



# Influence of the photoexcitation process on the dynamics of triplet excitons in organic polymers



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## ABSTRACT

In this work we adopt a model Hamiltonian approach to investigate exciton generation and its subsequent dynamics in conjugated polymers. By using a modified version of the Su–Schrieffer–Heeger model Hamiltonian to include temperature effects, interaction between polymer chains, and different photoexcitation processes, we study the dynamics of triplet excitons in the system. The temperature is incorporated in the method by means of a classical Langevin equation, and Ehrenfest molecular dynamics is used to describe the time evolution of the system. We were able to distinguish the response of the oscillating electric dipole for different excitations at nonzero temperatures based on the amplitude and frequency.

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## 1. Introduction

Polymer-based solar cells have been recently studied as a potential replacement for conventional ones. Besides low-cost, organic solar cells have other advantages such as low toxicity, favorable mechanical properties, adjustable electronic properties and ease of fabrication. Despite the continued interest in the electronic properties of these novel materials, an understanding of the underlying processes involved in the charge transport remains far from satisfactory [1].

The whole mechanism of charge transport in inorganic photovoltaic materials is well understood, but an equivalent understanding of the behavior of organic excitons is still absent. This fact is partially due to the differences in the nature between inorganic and organic charge carriers and of the respective excitons, which in turn are responsible for several of the properties that make organic photovoltaics attractive.

It is well known that the efficiency of transport in conventional semiconductors is limited by thermal lattice deformations called phonons because it tends to occur in delocalized states. In organic semiconductors, however, a similar kind of delocalized transport mechanism would decrease the mean free path of such carriers to a length smaller than the mean interatomic distance. This conclusion leads one to consider the electronic transport through hopping between localized states in organic materials [2]. Particularly,

it is known that in organic semiconductors, collective nonlinear excitations resulting from the coupling between electrons and phonons are responsible for the charge conduction. Subsequently, organic excitons arise from the interaction between oppositely charged quasi-particle (e.g. polarons) in the same fashion as inorganic excitons arise from interactions between electrons and holes. Thus, interestingly enough, in these systems the charge transport is actually phonon enabled, rather than being phonon limited. Since this transport mechanism has frequently been confirmed by experimental research [3], one concludes that thermal effects must play a dramatically different role in organic conduction when compared to its role in conventional electronics.

Features such as current–voltage expressions derived for inorganic systems have proven to be applicable for organic systems only under certain circumstances. Thermal effects and the varying nature of the organic exciton leads the systems to regimes in which a clear understanding of the transport mechanism is missing. In spite of the fact that temperature effects have been the target of many theoretical and experimental studies, few theoretical works have dealt with the contribution of the kind of excitation performed to create the exciton.

Another important difference between the two types of photovoltaics lies in the major challenge that each technology must face in order to create free charge carriers from excitons. While the efficiency of both organic and inorganic photovoltaics is determined by the absorption rate of incident photons, the main issue for organic photovoltaics lies in the dissociation of the exciton that is typically an order of magnitude more bounded than in the inorganic case [4]. Once the electron hole pair is formed, the structure

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is much too stable to yield free carriers by mere thermal excitation, and we must either consider other kinds of excitations or create less stable excitons. Thus, in the case of organic photovoltaics, the type of exciton in terms of the photoexcitation level also plays an important role in the transport mechanism.

An interesting issue is discussed in a recent experimental paper by Kobayashi and coworkers [5]. In their work it was possible to relate the fast exciton's geometrical relaxation time to the transition from a free exciton to form a bound polaron pair in organic based compounds. It is then highly desirable to determine possible phenomenological reasons behind this ultrafast relaxation of excitons, as well as to predict how the excitation level affects the relaxation time.

In this sense, we dedicate this work to the description of the photoexcitation influence over the behavior of the excitons in conjugated polymers. By considering a version of the SSH hamiltonian [6] modified to include temperature effects and interchain interactions we consider a pair of conjugated polymer chains in which we perform several kinds of photoexcitations to create excitons of different natures at nonzero thermal regimes [7]. As temperature induces relaxations through oscillating dipoles we relate the amplitude and frequency of these oscillations to the kind of excitation considered. We thus determine the processes of exciton relaxation in terms of these oscillations through the use of the presently developed model.

This work is organized as follows: in Section 2 we describe our model; Section 3 is devoted to the presentation of our main results that we summarize in Section 4.

## 2. Methodology

We considered a Hamiltonian of the type  $H = H_1 + H_2 + H_{int}$ , where  $H_1$  and  $H_2$  stand for a typical SSH hamiltonian [6] such as:

$$H_j = -\sum_{n,s} t_{j,n,n+1} \left( C_{j,n+1,s}^\dagger C_{j,n,s} + H \cdot c \right) + \sum_n \frac{K}{2} y_n^2 + \sum_n \frac{p_n^2}{2M}, \quad (1)$$

where  $j = 1$  or  $2$  and refers to the index of each chain. Here  $n$  indicates the sites of the chain. The operator  $C_{n+1,s}^\dagger$  ( $C_{n,s}$ ) creates (annihilates) a  $\pi$ -electron state with spin  $s$  at the  $n$ th site;  $K$  is the harmonic constant that describes a  $\sigma$  bond and  $M$  is the mass of a CH group. The parameter  $y_n$  is defined as  $y_n \equiv u_{n+1} - u_n$  where  $u_n$  is the lattice displacement of an atom at the  $n$ th site.  $p_n$  is the conjugated momentum to  $u_n$  and the quantity  $t_{j,n,n+1}$  is the hopping integral, given by

$$t_{j,n,n+1} = [1 + (-1)^n \delta_0] (t_0 - \alpha y_n), \quad (2)$$

where  $t_0$  is the hopping integral of a  $\pi$ -electron between nearest neighbor sites in the undimerized chain.  $\alpha$  is the electron-phonon coupling, and  $\delta_0$  is the Brazovskii–Kirova symmetry-breaking term, which is used to take the *cis* symmetry of the polymer into account. The parameters used here are  $t_0 = 2.5$  eV,  $M = 1349.14$  eV  $\times$  fs<sup>2</sup>/Å<sup>2</sup>,  $K = 21$  eV Å<sup>-2</sup>,  $\delta_0 = 0.05$ ,  $\alpha = 4.1$  eV Å<sup>-1</sup> and a bare optical phonon energy  $\hbar\omega_Q = \sqrt{4K/M} = 0.16$  eV. These values have been used in previous simulations and are expected to be valid in general for conjugated polymers [7–11].

In order to introduce electronic coupling between chains 1 and 2 we make use of an interaction Hamiltonian of the type:

$$H_{int} = -\sum_{s,n} t_\perp \left( C_{1,n,s}^\dagger C_{2,n,s} + C_{2,n,s}^\dagger C_{1,n,s} \right), \quad (3)$$

where  $t_\perp$  is the transfer integral between sites labeled by same index  $n$  in different chains; here  $t_\perp = 0.075$  eV [12,13].  $C_{1,n,s}^\dagger$  ( $C_{1,n,s}$ ) creates (annihilates) a  $\pi$  electron with spin "s" at the  $n$ th site of chain 1 while  $C_{2,n,s}^\dagger$  ( $C_{1,n,s}^\dagger$ ) annihilates (creates) a  $\pi$ -electron state at the corresponding site in chain 2.

According to our model we must simultaneously solve the time dependent Schrödinger equation for the electronic part and the Euler equation for the lattice. In order to solve these equations numerically, one must first obtain a stationary state that is self-consistent with all degrees of freedom of the system (the lattice plus electrons). Then, the time evolution of the system configuration will be described by the Equations of Motion.

The electronic wave function is the solution of the time-dependent Schrödinger equation:

$$i\hbar \dot{\psi}_{j,k,s}(n,t) = -t_{j,n,n+1} \psi_{j,k,s}(n+1,t) - t_{j,n-1,n}^* \psi_{j,k,s}(n-1,t) - t_\perp \psi_{j,k,s}(n,t), \quad (4)$$

where  $\hat{j} = 2, 1$  for  $j = 1, 2$ , respectively.

In order to solve this equation, the following expansion was introduced

$$\psi_k(t) = \sum_l C_{lk} \phi_l(t), \quad (5)$$

with  $C_{lk} = \langle \phi_l | \psi_k \rangle$ , where  $\{\phi_l\}$  is the set of eigenfunction of the electronic Hamiltonian at a given time  $t$ . The solution of the time-dependent Schrödinger equation [14] is then written as

$$\psi_{k,s}(n, t_{j+1}) = \sum_l \left[ \sum_m \phi_{l,s}^*(m, t_j) \psi_{k,s}(m, t_j) \right] \times \exp \left( -i \frac{\varepsilon_l \Delta t}{\hbar} \right) \phi_{l,s}(n, t_j), \quad (6)$$

where  $\{\varepsilon_l\}$  represents the eigenvalues of the electronic part of the Hamiltonian at a given time  $t_i$ , and the term in square brackets is the expansion coefficient.

The equation of motion that describes the site displacement and provides the temporal evolution of the lattice is obtained in a classical approach [15,6] by solving the Euler equation and obtaining a typical force expression. This equation is written as

$$F_n(t) = M \ddot{u}_n = -K[2u_n(t) - u_{n+1}(t) - u_{n-1}(t)] + \alpha[B_{n,n+1} - B_{n-1,n} + B_{n+1,n} - B_{n,n-1}], \quad (7)$$

where

$$B_{n,n'} = \sum_{k,s} \psi_{k,s}^*(n,t) \psi_{k,s}(n',t) \quad (8)$$

is the term that couples the electronic and lattice solutions, and the index  $j$  for chains was omitted. The primed summation represents a sum over the occupied states only. In our study we have simulated the electron removal from one chain and subsequent absorption of this electron by the other chain by changing the occupation of the electronic states. Once the system is made of two weakly interacting parallel chains, we remove an electron from an occupied molecular orbital and consider an unoccupied virtual molecular orbital in the sum.

In the spirit of the SSH model, the classical treatment of the lattice, we introduce temperature in our system by adopting the phenomenological approach of considering random vibrations for the CH groups. Several literature references show that this methodology that has been proved successful [7,9,11,16]. This was accomplished through the use of a canonical Langevin equation [17–19] in which  $\zeta(t)$  is a white stochastic signal (the fluctuation term) with the following properties:  $\langle \zeta(t) \rangle \equiv 0$  and  $\langle \zeta(t) \zeta(t') \rangle = W \delta(t - t')$ .  $\gamma$  is a stokes-like dissipation term. Including both terms in our force equation, Eq. (7), we obtain an effective force  $\tilde{F}_n$ :

$$M \ddot{u}_n = -\gamma \dot{u}_n + \zeta_n(t) + F_n(t) \equiv \tilde{F}_n \cdot (t). \quad (9)$$

The relationship between  $\zeta(t)$ ,  $\gamma$ , and the temperature  $T$  of the system is given by the fluctuation dissipation theorem. The damping constant  $\gamma$  can be determined by low temperature lattice thermal

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