Effect of interchain coupling on the excited polaron in conjugated polymers

CrossMark

Xiao-xue Li *, Gang Chen *

School of Physics and Technology, University of Jinan, Jinan 250022, PR China

ABSTRACT

Based on the one-dimensional extended Su–Schrieffer–Heeger model, we theoretically investigate the effect of interchain coupling on the formation and polarization of the single-excited state of polaron in conjugated polymers. It is found that there exists a turnover value of the coupling strength, over which the excited polaron could not be formed in either of the two coupled chains. Instead, a polaron-like particle is localized at the center of each chain. In addition, we also find that the reverse polarization of the excited polaron could be enhanced for some cases in polymer when the interchain coupling becomes strong until it exceeds the critical value.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

In the past decades, conjugated polymers such as polyacetylene have been extensively investigated from both theoretical and experimental viewpoints due to their abundant electrical, photonic and magnetic properties [1–4]. As the promising organic semiconductor materials, conjugated polymers possess strong electron-lattice coupling. The injection of an extra electron (or hole) could induce the lattice defect, and then the formation of the self-trapped elementary excitation called polaron [5]. In depth exploration of polaron's property is of great important for the application of conjugated polymers on organic devices.

In 2005, Gao et al. theoretically explored the single-photon excitation of a charged polaron [6]. They found that the polarization of the excited polaron was opposite to the external electric field. Besides, another similar polarization could also been obtained from biexciton [7,8] and high-energy exciton [9]. Reverse polarization is the peculiar property of organic molecules, and of great interest in both basic principle and technology.

Here, we should note that in previous researches, it is commonly held that the conjugated polymers possess quasi-one-dimensional structure. The two nearest-neighbor carbon atoms on the same polymer chain are connected with each other by covalent bond. While for the carbon atoms on different polymer chains, like molecular crystals, the coupling interaction between them is weak.

For this reason, in most theoretical researches on conjugated polymers, the effect of interchain coupling is completely neglected. However, it should be stressed that the polymer molecule is a π-stacked system. The interchain coupling interaction between two nearest-neighbor polymer chains caused by polymer's three-dimensional character should be taken into account. The coupling strength in solid film of polymer molecules is larger than that in dilute solution. The introduction of interchain coupling could not only well embody the π-stacked effect, but also determine the bulk property of the system. Therefore, researchers have to use the extended version of the Su–Schrieffer–Heeger (SSH) model [5,10,11] consisting of interchain coupling term, and then the three-dimensional structure of polymer molecules could be well described. Their results show that the effect of interchain interaction is significant, although the coupling strength is small. For example, Stafström et al. stimulated the interchain polaron transport in *trans*-polyacetylene molecule [12]. It is found that under the influence of strong interchain coupling, the polaron could be extended over several polyacetylene chains. An et al. stimulated the scattering process between positive and negative polarons in two coupled *trans*-polyacetylene chains [13]. It is found that for different initial conditions, i.e., the two oppositely charged polarons are localized on the same chain or on the different chains, the yield of exciton formed by polaron recombination under the same electric field is different. Thus we can see that the interchain coupling could indeed play a vital role in not only the formation (or localization) but also the recombination (or velocity) of polaron. Then we predict that how the interchain coupling affects

* Corresponding author.
E-mail addresses: sps_lixx@ujn.edu.cn (X.-x. Li), ss_cheng@ujn.edu.cn (G. Chen).

the property of elementary excitation in conjugated polymers will be a hot subject in future studies.

As early as 1998, Klimov et al. experimentally reported that the biexciton was not stable in solid film of polymer molecules with strong interchain coupling [14]. On the other hand, Gao et al. theoretically predicted that the efficiency of double-photon absorption of polymer molecules to form biexciton was low [15]. Then we speculate that the reverse polarization phenomenon of biexciton could not be easily observed experimentally. Recently we studied the effect of interchain coupling on the reverse polarization of high-energy exciton, and found that it tended to extend between the two coupled chains, and then its reverse polarization was reduced [16].

Is interchain coupling always unfavorable to reverse polarization of conjugated polymers? For the single-excited state of polaron, although it could be reversely polarized in an isolated polymer chain, the effect of interchain coupling on its formation and polarization is still not clear. Whether its reverse polarization depends sensitively on the coupling strength? Whether the introduction of an interchain electron-transfer term into SSH model could bring in some new interesting phenomena of the excited polaron? With these questions in mind, in this paper, we mainly consider a system consists of two coupled polyacetylene chains, and explore the effect of interchain coupling on the property of the charged polymer after single-photon absorption. The remainder of the paper is organized as follows. In Section 2, we establish model Hamiltonian, and outline the scheme of the self-consistent calculation between the static Schrödinger equation and the equilibrium condition. In Section 3, the calculated results and discussion are given. Finally, the conclusions drawn from the present study are summarized in Section 4.

2. Model and method

In the framework of tight-binding approximation, we establish the Hamiltonian consists of four parts,

$$H = H_{\text{ele}} + H_{\text{latt}} + H_E + H_\perp. \tag{1}$$

Based on the one-dimensional SSH model [5,10,11], we describe the electronic part of Eq. (1) as

$$H_{\text{ele}} = -\sum_n [t_0 - \alpha(u_{n+1} - u_n)](C_{n+1}^+ C_n + C_n^+ C_{n+1}), \tag{2}$$

where t_0 denotes the electron transfer integral between nth and $(n+1)$th carbon atoms in the case of non-dimerization, α the electron–lattice coupling constant, and u_n the displacement of nth carbon atom from its equilibrium position. C_n^+ and C_n denote the creation and annihilation operators of electron at site n, respectively.

The second part of Eq. (1) introduced by lattice distortion in polymer is given classically by

$$H_{\text{latt}} = \frac{1}{2}K\sum_n (u_{n+1} - u_n)^2 + K'\sum_n (u_{n+1} - u_n). \tag{3}$$

Here, K denotes the elastic constant, and the last linear term is introduced to stabilize the polymer chain under the free-end boundary condition [17,18].

A uniform electric field is applied along the chain so as to polarize the excited polaron. Then, the contribution from electron–electric field interaction to Hamiltonian is given as a scalar potential,

$$H_E = |e|E\sum_n (na + u_n)(C_n^+ C_n - 1). \tag{4}$$

e is the electron charge, E the field strength and a the lattice constant.

The last term in Eq. (1) describes the interaction between two coupled nearest-neighbor polymer chains [16,19–21],

$$H_\perp = -\sum_n t_\perp (C_{1,n}^+ C_{2,n} + C_{2,n}^+ C_{1,n}). \tag{5}$$

Here, $t_\perp$ denotes the orthogonal hopping integral of electron between chain 1 and chain 2 localized at the same site.

Given the above, we generalize the Hamiltonian for electron in polymer takes the form of

$$H_0 = -\sum_{n=1}^{2N} [t_0 - \alpha(u_{n+1} - u_n)](C_{n+1}^+ C_n + C_n^+ C_{n+1})$$
$$+ |e|E\sum_{n=1}^{2N} (na + u_n)C_n^+ C_n - t_\perp \sum_{n=1}^{N} (C_n^+ C_{n+N} + C_{n+N}^+ C_n). \tag{6}$$

To facilitate the calculation, we consider the system of two coupled parallel chains, each with a length of N units of Carbon–Hydrogen (CH) group. Then $n = 1 \sim N$ denotes chain 1, and $n = (N+1) \sim 2N$ chain 2, with the total CH group number of the system $2N$. The electron is in its eigen-state and satisfies the following stationary state Schrödinger equation

$$\varepsilon_\mu |\Phi_\mu\rangle = H_0 |\Phi_\mu\rangle \tag{7}$$

as its mass is much smaller than that of a CH group. In Wannier representation, the eigen-state $|\Phi_\mu\rangle$ of electron with eigen-value ε_μ could be expressed as $|\Phi_\mu\rangle = \sum_n Z_{\mu,n}|n\rangle$. $|n\rangle$ denotes the atomic orbital of the nth site, and $Z_{\mu,n}$ the wave function of electron localized on nth site, μth energy level. Then Eq. (7) becomes

$$\varepsilon_\mu Z_{\mu,n} = -[t_0 - \alpha(u_n - u_{n-1})]Z_{\mu,n-1}$$
$$- [t_0 - \alpha(u_{n+1} - u_n)]Z_{\mu,n+1}$$
$$+ |e|E(na + u_n)Z_{\mu,n} - t_\perp Z_{\mu,n+N} - t_\perp Z_{\mu,n-N}. \tag{8}$$

The total energy of the system is therefore given by

$$E = \sum_\mu^{\text{OCC}} \varepsilon_\mu + \frac{1}{2}K\sum_n (u_{n+1} - u_n)^2$$
$$+ K'\sum_n (u_{n+1} - u_n) - |e|E\sum_n (na + u_n). \tag{9}$$

Obviously, it is the function of atom's displacement u_n. Under the variation principle, u_n is determined by $\partial E(\{u_n\})/\partial\{u_n\} = 0$. Then we obtain the static equilibrium condition

$$u_{n+1} - u_n = -\frac{2\alpha}{K}\sum_\mu^{\text{OCC}} Z_{\mu,n}^* Z_{\mu,n+1} - \frac{K'}{K}$$
$$+ \frac{|e|E}{K}\left(\sum_{m=1}^{n}\sum_\mu^{\text{OCC}} Z_{\mu,m}^* Z_{\mu,m} - n\right). \tag{10}$$

Thus it can be seen that the lattice distortion u_n is determined self-consistently with the wave function $Z_{\mu,n}$. By solving Eq. (8) and Eq. (10) simultaneously, we can self-consistently calculate the lattice displacement and electron wave function at the lowest energy state of the system.

3. Results and discussion

In the present calculation, the parameters are taken as $t_0 = 2.5$ eV, $\alpha = 4.1$ eV/Å, $K = 21$ eV/Å^2, $a = 1.22$ Å for the trans-polyacetylene [5,10,11]. For each chain consists of N CH group,