Organic Electronics 25 (2015) 261–265

Contents lists available at ScienceDirect

Organic Electronics

journal homepage: www.elsevier.com/locate/orgel

Long-range Coulomb interaction effects on polarons in conjugated polymers

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ARTICLE INFO

Article history:
Received 10 June 2015
Received in revised form 28 June 2015
Accepted 28 June 2015
Available online 3 July 2015

Keywords:
Electron–electron interaction
Electron–lattice interaction, polaron
Multiconfigurational time-dependent
Hartree–Fock formalism

ABSTRACT

Combining the Su–Schrieffer–Heeger and Pariser–Parr–Pople model (SSH+PPP), we have studied the influence of electron–electron interactions on the motion and dissociation of a polaron in the presence of an electric field, with emphasis on the long-range Coulomb interactions. The multiconfigurational time-dependent Hartree–Fock (MCTDHF) formalism was used to compute the electron–electron interactions. How the saturated velocity and the critical dissociation electric field of the polaron are related to the on-site Coulomb repulsion and long-range Coulomb interactions has been investigated. It was found that the on-site Coulomb interaction does not favor the motion of a polaron. There is a critical strength of the long-range Coulomb interaction for which the polaron takes on the most localized configuration. Comparing with the results obtained using the extended Hubbard model, we found that competition between the long-range Coulomb interactions and the on-site Coulomb interaction leads to a non-monotonic dependence of both the saturated velocity and the critical dissociation electric field on the long-range Coulomb interactions.

1. Introduction

Conjugated polymers have been one of the ideal candidates for the development of optoelectronics devices, such as light-emitting diodes and organic photocells, because of their unique optical and electrical properties [1–4]. Most of the conjugated polymers are quasi-one-dimensional materials, where electron–phonon coupling mechanisms play an important role. In particular, extra electrons and holes tend to deform the lattice and induce self-trapped elementary excitations such as solitons, polarons and bipolarons, which are generally believed to be the main charge carriers in conjugated polymers [5–7]. The motion of the charge carriers along the polymer chain in the presence of an external electric field is one of the processes involved in the functioning of these devices. For example, it is widely accepted that in light emitting diodes, electrons and holes injected from metal electrodes can distort the polymer chain to form positive and negative polarons which then move as a unit under the influence of an electric field. When positive and negative polarons meet they can recombine to form an exciton. The exciton can then decay radiatively to emit a photon. Conversely, in organic solar cells, the polymers absorb sunlight generating charge carriers (usually polarons). These charge carriers likewise move through the photocell in the presence of the electric field, constituting the photocurrent. In order to increase the performance of devices, whether photo-emitting or photo-absorbing, a better understanding of the transport of charge carriers is required, especially of the transport of the polarons which are the predominant excitations in nondegenerate polymers.

A great deal of effort has been devoted to studying polaron dynamics in the framework of the Su–Schrieffer–Heeger (SSH) Hamiltonian [8–14]. It has been found that an electron or a hole injected from an electrode can form a polaron in the presence of a weak electric field [8]. The polaron then travels as an entity along the polymer chain and reaches a saturated velocity in the presence of a constant electric field [9–13]. If the electric field is very strong, the polaron dissociates due to the fact that the propagation speed of the lattice distortion can not keep up with the motion of the charge [13,14]. The disruption of a polaron in a strong electric field has been observed experimentally [15].

In the SSH model, only the electron–lattice (e–l) interactions are considered, and the electron–electron (e–e) interactions are totally ignored. In order to understand the role of the e–e interaction on polaron dynamical properties, several groups have described the polymer using the SSH Hamiltonian in combination with the Hubbard model or extended Hubbard model, where the on-site Coulomb repulsion and the nearest-neighbor interactions are considered. Using the SSH and extended Hubbard models in the

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http://dx.doi.org/10.1016/j.orgel.2015.06.045
1566-1199/

unrestricted Hartree–Fock approximation, Di et al. found that the localization of the polaron was strengthened and the saturated velocity of the polaron was decreased by both on-site Coulomb repulsion, U, and the nearest-neighbor interactions, V [16]. Recently, Zhao and coworkers have investigated the dependence of the velocity on the on-site Coulomb interaction U using an adaptive time-dependent density matrix renormalization group method. The results showed that the polaron velocity is suppressed by the on-site Coulomb interaction, U. The polaron moves with a supersonic velocity, about four times the velocity of sound in the small U limit, and approaches the velocity of sound for large U [17]. Using the same method as Zhao, Ma et al. confirmed the results of Zhao and also found that large V values favor polaron transport while small values of V suppress the polaronic motion [18].

From these studies, we can see that the on-site Coulomb interactions and nearest-neighbor interactions greatly influence the motion of polarons. However, in principle, e–e interactions include not only on-site Coulomb repulsion and nearest-neighbor interactions, but also long-range Coulomb interactions which are not included in the Hubbard or extended Hubbard model. The present paper reports a systematic numerical investigation of the influence of e–e interactions, especially the long-range Coulomb interactions, on polaron motion and stability. This work has been performed using the SSH Hamiltonian combined with the Pariser–Parr–Pople (PPP) model. The approach takes into account both e–l and e–e interactions in organic polymers. A multiconfigurational time-dependent Hartree–Fock (MCTDHF) method has been adopted to handle the e–e interactions [19]. The evolution of the electronic states and the atoms have been simulated using the nonadiabatic molecular dynamics method [20]. The aim of this work is to give a physical picture of the characteristics of polaron dynamics when long-range Coulomb interactions are taken into account, and to contribute to the understanding of the dynamic processes with the expectation that they may provide guidance to improve charge transport in organic optoelectronic devices. The paper is organized as follows: In Section 2, we present the SSH model modified to include e–e interactions via a PPP Hamiltonian for describing a polymer chain. Then the MCTDHF formalism is briefly introduced. In Section 3, the static and dynamic characteristics of polarons are described taking into account the long-range Coulomb interactions. A summary is given in Section 4.

2. Model and method

The SSH model [21] captures the characteristics of strong e–l coupling in conjugated polymers and the PPP model [22] includes the e–e interactions. We adopt the SSH+PPP model Hamiltonian for a polymer chain describing the system, so both e–e and e–l interactions are addressed. The overall Hamiltonian is described as follows:

$$H = H_e + H_l. \tag{1}$$

The first part is the electron Hamiltonian of the system, which can be written as,

$$\begin{aligned} H_e = & -\sum_{n,\sigma}[t_0 - \alpha(u_{n+1} - u_n) + (-1)^n t_e](c^\dagger_{n+1,\sigma}c_{n,\sigma} + h.c.) \\ & + U\sum_n \left(c^\dagger_{n\uparrow}c_{n\uparrow} - \frac{1}{2}\right)\left(c^\dagger_{n\downarrow}c_{n\downarrow} - \frac{1}{2}\right) \\ & + \frac{1}{2}\sum_{m,n\neq m}\sum_{\sigma,\sigma'} V_{mn}\left(c^\dagger_{m\sigma}c_{m\sigma} - \frac{1}{2}\right)\left(c^\dagger_{n\sigma'}c_{n\sigma'} - \frac{1}{2}\right) \\ & + |e|E(t)\sum_{n,\sigma}[(n+1)r_0 + u_n]\left(c^\dagger_{n\sigma}c_{n\sigma} - \frac{1}{2}\right). \end{aligned} \tag{2}$$

The first term in Eq. (2) is the e–l coupling Hamiltonian of the system described with the SSH model including a Brazovskii–Kirova-type symmetry breaking term [23], where the operator $c^\dagger_{n,\sigma}$ ($c_{n,\sigma}$) creates (annihilates) an electron at site n with spin σ, and t_0 denotes the hopping integral of π electrons for zero lattice displacement. α is the e–l coupling constant, and u_n is the displacement coordinate of the nth site. The second and third terms account for on-site Coulomb interactions and long-rang Coulomb interactions, respectively. U is the on-site Coulomb repulsion energy, and the effects of long-rang Coulomb interactions are described by the semiempirical Ohno potential V_{mn}, defined as

$$V_{mn} = \frac{U}{\sqrt{1 + (\beta r_{mn}/r_0)^2}}, \tag{3}$$

where r_{mn} denotes the distance between sites m and n, r_0 is the average bond length, and β is the shielding factor, which determines the ratio between the onsite and inter-site repulsion energies. The electric field is applied along the polymer chain, and its interactions are given in the fourth term of Eq. (2). Here, e is the electron charge. In our simulation, the field is constant after a smooth turn-on described by a half Gaussian time profile $E(t) = E_0 exp[-(t - t_c)^2/t_w^2]$ for $0 < t < t_c$ and $E(t) = E_0$ for $t > t_c$. For all results presented below, we chose $t_c = 75$ fs and $t_w = 25$ fs. The last part of Eq. (1) is the Hamiltonian for the lattice distortion that is described classically:

$$H_l = \frac{K}{2}\sum_n (u_{n+1} - u_n)^2 + \frac{M}{2}\sum_n \dot{u}_n^2, \tag{4}$$

where K is the elastic constant and M is the mass of a CH group.

The evolution of the electronic state with time is obtained by solving the time-dependent Schrödinger equation,

$$i\hbar\frac{\partial}{\partial t}|\Psi\rangle = H_e|\Psi\rangle. \tag{5}$$

The lattice configuration of the system $\{u_n\}$ is inversely determined classically by the electronic states in a nonadiabatic approach

$$M\ddot{u}_n = -\nabla_n\langle\Psi|H_e|\Psi\rangle - \nabla_n\langle\Psi|H_l|\Psi\rangle. \tag{6}$$

From Eqs. (5) and (6), one can see that the degrees of freedom of both the electron and lattice are coupled and should be evaluated self-consistently. It should be noted, however, that since the electronic part of the Hamiltonian H_e contains e–e interaction operators, it is generally impossible to solve exactly the full many-body problem described in Eq. (5) for systems with many interacting electrons. Here, we adopt the same technique as in Ref. [19] to solve the coupled differential Eqs. (5) and (6), i.e., the MCTDHF method which together with the Runge–Kutta method of order eight with step-size control, has been shown to be an effective approach for investigating the dynamics of conjugated polymers [24–26]. The parameters used in this paper are taken to be those for *cis*-polyacetylene, i.e., $t_0 = 2.1$ eV, $t_e = 0.05$ eV, $\alpha = 3.2$ eV/Å, $K = 21.0$ eV/Å^2, $r_0 = 1.22$ Å, $M = 1349.14$ eV fs^2/Å^2, $U = 4.1$ eV, and $\beta = 3.4$ [19]. These parameters reproduce well the band gap diagram of the polyacetylene. Although these parameters are chosen for polyacetylene, the results are expected to be qualitatively valid for other conjugated polymers.

3. Results and discussions

Let us start with the static properties of a polaron. A one-dimensional polymer chain containing 400 sites was considered, which is long enough to eliminate the boundary effects. The geometry of the polymer chain with no electric field can be