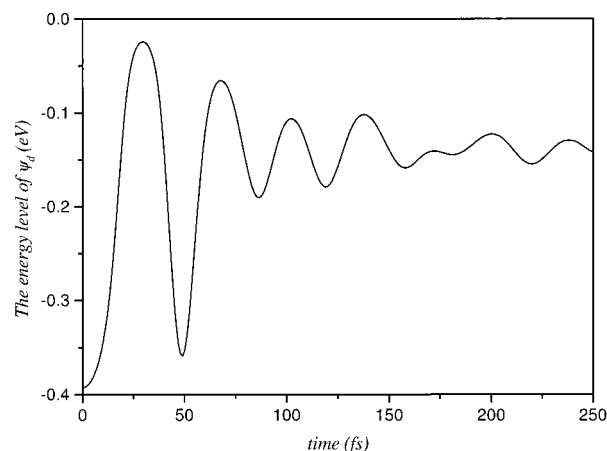
Figure 2. Evolution of the energy level of the lower gap state ψ_d.

sites. The initial lattice configuration is shown by the $t = 0$ curve of Figure 1. The electron−lattice interaction causes the interaction between these two single excitations, where the lattice configuration changes. The time-dependent lattice configurations are shown in Figure 1. At the beginning ($t = 0$), there are two peaks in the lattice configuration, which reflect two single excitations. First, these two peaks move closer and closer, indicating that single excitations have an attractive interaction. At the same time, the whole configuration vibrates with a period of about 40 fs. After $t = 160$ fs, two peaks merge into one peak, and the lattice configuration gradually steadies. This evolution of the lattice configuration tells us that two single excitations in one chain will attract each other and fuse into one double excitation.

During the fusion process, associated with the lattice relaxation, the electronic spectrum is also changing. Figure 2 shows the time evolution of the lower gap state ψ_d. At $t = 0$, the level is the HOMO of the single excitation. After vibrating several times, it gradually converges to the HOMO of the double excitation. Both the lattice configuration evolution (Figure 1) and the electronic spectrum evolution (Figure 2) show that the relaxation time for the excitation fusion is about 160 fs.

As mentioned in the Introduction, this paper only considers the electron−lattice interaction. Thus, the present result can only describe the fusion of a bipolaron. To fully describe the fusion from exciton to biexciton, the electron−electron interaction should be included, which will be considered in a future study.

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