

## Impact of Coulomb Interactions on the Exciton Dissociation in Polymer Heterojunctions

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### 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<sup>1-5</sup>. The photoexcitation mechanism in OSCs leads primarily to the formation of excitons. The exciton is a bound electron-hole pair formed due to the strong electron-lattice interactions presented by the organic materials. Consequently, to generate current, the excitons must first dissociate into free charges (polarons<sup>6-9</sup>). Once the excitons are the main responsible by the charge transport mechanism in donor-acceptor (D-A) polymer heterojunctions, studies considering channels for their dissociation in these materials are crucial to a more detailed description of the working principles of OSCs.

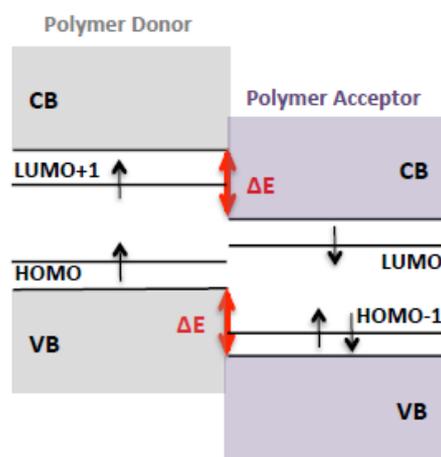
In this work, the role played by the Coulomb interactions on the exciton dissociation mechanism in conjugated polymers is numerically investigated using an extended version of the Su-Schrieffer-Heeger (SSH) model, which includes inter-chain interactions. Moreover, the model includes the band width ( $\Delta E$ ) of the donor and acceptor materials, once this is considered one of the most relevant molecular parameters which may affects the rate of the exciton dissociation and, consequently, the recombination between the polarons in a D-A interface. The results presented in this work may provide guidance to enhance the power energy conversion efficiency in OSCs, being of major interest.

### METHODS

The starting point for the simulations present a configuration in which one exciton lies in the donor chain. The acceptor chain, in its turn, can be occupied (or not) by an positive/negative polaron. For the cases depicted in Figure 1, a negatively

charged polaron is represented by the doubly occupied HOMO-1 (Highest Occupied Molecular Orbital) and the solely occupied LUMO (Lowest Unoccupied Molecular Orbital) 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.

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 with a band width  $\Delta E$ . 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  $\Delta_n$  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  $\pi$ -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,  $\alpha$  the electron-phonon coupling constant,  $u_n$  the displacement of a site from its equilibrium position, and  $\delta_0$  the Brazovskii-Kirova symmetry-breaking term that is introduced in order to lift the ground-state degeneracy for non-degenerated polymers<sup>10</sup>.  $\gamma \equiv ea/\hbar c$ , with  $a$  is the lattice parameter,  $e$  the absolute value of the electronic charge, and  $c$  is the speed of light. The external electric field is introduced in the model through the time-dependent vector potential, in which  $\mathbf{E} = -(1/c)\dot{\mathbf{A}}$ .

The contribution of the electron-electron interactions ( $H_{ee}$ ) to the model Hamiltonian can be placed as

$$H_{ee} = U \sum_{i,s} \left( C_{i,\uparrow}^\dagger C_{i,\uparrow} - \frac{1}{2} \right) \left( C_{i,\downarrow}^\dagger C_{i,\downarrow} - \frac{1}{2} \right) + \frac{1}{2} \sum_{i,j \neq i} V_{i,j} (n_i - 1)(n_j - 1)$$

in which  $U$  is the screened on-site Coulomb interactions,  $n_i = \sum_s C_{i,s}^\dagger C_{i,s}$  and  $V_{i,j}$  denotes the Ohno potential<sup>11</sup> defined as

$$V_{i,j} = \frac{U}{\sqrt{1 + (\beta r_{ij}/r_0)^2}}$$

for  $i$  and  $j$  running over the sites of the same chain.  $V_{i,j}$  defines the long-range electron-electron interactions, in which  $\beta$  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

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

where  $\sum_{\langle i,j \rangle, s}$  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  $t_{i,j}^\perp$  represents the

interchain hopping integral as a function of the inter-chain distance  $d$  and has the form of

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

for the nearest hopping and

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

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

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

where  $K$  is the harmonic constant of a  $\sigma$  bond,  $M$  is the mass of a CH group, and  $i$  runs over the sites of both chains<sup>12</sup>.

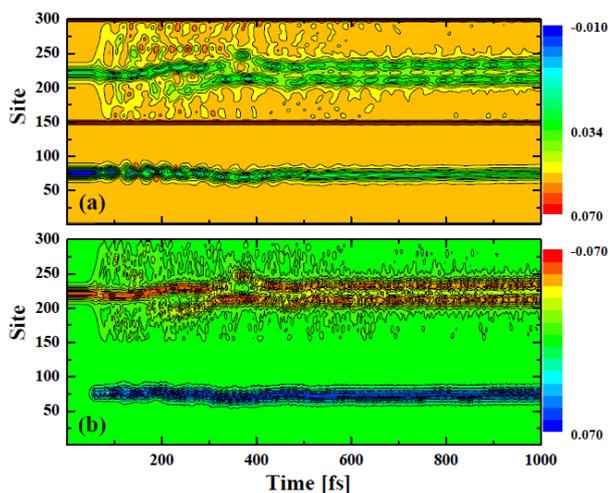
Recently, Miranda *et al.* developed a set of parameters to use when Coulomb interactions are considered<sup>13,14</sup>. Thus, we adopt this parameters developed by them:  $t_0 = 2.1$  eV,  $\alpha = 3.2$  eV/Å,  $\delta_0 = 0.05$  eV,  $K = 21.0$  eV/Å<sup>2</sup>,  $M = 1349.14$  eV fs<sup>2</sup> / Å<sup>2</sup>,  $r_0 = 1.22$  Å,  $\beta = 3.4$ .

## RESULTS AND DISCUSSION

Here we discuss a case where the exciton dissociation takes place in the presence of a negatively charged polaron in the acceptor chain. In this way, Figure 2 depicts the exciton dissociation mechanism followed by the interaction of two polarons with same charge and parallel spin configuration. One can see, in Figure 2(a), that at the first few femtoseconds, the exciton can keep its shape deforming deeply the donor chain (dark-blue region), leading the total charge in that chain to be zero, whereas the negative polaron remains unaltered in the acceptor chain with a lattice deformation degree (green region) shallower than to the exciton. At this stage, the inter-chain interactions are significantly weak, still increasing, and are not strong enough to appreciate the exciton dissociation. After that, the inter-chain interactions reach its full strength and the exciton dissociation (the transfer of an electron to the acceptor chain) takes place.

As can be noted 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 take 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 ( $\Delta E$ ) of 0.8 eV.

## CONCLUSIONS

In summary, the exciton dissociation dynamics between in polymer D–A considering the presence of a negatively charged polaron in polymer heterojunctions has been theoretically investigated combining the SSH and the extended Hubbard models in the scope of a nonadiabatic evolution method. An Ehrenfest Molecular Dynamics is performed by using a one-dimensional tight-binding model which includes lattice relaxation. The results show that, among others, one of the possible channels for the interaction between the polaron and exciton, if the electrons in the polaron and exciton has parallel spins, is the formation of three polarons one positively and two negatively

charged. This understanding of the exciton dissociation and the charge carrier interaction in D–A polymer heterojunctions can pave the way to improve charge transport efficiency in OSCs.

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