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Effect of electron-electron interaction on scattering process of oppositely charged polarons in conjugated polymers

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ABSTRACT

By using one-dimensional tight-binding Su-Schrieffer-Heeger model modified to include electron-electric field interaction and electron-electron interaction, we simulate the scattering process of oppositely charged polarons with spin parallel and antiparallel, respectively. It is found that at weak field, the electron-electron interaction is dominant. Under the effect of strong Coulomb attraction, the polarons with spin antiparallel could not be separated after collision, and ultimately recombine into the singlet exciton. While in case of spin parallel, the strong Coulomb repulsion makes no collision occur unless strengthening the electric field. At moderate field, the electron-electron interaction could facilitate the recombination of polarons into triplet exciton rather than singlet. It is obtained that there exists competition between electron-electric field interaction and electron-electron interaction, a suitable strength of which could promote the formation of exciton in conjugated polymers.

1. Introduction

During the past decades, lots of efforts have been devoted to conjugated polymers for their abundant available optical and electrical characteristics. The potential applications of polymers have attracted more and more attentions, and then a series of polymer-based organic optoelectronic devices have emerged, such as polymer light emitting diodes and polymer photovoltaic cells [1–3]. It is widely believed that polymers are the most promising organic materials. In comparison with conventional inorganic semiconductors, organic polymers possess strong electron-lattice interaction. The doped charge into them could induce the localized lattice deformation, and is trapped itself therein. Then the self-trapped elementary excitation, i.e. polaron is formed [4]. It should be aware that since polaron is the elementary carrier in organic materials, intensive study on its dynamical evolution is of great importance to the improvement of conductivity and light-emitting performance of the above mentioned organic devices.

Early in 2008, An et al. have simulated the scattering process of oppositely charged polarons in conjugated polymers by using the one-dimensional tight-binding Su-Schrieffer-Heeger (SSH) model [5]. They find that under the effect of electric field, the polarons may recombine into exciton, pass through each other, or be dissociated, which depends on the field strength. However, SSH model has its limitation because it only considers electron-lattice interaction, but completely ignores electron-electron interaction [4,6,7]. Therefore, there is no spin-related term in Hamiltonian of system so as to break the spin degeneracy of energy levels, and then the formed singlet and triplet excitons could not be distinguished from each other.

As is known, in case of non-polarized carrier injection into conjugated polymers, the spin orientation of the formed polaron is random. It may be up or down with the equal probability. In the absence of spin-related interaction, such as Zeeman effect, spin-orbital coupling, and hyperfine interaction, the spin of polaron is unchanged during its dynamical evolution process. Then the spin-independent polaron recombination statistically yields singlet or triplet exciton with the ratio of 1:3. As the emission of photon originates from the radiative decay of singlet exciton into ground state, rather than triplet, the electroluminescence efficiency of polymer light emitting diodes is then limited to 25%.

By using SSH model modified to include electron-electron interaction in form of the extended Hubbard model, Li et al. further explore the recombination of polarons into exciton [8]. They find that in presence of on-site repulsion, the triplet is much more stable than singlet. Through adopting the same method, Lei et al. discuss the effect of spin polarization angle on scattering process of polarons [9]. They find that in case of spin-parallel, the yield of triplet exciton increases with the

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enhancement of electron-electron interaction. While in case of spin-antiparallel, the formation of singlet exciton becomes independent. However, in their works, as the electric field is fixed to be moderate, its effect on polaron recombination has not been taken into account. In fact, there is competition between electron-electric field interaction and electron-electron interaction. Although it is difficult to confirm which one is dominant, we can guess that it may depend on the interaction strength.

We should mention that early in 2007, Di et al. have presented that under the effect of a fixed electric field, the motion of polaron is restrained by electron-electron interaction since its localization is strengthened [10]. In addition, they point out that there is a threshold field, over which the polaron is no longer stable, and the charges are decoupled from the lattice deformation. The value of this critical electric field is found to be closely related to the strength of electron-electron interaction. The same conclusion has been obtained by Ma et al. [11]. They demonstrate that each site of lattice tends to be occupied by one electron when the on-site electron-electron Coulomb repulsion is enhanced. As a result, the charge density is distributed more locally, and then the width of lattice defect becomes narrower. As the velocity of polaron depends on the delocalization level of its defect, its transport is then restrained. However, these works focus on the dynamical evolution of a single polaron, rather than the scattering process between polaron pair, so their spin orientation has not yet been taken into account.

In subsequent research, Ma et al. get that the electron-electron interaction could also influent the condition of soliton collision [12]. They point out that with the increase of interaction strength, the minimum distance between the two charged solitons during their collision process is significantly widened. Under the effect of strengthened Coulomb repulsion, the two solitons can hardly move towards each other more closely for complete contact. Meng et al. research the dissociation of exciton generated from photoexcitation in polymers under the effect of both electric field and electron-electron interaction [13]. They find that the electron-electron interaction is unfavorable for exciton dissociation as the attraction between electron and hole localized on excitonic lattice deformation is enhanced. Therefore, the value of critical electric field increases so as to split exciton into free electron and hole. Sun et al. investigate the scattering process between polaron and bipolaron [14]. They find that with the enhancement of electron-electron interaction, the attraction between the oppositely charged polaron and bipolarons becomes strong. Then it is easier for them to recombine rather than pass through each other. From these works we conclude that the Coulomb repulsion/attraction between two charge carriers could be significantly enhanced by electron-electron interaction.

Not only that, after taking into account spin multiplicity, more interesting results could be obtained. For example, Sun et al. investigate the spin-dependent scattering process between polaron and exciton [15]. It is found that in case of spin-parallel, polaron could pass through exciton easily. While in case of spin-antiparallel, the electron-electron interaction leads to the strong repulsion between them, and the product of their collision could be modulated by the external electric field. Di et al. explore the recombination of polaron pair [16]. They find that for the two polarons with the same charge and spin, their collision is elastic as the Coulomb repulsion between them is strong. While for the ones with the opposite spin, they could recombine into bipolaron. This process is related on the applied electric field and the electron-electron interaction. Then we are aware that in order to obtain the desired product after collision between charge carriers with spin parallel or antiparallel, it is needed to modulate the strengths of both electric field and electron-electron interaction to a suitable value.

Recently, Sun et al. present the spin-dependent polaron recombination, and distinguish between the formed singlet and triplet excited states [17]. They focus on the competition between electric field and interchain coupling, rather than electron-electron interaction. Silva et al. simulate the scattering dynamics of several polarons localized in a single polymer chain so as to discuss the influence of carrier concentration without considering the spin multiplicity of polarons and the effect of electron-electron interaction [18]. These works provide the important enlightenment to our present work.

In this paper, by using the modified SSH model after including electron-electron interaction, and the non-adiabatic dynamical evolution method [19], we simulate the polaron collision under the effect of different electric fields, with two cases being discussed respectively, i.e., the spin orientation of the two oppositely charged polarons is parallel or antiparallel. The paper is organized as follows. In Section 2, we give the model and method. The results and discussion are presented in Section 3. In Section 4, the conclusion is briefly summarized.

2. Theoretical methods

We consider an isolated polyacetylene chain with *cis* configuration, and establish the Hamiltonian in form of $H = H_{\mathrm{SSH}} + H_E + H_{\mathrm{e-e}}$.

The first term

$$H_{\mathrm{SSH}} = -\sum_{n,s} t_{n,n+1}(C^{+}_{n+1,s}C_{n,s} + C^{+}_{n,s}C_{n+1,s}) + \frac{1}{2}K\sum_{n}(u_{n+1}-u_n)^2 + \frac{1}{2}M\sum_{n}\dot{u}_n^2 \tag{1}$$

is the famous SSH model, which contains electron-lattice interaction, elastic potential energy and kinetic energy of lattice atoms [4,6,7]. Here, $t_{n,n+1} = t_0\text{-}\alpha(u_{n+1}\text{-}u_n)\text{-}(\text{-}1)^n t_{\mathrm{e}}$ denotes the intrachain hopping integral between sites n and $n+1$, and t_0 between two nearest sites without dimerization. α is the electron-lattice coupling constant, and u_n the displacement of site n from its equilibrium position. The symmetry breaking term t_{e} is included to describe *cis*-polyacetylene with non-degenerate ground-state structure [20]. $C^{+}_{n,s}$ and $C_{n,s}$ are creation and annihilation operators of electron with spin s at site n, respectively. K denotes the elastic constant and M the mass of Carbon-Hydrogen group.

The second term

$$H_E = |e|E(t)\sum_{n,s}(na+u_n)\left(C^{+}_{n,s}C_{n,s}-\frac{1}{2}\right) \tag{2}$$

denotes the additional energy introduced by electron-electric field interaction. e is the electron charge, and a the lattice constant.

The third term

$$H_{\mathrm{e-e}} = \frac{U}{2}\sum_{n,s}\left(C^{+}_{n,s}C_{n,s}-\frac{1}{2}\right)\left(C^{+}_{n,-s}C_{n,-s}-\frac{1}{2}\right) \tag{3}$$

is the extended Hubbard model obtained from the Hartree-Fock approximation to describe the electron-electron interaction [21]. Here, U denotes the interaction strength between two on-site electrons with opposite spin orientation. In our calculation, the value of U ranges from 0 to 4eV, which has been proved to be reasonable in description of polyacetylene [4,22].

In Wannier representation, the electronic state $|\Psi_\mu(t)\rangle$ on μth energy level is expanded as

$$|\Psi_\mu(t)\rangle = \begin{vmatrix}\Psi_{\mu,\uparrow}(t)\\ \Psi_{\mu,\downarrow}(t)\end{vmatrix} = \sum_n \begin{pmatrix}\psi_{\mu,\uparrow}(n,t)\\ \psi_{\mu,\downarrow}(n,t)\end{pmatrix}|n\rangle. \tag{4}$$

Here, the amplitude $\psi_{\mu,s}(n,t)$ is obtained by solving the time-dependent Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}\psi_{\mu,s}(n,t) = -t_{n-1,n}\psi_{\mu,s}(n-1,t) - t_{n,n+1}\psi_{\mu,s}(n+1,t) + \left\{|e|E(t)(na+u_n) + U\left[\rho^{-s}_{n,n}(t)-\frac{1}{2}\right]\right\}\psi_{\mu,s}(n,t). \tag{5}$$

The temporal evolution of lattice displacement u_n is described by the classical Newton equation of motion