

# Integral encounter theory of strong electron transfer

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(Received 30 November 2004; accepted 21 January 2005; published online 30 March 2005)

The integral encounter theory (IET) has been extended to the reactions limited by diffusion along the reaction coordinate to the level crossing points where either thermal or hot electron transfer occurs. IET describes the bimolecular ionization of the instantaneously excited electron donor  $D^*$  followed by the hot geminate backward transfer which precedes the ion pair equilibration and its subsequent thermal recombination. We demonstrate that the fraction of ion pairs which avoids the hot recombination is much smaller than their initial number when the electron tunneling is strong. © 2005 American Institute of Physics. [DOI: 10.1063/1.1871935]

## I. INTRODUCTION

The integral encounter theory is a new and universal method of chemical kinetics.<sup>1</sup> Using the integral kernels instead of the rate constants accounts for the memory effects in photochemistry and proved to be very useful in kinetic investigations of fluorescence, photoconductivity, chemiluminescence, and electrochemistry.<sup>2</sup> Up to the present the electron transfer rates used in integral encounter theory (IET) as an input data were borrowed from the perturbation theory which implies that the nonadiabatic tunneling is weak and the initial vibrational equilibrium distribution of the reactants is never violated. However, the latter is not in equilibrium from the very beginning if the system approaches the crossing point not from below but from above, moving down to the bottom of the well. This is a case when the system is prepared by forward electron transfer in the point  $q_1$  (Fig. 1) and moves down passing the point  $q_2$  where the hot backward transfer occurs.

The influence of nonequilibrium and especially coherent vibrational motion on electron transfer in donor-acceptor pairs at fixed interparticle distance has received considerable attention in theoretical studies.<sup>3–15</sup> Among them the perturbation theory was revised and the generalized golden rule was proposed.<sup>7,8</sup> Unfortunately, the tunneling in such theories remains weak and the yield of hot recombination is always small. The nonperturbative electronic coupling analysis limited by the case of weak interaction of the donor-acceptor pairs with the solvent was developed and the manifestation of the coherent underdamped motion on the reactant free energy surface in ultrafast electron transfer was investigated.<sup>9,11</sup>

The situation changes qualitatively if the same problem is considered within the stochastic approach assuming that the motion along the crossing levels is diffusional while the tunneling can be considerably stronger. This approach, proposed long ago,<sup>16,17</sup> was many times applied to the thermal

transfer starting from the equilibrium state. When the tunneling becomes strong and the perturbation theory inapplicable, it results in so-called solvent controlled limit. The transfer rate in this case is limited by diffusion along the reaction coordinate to the crossing point. The thermal charge separation (ionization) at  $q_1$  and thermal recombination at  $q_2$  can be both limited by the diffusion (from the bottom of the corresponding wells to the crossing points) when the short interparticle distance makes the tunneling strong. The hot electron transfer considered in the same way in Ref. 3 also becomes strong at short distances and under definite conditions (case  $E$  in Ref. 3) the yield of hot recombination products is much larger than in perturbation theory. Since the interparticle distances in solutions are different, the authors of Ref. 3 proposed to average over them assuming that particles are immobile. Their recipe is an appropriate one for only solid solutions. In liquids the diffusion in real space and along the reaction coordinate should be considered simultaneously. It was once done for forward thermal transfer using differential encounter theory.<sup>18</sup>

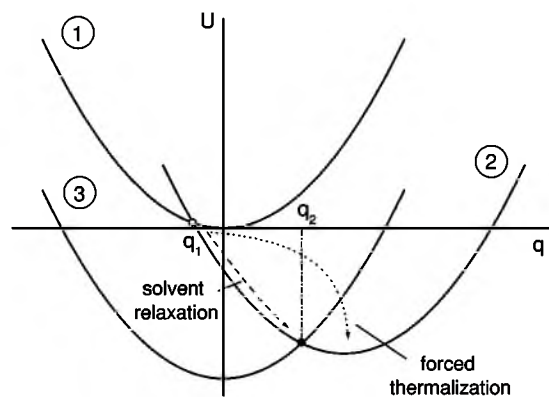


FIG. 1. The energy level scheme for the excited (1), charge separated (2), and the ground (3) states of the donor-acceptor pair at the contact distance.  $q_1$  and  $q_2$  are the crossing points for forward and backward transfer, respectively. The dashed arrow represents the solvent relaxation process and the dotted arrow represents the forced thermalization procedure used in numerical simulations (see Sec. VI).

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