Polaron Dynamics in Impurity-doped Conjugated Polymers

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Abstract. Transport process of a charged polaron in impurity-doped conjugated polymers is investigated by using a nonadiabatic evolution method. Effect of the impurity ion on the polaron motion in a system of two-chains is focused. It is found that an impurity ion acts as a barrier or well rather than a bridge, which is not favourable for the polaron transport between chains.

1. Introduction

Charge transport in conjugated polymers has attracted much interest since the discovery in 1977 that trans-polyacetylene can be doped to exhibit a very high electrical conductivity. Up to now extensive researches about soliton and polaron carrier dynamics have been done in an infinite chain [1-3]. Considering the actual materials, effect of impurity ions on charge transport was recently analyzed by Silva et al [4-5]. They concluded that a polaron could be trapped or scattered by an impurity ion depending upon the interaction of polaron-ion. Wu et al. further studied two kinds of dynamical process, one is the field-induced depinning of a charged polaron and the other is the scattering of a polaron by a repulsive impurity [6].

However, all the present investigations are focused on a single chain. In actual organic materials, the lengths of molecular chains are limited. It is certainly that a polaron will hop among chains during its transport process. In this process, the dopant ions sited at the interspaces of the chains will affect the hopping of charged polarons to some extent. In this paper, we model a two-chain system with an impurity ion at the interspace and calculate the dynamics of a polaron under an external electric field.

This contribution is organized as follows: In the following section, the model and the method of simulation are explained briefly. In section 3 the results are presented and discussed. The last section is devoted to concluding remarks.

2. Model and method

Considering a two-chain system with an impurity ion at the interspace, we employ the extended Su-Schrieffer-Heeger model [7-8]. Under an external electric field, the Hamiltonian is described as

\[
H(t) = -\sum_{n,n'} t_{nn'} c_n^+ c_{n'} + \frac{K}{2} \sum_n (u_{n+1} - u_n)^2 + \frac{M}{2} \sum_n \dot{u}_n^2 + e|E(t)| \sum_n (na + u_n)(c_n^+ c_n - 1) + V_0 c_m^+ c_m
\]  

(1)

\(t_{nn'}\) being the hopping integral between site \(n\) and \(n'\).

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\[
\begin{aligned}
t_{\text{on}} &= \begin{cases} 
  t_0 + \alpha (u_n - u_{n'}) - t_e \cdot (-1)^n & \text{intra-chain hopping with } n' = n \pm 1 \\
  t_{11}, t_{12} & \text{inter-chain hopping}
\end{cases}
\end{aligned}
\]

where \( t_0 \) is the transfer integral in a regular lattice, \( \alpha \) the electron-lattice coupling constant and \( u_n \) the displacement coordinate. \( t_e \) is introduced to lift the ground-state degeneracy for non-degenerate polymers such as cis-polyacetylene. \( K \) is the elastic constant and \( M \) the mass of a CH group. \( V_0 \) is the potential strength of the impurity ion acting on \( \pi \)-electrons at site \( m \). Spin index \( s \) is neglected through the whole paper. An external electric field is applied along the chains. At the beginning, the field is smoothly exerted with the form of half-Gaussian function as

\[
E(t) = E_0 \exp[-(t - T_C)/T_W^2].
\]

Then it keeps \( E(t) = E_0 \) when \( t \geq T_C \). For the interchain hopping, the nearest and the next-nearest neighbour terms are included in the present model, which are denoted by \( t_{11} \) and \( t_{12} \) separately.

The evolution of the lattice configuration is determined by the equation of motion

\[
M \ddot{\rho}_n = -K(2u_n - u_{n+1} - u_{n-1}) + 2\alpha(\rho_{n,n+1} - \rho_{n,n-1}) + 4\kappa |E(\rho_{n,n} - 1)|
\]

where the density matrix \( \rho \) is defined as

\[
\rho_{n,n'} = \sum_\nu \Psi_\nu(n,t) f_\nu \Psi_\nu^\dagger(n',t)
\]

\( f_\nu \) is the time-independent distribution function. The electronic wave functions is described as

\[
\hbar \frac{\partial}{\partial t} \Psi_\nu(n,t) = t_{n,n'} \Psi_\nu(n,t) + eE(t)(na + u_n) \Psi_\nu(n,t) + V_0 \Psi_\nu(m,t)
\]

The coupled differential equations (3) and (5) are solved with a Runge-Kutta method [9] of order eight with step-size control.

Selecting parameters referring to that of polyacetylene [10], \( t_0 = 2.5 \text{eV} \), \( \alpha = 4.1 \text{eV/Å} \), \( K = 2\text{eV/Å}^2 \), \( a = 1.22 \text{Å} \), \( M = 1349.14 \text{eV·fs}^2/\text{Å}^2 \). Polymers with a degenerate ground state such as trans-polyacetylene are described by the SSH model widely, in which the confinement constant is set \( t_e = 0 \). Here we take \( t_e = 0.05 \text{eV} \) to describe polymer chains with a nondegenerate ground state such as cis-polyacetylene. The parameter values of the interchain coupling are set as \( t_{11} = 0.1 \text{eV} \) and \( t_{12} = 0.05 \text{eV} \). Although these parameters are chosen for polyacetylene, the results are expected to be qualitatively valid for other conjugated polymers with a nondegenerate ground state.

3. Results and discussion

It has been known that, in a single chain system, an impurity ion will scatter or trap a charged polaron and therefore affect the moving of the polaron to much extent. There is a threshold field for the polaron passing through the impurity. The strength of the threshold field increases linearly with the impurity potential [4-6].

![Figure 1. Sketch of the two-chain system with an impurity ion.](image)
there is a donor impurity ion, as shown in fig.1. A negative charged polaron forms initially at the far left of the first chain. It moves to right along chain under the external electric field. As a polaron will dissociate under a strong electric field [2], we adjust the strength of the field to keep the entirety of the polaron when it is far apart from the coupling region.

Firstly, we consider the case without any impurity ions. It is found that the polaron will relax in the coupling region for about 300fs under the electric field $D_{AV}/10^{3.1} \times 3^{-}$ and then migrate into the second chain. The polaron continues to move in the second chain under the external field. Then for the case with a weak impurity potential, it is found that the polaron can pass through the coupling region and keep its entirety unchanged. But it will spread in the coupling region and relax a longer time than the case without impurity. In fig. 2 we show the evolution of lattice configuration and charge density distribution under the electric field $D_{AV}/10^{3.1} \times 3^{-}$ with impurity potential $V_0 = -0.25eV$. It can be seen that the polaron relaxes about 600fs in the coupling region, and then it accumulates in the second chain and continues moving.

In the case of a strong impurity potential, it is found that a large field is needed to drive the polaron passing the coupling region. The picture becomes complex in such a condition as a stronger field would dissociate the polaron, while a weaker field could not drive the polaron. Here we only consider the case that the polaron does not dissociate before it enters the coupling region. One result is shown in fig.3 with the impurity potential $-1.0eV$. A field strength of at least $1.55 \times 10^{-3} V/\AA$ is needed to drive the polaron passing through the impurity ion in the case of a single chain. For a two-chain system, interchain coupling provides another mechanism for a polaron to pass through the impurity ion. Due to the strong impurity confinement, the polaron will be dissociated in the coupling region. Part of the electronic charge will pass through the impurity ion and the left will be confined in the coupling region. We can understand it from the point of probability. Evolution of the net electronic charge distribution in the coupling and uncoupling region (first and second chain) are shown in fig.3 separately by dashed, solid and dot line. Therefore, in the case of a strong impurity ion, a polaron could not keep its entirety. It will be dissociated into extended state when it passes through the impurity ion. In this case, the dissociation of a polaron may arise from two forces: the driving electric field and the impurity potential respectively. The electric field force drives the polaron moving along the chain; while the force produced by the impurity potential intends to trap the polaron. There exists a competition between the two forces. In the case of our calculation above, the two forces are so strong that the polaron can not keep its original shape. Of course, as there is interchain coupling in actual
materials, a charged carrier can transport by hopping among chains, although it could not keep its entirety like a polaron. The mobility will depend upon the interchain coupling as well as the impurity confinement.

![Figure 3](image_url)

**Figure 3.** Evolution of the electronic charge distribution in a two-chain system containing a site impurity $V_0 = -1.0\text{eV}$ with $E = 2.1 \times 10^{-3}\text{V/Å}$. Dashed line: the net charge in the coupling region; solid line and dot line: the net charge in the uncoupling region of the first chain and second chain separately.

4. **Summary and conclusion**

Polaron transport in actual polymers was investigated through its dynamic process in a two-chain system. Impurity potential as well as interchain coupling was included. It was found that in the case of a weak impurity confinement, a polaron can keep its entirety, hop between chains and pass through the impurity ion. But in the case of a strong impurity confinement, the polaron will be dissociated. Under a suitable driving field, part of the dissociated charge will pass through the impurity ion and the left will be confined by the impurity. The competition between the interchain coupling and the impurity confinement and its effect on the polaron transport was discussed. A detailed investigation containing more chains will be carried out in the future.

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**References**

[1] D. M. Basko and E.M. Conwell 2002 *Phys. Rev. Lett.* **88** 056401
[2] Åsa Johansson and Sven Stafström 2001 *Phys. Rev. Lett.* **86** 3602
[3] Åsa Johansson and Sven Stafström 2002 *Phys. Rev. B.* **66** 085208
[4] H.W. Streitwolf 1998 *Phys. Rev. B.* **58** 14356
[5] Cleber da Silva Pinheiro and Geraldo Magela e Silva 2002 *Phys. Rev. B.* **65** 094304
[6] Y.H. Yan, Z. An, and C.Q. Wu 2004 *European Physical Journal B.* **42** 157
[7] W. P. Su and J. R. Schrieffer 1981 *Phys. Rev. Lett.* **46** 738
[8] W. P. Su, J. R. Schrieffer, and A. J. Heeger 1980 *Phys. Rev. B.* **22** 2099
[9] R.W. Brankin, I. Gladwell, and L.F. Shampine, RKSUITE: Software for ODE IVPS, http://www.netlib.org.
[10] A. J. Heeger, S. Kivelson, J. R. Schrieffer, and W. P. Su 1988 *Rev. Mod. Phys.* **60** 781