# Coupled Electronic-Structural Dynamics with Local Decay-of-Mixing

Luis G. C. Rego
Department of Physics,
Universidade Federal de Santa Catarina, Florianópolis, SC, Brasil

Charge transfer (CT) and electronic excitation dynamics (EED) are ubiquitous in photochemistry. They constitute the underlying mechanisms for electron transfer reactions, light-harvesting in natural and artificial molecular structures, energy transduction phenomena, and many other processes. They are often influenced by the non-adiabatic coupling between electronic and nuclear degrees of freedom.

In this talk I describe a hybrid QM-MM self-consistent method that incorporates non-adiabatic electronic quantum dynamics into molecular mechanics, for simulations of large scale atomistic structures subject to complex structural deformations [1-3]. Simulations are carried out within the framework of the Ehrenfest method and the Coherent Switching with Decay-of-Mixing (CSDM) method, proposed by Truhlar and collaborators [4]. The CSDM method aims to introduce decoherence into the electronic non-adiabatic dynamics as a result of the nuclear motion. However, as proposed, the CSDM method applies decoherence globally to the excited quantum state, which is adequate for small molecular systems, but leads to nonphysical excessive nonphysical decoherences in the case of charge transfer. This is due to the fact that remove adiabatic states contribute equally to decoherence as local states. To solve this issue we propose a Local Decay-of-Mixing (LDM) that does not rely on ad-hoc relaxation constants. We present results for photo-induced charge transfer driven by vibrational relaxation for chromophores on extended solid interfaces.

[1] J. Phys. Chem. Lett., **9**, 5926 (2018)
[2] J. Phys. Chem. C, **123**, 5692 (2019)
[3] J. Phys. Chem. C, **123**, 23760 (2019)
[4] J. Chem. Theory Comput., **16**, 4098 (2020)