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Correlation effects on the dynamics of bipolarons in nondegenerate conjugated polymers

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By employing an adaptive time-dependent density-matrix-renormalization-group method, we investigate the dynamics of a charged bipolaron in the presence of both electron-phonon and electron-electron interactions. We use a Su-Schrieffer-Heeger model modified to include electron-electron interactions via a Hubbard Hamiltonian, a Brazovskii-Kirova symmetry-breaking term, and an external electric field. Our results show that the velocity of the bipolaron increases first and then decreases with the increasing of the on-site Coulomb interaction, U . Furthermore, the dependence of the bipolaron velocity, bipolaron effective mass, and bipolaron stability on the lattice structures is discussed. © 2009 American Institute of Physics. [DOI: 10.1063/1.3155207]

I. INTRODUCTION

Conjugated polymers, as quasi-one-dimensional materials, have a property that their lattice structure can be easily distorted due to the strong electron-lattice interactions.¹ As a result, charge injections or photoexcitations will induce self-trapped elementary excitations, such as solitons,^{2,3} polarons,⁴ and bipolarons.⁵ It has been generally accepted that the charge carriers in conjugated polymers are these excitations including both charge and lattice distortion.¹ There have been considerable research works devoted to the study of those nonlinear elementary excitations in conjugated polymers.⁶ The motivation behind these works stems from the fact that these excitations play an important role in organic optoelectronic devices, including light-emitting diodes, field-effect transistors, photocells and lasers,⁷ and so on. The formation and transport of such charge carriers are believed to be of fundamental importance.

Recently, UV visible near-infrared spectroscopy studies on poly(*p*-phenylene vinylene) combined with the follow up of the kinetics of doping with iodine vapor were reported and interpreted as direct observations of the formation of polaronic charge carriers.⁸ However, by following different doping levels with I_2 doping, bipolaron formation is identified as well, showing that polarons and bipolarons coexist in the oxidized polymer. Both polarons and bipolarons, which are composite particles with internal structure, can be formed in nondegenerate conjugated polymers, such as poly(phenylenevinylene) and polythiophene. The bipolarons are spinless species with charge $\pm 2|e|$, in contrast to the spin-bearing polarons (spin 1/2, charge $\pm 2|e|$). Therefore, the properties of the transport and the recombination of bipolarons will be much different from that of polarons. The existence of bipolarons is likely to play an important role in understanding the

operation of these optoelectronic devices based on conjugated polymers.⁵ There have been considerable amounts of research works devoted to the properties of bipolarons, for example, the formation and stability of bipolaron,^{9–14} the infrared active vibrational modes around a bipolaron,^{15,16} and the bipolaron lattice at metal-polymer interface.¹⁷ However, most of these works were focusing on the static properties of bipolarons. Most of processes in organic optoelectronic devices, such as the injection of charge from electrodes, the transport of charge carriers, and the recombination of oppositely charged polarons and/or bipolarons, are dynamical processes accompanying with both charge motion and lattice distortion driven by applied electric field. Therefore, a real time dynamical model should be much appropriate for the simulations of these processes.

The lattice dynamics^{18–27} has been widely used to simulate the formation of these nonlinear elementary excitations induced by photoexcitations or charge injections, and their motion driven by applied electric field, within the tight-binding Su-Schrieffer-Heeger (SSH) model³ as well as its extended versions for nondegenerate polymers.⁴ For example, it has been shown that the photocarriers (charged polarons) are generated directly by photoexcitations with a quantum yield about 25%.¹⁸ Importantly, the formation mechanism of charged polarons can only be understood within the dynamical scheme. In the presence of external electric fields, solitons as well as polarons move as one entity consisting of both the charge and the lattice deformation with a stationary velocity after being accelerated for a short time. A breatherlike lattice oscillation is developed behind the polaron, which bears the increased energy due to the electric field acting on the polaron.¹⁹ Solitons are shown to have a maximum velocity $2.7v_s$, where v_s is the sound velocity.^{26,27} The situation is different for polarons, which have a maximum velocity $4v_s$.²⁰ At extremely high electric field

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strengths, the soliton or polaron becomes unstable and dissociates due to the charge moving faster and not allowing the distortion to occur.

Because both electron-phonon and electron-electron interactions are expected to be important features of the electronic structure of organic materials, it is necessary to address the role of these interactions on charge carriers. In the SSH model, however, only the electron-lattice interactions are considered while the electron-electron interactions are ignored. Therefore, it should be asked, how the electron correlation affects the dynamical properties of polymers. Many research works have suggested that the electron correlation effect is of fundamental importance for understanding the physics properties of conjugated polymers,⁶ for example, the branch ratio between the singlet and the triplet excitons in polymer-based light-emitting diodes.^{28–31} Recently works on the dynamics of solitons and polarons in conjugated polymers show that the adaptive time-dependent density-matrix-renormalization-group³² (t-DMRG) method is an efficient approach to perform a real time dynamics of many-body systems including both electron-electron and electron-phonon interactions.^{33–35} In this paper, we apply the t-DMRG method on this system with both electron-phonon and electron-electron interactions, and investigate the dynamics of bipolarons.

In realistic devices, the charge transport is largely limited by interchain hopping rather than by intrachain processes. Even so, it is still very important and well worth to study the intrachain processes in depth theoretically because the charge transport in polymers is not well understood. For this reason, we focus on the dynamics of charged bipolarons driven by an external electric field in a single conducting polymer chain. In fact, the rapidly developing investigations in the area of nanometer-scale systems and its concomitant potential technological applications in real devices have induced considerable interest in the study of electrical transport through single conductive molecules or molecular wires.³⁶

The paper is organized as follows. In Sec. II, we present SSH model modified to include electron-electron interactions via a Hubbard Hamiltonian for a polymer chain under the influence of an external electric field and describe the dynamical evolution method used in this work. In Sec. III the dynamical evolution of a bipolaron under an applied electric field will be discussed. A summary is given in Sec. IV.

II. MODEL AND METHOD

The model Hamiltonian we consider for a polymer chain in this paper takes the following form:

$$H = H_{\text{el}} + H_{\text{latt}} + H_E. \quad (1)$$

The first part is to describe the electron energy, which contains both the electron-lattice coupling and electron-electron interactions, modeled by Hubbard extension of an SSH-type Hamiltonian,^{37–39}

$$H_{\text{el}} = - \sum_{i,\sigma} t_i [c_{i,\sigma}^\dagger c_{i+1,\sigma} + H.c.] + U \sum_i c_{i\uparrow}^\dagger c_{i\uparrow} c_{i\downarrow}^\dagger c_{i\downarrow}, \quad (2)$$

where $t_i \equiv t_0 - \alpha(u_{i+1} - u_i) + (-1)^i t_e$ is the hopping integral between sites i and $i+1$; α describes the electron-lattice coupling between neighboring sites due to the lattice bond stretch or compression; u_i is the monomer displacement of site i from its undimerized equilibrium position; and t_e is the Brazovskii–Kirova symmetry-breaking term introduced for nondegenerate polymers.⁴ U is the on-site Coulomb interaction; $c_{i,\sigma}^\dagger (c_{i,\sigma})$ is the creation (annihilation) operator of an electron with spin σ at the site i .

The second part in Eq. (1) is to describe the lattice elastic potential energy and the kinetic energy,

$$H_{\text{latt}} = \frac{K}{2} \sum_i (u_{i+1} - u_i)^2 + \frac{M}{2} \sum_i \dot{u}_i^2, \quad (3)$$

where K denotes the force constant originating from the σ -bond between carbon atoms, and M is the mass of a site, such as that of a CH unit for *trans*-polyacetylene.

The electric field $E(t)$ is included in the Hamiltonian as a scalar potential. This gives the following contribution to the Hamiltonian:

$$H_E = |e|E(t) \sum_{i,\sigma} (ia + u_i) \left(c_{i,\sigma}^\dagger c_{i,\sigma} - \frac{1}{2} \right). \quad (4)$$

The model parameters used in this work are those generally chosen for *trans*-polyacetylene:¹ $t_0 = 2.5$ eV, $K = 21.0$ eV/Å², $\alpha = 4.1$ eV/Å, $a = 1.22$ Å, $M = 1349.14$ eV fs²/Å², t_e is between 0 and 0.2 eV, and a bare optical phonon energy $\hbar\omega_0 = \hbar\sqrt{4K/M} = 0.16$ eV. All energies are given below in units of the hopping integral t_0 .

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. The total energy is obtained by the expectation value of Hamiltonian (1) at the ground state $|g\rangle$,

$$E_t = \langle g | H_{\text{el}} | g \rangle + \frac{K}{2} \sum_i (u_{i+1} - u_i)^2. \quad (5)$$

The electronic states are determined by the electronic part of Hamiltonian (2) and the lattice configuration of the polymer $\{u_i\}$ is determined by the minimization of the total energy in the above expression,

$$u_{i+1} - u_i = - \frac{\alpha}{K} \sum_\sigma \langle g | c_{i,\sigma}^\dagger c_{i+1,\sigma} + H.c. | g \rangle + \lambda, \quad (6)$$

where λ is a Lagrangian multiplier to guarantee the polymer chain length unchanged, i.e., $\sum_i (u_{i+1} - u_i) = 0$. The initial configuration of a bipolaron in the following dynamical evolution will be obtained from the solution of the above self-consistent Eq. (6) at the ground state.

At $t=0$, the polymer chain contains a positively charged bipolaron at the center. When an electric field is turned on, the lattice configuration at any time $t(>0)$ should be governed by the Newtonian equations of motion,

$$\begin{aligned}
M\ddot{u}_i(t) = & -K[2u_i(t) - u_{i+1}(t) - u_{i-1}(t)] \\
& + \alpha \sum_{\sigma} [\langle \psi(t) | c_{i,\sigma}^{\dagger} c_{i+1,\sigma} + H.c. | \psi(t) \rangle \\
& - \langle \psi(t) | c_{i-1,\sigma}^{\dagger} c_{i,\sigma} + H.c. | \psi(t) \rangle] - |e|E(t) \\
& \times \left[\langle \psi(t) | \sum_{\sigma} c_{i,\sigma}^{\dagger} c_{i,\sigma} | \psi(t) \rangle - 1 \right], \quad (7)
\end{aligned}$$

where $|\psi(t)\rangle$ are the time-evolved states at time t . In principle, the time evolution can be done by operating on $|\psi(t)\rangle$ with the time-evolution operator,

$$|\psi(t + \Delta t)\rangle = e^{-iH(t)\Delta t/\hbar} |\psi(t)\rangle = e^{-i\tau H(t)} |\psi(t)\rangle. \quad (8)$$

The time development of the lattice distortions and the electronic wave functions are obtained by solving the coupled Newtonian equation of motion Eq. (7) and the time-dependent Schrödinger equation Eq. (8).

The real time dynamics of such a many-body system including both electron-phonon and electron-electron interactions is a challenge work. A recently developed numerical method, the adaptive t-DMRG (adaptive t-DMRG),³² which is an efficient implementation of Vidal's time-evolving block-decimation (TEBD) algorithm⁴⁰ in the DMRG framework,⁴¹ enables us to perform this task. The key idea of t-DMRG is to incorporate the second order Suzuki–Trotter decomposition of the time-evolution operator Eq. (8) into the DMRG finite-system algorithm. The two main conditions for this method to be applicable, namely, that the system must be one dimensional and have nearest-neighbor interactions only, are met for the present system. Details about this method can be found in recent papers.^{33–35} The t-DMRG results show excellent agreement with exact results in the noninteracting case because of the introduction of classical phonons, which will reduce the DMRG truncation error significantly. In this paper, we present quasixact numerical results of the real time dynamics of the Hamiltonian Eq. (1) for realistic sizes of up to $N=128$ sites.

III. RESULTS AND DISCUSSIONS

In this section, we present our results on the motion of bipolarons in the presence of an external electric field. In our simulation, a polymer chain with total sites $N=128$ is considered. The starting geometry is obtained by minimizing the total energy of the chain where the electronic band is half filled with two extra holes. In order to reduce the lattice vibration in the accelerated process of the bipolaron, the electric field is turn on smoothly, that is, the field strength changes as $E(t)=E_0 \exp[-(t-t_c)^2/t_w^2]$ for $0 < t < t_c$, $E(t)=E_0$ for $t_c < t$ with t_c being a smooth turn-on period, and t_w being the width. Here, we take $t_w=10$ fs and $t_c=20$ fs.

The time evolution of the charge center X_c of the bipolaron under a moderate electric field, $E_0=2.0$ mV/Å, is shown in Fig. 1. When the electric field is turned on, the bipolaron is accelerated first, and then moves with a constant velocity as one entity consisting of both charge and lattice defect. The stability for the bipolaron velocity occurs because the moving bipolaron shall emit localized phonon-multibreather excitations, which bear the increased energy of

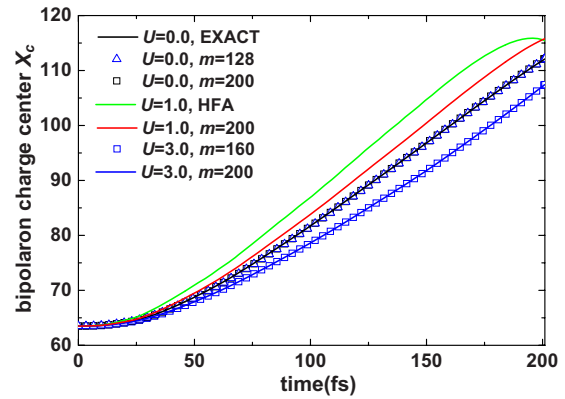


FIG. 1. (Color online) The time evolution of the charge center X_c of the bipolaron for different numbers of states m kept in DMRG, calculated with parameters $t_c=0.02$ and $E_0=2.0$ mV/Å.

the system due to the external electric field.¹⁹ The velocity is scaled by the sound velocity $v_s=\sqrt{4K/Ma/2}$ and is averaged in order to cancel out the fluctuations because only the stationary velocity is focused below. In order to confirm the validity of our results, we compare the t-DMRG calculations with the exact numerical results for a noninteracting ($t_c=0.02$, $U=0$) chain of the same set of parameters described above. The excellent agreement was found in both the charge center X_c and the staggered bond parameters (not shown in the figure) up to time $t\sim 200$ fs even when keeping $m=128$ states per block. In the following we always keep $m=200$ states per block and use a time step $\tau=0.05$ (in unit of \hbar/t_0).

When the Coulomb interaction is turned on, the velocity of the bipolaron increases first and then decreases with increasing of the on-site Coulomb interaction. In addition, one can find that the bipolaron velocity calculated by the t-DMRG method is smaller than that obtained at the unrestricted Hartree–Fock level. The electron correlation effects have been considered in t-DMRG calculations, thus, it indicates that the motion of bipolarons is more suppressed by the electron correlation effects. Moreover, it should be noted that the bipolaron velocity depends not only on the electron-electron interaction, but also on the electron-phonon coupling constant, the sound velocity, etc. In what follows, in order to study the electron correlation effects on the bipolaron dynamics, we will only focus on the stationary velocities of the bipolaron for different electron-electron interaction strengths with the condition that the other parameters are fixed.

As described above, the motion of a charged bipolaron has been presented in the weak coupling region ($U\leq 3.0$), based on the SSH and Hubbard model (HM). Figure 2 shows the stationary velocity of a bipolaron varies with the on-site Coulomb interaction U for different parameters t_e . In Fig. 2, we see that velocity of the bipolaron decreases with the increase in parameter t_e at $U=0$ limit. This is because the difference in hopping integrals between the nearest-neighboring bonds becomes large when t_e increases. Moreover the large difference in hopping integrals is unfavorable for bipolaron motion. As a result, bipolaron velocity decreases as t_e increases. In addition, one can find that the velocity of the

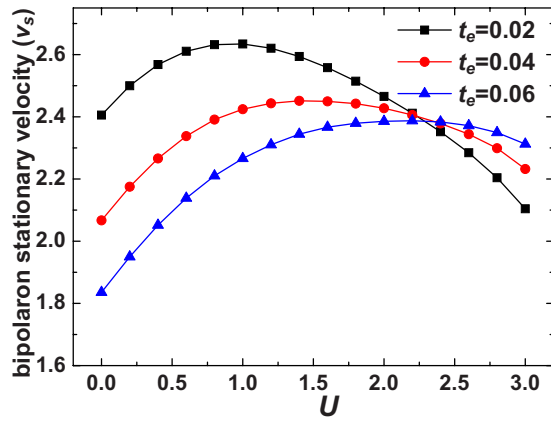


FIG. 2. (Color online) The stationary velocity of a bipolaron driven by an external electric field ($E_0 = 2.0$ mV/Å) as a function of U for different parameters t_e .

bipolaron increases first, then decreases with the increase in the on-site Coulomb interaction for all the different t_e . To understand the electron correlation effects on the dynamics of bipolarons, we explore the relation between the stationary velocity of the bipolaron and its localization from a static view. In Fig. 3 we show the excessive electron charge distribution of a static charged bipolaron calculated with different U . Clearly, due to the existence of a bipolaron, there are large charge fluctuations within the lattice defect. With the on-site repulsion U increases, a large charge fluctuation becomes increasingly unfavorable and the excessive charge density tends to be equally distributed at different CH monomers. Consequently, the charge oscillation is reduced substantially with the increase in Hubbard U . In fact, in the case of not too large U , the increase in the on-site Coulomb interaction can improve the bipolaron transport because the on-site repulsion makes the electrons (or holes) hop to the neighbor site more easily, just as similar as that of a soliton.³⁴ On the other hand, in contrast to the polaron, the width of the bipolaron is broadened by the Hubbard U because the Coulomb repulsive does not favor two different particles to occupy the same site. The staggered bond order parameter $\delta_i = (-1)^i(2u_i - u_{i-1} - u_{i+1})/4$ of a static bipolaron is shown in the inset of Fig. 3 for several values of U . It is found that the width of the

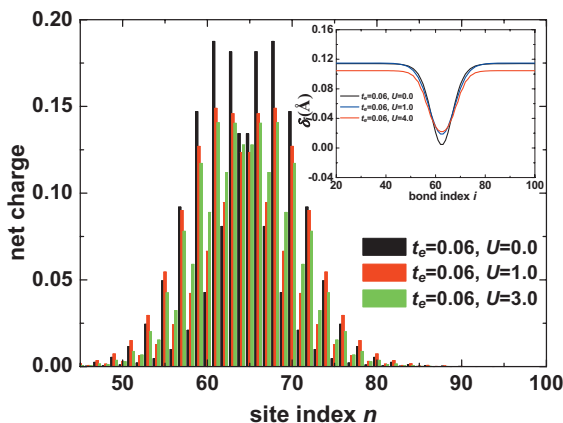


FIG. 3. (Color) The net charge of a static charged bipolaron as a function of the site index calculated with different U values. The inset shows the staggered bond order parameter δ_i of a static bipolaron for several values of U .

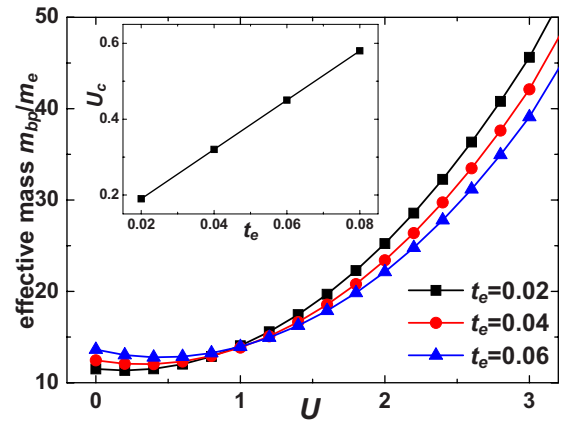


FIG. 4. (Color online) The U -dependence of the bipolaron effective mass m_{bp} scaled by the free electron mass m_e . The inset shows the critical value U_c when the bipolaron becomes unstable and breaks into two bounded polarons for different t_e .

bipolaron is an increasing function of the Hubbard U . In general, the broader the bipolaron width is, the smaller the effective mass is (see Fig. 4).³³ Along with the reduction in effective mass, the bipolaron becomes unstable and the stationary velocity of the bipolaron increases. Therefore, the stationary velocity of a charged bipolaron increases while the value of U increases, as displayed in Fig. 2. When the on-site Coulomb interactions U increase further and become to be dominant, the strong Coulomb interactions destabilize the bipolaron, and the complex particle is a two bounded polaron rather than a bipolaron. In addition, the electrons localized in the bipolaron have to overcome the potential barrier induced by Hubbard U in order to move from one site to another because of the lattice tending to be singly occupied in the spin-density-wave phase, thus the velocity of the bipolaron decreases.

In connection with the stationary of the velocity, it is interesting to trace the behavior of the effective mass of bipolarons. The effective mass m_{bp} of the bipolaron can be calculated by using the same method described in Ref. 33. First, the static lattice configuration is smoothed by spline interpolation, allowing us to compute the configuration at any desired points. Then, the bipolaron effective mass can be determined by calculating the energy of a slowly moving domain wall,

$$u(x, t) = u(x - v_{bp}t, t). \quad (9)$$

Using the adiabatic approximation for the electronic motion, one can show that the effective mass of the bipolaron is related δu_i for a small change in domain wall position, by

$$\frac{1}{2} \sum_i M \dot{u}_i^2(t) = \frac{1}{2} m_{bp} v_{bp}^2. \quad (10)$$

It is clear that the effective mass will appear in the transport coefficients of the bipolaron.

In Fig. 4, the U -dependence of the effective mass m_{bp} scaled by the free electron mass m_e is summarized. From the staggered bond order parameters of the bipolarons at $U=0$ limit, we give the bipolaron effective masses as $11.5m_e$, $12.5m_e$, and $13.6m_e$ for $t_e/t_0 = 0.02$, 0.04 , and 0.06 , respec-

tively, which are heavier than the effective mass of soliton [about $6.0m_e$ (Ref. 3)] and polaron [about $3.3m_e$ (Ref. 33)]. As stated above, one can find that the effective mass decreases first and increases subsequently, which is consistent with the observed dynamic behavior of bipolarons under the influence of an external electric field, although the critical points are slightly different. This is because that we obtain the effective mass from the static geometry structure of the bipolaron and assume that the geometry does not change when it moves. In fact, the moving bipolaron shall emit phonons to keep its steady motion,¹⁹ and the width of a moving bipolaron shows small oscillations in time because of the excitation of amplitude modes. Therefore, the obtained effective mass of the bipolaron may be slightly different from that of a moving bipolaron.

As is well known that the existence of bipolarons is challenged by the Coulomb repulsion,^{13,14} therefore, the minimum value of effective mass can be considered as the crossover when the bipolaron becomes unstable and breaks into two bounded polaron. The corresponding critical values of U_c for different t_e shown in the inset of Fig. 4 form a straight line. The critical values U_c for this crossover are about $U/t_0=0.19$, 0.32, and 0.45 for $t_e/t_0=0.02$, 0.04, and 0.06, respectively. It indicates that bipolarons in the materials with strong Brazovskii–Kirova symmetry-breaking energy are more stable. When the Hubbard U is sufficient large, the bipolaron will dissociate into two bounded polaron. At $U=\infty$ limit, the SSH Hamiltonian can be mapped onto a two-body system plus classical phonons.³³ Furthermore, the lattice defect should be two independent acoustic polarons because no electron exchange or spin exchange are allowed between these two particles. The dynamics of an acoustic polaron has been extensively studied via analytical⁴² and numerical⁴³ techniques, and its stationary velocity is the sound velocity of the system.

IV. SUMMARY

In summary, the effects of electron-electron interaction on the motion of a bipolaron driven by an external electric field in nondegenerate conjugated polymers are investigated by using an adaptive t-DMRG method. We give both the static and the dynamic properties of bipolarons in the case of Hubbard U varying from zero to infinite. Our results show that the motion of the bipolaron is first enhanced, and then suppressed as the on-site Coulomb interaction increases. Accordingly, the effective mass first decreases then monotonically increases to the asymptotic value. Additionally, the stability of a bipolaron relative to a pair of polarons as a function of on-site Coulomb interaction is also discussed.

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