A new perspective on optoelectric conversion in conjugated polymers*

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Photoexcitation of a neutral soliton will create a polaron and a charged soliton. According to a tight-binding model and a nonadiabatic method, we investigate the dynamical process of these two photogenerated charge carriers in an external electric field. It is found that the polaron and the soliton can pass through each other, which excludes the possibility of carrier recombination that usually occurs in existing organic solar cells. The results indicate a more efficient way to realize the optoelectric conversion by photoexciting polymer materials with soliton defects. On the other hand, it is found that solitons take on greater stability than polarons during collision.

Keywords: polaron, soliton, optoelectric conversion

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1. Introduction

In the past few years one has witnessed a rapid growth of interest in conjugated polymers due to their promising application in a variety of optoelectric devices, such as field-effect transistors, light-emitting diodes and solar cells.[1−5] Cells made with a single polymer and two electrodes tend to be inefficient because the photogenerated excitons are usually not split by the built-in electric field.[6,7] The performances of the polymer solar cells have been improved by the use of a bulk-heterojunction. In a bulk-heterojunction, excitons need to diffuse a much shorter distance to the interface and the charge generation takes places throughout the bulk, leading to a high charge generation efficiency. Some solar cells made of organic materials may compete with current inorganic solar cells. The drawback of the bulk-heterojunction concept, however, is the fact that the collection of photogenerated charges becomes strongly dependent on the morphology of the blend.[8,9]

A great deal of theoretical research has also been devoted to the polymer optoelectric properties and several approaches to improving the optoelectric conversion efficiency have been suggested.[10−14] Solitons are very important excitations in trans-polyacetylene(tPA). It has been demonstrated that a neutral soliton will convert to a negatively charged polaron and a positively charged soliton by photoexcitation, i.e., $S^0 + h\nu \Rightarrow S^+ + P^-$.[15] Different from photogenerated excitons which are not separated efficiently into free charge carriers (P^- and P^+), the photogenerated S^+ and P^- are separated immediately after photoexcitation. Thus, the optoelectric conversion becomes possible. In this paper, we present a detailed study of the dynamical process of the photogenerated charge carriers in the presence of an external electric field after photoexcitation, that is, polaron–soliton collision. Particularly, it should be noted that the polymer chain adopted here is specified to be tPA due to the requirement that solitons exist in degenerate systems.

2. Model and method

For a chain-like organic molecule, we can describe it in the framework of the tight-binding model.[16] The Hamiltonian is expressed as

$$H = H_0 + H_{\rm E} + H_{\rm e-e}, \tag{1}$$

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where H_0 describes the electron–lattice interaction, which has the following form:

$$H_0 = -\sum_{n,s} t_{n,n+1}(\hat{c}^+_{n,s}\hat{c}_{n+1,s} + \hat{c}^+_{n+1,s}\hat{c}_{n,s}) + \frac{K}{2}\sum_n (u_{n+1}-u_n)^2 + \frac{M}{2}\sum_n \left(\frac{\partial u_n}{\partial t}\right)^2, \quad (2)$$

where $t_{n,n+1} = [t_0 - \alpha(u_{n+1} - u_n)]$ is the hopping integral of π electrons between sites n and $n+1$, α represents the electron–lattice coupling constant, u_n is the monomer displacement of site n, $\hat{c}^+_{n,s}(\hat{c}_{n,s})$ denotes the electron creation (annihilation) operator on site n with spin s, K is the elastic constant, and M refers to the mass of a CH group.

The contribution from the external electric field is

$$H_E = \sum_n eE(t)(na + u_n)(\hat{c}^+_{n,s}\hat{c}_{n,s} - 1), \quad (3)$$

with e is the electronic charge and a the lattice constant. To avoid the drastic vibration of lattice atoms, the electric field $E(t)$ is applied with a linear function $E_0 t/t_c$. After $t = t_c$, the electric field becomes a constant the same as E_0.

H_{e-e} is the electron–electron interaction, which is treated as the Hartree–Fock approximation for simplicity

$$H_{e-e} = \frac{U}{2}\sum_{n,s} \hat{c}^+_{n,s}\hat{c}_{n,s}\hat{c}^+_{n,-s}\hat{c}_{n,-s} + \frac{V}{2}\sum_{n,s,s'} \hat{c}^+_{n,s}\hat{c}_{n,s}\hat{c}^+_{n+1,s'}\hat{c}_{n+1,s'}, \quad (4)$$

where U and V denote the on-site repulsion and the nearest-neighbour repulsion, respectively.

The evolution of the system proceeds by following the equation of motion of the electronic state $\Psi_\nu(n,t)$

$$\mathrm{i}\hbar\partial_t \Psi_\nu(n,t) = H_{\mathrm{ele}}\Psi_\nu(n,t), \quad (5)$$

and the equation of motion of the lattice displacement u_n

$$M\ddot{u}_n = -K[2u_n(t) - u_{n+1}(t) - u_{n-1}(t)] + 2\alpha[\rho_{n,n+1}(t) - \rho_{n-1,n}(t)] + eE(t)[\rho_{n,n}(t) - 1] - \lambda M\dot{u}_n(t), \quad (6)$$

where the element of the density matrix is defined as

$$\rho_{n,n'} = \sum_\nu \Psi^*_\nu(n,t) f_\nu \Psi_\nu(n',t), \quad (7)$$

with f_ν being the time-independent distribution function depending on the initial occupation (being 0, 1, or 2). In the following, we will focus on the evolution of the charge distribution defined as $\rho_n = \rho_{n,n} - 1$ and the staggered lattice configuration in the form $y_n = (-1)^n(2u_n - u_{n-1} - u_{n+1})/4$.

At an arbitrary time, the electronic state $\Psi_\nu(n,t)$ can be expanded on the basis of the instantaneous eigenstates into $\Psi_\nu(n,t) = \sum_\mu C_{\nu,\mu}(t)\phi_\mu(n,t)$, where $\phi_\mu(n,t)$ are solutions to the time-independent Schrödinger equation at that moment, i.e., $H_{\mathrm{ele}}\phi_\mu(n,t) = \varepsilon_\mu(t)\phi_\mu(n,t)$.

The above coupled differential equations (5) and (6) are solved by the Runge–Kutta method of order eight with step size controlled.

3. Results and discussion

We consider a finite tPA chain containing 299 monomers. The values of the parameters in the Hamiltonian are chosen as those generally used:[17] $t_0 = 2.5$ eV, $\alpha = 4.1$ eV/Å, $K = 21$ eV/Å^2, $a = 1.22$ Å, $M = 1349.14$ eV $\cdot$ fs^2/Å^2 (1 Å = 0.1 nm), and e–e interaction $U = 2.0$ eV, $V = U/3$.

We focus on the motion of the photogenerated charge carriers P^- and S^+ upon photoexcitation of a neutral soliton. P^- and S^+ have existed in the polymer chain before the field is applied, and we take this conformation as the initial condition. The soliton and polaron are separated far from each other so that they can have enough space to travel before collision.

In Fig. 1(a) we show the initial charge distribution ρ_n and the accompanying lattice configuration y_n. The structure of the energy levels corresponding to this conformation is presented in Fig. 1(b). Three energy levels are localized in the energy gap, among which the two shallow ones near the band edge are the polaron energy levels and the deep one at the midgap belongs to the charged soliton. According to the charge quantities carried by these two quasi-particles, the three localized energy levels ε_{149}, ε_{150} and ε_{151} accomodate 1, 0, and 2 electrons, respectively. After the electric field is turned on, the polaron and the soliton start to move and collide with each other after some time. We have performed simulations for a wide range of the applied field from 5×10^3 V/cm to 4×10^5 V/cm. The reason for this choice of the field is that for a single polaron (or a single soliton) under higher field, it cannot be kept localized but becomes dissociated.[18] It is interesting to find that the photogenerated S^+ and P^- can pass through each other.

Meanwhile it can be recognized that above the field $E = 10^5$ V/cm, the polaronic lattice distortion and the charge no longer move together as an entity after collision, that is, the polaron becomes dissociated after collision with the soliton at field $E \geq 10^5$ V/cm, while the soliton can keep its localized state well.

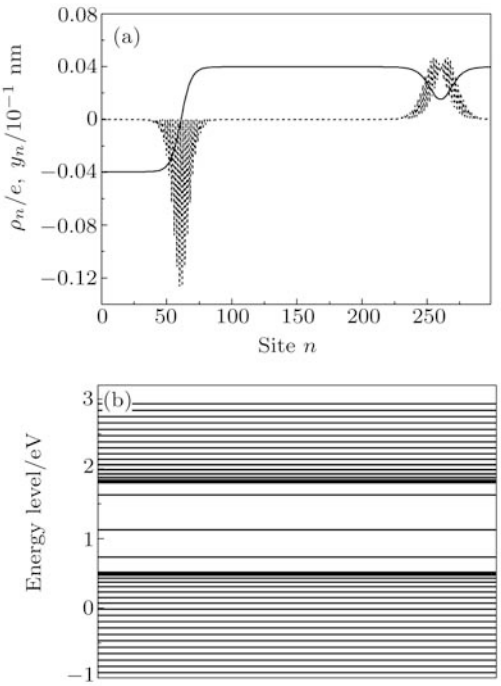


Fig. 1. Initial conformation of the system: (a) lattice configuration y_n (solid line) and charge distribution ρ_n (dot line), and (b) the structure of the energy levels.

To see the picture clearly we first illustrate the dynamical behaviour of the system at a field $E = 0.8\times10^5$ V/cm, lower than the critical value 10^5 V/cm. Depicted in Fig. 2(a) is the evolution of the charge distribution ρ_n. It can be seen from the picture that in the presence of the electric field the polaron (dark) and the soliton (white) enter into a motion state after a waiting time for energy accumulation. After a short acceleration phase they move each with a constant velocity and the soliton moves a little slowly than the polaron. At about 400 fs, they meet and collide with each other. Figure 2(b) shows the charge distribution and the corresponding lattice configuration at a few typical times. We can see some lattice vibrations induced by the applied field. After 400 fs, lattice vibration increases due to the collision between these two quasi-particles. It is found that the polaron can pass through the soliton kink and the electrons are still coupled with the lattice distortions after collision. Detailed studies of scattering between other excitations in conjugated polymers, e.g. polaron–bipolaron collision, two oppositely charged polaron collision, were carried out in Refs. [11]–[14]. The behaviour of soliton–polaron collision we discuss here is similar to that of polaron–bipolaron scattering in Ref. [11]. The polaron and the bipolaron can pass through each other depending on the strength of applied field.

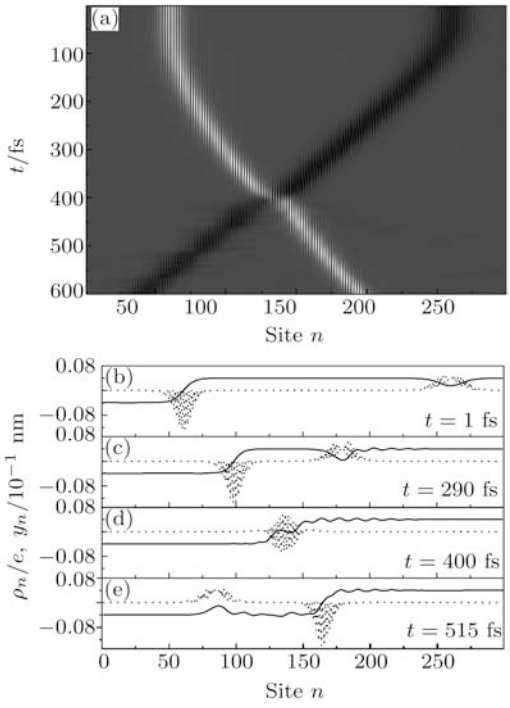


Fig. 2. Time evolutions of (a) charge distribution ρ_n, and (b)–(e) charge distribution (dot line) and lattice configuration (solid line) at several typical times $t = 1, 290, 400, 515$ fs under an external electric field $E = 0.8 \times 10^5$ V/cm.

Next we present the results at a higher field $E_0 = 1.2 \times 10^5$ V/cm for comparison. It has been well known that for such a strength of the field, a single polaron (or soliton) can move along the polymer chain with keeping integrity. Plotted in Fig. 3 are the lattice configuration and the charge distribution at several typical times. Figures 3(b) and 3(d) show the lattice configuration and the electronic distribution before and after they meet, respectively. After the polaron passes through the soliton kink, the charge escapes from the polaronic lattice distortion and becomes delocalized in the whole chain. The lattice distortion is left behind. However, the soliton continues to move as an entity, which implies that the soliton is more stable than the polaron under the same electric field. The characteristics of polaron dissociation can also be reflected by the behaviours of the instantaneous eigenlevels, see Fig. 4. Accompanied with the

dissociation, the localized polaron state becomes delocalized, so that the localized polaron levels disappear. Instead, they melt into the continnum bands. The soliton level stays localized in the gap.

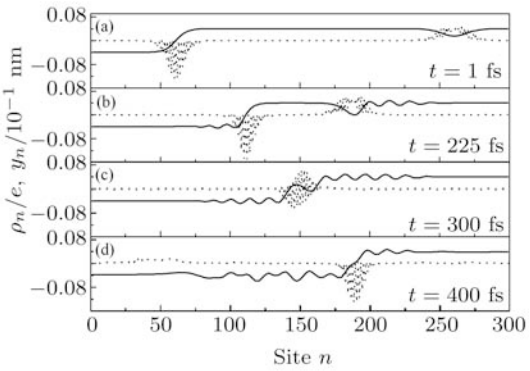


Fig. 3. Curves for charge distribution ρ_n (dot line) and the lattice configuration y_n (solid line) at $t = 1, 225, 300, 400$ fs from the top to the bottom under field $E = 1.2 \times 10^5$ V/cm.

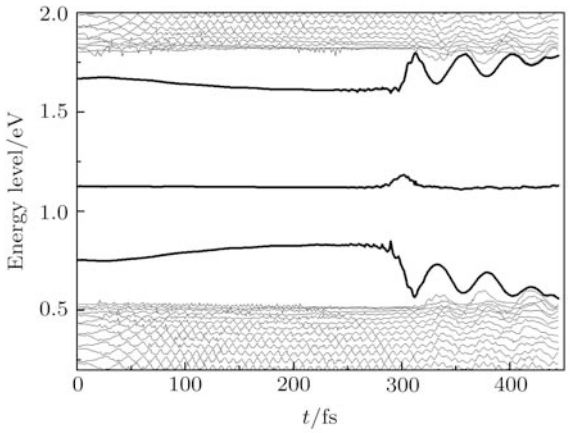


Fig. 4. Evolutions of the polaron levels $\varepsilon_{151}, \varepsilon_{149}$ and the soliton level ε_{150} under field $E = 1.2 \times 10^5$ V/cm.

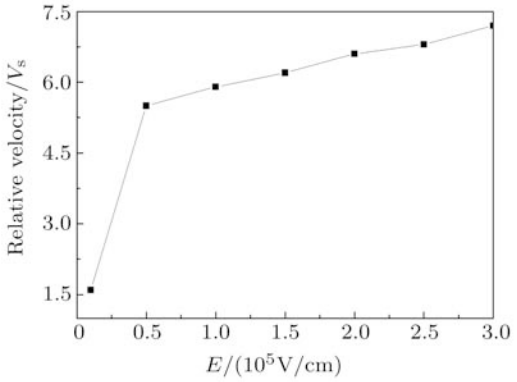


Fig. 5. Field dependence of the relative velocity of the collision between two quasi-particles.

The dissociation of polaron is related to the relative velocity of the collision (in terms of the sound velocity V_s). Figure 5 shows the field dependence of relative velocity. The relative velocity increases with the enhancement of the electric field increasing. In the presence of a higher electric field, these two quasiparticles meet at a large relative velocity, so that the electron confined in the polaronic lattice distortion can be scattered out and becomes delocalized.

As discussed above, whether under low fields or in high fields, photogenerated charge carriers upon photoexcitation of a neutral soliton can pass through each other without recombination. Thus through our simulation, a more efficient way to realize the optoelectric conversion by photoexciting polymer materials with soliton defects may be suggested. Early polymer solar cells showed rather low solar power conversion efficiencies, because photoexcitation resulted in a strong Coulombically bond charge pair (referred to as exciton). Without addition of electron donating/accepting dopants or functional groups, the efficiency of charge carrier generation in polymer is low. The performance of solar cell has been improved by the use of a bulk-heterjunction architecture. In a bulk-heterjunction, excitons need to diffuse a much shorter distance to the interface and charge generation takes place throughout the bulk, leading to a high charge photogeneration efficiency. If the exciton decays in a time shorter than that necessary for diffusing to the interface, it will not contribute to the photogeneration of charges. However, two advantages lie in the process we have investigated. First, different from the photogenerated exciton, the charge carriers are separated directly upon photoexcitation. Moreover, charge collection is easier because the possible geminate recombination of the charge carriers is excluded. Therefore, the solar power conversion efficiency may be greatly improved.

4. Summary

Polymer, or plastic, solar cells have shown potential for harvesting solar energy in a cost-effective way. Significant efforts are being made to improve the performances of the polymer solar cells. High efficiency requires efficient light absorption and transport of charge carriers. It has been demonstrated that a neutral soliton will convert to a negatively charged polaron and a positively charged soliton by photoexcitation. The photogenerated products are separated from each other upon photoexcitation. Thus, the optoelectric conversion becomes easier via the photoex-

citation of the soliton. Another key issue in improving the efficiency of the organic solar cell is charge collection. Geminate recombination of the photogenerated charge carriers (oppositely charged polarons) before they transfer to the electrodes will greatly decrease the optoelectric conversion efficiency. Through our study on the field-drived dynamical process of the charge carriers, after photoexcitation of a neutral soliton, i.e., polaron–soliton collision, we find that the polaron and the soliton can pass through each other and keep integrity, which excludes the possible recombination of charge carriers. Thus, the efficiency of the optoelectric conversion may be greatly improved.

References

[1] Forrest S, Burrows P and Thompson M 2000 *IEEE Spectrum* **37** 29

[2] Peumans P, Yakimov A and Forrest S R 2003 *J. Appl. Phys.* **93** 3693

[3] Gao K, Xie S J, Li Y, Yin S, Liu D S and Zhao X 2009 *Chin. Phys.* B **18** 2961

[4] Tian R Y, Yang R Q, Peng J B and Cao Y 2005 *Chin. Phys.* **14** 1032

[5] Xiong Z H, Wu D, Vardeny Z V and Shi J 2004 *Nature* **427** 821

[6] Coakley K M and McGehee M D 2004 *Chem. Mater.* **16** 4533

[7] Andrés J A and Blau W J 2008 *Carbon* **46** 2067

[8] Street R A, Schoendorf M, Roy A and Lee J H 2010 *Phys. Rev.* B **81** 205307

[9] Holt J, Singh S, Drori T, Zhang Y and Vardeny Z V 2009 *Phys. Rev.* B **79** 195210

[10] Kirchartz T, Pieters B E, Taretto K and Rau U 2009 *Phys. Rev.* B **80** 035334

[11] Sun Z , Li Y , Gao K, Liu D S, An Z and Xie S J 2010 *Organic Electronics* **11** 279

[12] Meng Y, Liu X J, Di B and An Z 2009 *J. Chem. Phys* **131** 244502

[13] Sun Z, Li Y, Xie S J, An Z and Liu D S 2009 *Phys. Rev.* B **79** 201310

[14] An Z, Di B, Zhao H and Wu C Q 2008 *Euro. Phys. J.* B **63** 71

[15] Zhang D C, Liu D S, Mei L M, Xie S J and Sun X 2005 *Synth. Met.* **152** 369

[16] Gao K, Liu X J, Liu D S and Xie S J 2007 *Phys. Rev.* B **75** 205412

[17] Liu W, Li Y, Sun Z, Liu D S and Xie S J 2008 *Phys. Lett.* A **372** 4315

[18] Rakhmanova S V and Conwell E M 1999 *Appl. Phys. Lett.* **75** 1518