A Dynamical Model for Ultrafast Catalytic Electron Transfer

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Energy (resp. charge) focusing can be achieved by nonlinear self-trapping resulting into the formation of a Discrete Breather (resp. a polaron). Targeted Energy (rep. Electron) Transfer (TET) may be subsequently involved for transportation of focused energy (resp. charge) by a coherent transfer of the Discrete Breather (resp. the polaron) from an initial selected site to another selected site imbedded in a complex system. This effect requires that the two involved sites are conjugate that is the nonlinear parameters concerning these two sites are finely tuned for TET (Note that TET is quite different from Davydov theory where energy transportation is achieved by mobile polarons which behave as solitons.). Because of its high selectivity, TET may be controlled by small perturbations allowing a logical control of energy (resp.charge) transportation. We believe that this effect is potentially highly interesting for understanding a wide variety of puzzling biochemical reactions but also perhaps for realizing artificial nanodevices. In many cases, much of the energy released by biochemical reactions (for example the hydrolysis of ATP) cannot be spread as heat in the thermal bath (as assumed in standard chemist models) but should be kept focused and transported for triggering selected subsequent reactions. In our talk, we shall first recall the basic principle of TET and next describe a particular application of the concept of TET for understanding Ultrafast Electron Transfer (UFET) which occurs at low temperature for example in the Photosynthetic Reaction Center (PRC) (which has been intensively experimentally studied during the last decades).

We start from a variation of the standard Marcus theory for Electron Transfer in chemistry but in addition to the standard reaction coordinates which correspond to atomic displacements, we also involve the complex amplitudes of the electron at relevant sites (Donor, Acceptor, Catalyst,etc..) as *independant dynamical* variables. In other words, we skip out the standard adiabatic approximation where the electronic state is slaved to the atomic variables (nevertheless, our improved model recovers the standard Marcus results when the adiabatic approximation is valid that is far from the inversion point when the energy barrier does not vanish. In that most common regime, the atomic thermal fluctuations are necessary for a thermally activated electron transfer.).

In the vicinity of the inversion point when there is no (adiabatic) energy barrier, the electron dynamics is necessarily highly nonadiabatic. We show that its effective quantum dynamics is described by a nonlinear Schroedinger equation (with an extra damping term and a thermal random force). It comes out that UFET at low temperature necessarily involves TET but next, it is shown that irreversibility cannot be obtained with only two sites Donor and Acceptor, but requires a third Catalytic site which mediates ET. We describe the obtained trimer model analytically and demonstrate its efficiency for UFET by numerical simulations.

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[1] S. Aubry, G. Kopidakis, A.M. Morgante and G.P. Tsironis, Physica **B296** (2001), 222–236

[2] S. Aubry and G. Kopidakis, Int. J. of Mod. Phys. B **17** 3908-3921 (2003);ibid. J. of Biol. Phys. **31** (2005) 375 - 402

[3] G. Hervé and S. Aubry, Physica **216D** (2006) 235-245