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Theory of Electron Transfer from the Excited State of an Adsorbed Dye to the Conduction Band of a Semiconductor

K.L. Sebastian[1,2] and M. Tachiya[2]
[1]*Indian Institute of Science*
[2]*National Institute for Advanced Industrial Science and Technology*

We consider the process of photoinduced heterogenous electron transfer [1-5]. A molecule, attached to a semiconductor surface, is excited to an upper electronic state by a laser pulse. The electron in the upper excited orbital can tunnel into the conduction band of the semiconductor, leaving the molecule ionized and perhaps vibrationally excited. Experimentally, electron injection times are of the order of tens to hundreds of femtoseconds. One can produce the molecule in a vibrationally coherent state and study its evolution, after electron injection. Such vibrational wave packet states, were found to continue their motion for several hundred femtoseconds in the product state, implying that electron donation occurs from a non-relaxed vibrational population of the donor.

We first study of the purely electronic problem, using an Anderson like Hamiltonian, which takes only the excited orbital of the adsorbate into account. The solid is represented as a single band of finite bandwidth. Using a Green's function approach, we calculate the exact survival probability of the excited state, for arbitrary bandwidths. We show that that the existence of a split-off state can play an important role in the total injection probability. In the wide band limit, the survival probability decays exponentially, but for finite band widths it does not. We also introduce a "pole approximation", which is easy to use, and leads to good approximate results for the adsorbate density of states and survival probability. It consists of looking for the poles of an appropriately analytically continued, adsorbate Green's function and using them alone, to calculate the quantities of interest. In the wide band limit the method is exact, but for finite bandwidths too, it leads to good agreement with exact calculations.

We also study the influence of vibrational motion, on the electron transfer. As the electron hops into the solid, the molecule is ionized, causing a change in the vibrational

Hamiltonian. We use the simplest model that includes this effect too (see Ramakrishna et. al. [1]). Further the model is of great theoretical interest as it is the simplest Hamiltonian, that has a continuum of electronic states, coupled to vibrational states.

We show how one can eliminate the electronic states exactly and reduce the problem to one of just vibrational motion. Any calculation that needs to be performed can, in principle proceed as if it is just for vibrational motion of the molecule. However, the vibrational motion is now governed by a non-Hermitian Hamiltonian and the calculation, naturally, is more involved. The method works for arbitrary density of states for the conduction band, into which electron injection occurs and can be used to calculate the survival probability in any given vibrational state.

We show that in this case too, the quantities of interest are all contained in an "adsorbate Green's operator", which acts on the space of vibrational wave functions. Its analytic continuation in the complex plane has poles and one can again use the pole approximation. In the wide band limit, this is exact, and leads to the interesting result that the survival probability is independent of vibrational motion in this limit, in agreement with the conclusions of [1]. Further, we show that in this limit, the vibrational dynamics is particularly simple. All that one has to do is, to assume that each one of the vibrational state has a finite lifetime, which is just the lifetime of the electron in the adsorbate state. In the case of finite bandwidth, one has to look for the poles of the Green's operator and use them in the calculations. We report results of calculations using this approximate method too.

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