Interchain Pair Hopping of Solitons and Polarons via Dopants in Polyacetylene

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Abstract

Interchain hopping of solitons and polarons in polyacetylene is studied by numerical simulation of their motion under an electric field. Use is made of the Su-Schrieffer-Heeger model supplemented with intrachain electron-electron interactions and dopant potentials. We find that charged solitons can hop to the opposite chain by forming bound pairs (bipolarons). For the case of polarons also, hopping in a pair is more favorable than single polaron hopping. Interchain hopping of a polaron pair is more efficient than that of a soliton pair.

I. INTRODUCTION

The mechanism of charge hopping among chains is one of the intricate unsettled questions related to understanding of the electronic properties of conducting polymers. \[1\] It is expected that charged solitons or polarons play a major role in conduction processes in polyacetylene. Motion of such nonlinear excitations can contribute directly to the conduction. \[2,3\] Polyacetylene, however, has a complex structure composed of polymer chains with finite
lengths and dopant ions (Fig. 1). A difficulty in the charged soliton model is that a single
soliton cannot hop to neighboring chains, since there exists a large activation barrier for
inversion of the phase of bond alternation over a large region. The difficulty can be removed
by consideration of pairs of solitons, i.e. bipolarons. Interchain hopping of polarons, which is
another conduction mechanism, is considered to be much easier. It is crucial to consider the
dynamics of the nonlinear excitations by taking into account the three-dimensional effects,
such as dopant potentials and interchain interactions.

Silva and Terai [4] investigated the effect of the interactions between two chains of poly-
acetylene on the dynamics of solitons, and found that the motion of a soliton is suppressed
by a confinement effect and that the amount of the charge transfer between the two chains
via charged and neutral solitons is quite small. The effect of a dopant has been usually
incorporated as the Coulomb potential for electrons. Yamashiro and coworkers pointed out
that interchain transfers are enhanced by the presence of the valence orbitals of the dopant
ions. [5]

We study here interchain hopping of solitons and polarons in polyacetylene by numerical
simulation of their motion under an electric field. We consider two neighboring chains that
are coupled with each other through dopant ions as shown in Fig. 1(b). One of these chains
contains a pair of solitons or polarons in the initial state. The effects of a dopant are twofold:
the Coulomb potential and enhancement of interchain transfer around the dopant. In our
model, the interchain transfer is assumed to occur in a small region around the dopant, and
is neglected in the other regions, for simplicity.

The effect of chain ends on the motion of the nonlinear excitations is also important.
For discussion of this effect the dopant is located near the end of one of the chains, chain
a in Fig. 1(b). The other chain (chain b) is arranged so that the dopant is located near
its midpoint. Thus we choose the structure shown in Fig. 1(b), and it seems reasonable to
regard this structure as a typical example of part of the three-dimensional complex structure
shown in Fig. 1(a).
II. MODEL AND NUMERICAL METHOD

The model Hamiltonian is given by

\[ H = H_a + H_b + H_{e-e} + H_{\text{int}} + H_{\text{imp}}. \] (2.1)

The first two terms, describing the two chains a and b, are the Su-Schrieffer-Heeger model \cite{6} modified to include the electric field.

\[ H_\lambda = -\sum_{i\sigma}(t_0 - \alpha y_{\lambda,i})[e^{i\gamma A}c_{\lambda,i+1\sigma} + h.c.] \]
\[ + \frac{K}{2} \sum_i y_{\lambda,i}^2 + \frac{M}{2} \sum_i \dot{u}_{\lambda,i}^2 - \Gamma(u_{\lambda,N} - u_{\lambda,1}), \] (2.2)

where \( \lambda = a, b \) and \( y_{\lambda,i} = u_{\lambda,i+1} - u_{\lambda,i} \). Here, \( t_0 \) is the hopping integral between the nearest neighbor sites, \( \alpha \) the electron phonon coupling constant, \( u_{\lambda,i} \) the displacement of the \( i \)th CH unit on the chain \( \lambda \), \( c_{\lambda,i\sigma} \) the annihilation operator of an electron at the \( i \)th site with spin \( \sigma \) on the chain \( \lambda \), \( K \) the spring constant, and \( M \) the CH mass. The electric field is applied in a direction parallel to the chain axis, being given by the time dependent vector potential, \( E = -\dot{A}/c. \) \cite{7} The parameter \( \gamma \) is defined by \( \gamma = ea/\bar{h}c \), where \( e \) is the absolute value of the electron charge, \( a \) the lattice constant, and \( c \) the light velocity. We adopt the open boundary condition for each chain. The last term in eq. (2.2) is added to keep the chain length constant. The third term in eq. (2.1) describes the short-range intrachain electron-electron interactions.

\[ H_{e-e} = U \sum_{\lambda,i} n_{\lambda,i\uparrow}n_{\lambda,i\downarrow} + V \sum_{\lambda,i} n_{\lambda,i}n_{\lambda,i+1}, \] (2.3)

with \( n_{\lambda,i\sigma} = c_{\lambda,i\sigma}^\dagger c_{\lambda,i\sigma} \) and \( n_{\lambda,i} = \sum_{\sigma} n_{\lambda,i\sigma} \). The parameters \( U \) and \( V \) are the on-site and nearest neighbor Coulomb repulsion, respectively. The two chains are of the same size. Chain b is shifted by \( i_0 \) sites with respect to chain a. The interaction between two chains is represented by

\[ H_{\text{int}} = -t_\perp \sum_{\sigma,i=p}^q (c_{a,i\sigma}^\dagger c_{b,i-i_0\sigma} + c_{b,i-i_0\sigma}^\dagger c_{a,i\sigma}), \] (2.4)
where \( p \) and \( q \) denote the first and last site in the interaction region around the dopant. The last term of eq. (2.1) represents the dopant potential, which is approximated by a square-well potential,

\[
H_{\text{imp}} = V_{\text{imp}} \sum_{\sigma, i=p}^{q} (c_{a,i\sigma}^\dagger c_{a,i\sigma} + c_{b,i-i_0\sigma}^\dagger c_{b,i-i_0\sigma}).
\] (2.5)

We use the following values of parameters: \( t_0 = 2.5 \text{eV}, t_\perp = 0.1 t_0, K = 21 \text{eV/} \AA^2, \alpha = 4.1 \text{eV/} \AA, a = 1.22 \AA, V_{\text{imp}} = -0.1 t_0, U = t_0, V = t_0/2 \) and \( \Gamma = 5.13 \text{eV} \). The chain sizes are \( N_a = N_b = 120 \) and the total number of electrons is \( N_e = 242 \), corresponding to two excess electrons in the system. The center of the dopant is located at the 105th site in the coordinate of chain \( a \). The endpoints of the interaction region are set to be \( p = 100 \) and \( q = 110 \). The shift of chain \( b \) with respect to chain \( a \) is \( i_0 = 46 \), so that the dopant is located near the center of chain \( b \).

The initial states are prepared self-consistently in the Hartree-Fock approximation, in which chain \( a \) contains two solitons or polarons, one of which is pinned by the dopant and the other of which is free to move. The time evolution of the electronic wavefunction is determined by use of the time-dependent HF equation, and the motion of the lattice by use of an equation of motion. In solving the time dependent HF equation we use the method of fractal decomposition for exponential operators. For the equation of motion the time differential equation is integrated with discretization of the time with an interval \( \Delta t \). The interval \( \Delta t \) is chosen to be \( \Delta t = 0.0025 \omega_Q^{-1} \) throughout this work. Here in our simulations the unit of time is the inverse of the bare optical phonon frequency \( \omega_Q = \sqrt{4K/M} \approx 2.5 \times 10^{-14} \text{s}^{-1} \) and that of the electric field is \( E_0 = \hbar \omega/ea \approx 1.3 \times 10^7 \text{V/cm} \).

### III. RESULTS AND DISCUSSION

#### A. Case of a pair of solitons

In the following we show the results in terms of the smoothened quantities of the bond variable and the excess charge distribution, defined as
\[
\tilde{y}_{\lambda,i} = (-1)^i (y_{\lambda,i-1} - 2y_{\lambda,i} + y_{\lambda,i+1})/4,
\]
(3.1)
\[
\tilde{\rho}_{\lambda,i} = (\rho_{\lambda,i-1} + 2\rho_{\lambda,i} + \rho_{\lambda,i+1})/4,
\]
(3.2)
where the excess charge density is calculated from the time-dependent wavefunctions \( \{\Psi_{\lambda\nu}(i, t)\} \),
\[
\rho_{\lambda,i}(t) = \sum'_{\nu} |\Psi_{\lambda\nu}(i, t)|^2 - 1.
\]
(3.3)
The prime attached to the summation symbol denotes a sum over occupied states.

Figure 2 shows a typical example of hopping of a pair of solitons from chain a to b in three-dimensional representation of \( \tilde{y}_{\lambda,i} \) and \( \tilde{\rho}_{\lambda,i} \) as functions of time and space. The free soliton on chain a is accelerated by the field and collides with the pinned soliton, resulting in formation of a bipolaronic state. In chain b small oscillations are generated after the field is switched on. Their amplitudes increase upon the collision and sometimes the oscillations induce bipolaronic lattice distortion. In such a case the soliton pair can easily hop to the neighboring chain. After the hopping, one of the solitons is pinned by the dopant and the other begins to move toward the chain end.

We have performed numerical simulations for various strengths of the field for changing of the incident velocity of the free soliton at the collision with the pinned soliton. In Fig. 3 we display the time dependence of the excess charge density on chain a, which is defined by
\[
\rho_a(t) = \sum_{i=1}^{N_a} \rho_{a,i}(t).
\]
(3.4)
In the initial state \( \rho_a(0) \) has almost \( 2|e| \), since there exist a pair of charged solitons on chain a. A slight deviation from \( 2|e| \) is due to partial flow of charge from the pinned soliton to chain b. The deviation increases and fluctuates after the two solitons form a bipolaron. In the case of a weak field (i.e. low incident velocity at the collision), the soliton pair does not show any sign of hopping at least within the longest time of our simulations. For a stronger field (high incident velocity), \( \rho_a(t) \) falls to about zero suddenly, indicating that the hopping of two electrons occurs simultaneously. There is a threshold velocity for the hop. This means that there is a potential barrier for the hopping. The time interval between
the collision and completion of the hop is not a simple function of the field strength (the 
incident velocity), but a rather chaotic one. The occurrence of the hop depends on the 
mutual motion of the soliton pair on chain a and the lattice oscillation on chain b. Namely, 
the hopping occurs under the conditions that the amplitude of the bipolaron becomes small 
on chain a and instantaneously becomes large on chain b. Therefore a slight difference in 
parameters results in a drastic change in the hopping time. Bipolaronic lattice distortion 
on the opposite chain is necessary for the hop to occur. The lattice fluctuations at finite 
temperature may affect the hopping, perhaps they make the hop easier.

The location of the dopant affects the hopping probability. If the dopant is located near 
the midpoint of chain a, the probability of hopping of the soliton pair is very low. When 
the field is sufficiently strong, the pinned soliton is pushed out by its collision with the free 
soliton and begins to move within chain a. In the case that the dopant is located near the 
chain end, even if the pinned soliton is pushed out, it is immediately reflected at the chain 
end, resulting in the formation of a bipolaron again. Bipolaron formation is necessary for the 
hopping to occur. Therefore, the hopping probability is larger when the dopant is located 
near the chain end.

**B. Case of a pair of polarons**

For the case of a pair of polarons three-dimensional representations of $\tilde{y}_{\lambda i}$ and $\tilde{\rho}_{\lambda i}$ are 
shown in Fig. 4. The hopping process seems qualitatively different from that for the soliton 
pair. The polaron pinned by the dopant in the initial state hops back and forth between the 
two chains in the electric field. The bipolaronic state observed in the case of the soliton pair 
does not appear as an intermediate state during the hop. The intermediate state in this case 
is such that each chain contains one polaron around the dopant. After the hopping, one of 
the two polarons is pinned by the dopant over the two chains and the other one is moved on 
chain b by the field. For the case of a single polaron, hardly any charge transport over the 
two chains due to interchain hopping through the dopant takes place, because of trapping
by the dopant potential. In Fig. 5 we show the time dependence of the excess charge density on chain $a$, $\rho_a(t)$, for several field strengths. Before the collision, $\rho_a(t)$ oscillates at around $1.5|e|$ due to the back-and-forth motion of the polaron pinned over the two chains. For the case $E = 0.01E_0$, two polarons are pinned by the dopant after the collision and there exists one polaron per chain. Therefore amount of the excess charge density on chain $a$ is $|e|$ on average. This case does not contribute to the charge transport from chain $a$ to chain $b$. In the stronger field cases the charge transport occurs by the polaron hopping. Then $\rho_a$ decreases by $|e|$ on average. The potential barrier for the hopping of a polaron pair is smaller than that for the hopping of a soliton pair. In contrast to the case for a soliton pair, the polaron pair hops almost irrespective of the dopant location relative to the chain end. When the two polarons collide, the hopping occurs almost instantaneously. Therefore, the time of the hop varies monotonically with the field strength, not in a chaotic manner.

It seems that the back-and-forth motion of the pinned polaron before the collision is induced mainly by the external field. For the parameter set used in our simulations, the energy difference between the state of the polaron being almost localized on one chain and the state of delocalization over the two chains is quite small. Therefore the oscillation can be induced by weak disturbance. This is considered to be one of the reasons for the small potential barrier for the polaron pair hopping.

It is worth noting that the final states result in formation of a pair of solitons or a pair of polarons depending on whether the initial state is a pair of solitons or pair of polarons. For a single chain with no electron-electron interaction, it has been shown by use of the TLM model [12] that a two-polaron state is unstable against a two soliton-state. [13] This is supported by the results of a numerical study on the dynamics of a polaron pair: it was observed that two polarons dissociate into a pair of solitons after their collision. [14] In our two-chain system, a two-polaron state, not a two-soliton state, appears after the collision (hopping) of a pair of polarons. One of the reasons for this may be that the delocalization of polarons over the two chains stabilizes the polaron pair state.

In summary, we have numerically investigated interchain hopping of a pair of solitons
and a pair of polarons. We found that charged solitons can hop to the opposite chain by forming a composite (bipolaron) in the electric field parallel to the chains. The existence of both the dopant and the chain end assists the hopping. The bipolaronic lattice distortion on the opposite chain is necessary for the hop to occur. There exists a finite potential barrier for the hopping. For the case of polarons also, hopping in a pair is more favorable than single polaron hopping. Interchain hopping of a polaron pair is more efficient than that of a soliton pair.

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REFERENCES

[1] H. G. Kiess (Ed.): *Conjugated Conducting Polymers*, Springer Series in Solid-State Sciences 102 (Springer-Verlag, Berlin, 1992).

[2] M. Kuwabara and Y. Ono: J. Phys. Soc. Jpn. 63 (1994) 1081.

[3] M. Kuwabara and Y. Ono: J. Phys. Soc. Jpn. 64 (1995) 2106.

[4] G. M. Silva and A. Terai: Phys. Rev. B47 (1993) 12568.

[5] A. Yamashiro, A. Ikawa and H. Fukutome: Synthetic Metals 65 (1994) 233.

[6] W. P. Su, J. R. Schrieffer and A. J. Heeger: Phys. Rev. Lett. 42 (1979) 1689; Phys. Rev. B22 (1980) 2099.

[7] Y. Ono and A. Terai: J. Phys. Soc. Jpn. 59 (1990) 2893.

[8] K. Yonemitsu, Y. Ono and Y. Wada: J. Phys. Soc. Jpn. 57 (1988) 3875.

[9] A. Terai: in *Relaxation in Polymers*, edited by T. Kobayashi (World Scientific Publishing Co., Singapore, 1993), p. 269.

[10] M. Suzuki: Phys. Lett. A146 (1990) 319; Phys. Lett. A165 (1992) 387; J. Phys. Soc. Jpn. 61 (1992) 3015; Proc. Japan Acad. 69 Ser. B (1993) 161.

[11] A. Terai and Y. Ono: Prog. Theor. Phys. Suppl. No. 113 (1993) 177.

[12] H. Takayama, Y. R. Lin-Liu and K. Maki: Phys. Rev. B21 (1980) 2388.

[13] Y. Onodera and S. Okuno: J. Phys. Soc. Jpn. 52 (1983) 2478.

[14] A. Terai and Y. Ono: Synthetic Metals 69 (1995) 681.

Fig. 1. Schematic illustration of (a) polymer chains with dopants and (b) the system studied here.
Fig. 2. Stereographic representation of the site \((i)\) and time \((t)\) dependences of (a) the bond variable and (b) the excess charge density for the case of a pair of solitons. The interchain interaction region is depicted as the region between two lines in the bottom \(i - t\) plane.

Fig. 3. Time dependence of the excess charge density on chain a for a pair of solitons.

Fig. 4. Stereographic representation of the site \((i)\) and time \((t)\) dependences of (a) the bond variable and (b) the excess charge density for the case of a pair of polarons.

Fig. 5. Time dependence of the excess charge density on chain a for a pair of polarons.
(a)

chain a

D^+

chain b

(b)
(a)
(b)
