A density matrix approach to photoinduced electron injection

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Abstract

Electron injection from an adsorbed molecule to the substrate (heterogeneous electron transfer) is studied. One reaction coordinate is used to model this process. The surface phonons and/or the electron-hole pairs together with the internal degrees of freedom of the adsorbed molecule as well as possibly a liquid surrounding the molecule provide a dissipative environment, which may lead to dephasing, relaxation, and sometimes excitation of the relevant system. In the process studied the adsorbed molecule is excited by a light pulse. This is followed by an electron transfer from the excited donor state to the quasi-continuum of the substrate. It is assumed that the substrate is a semiconductor. The effects of dissipation on electron injection are investigated.

Key words: electron transfer, density matrix theory, molecules at surfaces

1 Introduction

In recent years electron transfer (ET) between molecular adsorbates and semiconductor nanomaterials and surfaces has been subject of much research [1]. The injection of an electron into the conduction band is a prototype reaction

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for a lot of electrochemical and photoelectrochemical interfacial processes such as photography, solar energy conversion, quantum dot devices, etc. [1]. Interfacial ET between discrete molecular levels and a conducting surface is the simplest of all surface reactions: it involves only the exchange of an electron, and so no bonds are broken [2].

The ultrafast nature of the charge injection from adsorbed molecules to the conduction band of semiconductor surfaces was shown in recent experiments [3–5]. The theoretical description of such experiments demands an adequate treatment of the ET dynamics to be able to describe short time-scale phenomena such as coherences. This can be done within the reduced density matrix (RDM) description used in the present contribution.

Recently [6,7] the electron injection from a chromophore to a semiconductor conduction band was described using the time-dependent Schrödinger equation, thus neglecting relaxation processes. The neglect of relaxation processes was motivated by the experimental finding that injected electrons relax only within 150 fs in the perylene-TiO$_2$ system. Here we include relaxation to be able to treat a larger class of experiments where, for example, the adsorbed molecule is surrounded by a liquid environment, and longer times.

2 Theory

In the RDM theory the full system is divided into a relevant system part and a heat bath. Therefore the total Hamiltonian consists of three terms – the system part $H_S$, the bath part $H_B$, and the system-bath interaction $H_{SB}$:

$$ H = H_S + H_B + H_{SB}. \quad (1) $$

The RDM $\rho$ is obtained from the density matrix of the full system by tracing out the degrees of freedom of the environment. This reduction together with
a second-order perturbative treatment of $H_{SB}$ and the Markov approximation leads to the Redfield equation [8–11]:

$$\dot{\rho} = -i[H_S, \rho] + \mathcal{R}\rho = \mathcal{L}\rho. \quad (2)$$

In this equation $\mathcal{R}$ denotes the Redfield tensor. If one assumes bilinear system-bath coupling with system part $K$ and bath part $\Phi$

$$H_{SB} = K\Phi \quad (3)$$

one can take advantage of the following decomposition [12,11]:

$$\dot{\rho} = -i[H_S, \rho] + [\Lambda\rho, K] + [K, \rho\Lambda^\dagger]. \quad (4)$$

The $\Lambda$ operator can be written in the form

$$\Lambda = \int_0^\infty d\tau \langle \Phi(\tau)\Phi(0) \rangle K I(-\tau) \quad (5)$$

where $K I(-\tau) = e^{-iHt}Ke^{iHt}$ is the operator $K$ in the interaction representation.

The system bath interaction is taken to be linear in the reaction coordinate as well as in the bath coordinates. Neither the rotating wave nor the secular approximation have been invoked. The so-called diabatic damping approximation which has numerical advantages [13] is not used because it could lead to wrong results in the present system studied [14,15].

In the following we direct our attention to ET between an excited molecular state and a conduction band. The Hamiltonian modeling this system consists of the ground and one excited state of the molecule and a quasi-continuum describing the conduction band together with one vibrational coordinate

$$H = \sum_a H_a |\phi_a\rangle \langle \phi_a| + \sum_k (V_{ke}|\phi_k\rangle \langle \phi_e| + H.c.) \quad (6)$$
Here $a$ can be equal to $g$ for the ground state, $e$ for the excited state, and $k$ for the quasi-continuum. As in Ref. [6] we choose the frequency of the vibrational mode to be $\hbar \omega_{\text{vib}} = 0.1$ eV. The coupling between the excited state and the continuum states is assumed to be constant: $V_{ek} = 0.1$ eV. A box-shaped uniform density of states is used. Instead of modeling the excitation from the ground state explicitly we assume a $\delta$-pulse. The excited state potential energy surface is shifted 0.1 Å along the reaction coordinate with respect to the ground state potential energy surface. This results in an initial vibrational wave packet on the excited state with significant population in the lowest 4 - 5 vibrational states. The shift between the excited state energy surface and the continuum parabola is 0.2 Å. The thermal bath is characterized by its spectral density $J(\omega) = \sum_m \gamma_m \delta(\omega - \omega_m)$. Because all system oscillators have the same frequency the coupling to the bath can be given by one parameter $\gamma_1$ in the diabatic damping approximation. Denoting the effective mass of the harmonic oscillator by $M$ the strength of the damping is chosen as $\gamma_1 \pi/(M \omega_{\text{vib}}) = 0.1$ eV.

To be able to study the effects of dissipation we do not model the quasi-continuum with such a large number of electronic states as in Ref. [6]. In that work a band of width 2 eV was described using an energy difference of 2.5 meV leading to 801 electronic surfaces. These calculations are already demanding using wave packet propagation but almost impossible using direct density matrix propagation. For doing such a large system one would have to use the Monte Carlo wave function scheme [16,17]. We use a much simpler model and describe only that part of the conduction band which really takes part in the injection process. The total width of the conduction band may be significantly larger. In the following, a band of width 0.75 eV is treated with 31 electronic surfaces. In each of these electronic states five vibrational states are taken into account. We are aware that this is only a minimal model but hope that it catches the effects of dissipation on the electron injection process.
3 Results

Here we look at two different populations arising in the process of electron injection. The time-dependent population of the electronic states in the conduction band is calculated as the sum over the vibrational levels of each electronic surface $P(k, t) = \sum_\nu P_{k,\nu}(t)$. As a second quantity we look at the time-dependent population of the vibrational levels of the excited molecular state $P_e(\nu, t)$. These two probability distributions give some hints on the effect of dissipation.

Figure 1 shows the electronic population for the quasi-continuum, i.e. the probability distribution of the injected electron, versus the energy of the conduction band. As described above, the four lowest vibrational states are populated significantly at $t = 0$. The structure arising in the upper panel of Fig. 1 was already explained by Ramakrishna et al. [6]. It can be estimated using the golden rule. The electronic probabilities in the quasi-continuum are given as

$$P(k, t) \approx \sum_{\mu, \nu} P_{\mu}^{(i)} |\langle \chi_{i\mu} | \chi_{k\nu} \rangle|^2 \delta(E_0 + \mu \hbar \omega_{\text{vib}} - E - \nu \hbar \omega_{\text{vib}})$$

where $P_{\mu}^{(i)}$ is the initial vibronic distribution in the excited state and $|\chi_{i\mu}\rangle$ and $|\chi_{k\nu}\rangle$ are the vibronic parts of the wave packet in the excited and quasi-continuum states, respectively. The energy $E_0$ denotes the middle of the band.

Turning on dissipation two effects can be seen. First, the vibrational populations in the excited state of the molecule no longer only decay into the quasi-continuum states but also relax within the excited state (see Fig. 2). Second, the vibrational populations also relax within the quasi-continuum states. The recurrences back into the excited state become much smaller. Only those parts of the wave packet which are still high enough in energy can go back to the molecule.
In summary, we extended the work by Ramakrishna, Willig, and May [6] by including relaxation processes into the description of electron injection into the conduction band of a semiconductor. This will, at least, become important for modeling electron injection in the presence of a fluid surrounding the attached molecule.

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Fig. 1. Probability distribution of the injected electron $P(k, t)$ without dissipation (upper panel) and with dissipation (lower panel).
Fig. 2. Population of the vibrational levels of the excited molecular state $P_{\nu}(\nu, t)$ without dissipation (upper panel) and with dissipation (lower panel).

The lowest vibrational state is populated most at $t = 0$. The higher the vibrational quantum number the less populated is the level.
