Impact of Coulomb Interactions on the Exciton Dissociation in Polymer Heterojunctions

Gesiel G. Silva, Luiz A. R. Junior & Antonio L. A. Fonseca

Introduction

Organic Solar Cells (OSCs) have attracted considerable interest currently by combining features that make them amenable to manufacturing with low environmental impact and potentially cost–effective to promising new photovoltaic technologies than their inorganic counterparts[1–3]. In these devices, the charge transport is one of the most important physical processes that should be intensively investigated in order to improve the power energy conversion effciency[4,5]. The charge transport mechanism in polymer–based materials are generally dominated by hopping (nonadiabatic) process of charge carriers between localized electronic states[6]. Due to the strong electron–lattice interactions in these materials, the conventional self–localized charge carriers are polarons which possess spin $\pm 1/2$ and charge $\pm e$[7]. However, when the photoexcitation process results in a large concentration of polarons, two acoustic polarons of same charge and antiparallel spins, for example, can recombine to form an bipolaron, that are spinless structures with charge $\pm 2e$[8]. An exciton, in its turn, is a bound electron–hole pair structure, which can be accomplished by charge injection or photoexcitation mechanisms resulting on the emergence of self–localized electronic states. The photoexcitation mechanism in OSCs leads primarily to the formation of excitons and consequently, to generate current, the excitons must first dissociate into free charges. Once that these structures are the main responsible by the charge transport mechanism in donor-acceptor (D–A) polymer heterojunctions, studies considering channels for their interaction in these materials, although crucial to a more detailed description of the charge transport, lacking theoretically andare also very few experimentally.

From the theoretical point of view, the generation of charge carriers in conjugated polymers was numerically investigated using an extended version of the Su–Schrieffer–Heeger (SSH) model that includes inter–chain interaction. It was obtained that the recombination between a polaron and an exciton can generates four kind of products, i. e, a triplet exciton, a singlet exciton, an excited polaron, and a bipolaron depending on the inter–chain coupling strength. However, one of the most relevant molecular parameters which may affects the rate of the exciton dissociation and, consequently, the recombination between the structures present in a photovoltaic interface is the band widths (ΔE) of the donor and acceptor materials, as shown in Figure 1. From these results, one can see that further detailed investigations about the possible channels for the charge carrier formation mechanism in polymer D–A heterojunctions and its impact on the charge transport can be a key

to enhance the power energy conversion effciency in OSCs being of major interest.

Sun and Stafstrom recently investigated how exciton dissociation is affected for temperature effects, intensity of the external electric field and inter-chain interaction strenght[9]. For the Coulomb interaction (U), they adopted 4.1 eV for interaction between the sites. In this scope, our goal was to investigate the influence of Coulomb interaction for different distances (d) inter-chain, or to vary Coulomb interaction for different distances. In this sense, we vary d from 1 to 10 Å and, for each d, varies U between 0.5 and 4.5 eV with increase of 0.5 eV.

The starting point for the simulations present a configuration in which one exciton lies in the donor chain while the acceptor chain contains an electron–polaron. In this case, the negatively charged polaron is represented by the doubly occupied HOMO-1 and the solely occupied LUMO levels. On the other hand, the exciton is denoted by electrons with parallel spin orientation in the HOMO and LUMO+1 levels, as shown in Figure 1.

Methods

The overall Hamiltonian of our model is $H = H_{intra} + H_{inter} + H_{latt}$. The term $H_{intra} = H_{elec} + H_{ee}$ represents the intra-chain electronic part.
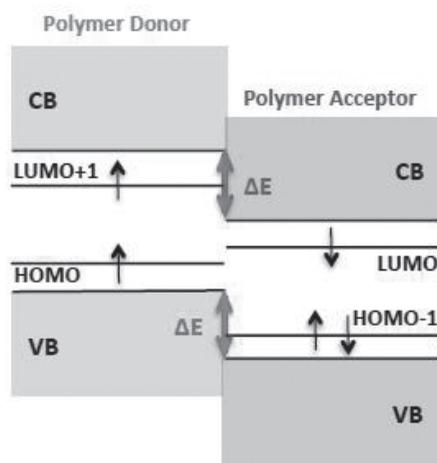
Figure 1. Schematic diagram of the energy levels for a D–A polymer heterojunction. Here, CB represents the conduction band whereas VB denotes the valence band.

In this way, H_{elec} can be expressed in the following form

$$H_{elec} = \sum_{i,s} \Delta_n C_{n,s}^\dagger C_{n,s} - \sum_{i,s} t_{n,n+1}(C_{n,s}^\dagger C_{n+1,s} + C_{n+1,s}^\dagger C_{n,s})$$

in which Δ_n denotes the on-site energy of site n. Here, the label n runs over the sites off both donor and acceptor chains without a specific index for the two different chains. In order to implement the D–A polymer heterojunction, the on-site energy for all sites of the donor chain is settled as $\Delta_n = \Delta E$ whereas for the sites of the acceptor chain $\Delta_n = 0$. The operator $C_{n,s}^\dagger$ ($C_{n,s}$) creates (annihilates) a π-electron state at a particular site n with spin s. $t_{n+1,n} = e^{-i\gamma A(t)}[(1+(-1)^i \delta_0) t_0 - \alpha(u_{n+1} - u_n)]$ is the intra-chain transfer integral where t_0 is the transfer integral between nearest neighboring sites in a dimerized lattice, α the electron-phonon coupling constant, u_n the displacement of a site from its equilibrium position, and δ_0 the Brazovskii-Kirova symmetry-breaking term that is introduced in order to lift the ground-state degeneracy for non-degenerated polymers[10]. $\gamma \equiv ea/\hbar c$, with a is the lattice parameter, e the absolute value of the eletronic charge, and c is the spped of light. The external electric field is introduced in the model through the time-dependent vector potential, in which $E = -(1/c) A$[6].

The contribution of the electron-electron interactions (H_{ee}) to the model Hamiltonian can be placed as in which U is the screened on-site Coulomb interactions,

$$H_{inter} = -\sum_{\langle i,j \rangle,s} t_{i,j}^\perp (C_{i,s}^\dagger C_{j,s} + C_{j,s}^\dagger C_{i,s}) + \frac{1}{2}\sum_{i,j} V_{i,j}(n_i - 1)(n_j - 1)$$

$n_i = \sum_s C_{i,s}^\dagger C_{i,s}$ and $V_{i,j}$ denotes the Ohno potential[11] defined as for i and j running over the sites of the same chain. $V_{i,j}$

$$V_{i,j} = \frac{U}{\sqrt{1 + (\beta r_{ij}/r_0)}}$$

defines the long–range electron–electron interactions, in which β denotes screening factor, $r_{i,j}$ is the distance between sites *i* and *j*, and r_0 the average bond length.

The inter-chain interactions (H_{inter}) has the form

$$H_{inter} = - \sum_{\langle i,j \rangle, s} t^{\perp}_{i,j} (C^{\dagger}_{i,s} C_{j,s} + C^{\dagger}_{j,s} C_{i,s})$$
$$+ \frac{1}{2} \sum_{i,j} V_{i,j} (n_i - 1)(n_j - 1)$$

where $\sum_{(i,j)s}$. establishes that the sum is restricted to pairs of nearest and next nearest neighboring sites at different chains, *i* and *j* are the sites index of opposite chains, and $t_{i,j}$ represents the interchain hopping integral as a function of the inter–chain distance d and has the form of

$$t^{\perp}_{i,j} = \frac{t_0}{10} exp(1 - d/5)$$

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$$t^{\perp}_{i,j} = \frac{t_0}{10} exp\left(1 - \frac{\sqrt{d^2 + r_0^2}}{5}\right)$$

for the next nearest hopping. Here, $V_{i,j}$ denotes the inter–chain Coulomb interactions.

The last term in our model Hamiltonian describes the lattice backbone where K is the harmonic constant of a σ

bond, M is the mass of a CH group, and i runs over the sites of both chains[12]. Recently, Miranda et al. developed a set of parameters to use when Coulomb interactions are considered[13,14]. Thus, we adopt this parameters developed by them: t_0=2.1 eV, α=3.2 eV/Å, δ_0=0.05 eV, K=21.0 eV/Å2, M=1349.14 eV fs2 / Å2, r_0=1.22 Å, β=3.4.

$$H_{latt} = \frac{K}{2} \sum_i (u_{i+1} - u_i)^2 + \frac{M}{2} \sum_i \dot{u}_i^2$$

Results and Discussion

As we can see in Figure 2(a), two similar lattice distortions appears in the acceptor layer, which depicts the time evolution of the staggered order parameter for the bond length. These well localized lattice structures denote the presence of two negative polarons in the acceptor layer whereas the donor layer contains only one localized lattice structure with similar degree of distortion, which denotes the presence of a negative polaron. It is easy to conjecture that, due to the parallel spin configuration presented by the electrons in the LUMO and LUMO+1 levels (two spin up electrons), the bipolaron formation can not takes place. Moreover, one can see from Figure 2(b), which displays the time evolution of the mean charge density, that a positive amount of charge rises in the polymer donor coupled to the shallower lattice deformation, whereas two negative structures appears in the polymer acceptor, which indicates that the former neutral excited structure is now a positively charged polaron and the two structures present in the acceptor layer are negatively charged polarons.
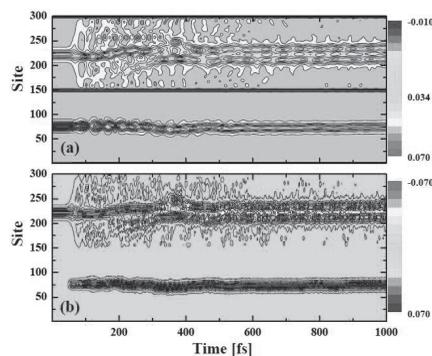
Figure 2. Time evolution (a) of the staggered order parameter of the bond length and (b) the mean charge density for a system with inter–chain distance (d) of 5 Å and band offset strength (ΔE) of 0.8 eV.

Acknowledgments

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