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Dissociation of bipolaron in non-degenerate polymer chain at high electric fields ☆

Y.H. Yan *, C.Q. Wu

Department of Physics, Fudan University, Shanghai 200433, China

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Abstract

We investigate the dynamics of bipolaron in non-degenerate polymer (e.g. PPV) in an external electric field by using a nonadiabatic evolution method, which allows transition between instantaneous electronic states. When the applied electric field exceeds a critical value, a bipolaron is found to dissociate like the case of polaron due to the lattice distortion not being able to follow the fast moving electrons. The critical value is estimated to be of order 10^6 V/cm. This result is consistent with experiment in that a large increase in current in PPV occurs at high fields. At a given electric field, the saturation velocity of bipolaron will decrease with the increase of non-degenerate parameters t_e.

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Keywords: Polymer; Bipolaron; Nonadiabatic dynamics

1. Introduction

Conjugated polymers have attracted much interest for their potential applications, e.g., organic light emitting diodes, field effect transistors, solar cells, etc. [1,2]. Due to the strong electron–lattice interactions, it is well known that additional electrons or holes in conjugated polymers will induce self-localized excitations, such as solitons [3] (only in *trans*-polyacetylene), polarons and bipolarons [4]. As a result, it has been generally accepted that the charge carriers in conjugated polymers are these excitations including both charge and lattice distortion [5]. Therefore, it is of fundamental importance to study the dynamics of charge carriers in polymers.

There have been extensive studies on soliton and polaron dynamics in conjugated polymers under the influence of external electric fields [6–12]. One of the major issues is the stabilities of those elementary excitations in electric fields. It has been shown that solitons and polarons can move with a constant speed along the polymer chain in electric field with strength below a critical value. Solitons are shown to have a maximum velocity of $2.7v_s$ [6,7], with v_s being the sound velocity, while the maximum velocity of polarons is about $4v_s$ [8,9]. Furthermore, it has been shown that the polaron can survive under the field up to about 4×10^5 V/cm [9,10]. In an even higher electric field, polaron will dissociate due to the lattice distortion not being able to following the faster moving electron. Here, it should be pointed out that polaron is referred to as the optical polaron, which is much different from the acoustic one. Acoustic polaron can only reach a maximum velocity near v_s [13,14].

There is also much effort devoted to the study of bipolaron [5], the elementary excitation in non-degenerate polymers, such as poly(p-phenylene vinylene) (PPV), the polymeric material adopted mostly in organic opto-electronic devices [1]. In static case, it was shown that at the large electron–phonon coupling, the bipolaron remains stable up to relatively large Hubbard U [15,16]. As for the dynamical behavior, the motion of a bipolaron (together with a polaron) under the influence of an electric field through a single-site impurity was discussed [17]. How-

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* Corresponding author.
E-mail address: yhyan@fudan.edu.cn (Y.H. Yan).

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ever, it is not clear how high electric fields a bipolaron can sustain and what velocity it can reach. But one can expect that just like the case of polaron, there exists a critical electric field above which a bipolaron begins to dissociate.

In the present Letter, we will discuss the bipolaron dynamics in high electric fields in terms of a modified SSH Hamiltonian. Recent experiments show that a rapid increase in current occurs in PPV when the electric field is up to 1–2 $\times 10^6$ V/cm, and the estimated mobility of 0.1 $\mathrm{cm}^2/(\mathrm{V\,s})$ is 5 orders of magnitude higher than the mobility in low fields [18,19]. We will show that this can be explained by the bipolaron dissociation. The Letter is organized as follows. In the following section, we present a tight-binding one-dimensional model for non-degenerate polymer chain in electric field and then describe the dynamical method. The results will be presented in Section 3 and the summary of this work is given in Section 4.

2. Model and method

The Hamiltonian we consider in this Letter is as follows

$$H = H_e + H_{\mathrm{latt}}. \tag{1}$$

The electronic part is

$$H_e = -\sum_n t_n \left[e^{-i\gamma A(t)} c_{n+1}^{\dagger} c_n + \mathrm{h.c.} \right], \tag{2}$$

where $c_n^{\dagger}$ (c_n) creates (annihilates) an electron at site n, $t_n = t_0 - \alpha(u_{n+1} - u_n) + (-1)^n t_e$ is the hopping integral between sites n and $n+1$, α describes the electron–lattice coupling between neighboring sites due to the lattice bond stretch or compression, u_n is the monomer displacement of site n, and t_e is the Brazovskii–Kirova symmetry-breaking term [4] introduced for non-generate polymers. The vector potential $A(t)$ is introduced to describe a uniform external electric field along the chain at the periodic boundary condition. The relation between the potential $A(t)$ and the uniform electric field $E(t)$ is given by $E(t) = -(1/c)\partial A(t)/\partial t$. And $\gamma \equiv ea/\hbar c$ is a constant quantity with c the light speed, e the absolute value of the electronic charge, and a the lattice constant. The polymer lattice is treated classically, so

$$H_{\mathrm{latt}} = \frac{K}{2} \sum_n (u_{n+1} - u_n)^2 + \frac{M}{2} \sum_n \dot{u}_n^2, \tag{3}$$

where K is the elastic constant and M the mass of a basic group. The model parameters we use in this work are those generally chosen for polyacetylene [5]: $t_0 = 2.5$ eV, $\alpha = 4.1$ eV/Å, $K = 21$ eV/Å^2, $M = 1394.14$ eV fs^2/Å^2, $a = 1.22$ Å, and t_e is between 0 and 0.2 eV. In fact, in PPV-type polymers, the phenyl ring torsion will modulate the hopping integral t as $t\cos\theta$, where θ is the torsion angle [20,21]. But one can expect that small magnitude of the torsion ($\theta \sim 20°$ in PPV) does not change the bipolaron state very much. So for simplicity, we do not take into account the phenyl ring torsion effect.

In the absence of an external electric field, we can determine the static structure or the initial conditions by the minimization of the total energy of the system. When an electric field is turned on, the lattice configuration at any time t (> 0) should be governed by the Newtonian equations of motion,

$$M\ddot{u}_n = F_n(t), \tag{4}$$

where the force acting on the nth site consists of two parts: one part comes from the spring force of the bond stretch or compression and the other comes from the force of the electron–lattice interaction,

$$F_n(t) = -K(2u_n - u_{n+1} - u_{n-1}) + \alpha\left[e^{i\gamma A(t)} (\rho_{n,n+1} - \rho_{n-1,n}) + \mathrm{c.c.} \right], \tag{5}$$

here, the element of the density matrix is defined as

$$\rho_{n,m}(t) = \sum_k \psi_k(n,t) f_k \psi_k^*(m,t), \tag{6}$$

f_k is the time-independent distribution function determined by initial occupation (being 0, 1 or 2). The evolution of the electronic wave function $\psi_k(n,t)$ is determined by the time-dependent Schrödinger equation

$$i\hbar\dot{\psi}_k(n,t) = -t_n e^{-i\gamma A(t)} \psi_k(n+1,t) - t_{n-1} e^{i\gamma A(t)} \psi_k(n-1,t). \tag{7}$$

The coupled differential equations (4) and (7) could be solved numerically by use of the Runge–Kutta method.

3. Numerical results

Now, we present our numerical results on the dynamics of bipolaron. We take the optimized bipolaron configuration obtained in the absence of electric field as the initial condition. In order to reduce the lattice vibration in the accelerated process of the charged bipolaron, the electric field is turned on smoothly, that is, the field strength changes as $E(t) = E\exp[-(t-t_c)^2/t_w^2]$ for $0 < t < t_c$, $E(t) = E$ for $t > t_c$ with t_c being a smooth turn-on period, and t_w the width. In the simulation, we take $t_w = 25$ fs and $t_c = 75$ fs.

Fig. 1 shows the saturation velocity of bipolaron as a function of the electric field strength with different parameters t_e.

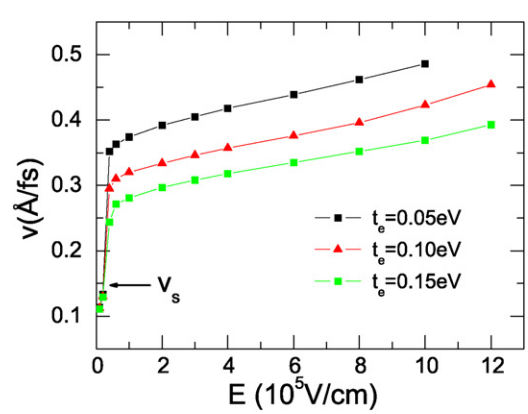

Fig. 1. The saturation velocity of bipolaron as a function of the electric field strength for different parameters t_e. The arrow indicates the position of the sound velocity.

From this figure, we observe that there is a change from a velocity below the sound velocity to a supersonic velocity around an electric field value of about 2.5×10^4 V/cm. The reason is that in low electric field, there is strong coupling between the bipolaron and the acoustic phonon [22]. The characteristic velocity of acoustic phonon is $v_s = \sqrt{4K/M}a/2 \approx 0.15$ Å/fs, therefore the bipolaron velocity cannot exceed sound velocity in low fields. When the electric fields become stronger, the bipolaron will be drawn out of the acoustic phonon trap. And then bipolaron velocity almost linearly increases with respect to the electric field strength E. In a given electric field, we see that velocity of bipolaron decreases with the increase of parameter t_e. This is because the difference of hopping integrals between the nearest-neighboring bonds becomes large when t_e increases. And the large difference of hopping integrals is unfavorable for bipolaron motion. As a result, bipolaron velocity decreases as t_e increasing.

In Fig. 1, we also observe that bipolaron can sustain to electric field 10^6 V/cm. That means, bipolaron keeps its shape while moving at a constant speed in electric field with strength up to $E \sim 10^6$ V/cm. This electric field value is much larger than that for polaron, which is estimated to be about 4.0×10^5 V/cm [8,9]. Therefore, bipolaron is more stable than polaron in electric fields. This could be understood in terms of binding energy, which is defined as the energy difference between the system with dimerized configuration (two extra electrons occupying the bottom level of conduction band) and the system with optimized configuration (two extra electrons occupying bipolaron energy level). The binding energy of bipolaron is about 0.36 eV (varying little with t_e), much larger than that of polaron, which is about 0.06 eV. At $t_e = 0.05$ eV, the critical electric field strength E_c, above which bipolaron dissociates, is estimated to be about 1.1×10^6 V/cm, and it is a little higher for a larger t_e.

In Fig. 2 we show the charge distribution ρ_n ($\equiv \rho_{n,n} - 1$) and lattice configuration y_n [$\equiv (-1)^n(u_{n+1} - u_n)$] of bipolaron at four different times in field 1.2×10^6 V/cm, which is just above the critical value. At the first 300 fs, the bipolaron moves with the lattice distortion accompanying the charge. And the distortion first becomes deeper and then goes more and more shallow. At around $t = 300$ fs, the bipolaron begins to dissociate since the lattice distortion can no longer follow the electron motion. Thereafter the charge held previously by the lattice distortion is distributed in the whole chain and becomes delocalized completely. From the lattice configurations at different times, we also observe breathers—spacial localized and time periodic vibrational excitations—emitted by the motion of bipolaron in the action of the applied electric field as in the case of polaron [11]. Here we should mention that the breather or phonon vibration left after the bipolaron dissociation is unfavorable for the charge mobility. But just as in metals where electron are also scattered by phonons, one still observe that the conductivity is much large. Therefore we can expect that charge mobility will increase after the bipolarons dissociate into free electrons in polymers.

The dissociation process is also reflected in Fig. 3 (lower panel), which shows the evolution of the bipolaron energy level,

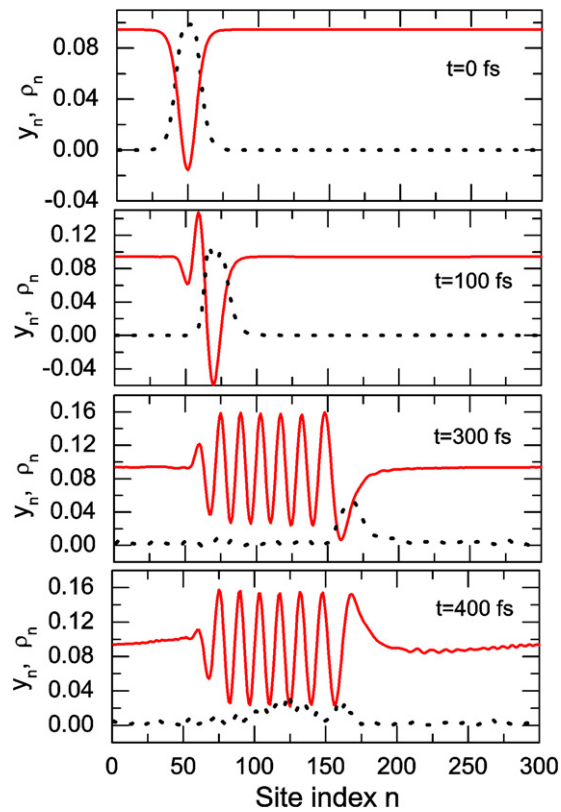

Fig. 2. Lattice configuration (solid lines) and charge distribution (dotted lines) at different times in the electric field $E = 1.2 \times 10^6$ V/cm, $t_e = 0.05$ eV.

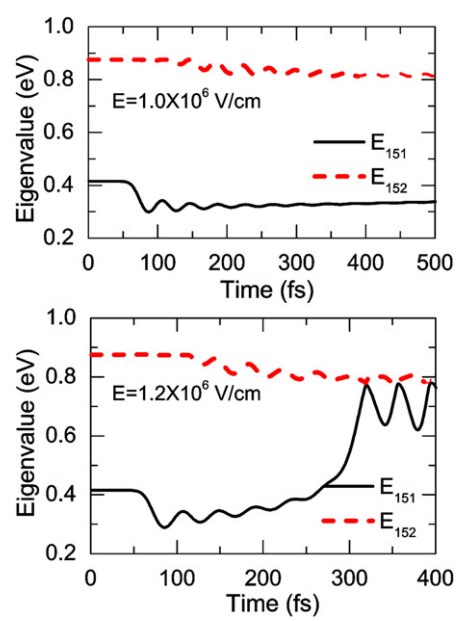

Fig. 3. Energy evolution in the electric field $E = 1.0 \times 10^6$ V/cm and $E = 1.2 \times 10^6$ V/cm. E_{152} is the bottom energy level of the conduction band, and E_{151} is the bipolaron level. $t_e = 0.05$ eV.

E_{151}, and the lowest energy level of the conduction band, E_{152}. From this figure, we observe that the bipolaron energy level first becomes deeper and then, around 300 fs, moves towards the conduction band. As a comparison, we also show the energy evolution in field 1.0×10^6 V/cm (upper panel). In this

situation, bipolaron does not dissociate and we observe that the bipolaron energy level exists all the time. Since it is well understood that free (unbound) electrons will move much faster than that of electrons bound by polarized phonon clouds, one might expect that a large increase of charge mobilities will occur when the polaron or bipolaron is dissociated by high electric field. In fact, experiments have shown that in PPV, the estimated mobility at high electric field $1–2 \times 10^6$ V/cm is 5 orders of magnitude larger than the mobility in low fields [18,19]. Therefore we might attribute this increase to the dissociation of bipolarons.

Furthermore, we consider the formation of a bipolaron in the presence of a constant electric field, for which the initial lattice configuration is taken as a perfectly dimerized one with two extra electrons occupying at the bottom of the conduction band. In the presence of a weak electric field, it takes about 100 fs to form a bipolaron in the polymer chain. The formatted bipolaron is moving at a low speed, which depends on the strength of applied electric fields. But the situation is different in an electric field $E > 8 \times 10^4$ V/cm, where a bipolaron will not form in the chain at all. The observation is only that the chain is distorted in a somewhat random way and the two added electrons remain unbound. It should be pointed out that the critical electric field for the formation of a bipolaron is a little larger than that for a polaron.

4. Summary

In summary, we have investigated the dynamics of bipolaron in non-degenerate polymer chain in high electric fields by solving the time-dependent Schrödinger equation for the electronic wave function and the Newtonian equation of motion for the lattice simultaneously. We do not take into account the electron–electron interaction since the system is not a strongly correlated one. It is shown that a bipolaron is much more stable than a polaron, that is, a bipolaron sustains in an electric field up to 1.0×10^6 V/cm. Above this critical electric field, the bipolaron will dissociate due to the lattice distortion not being responded simultaneously to the fast moving electrons. This result is consistent with the experiment in that a rapid increase in current occurs in PPV when the electric field is up to $1–2 \times 10^6$ V/cm. The dependence of bipolaron velocities on the electric fields and the non-degenerate parameters is also discussed.

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