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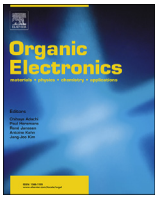

Phase-breaking effect on polaron transport in organic conjugated polymers

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ABSTRACT

Despite intense investigations and many accepted viewpoints on theory and experiment, the coherent and incoherent carrier transport in organic semiconductors remains an unsettled topic due to the strong electron-phonon coupling. Based on the tight-binding Su-Schrieffer-Heeger (SSH) model combined with a non-adiabatic dynamics method, we study the effect of phase-breaking on polaron transport by introducing a group of phase-breaking factors into π-electron wave-functions in organic conjugated polymers. Two approaches are applied: the modification of the transfer integral and the phase-breaking addition to the wave-function. Within the former, it is found that a single site phase-breaking can trap a polaron. However, with a larger regular phase-breaking a polaron becomes more delocalized and lighter. Additionally, a group of disordered phase-breaking factors can make the polaron disperse in transport process. Within the latter approach, we show that the phase-breaking can render the delocalized state in valence band discrete and the state in the gap more localized. Consequently, the phase-breaking frequency and intensity can reduce the stability of a polaron. Overall, the phase-breaking in organic systems is the main factor that degrades the coherent transport and destroys the carrier stability.

1. Introduction

Energy migration and carrier transport are important current topics in organic semiconductors and devices. Although the organic conductance has been effectively improved and the organic devices, such as organic solar cells (OSC) and organic light emitting diodes (OLED), have been successfully fabricated, some basic physical phenomena in organic electronics are still controversial. For example, there is no consistent conclusion on the organic transport mechanism whether band-like transport or hopping is the dominant mechanism. This controversy is recently shown to relate closely to the coherence or incoherence of the transport mechanism.

The specific nature of organic semiconductors on physical and structural basis determines their transport performance. In traditional inorganic semiconductors and metals, the rigid periodic lattice structure makes the electronic state behave in the form of a Bloch wave. The band-like transport mechanism dominates, which leads to a high mobility. Simple lattice structure and the absence of electron-phonon coupling make the effective transport easily understood. While in organic semiconductors, the strong electron-phonon coupling causes the carriers or excited states to couple with the soft lattice resulting in the formation of spatially localized self-trapped states, such as polarons, bipolarons or excitons. These quasi-particles are heavier and move slower than the usual electrons and holes. As a result, the mobility is adversely affected even in organic crystals. Moreover, the actual material microstructure is not as perfect as one would expect. Besides electron-lattice interaction, there also exist the structural diversity, impurities and thermal effects. All these factors complicate the transport mechanism. Up to now, much work has been done to study carrier transport in organic molecular crystals or polymers [1]. In 2006, Troisi and Orlandi used a one-dimensional semiclassical model to compute charge carrier mobility in the presence of thermal fluctuations of the electronic Hamiltonian. This transport mechanism explains several contrasting experimental observations pointing sometimes to a delocalized “band-like” transport and sometimes to the existence of strongly localized charge carriers [2]. The effects of structural diversity [3] and impurities are also considered as the diagonal or non-diagonal disorder, and the thermal effect has been modeled by dynamic disorder exerting a random force on lattice

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sites [4,5]. The comprehensive effect of these factors leads to the inferior transport performance of organic semiconductors.

From what is stated above, we can infer that the poor mobility should be intrinsic to organic materials. However, two promising facts are worth considering. One is the high mobility at low temperature. The negative temperature coefficient of mobility is the fingerprint of the band-like transport mechanism. In one experiment, Sakanoue and Sirringhaus found that in the crystalline pentacene or polymer at low temperature, the mobility is high and “thermally deactivated”, e.g. it decreases with rising temperature [6]. Early investigation by Palstra and coworkers also showed that the mobility of crystal pentacene decreased with temperature and impurity [7]. This phenomenon should be attributed to degeneration of band-like or coherent transport caused by thermal lattice fluctuations. The other fact is the observation of room-temperature coherence. In 2009, Scholes observed efficient coherent transport in organic semiconductors at room temperature [8,9], which offered the possibility of efficient transport of charge and energy in the organic material. It is considered that coherent transport dominated at short times if the polymer chains were protracted, while incoherent transport dominated if the chains were folded seriously. Cho et al. experimentally measured electron transport properties during an ultrashort time and found the transition from coherent transport to incoherent transport [10]. Recently, Takeya et al. reduced molecular thermal vibrations by pressurizing the material and also experimentally obtained the corresponding result [11]. As the intermolecular spacing decreases the coupling is enhanced, which leads to the electron transport from incoherent to band transport in the organic crystal. These observations indicate that coherence supports effective transport and the structural disorder and thus the phase disorder should be responsible for the reduction of mobility. Impurities or defects are easily created in the organic samples; thermal effect is apparent for organic materials with light atoms. Moreover, the electron-electron interaction is also an important source of phase-randomizing collisions. For effective carrier transport and energy migration, investigations on the coherent mechanism and keeping track of phase information are necessary.

Rapid progress has been made in studying coherent transport. Scholes and coworkers proposed some methods to define coherence in theory [12], such as the relative coupling strength theory. In experiment, they also observed the cross peak in two dimensional electronic spectroscopy [13], implying the existence of a coherent process. These theoretical descriptions can well present the coherence phenomenon in organic semiconductors and have played a guiding role in experiments, but the analysis of intrinsic phase information of the wave-function which is the root cause of all the coherence phenomena has been obviously lacking. In 2012, Yao et al. considered the decoherence process in organic amorphous semiconductors by introducing a decoherence time, and how the type of transport is changed from coherent to incoherent [14]. With Monte Carlo simulation, they obtained the dependence of diffusion coefficient on decoherence time, which is consistent with some experimental observations [15]. In many previous works on π-conjugated molecules or polymers, an atomistic simulation dynamic approach has been widely used to describe the dynamic behaviors of carriers in organic semiconductors, such as polaron transport and dissociation, polaron collisions and exciton production [16–20]. In these investigations, the phases of the electronic states are strictly determined by the Hamiltonian. From the perspective of coherence, the electronic phase is supposed to be reserved, which means a coherent transport. Obviously, this kind of treatment is deficient when involving phase-breaking processes.

In this paper, we consider this question in the context of phase conservation. In a highly conjugated polymer, as the main carrier, a polaron is a combination of an electron (hole) and the lattice distortion. How the phase of the π-electron wave-function affects the polaron should be considered by invoking the electron-phonon coupling. Consequently, this paper is organized as follows. The model and method are described in the next section. A qualitative analysis is also given in this section. Then in section three we present calculations on a polaron and its dynamics based on two phase-breaking mechanisms we proposed. Finally in section four, we discuss the phase-breaking effect and conclude that phase-breaking is unfavorable to carrier stability and its transport in the materials with band-like transport mechanism.

2. Model and method

In our previous works, we have studied polaron motion, dissociation and collisions. The behavior of a polaron (bipolaron or exciton) is closely related to the electron-phonon coupling. For a conjugated polymer chain described by the SSH model, the evolution of the electronic wave-functions and the lattice configuration is determined by Refs. [3,21,22].

$$i\hbar\frac{\partial}{\partial t}\varphi_{\mu,n}(t) = -t_{n-1}\varphi_{\mu,n-1} - t_{n+1}\varphi_{\mu,n+1} - e(na+u_n)\varphi_{\mu,n} \tag{1}$$

$$M\ddot{u}_n(t) = f_l + f_e + f_E \tag{2}$$

with the elastic force, electron-phonon coupling force and external electric field force separately given by

$$f_l = -K(u_{n+1} - 2u_n + u_{n-1}) \tag{2a}$$

$$f_e = \alpha\left(\rho_{n+1,n} + \rho_{n,n+1} - \rho_{n,n-1} - \rho_{n-1,n}\right) \tag{2b}$$

$$f_E = -eE\left(\rho_{n,n} - 1\right) \tag{2c}$$

where $t_n = t_0 - \alpha(u_{n+1} - u_n)$. All the notations have the normal meaning as in previous reference [23]. Normally, the non-adiabatic dynamic process is expressed by the solution of the coupled derivative equations consisting of the time-dependent Schrödinger equation and the Newton's equation of motion. We first prescribe an initial system state, of which the band structure and wave-function are determined. Starting with the initial state, the electron wave-function evolves following the time-dependent Schrödinger's equation. Meanwhile, due to the electron-phonon coupling, the lattice motion is controlled by the driving force in Eq. (2), which is partially determined by the electron state at previous time step. Therefore, the updated lattice structure determines the electron state of the next time step. With increasing time, the evolving electron wave-function and the lattice motion condition at every time step are determined.

In Eq. (2b), the density matrix is given by $\rho_{m,n} = \sum_{\mu}^{OCC}\varphi_{\mu,m}^{*}\varphi_{\mu,n}$, from which we can discern the importance of phase. For the diagonal terms, $\rho_{n,n}$ means the electronic density at site n. But for the off-diagonal terms, $\varphi_{\mu,n} = \left|\varphi_{\mu,n}\right|e^{i\theta_{\mu,n}}$, $\rho_{m,n} = \sum_{\mu}^{OCC}\left|\varphi_{\mu,m}^{*}\right|\left|\varphi_{\mu,n}\right| e^{i(\theta_{\mu,n}-\theta_{\mu,m})}$, the effect of phase is important. From the expression of the electron-phonon coupling term, we see that this force is sensitive to the phase difference between the neighboring sites. Therefore, if the phase is altered by some physical factors, it is expected that the lattice configuration or the carrier would be changed. It should be noticed that for usual rigid materials, the electron-phonon coupling α is very weak, and in this case the electron-phonon coupling force has been neglected.