Including quantum nonadiabatic effects into molecular dynamics simulations

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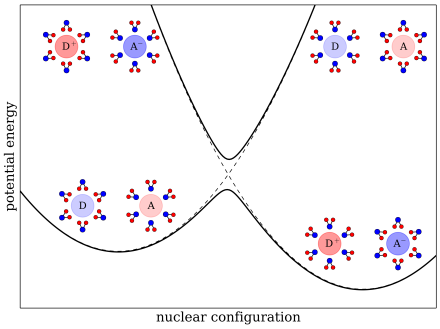

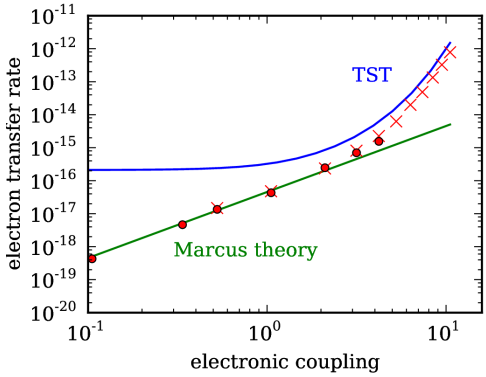

Nonadiabatic processes, such as those induced by photoabsorption or which describe electron transfer, are present in many areas of physical and biological science including chemical reactions, solar cells, vision, photosynthesis, DNA radiation damage and electronic spectroscopy. It is necessary to consider the excited electronic states in order to describe such processes correctly, and thus standard molecular dynamics techniques, which rely on the Born-Oppenheimer approximation, are not appropriate.

We have recently developed a nonadiabatic dynamics method [1], which like molecular dynamics simulations is based on trajectories and can therefore be applied to complex systems of interest. This new method employs a ring-polymer molecular dynamics (RPMD) [2] formulation of the nonadiabatic mapping approach [3] and is capable of describing the quantum effects of delocalization, zero-point energy and tunnelling as well as nonadiabaticity, without requiring the expensive propagation of nuclear wavefunctions.

We employ our nonadiabatic RPMD method to compute the rates of electron-transfer reactions and show how the important concept of the transition-state can be generalized to this type of reaction. This provides a simple extension to the commonly-used Marcus theory for systems with free-energy surfaces which cannot be described as harmonic oscillators [4].

The method also has the ability to simulate electronic spectroscopy in the condensed phase and describes the dynamics in a novel way with the ring polymer delocalized simultaneously over both the ground- and excited-states. As the method can in princple be efficiently combined with an on-the-fly calculation of the potential energy surfaces, it provides an excellent opportunity to interpret the absorption spectra of a wide variety of complex molecular systems.

[1] J. O. Richardson and M. Thoss, *J. Chem. Phys.*, **2013**, *139*, 031102.
[2] S. Habershon, D. E. Manolopoulos, T. E. Markland and T. F. Miller III, *Annu. Rev. Phys. Chem.*, **2013**, *64*, 387-413.
[3] G. Stock and M. Thoss, *Phys. Rev. Lett.*, **1997**, *78*, 578-581.
[4] J. O. Richardson M. Thoss, *J. Chem. Phys.*, **2014**, *141*, 074106.