Quantum modeling for injection of carriers coupled to a bath of vibration modes: application to hot and cold charge transfer states in organic solar cells

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We develop a quantum model for the injection of carriers in a material that presents strong electron-vibration coupling. This model, which can be solved numerically, is applied to the organic solar cells for which the electron transfer at the donor-acceptor interface is an essential step. We analyze how the electron-hole interaction and the nature of the recombination process impact the electron transfer. In particular this model explains, on a quantum basis, how one can get high injection yield with a cold charge transfer state as often observed experimentally.

The interfacial charge transfer (CT) between heterogeneous materials constitutes a key physical phenomenon central to a variety of light-induced energy transport and conversion processes such as photocatalysis, photovoltaics, energy storage, molecular electronics, etc... [1–8]. In the case of excitonic solar cells such as heterojunction bulk organic solar cells (OSC) the photon is absorbed in the donor zone and leads to the creation of an exciton which is stable because of the strong Coulomb interaction between the electron and the hole constituting it. The exciton must migrate to the donor-acceptor interface in order to dissociate [9, 10]. Yet once the charges are in separate phases, they still need to overcome their mutual Coulomb attraction which is larger than the thermal energy room (around 0.025 eV) otherwise they recombine [11–15]. Several phenomena have been identified as facilitators of charge separation such as, built-in electric fields at donor-acceptor interfaces, delocalization of the excitons and of the free carriers charges, the offset in energy levels between donor and acceptor, structural disorder etc... [16–22]. A central concept is that of the charge transfer state (CTS) which is the first state on which the electron hops on the acceptor side and on which it is coupled to local vibration modes. A much-debated issue is how the efficiency of the charge separation is related to the release of energy on these modes (hot CTS) or not (cold CTS).

On the theoretical side, the treatment of charge transfer in organic semiconductors is complex. Historically some phenomenological models were developed such as the Brahm-Onsager [23, 24] analytic model which is based on a classical picture that allows to describe separation in a strong Coulomb potential. The Marcus theory and related approaches are also much-used and describe charge transfer at the molecular level with incoherent hopping [19, 20, 25, 29]. Ab-initio electronic structure calculations [21, 22, 30] also bring much useful information concerning the electronic states and the electrostatic potential. For a fully microscopic understanding of the charge separation mechanism in these organic photovoltaic devices, numerical methods have been proposed such as exact diagonalization [31] and time-dependent density functional theory [32–34]. Yet the problem of describing properly the charge separation process is still largely open and new complementary approaches are needed.

In the present study we focus on the dynamics of the charge separation process. We assume a simple Holstein Hamiltonian which describes an electron that interacts with a bath of vibration modes on the acceptor side. In addition we include the electrostatic potential due to the electron-hole interaction near the donor-acceptor interface. The parameters of this Hamiltonian are estimated from ab-initio calculations. We show that it is possible to treat this model essentially exactly by combining the Dynamical Mean Field Theory and the quantum scattering theory. This avoids perturbative theories, such as the Fermi Golden Rule [35, 36], which is often used but is justified only at the weak electron-vibration coupling.

We analyze the conditions for the existence of a cold or hot charge transfer state which is much debated in the scientific community [19, 37–39, 40–44]. It is shown that even in the presence of the electron-hole attraction the electron can be injected into the acceptor with moderate initial energy such that the charge transfer state stays cold [19, 37]. This situation is observed in some systems and finds here a natural explanation on a quantum basis.

Our charge separation model is presented in Figure 1. We consider optical modes with frequencies higher than the thermal energy at room temperature so that all vibration modes are initially empty when the charge injection process starts. The red ball is the hole that is considered fixed and the black balls represent the
different positions of the electron. The state \(|I\rangle\) is the excited singlet state from which the electron can be injected into the charge transfer state (CTS) via the hopping integral \(m\). The electron can jump, on the sites \(i\) of the successive layers \(L=0,1,2...\) (the layer \(L=0\) is the CTS itself) and on each site it can excite phonons. We assume that the sites \(i\) are distributed on a Bethe lattice which is known to reproduce correctly the local environment of a compact system (see Supplementary Material (SM)). For simplicity, we take the standard limit of infinite coordination of this Bethe lattice in which case the mean-field solution is exact.

We consider throughout this letter a Holstein model for the electron-vibration coupling with one vibration mode per site \(i\) of the lattice. The total Hamiltonian \(H\) takes the form [45] [46].

\[
H = \varepsilon_I c_i^+ c_i - m(c_i^+ c_0 + c_0^+ c_i) - \sum_i \frac{V}{L_i + 1} c_i^+ c_i \\
+ \sum_i \hbar \omega a_i^+ a_i - \sum_{i,j} J_{i,j} (c_i^+ c_j + c_j^+ c_i) \\
+ \sum_i g_i c_i^+ c_i (a_i^+ + a_i) + H_R
\]

\(\varepsilon_I\) is the energy of the incoming electron of a molecule at the donor site. The hopping parameter \(m\) between the donor site and the CTS (site \(i=0\)) will be taken as weak compared to the pure electronic bandwidth \(4J\) so that we can take the limit \(m \to 0\). For a site \(i\) the electron creation (annihilation) operators are \(c_i^\dagger\) \((c_i)\). The electrostatic potential at site \(i\) which is on the layer \(L_i\) is \(-\frac{V}{L_i+1}\). It is due to the electron-hole interaction and is characterized by the parameter \(V\). The phonon creation (annihilation) operators of the local vibration mode at site \(i\) is \(a_i^\dagger\) \((a_i)\) and \(\hbar \omega\) is the phonon energy. \(J_{i,j}\) are the hopping matrix elements between nearest neighbors \(i\) and \(j\) on the Bethe lattice and are expressed from \(J\) as explained in the SM. \(g\) is the electron-vibration coupling parameter. The Hamiltonian \(H_R\) represents the recombination processes.

The injection process is analyzed in the full Hilbert space of the electron + vibration modes system (represented in Figure (2)). The initial state \(|I\rangle\) corresponds to the electron on the donor side with no vibration mode excited. The hopping term \(m\) allows the transfer to the CTS with zero phonons \(|0\rangle\). Then the electron-vibration coupling couples the states \(|0\rangle,|1\rangle,\ldots|n\rangle\) with \(n\) phonons created on the CTS and no other mode excited in the acceptor side. Starting from state \(|n\rangle\) there are two channels in which the electron leaves the CTS. Channel \(nA\) corresponds to the propagation on the acceptor side and channel \(nR\) corresponds to the recombination process. The probabilities of injection in channels \(nA\) \((nR)\) are \(\Phi_A^n\) \((\Phi_R^n)\). From these quantities, it is possible to express the quantum yield \(Y\) which is the probability for the electron to be injected into the acceptor and the average vibration energy \(E_{TS}\) on the CTS [47]. One has:

\[
Y = \sum_{n=0}^{\infty} \Phi_A^n = 1 - \sum_{n=0}^{\infty} \Phi_R^n \quad (2a)
\]

\[
E_{TS} = \sum_n n\hbar \omega[\Phi_A^n + \Phi_R^n] \quad (2b)
\]

The probabilities \(\Phi_A^n\) and \(\Phi_R^n\) of injection in the channels \(nA\) and \(nR\) are computed from the scattering theory [31] [48] [51] and depend only on the self-energies \(\Delta_A(\varepsilon_I - n\hbar \omega)\) and \(\Delta_R(\varepsilon_I - n\hbar \omega)\) which represent the effect of the corresponding channels. As shown in SM \(\Delta_A(z)\) is computed from the DMFT. Solving the coupled mean-field equations for an inhomogeneous model, as for the case with electron-hole interaction, is difficult with standard methods. In order to solve these equations we use a development in continued fraction which is very efficient [51] and for which the results are computed with a finite energy resolution. Here the resolution is in the range 0.1-0.2 \(J\) (see SM) which is sufficient for the present discussion.

The recombination process is modeled as an injection into a continuum and we discuss two limits where this continuum is either narrow with a width comparable to the electronic band or is much wider. We expect that the wide band limit is valid if the hole and the electron recombine by emission of a photon in the continuum of electromagnetic waves. This wide band limit can be a good approximation for other recombination pathways since the total energy of a few eV which is released is larger than the variation of energies considered for \(\varepsilon_I\). For a recombination process into a wide continuum we neglect the dependence of \(\Delta_R(z)\) with \(z\) and for simplicity
we take \( \Delta_R(z) = -i\hbar \Gamma \) where \( \Gamma \) is the recombination rate.

We discuss now the results obtained for the LDOS on the site \( |0\rangle \), the energy \( E_{TS} \) lost by the electron on the CTS and the quantum yield \( Y \) of the injection. All energies are given in unit of \( J \) (the pure electronic band-width is \( 4J \)) and for all cases we consider \( \hbar \omega = 1 \). The LDOS are given in units of \( 1/J \). We consider four cases that combine \( g = 1 \) or \( g = \sqrt{2} \) for the electron-vibration coupling parameter with \( V = 0 \) or \( V = 1.5 \) for the electrostatic potential parameter (see the expression of the Hamiltonian in equation [1]). Additional results for other values of the parameters confirm the behavior discussed here (see SM).

Figure (3) presents results in the absence of recombination. We consider first the upper part of the panels a) and b) which show the LDOS \( n(E) \) on-site \( |0\rangle \). Panel a) shows the results for \( g = 1 \) and for \( V = 0 \) (red) or \( V = 1.5 \) (blue). We define \( E_{\text{Min}} \) as the minimum energy of the spectrum in the bulk that is for \( V = 0 \). \( n(E) \) tends to zero at large energies but its spectrum is infinite. \( n(E) \) presents oscillations with minima separated by about \( \hbar \omega = 1 \) which indicates the pre-formation of polaronic bands. For \( V = 1.5 \) the electrostatic potential depends on the distance to the CTS and tends to zero far from the CTS. Therefore close to the CTS the electronic density is modified but far from the CTS one expect that the system is similar to the bulk that is to the case \( V = 0 \). For \( V = 1.5 \) there is a continuum part of \( n(E) \) which starts at the same minimum value \( E_{\text{Min}} \) as for \( V = 0 \). This is expected because the states of the bulk can propagate up to the site \( |0\rangle \) and give therefore contributions to the LDOS \( n(E) \) for all energies \( E > E_{\text{Min}} \). Yet the LDOS \( n(E) \) on state \( |0\rangle \) is strongly modified by the electrostatic potential induced by the electron-hole interaction. In addition there are localized states below the minimum energy \( E_{\text{Min}} \) of the bulk spectrum. These states are analogous to bound electronic states in atoms or to impurity states in semiconductors and are spatially localized around the CTS. One may expect that there is an infinite series of such states close to \( E_{\text{Min}} \) but their weight is too small to be detected numerically. Yet the results indicate that the total weight of the localized states (essentially the two peaks shown in panel a)) is about 0.34 which means that the continuum has a weight of about 0.66. This confirms that the electron-hole potential strongly modifies the LDOS. For the strongest electron-vibration coupling (\( g_1 = \sqrt{2} \), in panel b), the two lower subbands of the continuum are nearly separated by gaps for \( V = 0 \) and the global width is larger than for \( g = 1 \). As for panel a) the introduction of the electron-hole interaction strongly modifies the LDOS both in the continuum part and by the creation of localized states. The total weight of the localized states is about 0.20 and therefore the continuum weight is about 0.80. Note that very close to the bottom of the continuum there is narrow peak with a small weight of about 0.01. We cannot discriminate if this peak is below the continuum and localized or if it belongs to the continuum, but this has no impact on our discussion.

The lower part of the panels of figure (3) represents the average energy \( E_{ph} = -E_{TS} \) lost by emitting phonons on the CTS. In order to inject an electron in the bulk the initial energy \( \varepsilon_I \) must be larger than the minimum energy \( E_{\text{Min}} \) of the bulk spectrum. Depending on \( \varepsilon_I \) two regimes occur. If \( E_{\text{Min}} < \varepsilon_I < E_{\text{Max}} \) there is less than one phonon emitted on average, which is a cold transfer state regime [22]. One has \( E_{\text{Max}} \simeq 1.5 \) for \( g = 1 \) and \( E_{\text{Max}} \simeq 1 \) for \( g = \sqrt{2} \) so that the range of values \( \varepsilon_I \) for injecting electrons with a cold CTS is of about 4 i.e. close to the pure electronic bandwidth. At higher values of \( \varepsilon_I \) the electron can excite one or several phonons which corresponds to a hot CTS. The existence of these two regimes can be understood by considering the limit of small \( g \) and the energy conservation during the injection process. Indeed when \( \varepsilon_I \) is between \( E_{\text{Min}} = -2 \) and \( E_{\text{Max}} = 2 \) (the values of the bounds of the continuum for the pure electronic spectrum) the system does not need to emit phonons to inject an electron in the acceptor side. But when \( \varepsilon_I > E_{\text{Max}} \) it is necessary to emit a phonon prior to inject an electron in the band and when \( \varepsilon_I > 3J \) it is necessary to emit two phonons to inject electrons and so on. This leads to the staircase curve in the lower part of panel a). So the average energy of phonons for \( \varepsilon_I \) in the range \([E_{\text{Max}}, \infty]\) will be \( E_{TS} \simeq (\varepsilon_I - E_{\text{Max}} + \hbar \omega) \). We see that the case \( g = 1 \) is close to \( g \to 0 \). For \( g = \sqrt{2} \), oscillations which reflect the pre-formation of polaronic bands appear but the global trend is identical.

We focus now on the effect of the recombination. If the recombination is treated as injection in a narrow continuum the two channels \( nA \) and \( nR \) (see Figure 2) correspond to narrow bands and this is a situation similar to that of figure (3). As discussed previously the energy
conservation imposes the existence of a hot CTS for sufficiently large $\varepsilon_I$. For every $n$ the flux shares between $\Phi_A^n$ and $\Phi_R^0$ so that the yield $Y$ is partial.

The wide band limit of the recombination is completely different as we show now. We present only the case $g = 1$ in Figure 4 since results for $g = \sqrt{2}$ are qualitatively similar. The panel $a)$ shows the results are rather similar for both values of $V = 0$ and $V = 1.5$. When $\varepsilon_I \leq 2$ the recombination effect is moderate and the CTS is cold. This regime is rather similar to the cold state regime of Figure 3 without recombination. When $\varepsilon_I \geq 2$ the quantum yield decreases with a hot CTS regime. For even higher values of $\varepsilon_I$ the average energy $E_{TS}$ decreases meaning again a cold CTS regime with a small quantum yield $Y < 0.5$. This results from a regime of tunneling. Indeed, the condition of energy conservation implies that the electron can enter in the acceptor channels only after having excited several phonons. A simple physical image is that the excitation of several phonons, which is performed in a tunneling regime, requires a time that increases with $\varepsilon_I$. During this time there is a transfer in the recombination channels with small $n$ at a constant rate $\Gamma$ which leads to smaller yield and smaller number of phonons emitted.

In Panel b) of Figure 4 the results for $V = 1.5$ are summarized in a phase diagram with the two variables $\varepsilon_I$ and $\Gamma$. The red zone represents the hot CTS cases with more than one phonon emitted and the white zone represents the cold CTS regime. One sees that for a sufficiently strong recombination $\Gamma > \Gamma_C$ there is no more values of $\varepsilon_I$ leading to a hot CTS. Note that for energies between $-2$ and $E_{Min} \simeq -2.4$ (not shown here) the yield will decrease again and becomes zero if $\varepsilon_I < E_{Min}$.

To conclude the present model shows that in a large range of incident energies $\varepsilon_I$, of the order of the pure electronic bandwidth $4J$, there can be a high quantum yield of injection and a cold CTS despite the electron-vibration coupling. This is consistent with many experiments. This occurs even with a strong electron-hole interaction which changes deeply the spectral density and creates localized states. For large values of $\varepsilon_I$ we show that the energy conservation imposes the injection to occurs after several phonon excitations, which is as a tunneling process. In this regime the detailed characteristics of the recombination process has a strong influence on the quantum yield of the electron transfer. We emphasize that the present approach could be used to treat models with other characteristics, as for example multiple vibration modes frequencies. It should also be useful for transfer processes at interfaces in other photovoltaic systems or in photosynthetic systems.

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**FIG. 3.** The spectral density $n(E)$ and the average energy lost on the CTS $E_{ph}(\varepsilon_I)$ ($E_{ph} = -E_{TS}$) without recombination. The cyan curve represents $E_{ph}(\varepsilon_I)$ in the case where $g \rightarrow 0$. For panel (a) $g = 1$ and the potential parameter is $V = 0$ (red) and $V = 1.5$ (blue). For panel (b) $g = \sqrt{2}$ and the potential parameter is $V = 0$ (orange) and $V = 1.5$ (green). For both panels the horizontal dashed gray line indicates the limit of cold and hot CTS regimes.

**FIG. 4.** Panel $a)$ shows the quantum yield $Y(\varepsilon_I)$ and the average energy $E_{ph}(\varepsilon_I)$ lost on the CTS, with recombination $\Gamma = 0.1$ and for $V = 0$ (red) and $V = 1.5$ (blue). The horizontal dashed gray line indicates the limit of cold and hot CTS regimes. Panel $b)$ is a phase diagram as a function of the incident energy $\varepsilon_I$ and of the recombination rate $\Gamma$ for $V = 1.5$. It shows the zones of high yield ($Y > 0.5$) or low yield ($Y < 0.5$) and the zones of hot CTS (red) or cold CTS (white).
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