

Polaron Dynamics in Organic Molecular Stacks

Luiz A. R. Júnior

Introduction

Organic semiconductors have emerged as ideal candidates for the design of optoelectronic devices such as photovoltaics¹ and light-emitting² diodes due to present important traits which are required for the development of new green energy solutions. The potential advantages in terms of low cost, flexibility, and low environmental impact make these materials attractive for the electronics industry. In order to increase the device performance, a better understanding at a molecular and even at the atomic scale of the charge transport properties is absolutely required^{3,4}. Particularly, the polaron stability and dynamics are of critical importance for the device performance.

The charge transport in organic materials can be classified in three different processes, considering the temperature dependence: the small polaron model, which is dominated by the nonadiabatic hopping process; the adiabatic (large) polaron model, and the band-like transport³. Organic molecular crystals and stacks, i. e., 2D and 1D systems, respectively, are particularly interesting in this context since they can, depending on preparation techniques and the choice of molecular constituents, exhibit different combinations of these processes.

Semiconducting molecular crystals are recognized to exhibit two types of electron–phonon couplings: the local intra-molecular (Holstein-type) and the non-local inter-molecular (Peierls-type)³. A considerable amount

of theoretical work, focused on understanding the charge transport processes in organic semiconductors, has been performed in the framework of the Holstein–Peierls model in the last few years^{5–9}. Nevertheless, studies that take into account different electronic and lattice parameters to characterize the polaron stability and dynamics for different kind of molecular stacks, are not available in the literature. Furthermore, the role played by the anisotropy in the polaron stability and dynamics (when more than one stack is considered) is not completely understood and requires a more detailed understanding.

In this work, a systematic numerical investigation of the influence of different electronic and lattice parameters on the polaron stability in organic molecular stacks is performed using a semi-empirical Holstein–Peierls model. The approach takes into account both intra- and inter-molecular electron–lattice interactions to describe also the polaron dynamics in the system. These investigations are performed in one-dimensional systems (molecular stacks) by varying relations between the transfer integral (electronic parameter), force constant and the electron-phonon coupling (lattice parameters). The systems investigated here are designed to resemble single stacks in molecular semiconductors such as pentacene, anthracene, or rubrene. An Ehrenfest Molecular Dynamics approach is performed by using a one-dimensional tight-binding model including lattice relaxation. Temperature effects are included by means of a canonical Langevin equation. The aim of this work is to give a physical picture of the polaron stability and

transport in organic molecular stacks contributing to the understanding of these important processes that may provide guidance to improve the charge transport in organic optoelectronic devices.

Methods

In our model, each molecule is represented by a site with index i having two degrees of freedom where v_x^i is the site displacements involved in the antisymmetric non-local vibrational modes and is the single internal phonon mode coupled to the electronic system through of the local e-ph coupling, according as represented in Figure 1. In this way, the combined Holstein-Peierls Hamiltonian is described as $H_{HP} = H_{elec} + H_{latt}$ and can

$$H_{elec} = \sum_i \alpha_1 u_i \hat{c}_i^\dagger \hat{c}_i + \sum_i (J_{i+1,i} \hat{c}_i^\dagger \hat{c}_{i+1} + h.c.)$$

assumes the following form for the first part (electronic Hamiltonian): where $J_{i+1,i}$ is the inter-molecular transfer integral between two neighboring sites and is defined as

$$J_{i+1,i} = J_0 - [\alpha_2^x (v_{i+1}^x - v_i^x)] e^{-i\gamma \Lambda_x(t)}$$

The operator \hat{c}_i^\dagger (\hat{c}_{i+1}) creates (annihilates) a carrier at the i -th lattice site; J_0 is the transfer integral for a pristine lattice; $v = \frac{e\alpha}{\hbar c}$ with e being the absolute value of the electronic charge, c is the speed of light, and a is the lattice constant; α_1 and α_2^x are the e-ph coupling constants for intra-molecular and inter-molecular, and vibrations, respectively. The electric field is assumed to be static and included in the model by means of the time dependent potential vector $\Lambda_x(t) = -cE_t$.



Figure 1. Schematic representation of the one-dimensional Holstein-Peierls System

The last part in is H_{HP} the Hamiltonian of the lattice backbone ($H_{latt} = H_{latt,1} + H_{latt,2}$) which is described by the two separate harmonic oscillators, considering the intra- and inter-molecular modes:

$$H_{latt,1} = \frac{K_1}{2} \sum_i (u_i)^2 + \frac{M_1}{2} \sum_i (\dot{u}_i)^2$$

and

$$H_{latt,2} = \frac{K_2}{2} \sum_i (v_{i+1}^x - v_i^x)^2 + \frac{M_2}{2} \sum_i (\dot{v}_i^x)^2$$

where the force constants and the masses and refer to the intra- and inter- molecular oscillators, respectively. Here, we have used the following values for the above-mentioned parameters: $J_0, \alpha_1, \alpha_2^x, K^1$ and K_2 varying in the range [35-100] meV, [0.5-2.0] eV/Å, [0.5-2.0] eV/Å, [5-10] eV/Å, [1.0-5] eV/Å, respectively, $M_1 = 1.3 \times 10^9$ e (as/Å)² $M^2 = 2.6 \times 10^{10}$ eV(as/Å)², and $a = 3.5$ Å³⁻⁹. The dynamical simulations are carried out using a particular set of parameters depending on the kind of molecular stack.

The electronic dynamics is performed by means of the time-dependent Schrödinger equation. By introducing instantaneous eigenstates, the solution at each instant of time can be expressed in the form where $\phi_l(m)$ and ϵ_l are the eigenfunctions and eigenvalues

$$\psi(n, t + \Delta t) = \sum_l \left[\sum_m \phi_l^*(m) \psi(m, t) \right] \times e^{\frac{i\epsilon_l \Delta t}{\hbar}} \phi_l(n)$$

of H_{elec} at time t , respectively. The equations of motion for the lattice backbone are given by the newtonian equations for the intra-molecular displacement and for the antisymmetric inter-molecular vibrations similarly to reported in references^{4,5}.

Results and Discussion

We have mentioned above that our model considers two degrees of freedom. The distortions related to the polaron show a negative value for the intra-site displacements, which denotes a compression of the molecules due to the excess of charge. On the other hand, the inter-molecular distortions show a contraction (negative values) for the two neighboring inter-molecular displacements of the central molecule, where the polaron is initially localized, as represented in Figure 1. These contractions are followed by elongations (positive values) in the displacements of the other molecules. These elongations decrease with increasing numbers of molecules, in order to keep the constraint of fixed total displacements. The lattice geometry of the system is optimized using the resilient backpropagation, RPROP, algorithm. For the charge distribution presented by the optimized geometry, the polaron is localized initially at three molecules with its main contribution residing on a central molecule.

With this geometry configuration and charge localization in mind, we now turn to simulations for the polaron dynamics in a system which resembles a pentacene stack (just to present an overview about the results in this abstract). Figure 2 depicts the results for the polaron dynamics in a one-dimensional system (a molecular stack) consisting of 20 sites. The calculations are carried out considering an adiabatic approximation in which the wavefunction of the charge is assumed to be a single eigenstate (the lowest LUMO) of the total Hamiltonian. In other words, the charge associated with the polaron remains in the same state during transport process and only this state changes its position with time.

After the electric field is applied, it takes a while (about 250fs) for the charge to start moving but then it moves with a constant velocity of about 25 Å/ps. This velocity can be calculated from the molecular charge density (panel (a)) by counting the number of the sites that has been travelled during the simulation time. Beside the charge density, the intra-molecular displacements (u_i) (panel (b)) and intermolecular bond lengths, ($v_{i+1}^x - v_i^x$) (panel (c)) are also demonstrated.

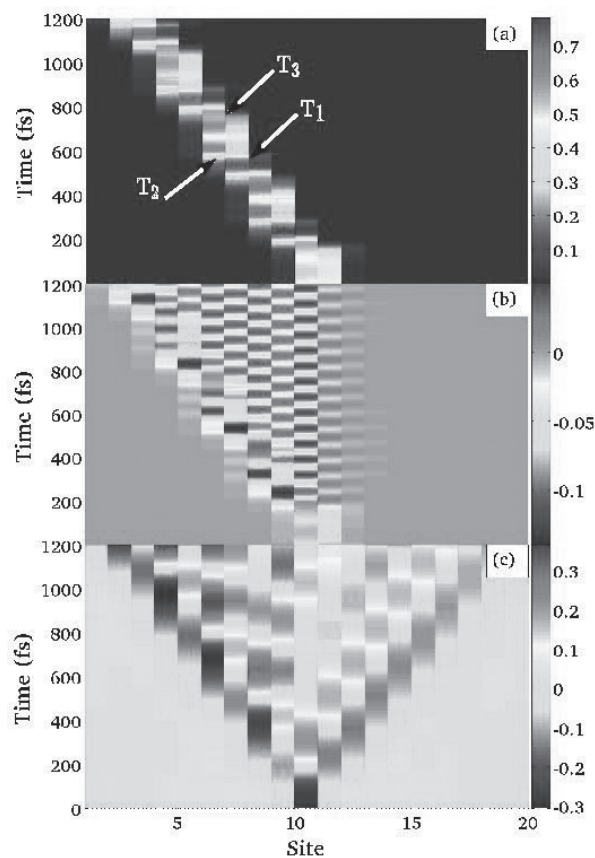


Figure 2. Polaron dynamics in a one-dimensional system (molecular stack): (a) molecular charge distribution, (b) intra-molecular displacement, and (c) inter-molecular bond length for $= 1.5 \text{ eV/\AA}$, $= 10.0 \text{ eV/}$, $= 0.5 \text{ eV/\AA}$, $= 1.5 \text{ eV/}$, $= 50 \text{ meV}$ and $= 2.0 \text{ mV/\AA}$.

Inspite of intra-molecular vibrations, inter-molecular distances, Figure 2(c), form traveling waves in the system which move with approximately the same velocity in the opposite direction of the polaron motion. In summary, when the polaron is situated on site i , the bond length between sites $i-1$ and i (in this case where the polaron moves in the $-x$ direction) will get contracted (blue color in panel (b) and (c)) which in turn will result in an expansion in the bond length between sites i and $i + 1$ (red color in panel (b) and (c)). It should be noted that the oscillatory behavior follows the classical mass-spring oscillator with a frequency $\sqrt{K_2/M_2}$.

It is important to get a view over the polaron transport phenomena according the transport mechanism described in the previous section. In Figure 2(a), it can be seen that the charge is localized on two sites in the beginning. It starts to move due to the applied force of electric field. One can describe the motion as an adiabatic process in which at each instant of time the charge goes from being centered on a single molecule (T1) to being shared equally between two neighboring molecules (T2) and then drifts and gets centered on the next molecule (T3). Obtain more details on this issue and how the transport is affected by changing different parameters is precisely the aim of this work.

Conclusions

In summary, a semi-empirical Holstein–Peierls model was used to study the polaron stability and mobility in crystalline organic semiconductors at a molecular level. The approach takes into account both intra- and intermolecular electron–lattice interactions as well as the effects of an external electric field. Furthermore, we have investigated the effects of the change of parameters on the polaron stability and mobility in order to simulate different kind of molecular stacks.

The results presented above are one of the evidences that the parameters may describe different types of interactions within a molecular crystal and that result in a stable mobile polaron. Nevertheless, the parameters that result in such a mobile polaron agree well with the interaction strengths that we can expect in molecular crystals. It is therefore plausible that the charge transport in terms of large polaron motion occurs in molecular crystals.

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Luiz A. R. Júnior^{a,b}

^aInstitute of Physics, University of Brasília, 70.919-970, Brasília, Brazil

^bUniversity of Brasília, UnB Faculty of Planaltina, 73.345-010, Brasília, Brazil