



A NONADIABATIC THEORY FOR ULTRAFAST CATALYTIC TRANSFER OF ELECTRONS AT LOW TEMPERATURE

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Electron transfer is a ubiquitous elementary process of chemical reactions[1]. Electron transfer is well described by the standard Marcus theory [2], based on an adiabatic hypothesis, as a thermally activated process with a characteristic energy barrier (figure 1). However, the fastest electron transfer occurs close to the Marcus inversion point characterized by a vanishing energy barrier in a regime where the adiabatic hypothesis breaks down. The need of an improved theory is thus a prerequisite to interpret the fast transfer at low temperature.

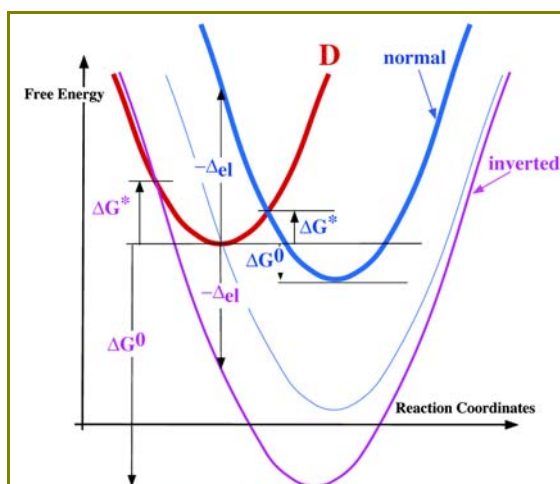


Figure 1. Free energy versus Reaction Coordinates of the system donor-acceptor when the electron is on the donor (top left curve D) or on the acceptor for several redox potentials in the normal regime (top right curve), at the inversion point (middle right curve) and in the inverted regime (bottom right curve). The chemical reaction energy is the distance between energy minima ΔG^0 . The energy barrier is ΔG^* . The electronic excitation energy on the donor at fixed reaction Coordinates is ΔeI .

We have constructed a quantum model of a weakly interacting electron in a *nonadiabatic* phonon bath, in a standard tight-binding scheme of the wave functions. The resulting effective equation that describes the tunneling of electrons is a discrete nonlinear Schrödinger equation with damping terms coming from the nonadiabaticity. These damping terms are necessary to dissipate

the transfer reaction energy and bring about its irreversibility. The thermal fluctuations of phonons introduce random forces in the effective equation at non-zero temperature.

Far from the inversion point, our model recovers fairly well the main predictions of the Marcus model in the standard situation of thermally activated and relatively slow electron transfer. Close to the inversion point, nonlinear effects liven up as the energy level of a given electronic state depends on its occupation density, modifying the transfer between Donor and Acceptor that was supposed to be resonant. This may induce an energy barrier and in any case to a slowing down of the transfer reaction.

We have already shown in previous works [3] that nonlinear tunneling can occur but it imposes an extra condition on the nonlinearities, stating that electronic states of the two molecules involved in the transfer must stay equal. In this case, the electronic density, initially on the donor molecule interacting weakly with the acceptor molecule in a nonlinear resonance, is going to slowly oscillate between the two molecules (as in the linear case) but the transfer will be done with a variation of the electronic level (not present in the linear case). This nonlinear tunneling of the electron is a coherent nonstochastic quantum process. However, the energy of the transfer reaction is zero and this ideal transfer case is physically marginal.

An acceptor molecule in nonlinear resonance with the Donor cannot accept irreversibly the transferred electron and will be named *catalysor* for now on in this note because it can induce spectacular catalytic effects to transfer the electron with a positive energy reaction on a third Acceptor molecule that is not initially in resonance with the Donor. The condition is simply that the oscillating electronic level of the Donor-Catalysor system must cross the unoccupied level of the acceptor molecule interacting weakly with the first system (figure 2). This resonance triggers the transfer of the electron from the Donor-Catalysor system to the acceptor molecule.

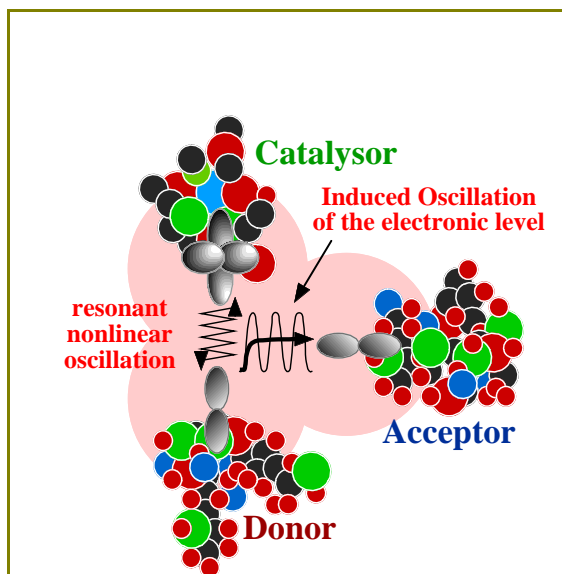


Figure 2. Scheme of a Donor-Acceptor electron transfer induced by a Catalysor. The electron, initially on the donor, oscillates between donor and catalysor, inducing a variation of the energy level. The electronic level resonates with the unoccupied level of the acceptor and the electron is irreversibly transferred with energy dissipation in the phonon bath.

Despite the further loss of the resonance, the reaction energy is dissipated with the charge fluctuations and the electron is irreversibly transferred in its fundamental state on the acceptor. This catalytic effect has been confirmed by numerical simulations of our effective equation of the electron transfer (figure 3) showing the transient passage on the catalysor and the total transfer in picoseconds, an ultrafast process compared to the activated case. The catalytic effect is still efficient at low temperature for cases where the direct transfer donor-acceptor is impossible due to a too high-energy barrier.

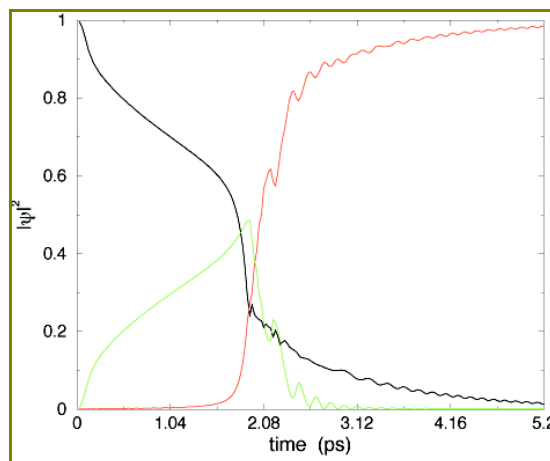


Figure 3. Electronic density as a function of time, on the Donor (in black), the catalysor (in green) and the acceptor (in red) in a realistic example: reaction energy of 0.375 eV, transfer integral of 0.01 eV and activation energy around 0.071 eV without catalysor. At zero temperature, the weak coupling with the catalysor induces a partial transfer on it and then a complete transfer on the acceptor.

Our approach can be extended to quantum excitation transfers and shed new light on the molecular logical functions in biochemistry reactions.

The crucial nonlinear resonance in the Donor-Catalysor system may be detuned by very small changes, coming for example from mutations in the biological world, leading to an inhibition of the electron transfer or at least a considerable slowing down. The photosynthetic reaction center of primitive bacteria, heavily studied experimentally [4], displays striking phenomena, qualitatively foreseen by our model.

References

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