Breather in the motion of a polaron in an electric field

J. F. Yu,1 C. Q. Wu,1,* X. Sun,1 and K. Nasu2

1Research Center for Theoretical Physics, Fudan University, Shanghai 200433, China
2Institute of Materials Structure Science, KEK, Tsukuba, Ibaraki 305-0801, Japan

(Received 19 January 2004; revised manuscript received 12 May 2004; published 24 August 2004)

It has been known that a charged polaron will reach a constant speed after being accelerated only for a short time in an electric field. Within a dynamical nonadiabatic evolution method, we simulate the motion of polaron under the influence of the electric field which is present for different periods. We find the lattice oscillation behind the polaron will be localized and separated with the moving polaron once the electric field is turned off. It is shown that the localized lattice oscillation is nothing but a breather, specifically, a moving multibreather excitation. Furthermore, it is the breather which bears the increased energy due to the electric field acting on the polaron, so that the polaron can move at a constant speed even in the presence of an electric field.

DOI: 10.1103/PhysRevB.70.064303 PACS number(s): 71.38.-k, 72.80.Le, 72.15.Nj, 71.23.An

I. INTRODUCTION

Recent years, organic electronic devices, e.g., light-emitting diodes, and, field-effect transistors, are attracting considerable interest because they have processing and performance advantages for low-cost and large-area applications.1 In these devices, organic polymers are used as the light-emitting and charge-transporting layers, in which the electron and/or hole are injected from the metal electrodes and transported under the influence of an external electric field. 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 solitons2 (only in trans-polyacetylene) and polarons.3 As a result, it has been generally accepted that the charge carriers in conjugated polymers are these excitations including both charge and lattice distortion.4

There have been extensive studies on soliton and polaron dynamics in conjugated polymers5–8 under the influence of external electric fields. It is shown that solitons as well as polarons keep their shape while moving along a chain. Solitons are shown to have a maximum velocity 2.7v_s, where v_s is the sound velocity.6,9 The situation will be different for polarons, which has been shown to be not created in electric fields over 6 × 10^4 V/cm due to the charge moving faster and not allowing the distortion to occur.7 A recent study by Johansson and Stafström8 deals with the polaron migration between neighboring polymer chains. The numerical results show that the polaron becomes totally delocalized, either before or after the chain jump for the electric field over 3 × 10^5 V/cm. A preexisted polaron in a single chain can survive under the field up to 10^6 V/cm.10,11

While the stability of polaron motion under an external electric field has been discussed, we will concentrate on the phonon excitation due to the motion of polaron under the influence of a moderate electric field in this paper. The work is motivated by the observation that a charged polaron will reach a constant speed after being accelerated only for a short time under an electric field.7,8 Within a dynamical nonadiabatic evolution method,6 we simulate the motion of polaron under the electric field which is present for different periods. We find the lattice oscillation behind the polaron will be localized and separated with the moving polaron once the electric field is turned off. It is shown that the localized lattice oscillation is nothing but a discrete breather, which has been a subject in nonlinear systems for more than a decade (see, e.g., Refs. 12–14). Furthermore, it is pointed out that it is the breather which bears the increased energy due to the electric field acting on the polaron, so that the polaron can move at a constant speed even in the presence of the field.

The paper is organized as follows. In the following section, we present a tight-binding one-dimensional model for a polymer chain under the influence of an external electric field and describe the dynamical evolution method. Main results are presented in Sec. III and the discussion and summary of this paper are given in Sec. IV.

II. MODEL AND METHOD

The model Hamiltonian we consider for a polymer chain in this paper takes the following form:2,6

\[ H = H_e + H_{\text{lat}}. \]  

The electronic part is

\[ H_e = - \sum_{n,\sigma} t_n [e^{-iyA(t)} c_{n+1,\sigma}^\dagger c_{n,\sigma} + \text{H.c.}], \]  

where \( t_n \) is the hopping integral between sites \( n \) and \( n+1 \) with \( \alpha \) being electron-lattice coupling constant and \( u_n \) being the monomer displacement of site \( n \) from its undimerized equilibrium position, \( c_{n,\sigma}^\dagger (c_{n,\sigma}) \) is the creation (annihilation) operator of an electron with spin \( \sigma \) at site \( n \), the parameter \( y \) is defined as \( y = ea \ell /hc \) with \( e \) being the absolute value of the electronic charge, \( a \) the lattice constant, and \( c \) the light velocity, and \( A(t) \) is the time dependent vector potential being related with the electric field \( E(t) \) along the chain direction as \( E(t) = -(1/c)\partial A(t)/\partial t \). The lattice part is

\[ H_{\text{lat}} = K \frac{1}{2} \sum_n (u_{n+1} - u_n)^2 + M \frac{2}{2} \sum_n u_n^2, \]  

where \( K \) represents the force constant originated from the \( \sigma \)-bond between carbon atoms and \( M \) the mass of a site, such
as that of a CH-unit for trans-polyacetylene.

In this work, we consider a chain of $N$-monomer with periodic boundary condition, and $N$ is taken to be large enough, such as 300 or 200 in some cases. Other model parameters are those generally accepted for trans-polyacetylene.

$$t_0=2.5 \text{ eV}, \quad K=21.0 \text{ eV/Å}^2, \quad \alpha =4.1 \text{ eV/Å}, \quad a=1.22 \text{ Å}, \quad \text{and } M=1349.14 \text{ eV fs}^2/\text{Å}^2.$$  

Before we go further for the dynamical evolution, we determine the static structure of a polaron in the absence of an external electric field.

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

$$E_t = \langle g | H | g \rangle + \frac{K}{2} \sum_n (u_{n+1} - u_n)^2. \quad (4)$$

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

$$u_{n+1} - u_n = -\frac{\alpha}{K} (\rho_{n,n+1} + \rho_{n+1,n}) + \lambda, \quad (5)$$

where $\lambda$ is a Lagrangian multiplier to guarantee the polymer chain length unchanged, i.e., $\sum_n (u_{n+1} - u_n) = 0$. $\rho_{n,m}$ is the element of density matrix, which will be given below. The initial configuration of a polaron in the following dynamical evolution will be chosen from the solution of the above self-consistent Eq. (5) at the ground state where the electronic band is half-filled with one more electron.

Now, we describe the nonadiabatic dynamical method that has been used for the dynamics of soliton and polaron in an electron-lattice interacting system. The evolution of the electron wave functions depends on the time-dependent Schrödinger equation

$$i\hbar \dot{\phi}_{n,\mu}(t) = -t_{n-1} e^{-i\gamma s} \phi_{n-1,\mu}(t) - t_{n} e^{i\gamma s} \phi_{n+1,\mu}(t). \quad (6)$$

The lattice displacements are determined classically by the following Newtonian equations of motion:

$$M \ddot{u}_n(t) = K [u_{n+1}(t) + u_{n-1}(t) - 2u_n(t)]$$

$$+ \alpha e^{-i\gamma s} \left[ \rho_{n,n-1}(t) - \rho_{n+1,n}(t) \right]$$

$$+ \alpha e^{i\gamma s} \left[ \rho_{n+1,n}(t) - \rho_{n,n+1}(t) \right], \quad (7)$$

where $\rho_{n,m}$ is the element of the density matrix defined as

$$\rho_{n,m} = \sum_{\mu} \phi_{n,\mu}(t) f_{\mu} \phi_{m,\mu}(t), \quad (8)$$

where $f_{\mu}$ is the time-independent distribution function determined by initial occupation (being 0, 1, or 2). The coupled differential Eqs. (6) and (7) can be solved numerically by use of the same technique in Refs. 6 and 8. The time step is chosen to be as small as 0.1 fs to avoid numerical errors.

In the real calculation, we choose the external field to be turned on smoothly, that is, we let $E(t) = E_0 \exp[-(t - t_0)^2/\tau_w^2]$ for $0 < t < t_c$, $E(t) = E_0$ for $t_c < t < t_{\text{off}}$, and $E(t) = 0$ for $t > t_{\text{off}}$ with $t_c$ being a smooth turn-on period, $\tau_w$ the width, and $t_{\text{off}}$ the time length for the electric field being on.

The evolution will be chosen from the solution of the above self-consistent Eqs. (4) and (5) with the $N$ electrons doubly occupying the lowest $N/2$ electronic levels, the extra electron occupying the lowest $(N/2+1)$-th level. With the polaron (both the lattice configuration and the electron occupancy) as the initial condition, we will focus on the time evolution of the lattice configuration $\{y_n\}$, which is defined as

$$y_n = (-1)^n(2u_n - u_{n-1} - u_{n+1})/4.0, \quad (9)$$

through the solving of the Eqs. (6) and (7).

In Fig. 1, we show the time evolution of a polaron at a moderate electric field $E_0 = 3 \times 10^4$ V/cm and the time length for the field presence $t_{\text{off}} = 150$ fs. As a comparison, we also show in Fig. 1 the result for the field being kept on ($t_{\text{off}} = \infty$). From the figure, we can see clearly that due to the influence of the electric field, the polaron will move with a quite stable shape while the lattice oscillation behind the polaron is caused. A very interesting thing is that the lattice oscillation is induced only with the field being on. Once the field is shut off, while the polaron moves at a constant speed the lattice oscillation will not be induced and the previous induced lattice oscillation will be quite stable.

In order to show the difference of the polaron motion between the case when the field will be switched off and when the field is kept on, we define the charge center $x_c$ as in Ref. 6.
cannot move faster due to the lattice character. This is what to induce lattice oscillation behind itself since the polaron the system increases steadily. Then the moving polaron has electric field is present on the moving polaron, the energy of this is coincident with that obtained in Ref. 8. Since the an electric field is applied, a charged polaron will reach a speed as compared with that in the case where the field is switched off. Then the polaron will move at a slightly slow speed, but in any case, the polaron polaron. It is clear that it is the drag that make a difference in by the field and then it drags the lattice deformation of the field is kept, the charge of the polaron will be forced ahead charge of the polaron will be forced ahead, that is the Su-Schrieffer-Heeger model. 2 We choose the lattice configuration into a ring of 200 sites. With the configuration and velocities as the initial condition, we do the simulation as done for the polaron motion but the electronic levels are filled only for the lower half part. The result is shown in Fig. 3, from which we can see clearly that the lattice oscillation exhibits the character of breathers, spatially localized, time periodic non-linear excitations, and it shows to be quite stable for a very long time. The lattice oscillation period is about \( T = 40.8 \) fs, which also coincides with that of breathers in the decay of an electron-hole pair into a soliton and antisoliton.9,15

As a comparison, let us see the temporal evolution of a breather in the discrete model (1) in the absence of external fields, that is the Su-Schrieffer-Heeger model.2 We choose the lattice configuration as the initial condition for simulation by

\[
\mathbf{u}_n = (-1)^n \mathbf{u}_0 (1 + \delta_n),
\]

where \( \mathbf{u}_0 \) is the dimerization magnitude, \( \delta_n \) is given as \( \delta_n = \sqrt{\epsilon} \text{sech}(\sqrt{12n\epsilon a\xi_0}) - \epsilon^2 \text{sech}^2(\sqrt{12n\epsilon a\xi_0}), \)

where \( \xi_0 = t_0 a / \alpha u_0 \) and \( \epsilon \) is the small expansion parameter which is related to the lattice oscillation period \( T .9,15 \) In our case, \( T = 40.8 \) fs, so \( \epsilon = 0.17 \). The result is shown in Fig. 4, from which we can see the time evolution of a breather.

By comparing what we have found in the motion of a polaron with the breather in Fig. 4, we know that is a multibreather state in Fig. 3. We show the lattice configuration \( \{y_n\} \) of this multibreather state at various times in Fig. 5, from which we have (1) the lattice oscillation induced by a moving polaron is a state of breathers, which is a spatially

\[
\mathbf{x}_c = \begin{cases} 
N\theta/2\pi, & \text{if } (\cos \theta_n) \geq 0 \text{ and } (\sin \theta_n) \geq 0; \\
N(\pi + \theta)/2\pi, & \text{if } (\cos \theta_n) < 0; \\
N(2\pi + \theta)/2\pi, & \text{otherwise},
\end{cases}
\]

where

\[
\theta = \arctan \frac{\sin \theta_n}{\cos \theta_n},
\]

and the average of \( \sin \theta_n \) and \( \cos \theta_n \) are defined as

\[
\sin \theta_n = \sum_n \rho_n \sin \theta_n, \quad \cos \theta_n = \sum_n \rho_n \cos \theta_n,
\]

with the probability weight \( \rho_n(=\rho_{n,n} - 1) \) and \( \theta_n = 2\pi n/N \).

In Fig. 2, we show the time evolution of the charge center \( x_c \) of the polaron under a moderate electric field. From it, we can see that the polaron begins to move at about \( t = 75 \) fs when the external field is increased to \( E_0 \) and the polaron gains enough energy. Then the polaron moves at a constant speed. At \( t = 150 \) fs, the polaron will be shocked if the field is switched off. Then the polaron will move at a slightly slow speed as compared with that in the case where the field is kept on. This is easy to understand. In the case where the field is kept, the charge of the polaron will be forced ahead by the field and then it drags the lattice deformation of the polaron. It is clear that it is the drag that make a difference in the speed of the polaron motion. But in any case, the polaron will move at a constant speed for a very long time.

Now, we can understand why the polaron moves at a constant speed no matter if the field is switched off or not. When an electric field is applied, a charged polaron will reach a constant speed after being accelerated only for a short time, this is coincident with that obtained in Ref. 8. Since the electric field is present on the moving polaron, the energy of the system increases steadily. Then the moving polaron has to induce lattice oscillation behind itself since the polaron cannot move faster due to the lattice character. This is what we have seen in Fig. 1. Once the field is switched off, the energy of the system will not be changed, then the moving polaron does not need to emit phonons to keep its steady motion. While the polaron moves at a constant speed, the previous induced lattice oscillation moves at a slower speed, which we will see below, so that the lattice oscillation will be separated from the moving polaron and becomes quite localized and stable.

To clarify the characteristic properties of the lattice oscillation induced by the moving polaron, we separate the lattice oscillation from the moving polaron by copying the lattice configuration \( \{u_n(t)\} \) and site velocities \( \{\dot{u}_n(t)\} \) at \( t = 600 \) fs excluding those at the 100 sites around the polaron into a ring of 200 sites. With the configuration and velocities as the initial condition, we separate the lattice oscillation part induced by the moving polaron.
localized, time periodic nonlinear excitation; (2) the nearest breathers have opposite phases; (3) the breathers have a small velocity [around 0.65\(v_s\), \(v_s \approx 1.53 \times 10^6\) cm/s] the sound velocity], though its connection with the moving polaron has been cut; and (4) the breather is a bound state of phonons, due to the nonlinear interaction within phonons, there exists a tendency for extended phonons to get together for the form of breathers, so we can see that there are more breathers at \(t=2400\) fs while those extended oscillation in front of the breathers fades away.

Finally we show in Fig. 6 the lattice configuration \(\{y_n\}\) at around \(t=600\) fs under an electric field of different strengths. Though the polaron velocity is slightly different for different electric fields, the number of induced breathers is the same. The amplitude and the distance between the nearest breathers depends on the strength of applied electric field. They are 0.007, 0.010, and 0.013 Å, and 7.0, 7.5, and 8.0 Å for the electric field \(E_0 = 1.0 \times 10^5\), \(E_0 = 2.0 \times 10^5\), and \(E_0 = 3.0 \times 10^5\) V/cm, respectively. Apparently, these breathers should have different energies since the strengths of the electric fields are different.

## IV. DISCUSSION AND SUMMARY

As is well known, discrete breathers are periodic localized oscillations that arise in discrete nonlinear systems. The study on the breathers, in particular, the discrete breathers, has a long history.\(^{12-14}\) While the static discrete breathers have been widely studied in nonlinear lattice systems since their existence was proven by MacKay and Aubry,\(^{16}\) the mobility of discrete breathers is still an open issue due to the fact that moving discrete breathers are not solutions of the dynamical equations of the system that can be obtained using continuation methods and a proof of existence of them has not been found so far. In spite of that, there still are many numerical works on it. For example, by a systematic numerical method, Chen \textit{et al}.\(^{17}\) constructed mobile breathers through an appropriate perturbation of the pinning mode in discrete \(\phi^4\) nonlinear lattices and analyzed properties of breather motion and determined its effective mass. In addition, in a DNA model with competing short- and long-range dispersive interactions, mobile breathers are found to exist for a wide range of the parameter values, and the mobility of these breathers is found to be hindered by the long-range interaction.\(^{18}\)

In conjugated polymers, which are modeled as electron-phonon interacting systems\(^2\) and nonlinear interactions in the lattice come from the integration over the electrons, the breather was first found at the decay of an electron-hole pair into a soliton and antisoliton.\(^{9,15}\) In the continuous version of the Su-Schrieffer-Heeger (SSH) model,\(^{19}\) the analytic solution of a breather [see Eq. (14)] was obtained by a low-amplitude expansion,\(^9,15\) and it has been shown to be a very accurate discrete breather in the discrete model of conjugated polymers, the SSH model, by both the adiabatic\(^9,15\) and nonadiabatic (see Fig. 4) dynamical evolution methods. Very recently, the breather of a bound soliton pair in trans-polyacetylene has been realized by sub-five-femtosecond optical pulses.\(^{20}\) A mobile multibreather excitation, what we found in this work, has not been reported before to the best of our knowledge not only in conjugated polymers but also in regular nonlinear lattice systems. A detailed investigation on it is underway.

Finally, one more interesting fact we should mention is that the breathers of significantly different amplitudes have

![Fig. 4. Stereographic presentation of the n and t dependence of the lattice configuration \(\{y_n\}\) in a ring of 200 sites. The initial \((t = 0)\) lattice configuration is given in Eq. (14).](image)

![Fig. 5. Lattice configuration \(\{y_n\}\) of the multibreather state at various times. All be the same as in Fig. 3.](image)

![Fig. 6. Lattice configuration \(\{y_n\}\) at around \(t=600\) fs under an electric field of different strengths. All others are the same as in Fig. 1 \((t_{eff}=\infty)\).](image)
almost the same oscillation period ($T \approx 41$ fs), but the analytic solution of a nonlinear equation\textsuperscript{9,15} indicates the amplitude is directly related with the oscillation period, which is actually a general property of a soliton. What does the phenomenon we found here imply? We are also waiting for the answer.

In summary, we have investigated the dynamical evolution of a polaron in a moderate-strength electric field. We found that the polaron under the influence of an external field has to emit phonons to keep its steady motion and these emitted phonons will be at a bound state, a moving multi-breather state, which bears the increased energy of the system due to the action of the field. The nearest breathers have opposite phases. The number of induced breathers is the same for different electric fields at the same duration. The amplitude and the distance between nearest breathers depend on the applied electric field while the oscillation period is determined only by the electron-phonon coupling system.

ACKNOWLEDGMENTS

This work was partially supported by the National Natural Science Foundation of China (Grant Nos. 90103034, 10321003, and 10374017) and the State Ministry of Education of China (No. 20020246006). One of the authors (C.Q.W.) is grateful to the Institute of Materials Structure Science of KEK for the hospitality during his visit there.

\textsuperscript{9}Corresponding author; electronic mail: cqw@fudan.edu.cn
\textsuperscript{1}I. H. Campbell and D. L. Smith, Solid State Phys. 55, 1 (2001) and references therein.
\textsuperscript{14}V. Fleurov, Chaos 13, 676 (2003).