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Scattering process between polaron and exciton in conjugated polymers

Zhen Sun,^{1,a)} Desheng Liu,² Sven Stafström,¹ and Zhong An³¹*Department of Physics, Chemistry and Biology, Linköping University, SE-58183 Linköping, Sweden*²*School of Physics, State Key Laboratory of Crystal Materials, Shandong University, 250100 Jinan, China*³*College of Physics, Hebei Normal University, 050016 Shijiazhuang, China*

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Scattering process between a negative polaron and an exciton in a polymer chain is investigated by using the Su–Schrieffer–Heeger model modified to include electron–electron interactions, the Brazovskii–Kirova symmetry breaking term, and an external electric field. It is found that the scattering process is spin dependent. If the polaron and the exciton have parallel spins, the polaron can easily pass through the exciton as if it “do not see” the exciton. If the polaron and the exciton have antiparallel spins, there exist strong repulsion between them. The polaron may be bounced back, be dissociated or pass through the exciton depending on the strength of the external electric field. In any of these cases, the polaron cannot break the exciton. © 2011 American Institute of Physics. [doi:10.1063/1.3548667]

I. INTRODUCTION

Conjugated polymers continue to attract commercial and scientific interest since they can be used to fabricate organic light-emitting diodes (OLEDs) (Ref. 1) which have unique set of characteristics, such as low cost, versatility of chemical synthesis, and ease of processing. Due to strong electron–phonon coupling, charge carriers in conjugated polymers are quite different from those in inorganic semiconductors and carry charge along with a local structural deformation, so called polarons or bipolarons.²

Another important excitation in the context of OLEDs is the exciton, which is a carrier of energy. Similar to the charge carrier, an exciton also couples strongly to phonons and is associated with a structural deformation. The exciton is created via absorption of a photon but could also be the result of interaction between two polarons with opposite charges. Since both polarons and excitons coexist in OLEDs, there exists high possibility of colliding between these excitations, and by studying the interaction between polaron and exciton we may get a deeper understanding of the properties of conjugated polymers in general, and OLEDs in particular.

The spin of an exciton may be triplet or singlet. Triplet excitons (TEs), due to their long lifetime, have high probability of colliding with polarons. Many experiments have shown that the density of TE is correlated with the density of charge carrier in a working OLED.^{3–6} Recently, Desai *et al.*⁷ suggested that the trapping of charge carriers at TEs in an OLED may be the origin of magnetoresistance. This stimulated some theoretical work on investigating the interaction between polaron and exciton. In a previous work, we simulated the bipolaron–exciton scattering process in conjugated polymers.⁸ The results showed that a bipolaron and an exciton can react with the production of a polaron and an excited polaron. Very recently, Li *et al.*⁹ and Meng *et al.*¹⁰ theoretically investigated the collision process between a polaron and a TE.

Li *et al.* simulated the collision process between a positive polaron and a TE and argued that the collision could induce the TE to emit light. Meng *et al.* simulated the scattering process between a negative polaron and a TE in a system composed of two coupled chains. Their results showed that the polaron–TE scattering can produce an excited polaron and convert the TE into a singlet exciton. Complementary to these interesting observations, in this work we focus on more details about the polaron–exciton scattering process.

Using a combined version of the Su–Schrieffer–Heeger (SSH) model¹¹ and the extended Hubbard model, we simulated the scattering process between a polaron and an exciton in a polymer chain in the presence of an external electric field. The simulations were performed using a nonadiabatic molecular dynamics method.¹² The aim of this paper is to give a microscopic picture of the polaron–exciton scattering process in conjugated polymers and contribute to understanding this important process in OLEDs.

II. MODEL AND METHOD

We use a SSH-type Hamiltonian which is modified to include electron–electron interactions and an external electric field. The electron–electron interactions are introduced by the extended Hubbard model. The total Hamiltonian is given by

$$H = H_0 + H_{ee}. \quad (1)$$

The first term of Eq. (1) is

$$H_0 = - \sum_{n,s} t_{n,n+1} (e^{i\gamma A} c_{n,s}^\dagger c_{n+1,s} + e^{-i\gamma A} c_{n+1,s}^\dagger c_{n,s}) + \frac{1}{2} K \sum_n (u_{n+1} - u_n)^2 + \frac{1}{2} M \sum_n \dot{u}_n^2, \quad (2)$$

where $t_{n,n+1} = t_0 - \alpha(u_{n+1} - u_n) + (-1)^n t_e$, t_0 is the transfer integral of π -electrons in a regular lattice, α the electron–lattice coupling constant, and u_n the lattice displacement of the n -th site from its equidistant position. t_e is introduced to

^{a)}Electronic mail: zhesu@ifm.liu.se.

lift the ground-state degeneracy for nondegenerate polymers, $\gamma \equiv ea/\hbar c$ is a constant quantity, c the light speed, e the absolute value of the electronic charge, and a the lattice constant. The vector potential $A(t)$ is introduced to describe a uniform external electric field along the polymer chain with periodic boundary condition, the relation between potential A and uniform electric field E is given by $E = -(1/c)\partial A/\partial t$. The operator $c_{n,s}^\dagger$ ($c_{n,s}$) creates (annihilates) a π -electron with spin s at the n -th site. The last two terms on the right hand side of Eq. (2) represent the lattice harmonic potential energy and the lattice kinetic energy, where K is the spring constant of a σ bond and M the mass of a CH group.

The second term of Eq. (1) expresses the electron–electron interactions,

$$H_{ee} = U_0 \sum_{n,s} \left(c_{n,s}^\dagger c_{n,s} - \frac{1}{2} \right) \left(c_{n,-s}^\dagger c_{n,-s} - \frac{1}{2} \right) + \sum_{n,s,s'} U_{n,n+1} \left(c_{n,s}^\dagger c_{n,s} - \frac{1}{2} \right) \left(c_{n+1,s'}^\dagger c_{n+1,s'} - \frac{1}{2} \right), \quad (3)$$

where U_0 is the on-site Coulomb repulsion strength. The nearest-neighbor Coulomb repulsion strength is assumed to have the form¹³

$$U_{n,n+1} = \frac{U_0}{\sqrt{1+x_{n,n+1}^2}} e^{-\beta x_{n,n+1}}, \quad (4)$$

where $x_{n,n+1} = |a + u_{n+1} - u_n|/a$ and β is the screening factor of the electron–electron interactions. In this paper, these extended-Hubbard-type interactions are treated within the unrestricted Hartree–Fock approximation.

The model parameters we use in this work are those generally chosen for polyacetylene,² $t_0 = 2.5$ eV, $\alpha = 4.1$ eV/Å, $t_e = 0.05$ eV, $K = 21.0$ eV/Å², $M = 1349.14$ eVfs²/Å², and $a = 1.22$ Å. The screening factor of electron interaction is set to $\beta = 1$. In this condition, $0.2U_0 \leq U_{n,n+1} \leq 0.3U_0$. Other values for $U_{n,n+1}$ are also used, such as $U_{n,n+1} = U_0/2$ or $U_0/3$,^{14,15} but our test calculations showed that these differences do not have distinct effect on the polaron–exciton scattering process.

Within the unrestricted Hartree–Fock approximation, the time-dependent Schrödinger equations for one-particle wave functions are expressed in the following form:

$$i\hbar \frac{\partial}{\partial t} \psi_{k,s}(n, t) = H_{n,n+1}^s(t) \psi_{k,s}(n+1, t) + H_{n,n-1}^s(t) \psi_{k,s}(n-1, t) + H_{n,n}^s(t) \psi_{k,s}(n, t) \quad (5)$$

with

$$H_{n,n+1}^s(t) = -t_{n,n+1} - U_{n,n+1} \rho_s(n, n+1, t), \quad (6)$$

$$H_{n,n-1}^s(t) = -t_{n-1,n} - U_{n,n+1} \rho_s^*(n-1, n, t), \quad (7)$$

$$H_{n,n}^s(t) = U_0 \left[\rho_{-s}(n, n, t) - \frac{1}{2} \right] + U_{n,n+1} \times \sum_{s'} [\rho_{s'}(n+1, n+1, t) + \rho_{s'}(n-1, n-1, t) - 1], \quad (8)$$

where the charge density $\rho_s(n, n', t)$ is expressed as

$$\rho_s(n, n', t) = \sum_k' \psi_{k,s}^*(n, t) \psi_{k,s}(n', t). \quad (9)$$

Here the sum over the index k is over occupied single-particle states in the initial stationary state. The equation of motion for the lattice is

$$M \ddot{u}_n = F_n(t) = -K[u_{n+1}(t) - u_{n-1}(t) - 2u_n(t)] + \alpha \sum_s \{ e^{i\gamma A} [\rho_s(n, n+1, t) - \rho_s(n-1, n, t)] + H.c. \}, \quad (10)$$

where $F_n(t)$ represents the force that the n -th site endured.

The above set of equations are numerically solved by discretizing the time with an interval Δt which is chosen to be sufficiently small so that the change of the electronic Hamiltonian during that interval may be negligible. For all the results presented below, we choose a time step of $\Delta t = 5as$.

By introducing electron instantaneous eigenstates at each moment, the solutions of the time-dependent Schrödinger equations can be put in the form¹²

$$\psi_{k,s}(n, t_{j+1}) = \sum_l \left[\sum_m \phi_{l,s}^*(m) \psi_{k,s}(m, t_j) \right] \times e^{-i(\epsilon_{l,s} \Delta t / \hbar)} \phi_{l,s}(n), \quad (11)$$

where $\{\phi_{l,s}(n)\}$ and $\{\epsilon_{l,s}\}$ are the eigenfunctions and the eigenvalues of the electronic part of the Hamiltonian H at a given time t_j . The lattice equations are written as

$$u_n(t_{j+1}) = u_n(t_j) + \dot{u}_n(t_j) \Delta t + \frac{F_n(t_j)}{2M} (\Delta t)^2, \quad (12)$$

$$\dot{u}_n(t_{j+1}) = \dot{u}_n(t_j) + \frac{F_n(t_{j+1}) + F_n(t_j)}{2M} \Delta t. \quad (13)$$

Hence, the electronic wave functions and the lattice displacement at the $(j+1)$ th time step are obtained from the j th time step.

At a given time t_j , the wave functions $\{\psi_{k,s}(n, t_j)\}$ can be expressed as a series expansion of the eigenfunctions $\{\phi_{l,s}\}$

$$\psi_{k,s}(n, t_j) = \sum_{l=1}^N C_{l,k}^s(t_j) \phi_{l,s}, \quad (14)$$

where $C_{l,k}^s$ are the expansion coefficients. The occupation number for energy level ϵ_l is

$$n_l(t_j) = \sum_{k,s}' |C_{l,k}^s(t_j)|^2. \quad (15)$$

FIG. 1. The schematic diagram of energy levels for a polymer chain containing a negative polaron and a neutral exciton.

$n_l(t_j)$ contains information concerning the redistribution of electrons among the energy levels.

In all simulations, we use staggered order parameter $r_n(t)$ and mean charge density $\bar{\rho}_n(t)$ to analyze the lattice and charge density evolution,

$$r_n(t) = \frac{(-1)^n}{4} \{u_{n-1}(t) + u_{n+1}(t) - 2u_n(t)\}, \quad (16)$$

$$\bar{\rho}_n(t) = \frac{1}{4} \sum_s \{ \rho_s(n-1, n-1, t) + 2\rho_s(n, n, t) + \rho_s(n+1, n+1, t) \}. \quad (17)$$

III. RESULTS AND DISCUSSIONS

It has been well known that the formation of polarons or excitons in polymers and the induced lattice distortion destabilize the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) and move these states into the energy gap.^{2,16} For a system containing a negative polaron and an exciton, there are four energy levels in the energy gap: two originate from the polaron and the other two from the exciton. There are many composite spin states in which electrons occupy these four intragap levels with different spins. We are interested in two of these, as shown in Figs. 1(a) and 1(b), respectively. In each of the composite spin state, the left two intragap levels ε_p^u and ε_p^d come from the polaron, in which the upper one is occupied by one electron and the lower one occupied by two electrons. The right two intragap levels ε_n^u and ε_n^d come from the exciton, and each of them is occupied by one electron. In composite spin state (a), the spins of the polaron and the exciton are parallel, while in composite spin state (b) the spins of the polaron and the exciton are antiparallel.

The starting geometry is obtained by minimizing the total energy of the chain with fixed occupation numbers as described above without the presence of the electric field. In this way we obtain the geometry for a chain containing a polaron and an exciton. In our simulations we use a 250-site chain, which is long enough to contain two independent excitations. Before the external electric field is turned on, the polaron is located at the 50th site while the exciton at the 150th site. They are separated well enough to ensure that there is no interaction between them at the beginning. Then with the electric

FIG. 2. Time dependence of r_n (a) and $\bar{\rho}_n$ (b) for the polaron–exciton collision corresponds to composite spin state (a), $E = 0.5 \times 10^5$ V/cm.

field being smoothly turned on, the charged polaron moves toward the neutral exciton and then collide with it.

We first discuss the polaron–exciton scattering process corresponding to composite spin state (a) in which the polaron and the exciton have parallel spins. We present the temporal evolution of staggered order parameter $r_n(t)$ and mean charge density $\bar{\rho}_n(t)$ in Figs. 2(a) and 2(b), respectively. In this simulation, the external electric field is set to $E = 0.5 \times 10^5$ V/cm. As we can see from Fig. 2(a), after some time (about 50 fs) the polaron begins to move as a result of the Coulombic force from the external electric field. It quickly reaches its saturation velocity and begins to overlap with the exciton after about 280 fs. To lower the system energy, the peak of polaron lattice deformation does not add on the peak of exciton lattice deformation. By exchanging their position the polaron passes through the exciton while the exciton experiences a small “position shift.” During the whole scattering process, the charge of polaron always couples with the lattice deformation, which can be seen from Fig. 2(b). The polaron holds its integrity very well after passing through the exciton.

However, the polaron cannot always pass through the exciton. If we lower the external electric field to below $E = 0.1 \times 10^5$ V/cm or increase the e – e interaction U_0 enough, the polaron will not be able to pass through the exciton. This means that there is weak repulsion between them.

In the following, we discuss the polaron–exciton scattering process corresponding to composite spin state (b), in

FIG. 3. Time dependence of r_n (a) and $\bar{\rho}_n$ (b) for the polaron-exciton collision corresponds to composite spin state (b), $E = 0.5 \times 10^5$ V/cm.

which the polaron and the exciton have opposite spins. The external electric field is set to $E = 0.5 \times 10^5$ V/cm as in the previous simulation. The temporal evolution of staggered order parameter $r_n(t)$ and mean charge density $\bar{\rho}_n(t)$ is displayed in Figs. 3(a) and 3(b), respectively. As shown in Fig. 3(a), when the polaron collides with the exciton, unlike composite spin state (a), it is repelled by the exciton. Evidently, there is strong repulsion between the polaron and the exciton in this case. Under the influence of the electric field, following the collision, the polaron turns back and then pushes the exciton moving together. From Fig. 3(b), we can see that the polaron also holds its integrity very well after the collision.

From the results above, we can conclude that the repulsion between a polaron and an exciton with antiparallel spins is much stronger than that with parallel spins. Obviously, this difference in behavior should be associated with the spins of the polaron and the exciton. In composite spin state (a), the electron in ε_p^u and the electrons in ε_n^u and ε_n^d are spin-parallel. Due to the Pauli principle, these electrons cannot occupy the same site when the polaron wave function and the exciton wavefunction overlaps. Compared with composite spin state (b), the overlapping of wavefunctions will not induce obvious energy increase, as the energy increase mainly comes from the on-site Coulomb repulsion strength U_0 . So the repulsion between a polaron and an exciton with parallel spins is much smaller than that with antiparallel spins.

If we increase the external electric field to $E = 2.0 \times 10^5$ V/cm the collision dynamics changes dramatically, as

FIG. 4. Time dependence of r_n (a) and $\bar{\rho}_n$ (b) for the polaron-exciton collision corresponds to composite spin state (b), $E = 2.0 \times 10^5$ V/cm.

shown in Figs. 4(a) and 4(b). From Fig. 4(a), we see that the polaron dissociates after colliding with the exciton. However, the exciton still keeps its integrity quite well. Due to the polaron dissociation, charge is no longer coupled to a local chain distortion but delocalizes over the whole system, as shown in Fig. 4(b). The delocalized charge hardly induces any lattice distortions. Instead the distortion pattern seen in Fig. 4(a) describes phonons which are created during the collision process.

If we continue to increase the external electric field as high as to $E = 2.5 \times 10^5$ V/cm the collision dynamics changes again, as shown in Figs. 5(a) and 5(b). From Fig. 5(a), we see that at about 240 fs the polaron begins to overlap with the exciton, then thrusts into the exciton pushed by the high electric field. After about another 100 fs, the polaron passes through the exciton. It recollects its charge and continues moving on. However, the polaron cannot recollect all his charge after the collision. This can be seen in Fig. 5(b). The charge confined by the polaron lattice deformation reduced a little after the collision. To see this clearly, we draw the time evolution of the occupation number of the intragap energy levels in Fig. 6.

We see that the occupation number of polaron level ε_p^u reduced from 1.0 to about 0.8 after the collision, while the occupation numbers of the two exciton levels hardly change. This shows that the exciton is quite stable during the scattering process whereas the polaron can either break or change its features as a result of scattering.

FIG. 5. Time dependence of r_n (a) and $\bar{p}_n$ (b) for the polaron-exciton collision corresponds to composite spin state (b), $E = 2.5 \times 10^5$ V/cm.

To test if the exciton can be broken by the polaron under any condition we have done a lot of other calculations in which we change some parameters such as e - e interaction and the electron-phonon coupling. All the results show that the exciton remains stable. We think that this is associated with the large binding energy difference between polaron and exciton. This binding energy difference can be seen from the level shift between ε_p^u and ε_n^u . In all the above simulations,

FIG. 6. Time evolution of the occupation number of the intragap energy levels, $E = 2.5 \times 10^5$ V/cm.

the binding energy of the polaron is much smaller than that of the exciton. The polaron is therefore easier to dissociate than the exciton, in agreement with our observation that in the collision between them, it is only the polaron that breaks. Furthermore, the binding energy difference does not change when we change the parameters, such as the external electric field, the e - e interaction and the electron-phonon coupling. Thus, we can conclude that a polaron never breaks an exciton.

IV. CONCLUSIONS

For two composite spin states, we have simulated the polaron-exciton scattering process in a polymer chain within a nonadiabatic evolution method, in which the electron wave function is described by the time-dependent Schrödinger equation while the polymer lattice is treated classically by a Newtonian equation of motion.

For composite spin state (a), the repulsion between the polaron and the exciton is very weak, the polaron can easily pass through the exciton even in weak external electric field. For composite spin state (b), the repulsion between the polaron and the exciton is much stronger than that for composite spin state (a). The polaron may be bounced back, be dissociated or pass through the exciton, which depends on the strength of the external electric field. Our results also show that the polaron always cannot break the exciton.

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- ¹J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burn, and A. B. Holmes, *Nature (London)* **347**, 539 (1990).
- ²A. J. Heeger, S. Kivelson, J. R. Schrieffer, and W. P. Su, *Rev. Mod. Phys.* **60**, 781 (1998).
- ³J. Kalinowski, W. Stampor, J. Szmytkowski, D. Virgili, M. Cocchi, V. Fattori, and C. Sabatini, *Phys. Rev. B* **74**, 085316 (2006).
- ⁴A. S. Dhoot, D. S. Ginger, D. Beljonne, Z. Shuai, and N. C. Greenham, *Chem. Phys. Lett.* **360**, 195 (2002).
- ⁵H. H. Liao, H. F. Meng, S. F. Horng, J. T. Shy, K. Chen, and C. S. Hsu, *Phys. Rev. B* **72**, 113203 (2005).
- ⁶D. Hertel and K. Meerholz, *J. Phys. Chem. B* **111**, 12075 (2007).
- ⁷P. Desai, P. Shakya, T. Kreouzis, W. P. Gillin, N. A. Morley, and M. R. J. Gibbs, *Phys. Rev. B* **75**, 094423 (2007).
- ⁸Z. Sun, Y. Li, S. J. Xie, Z. An, and D. S. Liu, *Phys. Rev. B* **79**, 201310(R) (2009).
- ⁹S. Li, G. P. Tong, and T. F. George, *J. Appl. Phys.* **106**, 074513 (2009).
- ¹⁰Y. Meng, X. J. Liu, B. Di, and Z. An, *J. Chem. Phys.* **131**, 244502 (2009).
- ¹¹W. P. Su, J. R. Schrieffer, and A. J. Heeger, *Phys. Rev. Lett.* **42**, 1698 (1979).
- ¹²Y. Ono and A. Terai, *J. Phys. Soc. Jpn.* **59**, 2893 (1990).
- ¹³C. Q. Wu, X. Sun, and K. Nasu, *Phys. Rev. Lett.* **59**, 831 (1987).
- ¹⁴G. M. e Silva, *Phys. Rev. B* **61**, 10777 (2000).
- ¹⁵K. Gao, X. Liu, D. Liu, and S. Xie, *Phys. Rev. B* **75**, 205412 (2007).
- ¹⁶D. K. Campbell, A. R. Bishop, and K. Fesser, *Phys. Rev. B* **26**, 6862 (1982).