NON-ADIABATIC DYNAMICS SIMULATION OF DEFECT TRANSPORT

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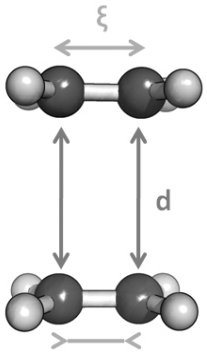
The dynamics of neutral and charged electronic defects is of highest interest. In biology it determines whether radiative and oxidative stress lead to damage which may alter the genetic code. In molecular electronics defect transport is a decisive factor with respect to conductivity. Due to the high complexity of the systems involved, defect dynamics offers considerable challenges to both theory and experiment. A further complication for modeling these processes is the coupling between electronic and nuclear degrees of freedom.

Non-adiabatic dynamics simulations [1], which have been very succesfully applied to photodynamic deactivation processes, also provide the necessary post Born-Oppenheimer corrections needed for an accurate description of defect transport processes. In particular surface hopping dynamics [2] provide a compact semi-classical description that suitably accounts for the reduced transfer probability in the weak coupling case.

Whereas the systems of interest are often of large spatial extent and environmental effects are important, a suitable smaller model system is favorable for examining the available computational methods and for understanding the physical effects. The ethylene dimer radical cation offers such a possibility. Diabatic energies are changed through double bond length alternation; the coupling is affected through the inter-monomer distance. It is observed that treating the two electronic states on an equal basis is necessary for getting even a qualitatively correct description and that dynamic electron correlation is not of high importance. In the case of weak coupling, non-adiabatic corrections are essential for describing the connection between the tunneling electron and the nuclear degrees of freedom. The dynamics results reflect the semi-classical description provided by Marcus theory.



[1] Worth, GA; Cederbaum, LS; *Annu. Rev. Phys. Chem.* 55 (2004) 127.
[2] Tully, JC; *Faraday Discussions* 110 (1998) 407.