New strategies for non-adiabatic dynamics with trajectories

I. Tavernelli[1]

[1]*IBM Research - Zurich, 8803 Rüschlikon, Säumerstrasse 4, Switzerland*

Initially restricted to a single adiabatic state, DFT-based molecular dynamics was recently extended to the non-adiabatic regime becoming an important tool for the study of photophysical and photochemical processes. Among the most commonly used trajectory-based non-adiabatic MD (NAMD) schemes are Ehrenfest dynamics and Tully's fewest switching surface hopping (FSSH). Despite their enormous impact in the quantum chemistry community, these methods suffer from many limitations e.g., the impossibility to describe wavepacket branching in Ehrenfest dynamics and the presence of over-coherence in FSSH. These failures are mainly associated to the approximate character of these approaches, which can hardly be improved due to the lack of a solid theoretical background.

To overcome these limitations, several alternative trajectory-based methods have been developed, which all share the common feature of being derived from a well defined mixed quantum-classical limit of the underlying exact time-dependent Schrödinger equation. Among others, there are multiple spawning [1], Bohmian dynamics [2], exact factorization [3] and the conditional wavefunction approaches.

In this talk, I will present some novel and promising trajectory-based NAMD schemes derived from different rigorous mixed quantum-classical limits of the exact coupled electrons-nuclei quantum dynamics [4]. In particular, I will describe the derivation and the implementation of two approaches based on the exact factorization theorem and Bohmian dynamics, respectively. Their advantages and disadvantages with respect to classical FSSH will also be discussed. These methods will then be applied (with suited approximations) to the study of the ultrafast electron and nuclear dynamics in several molecular systems in the gas and condensed phases.

[1] M. Ben-Nun, J. Quenneville , and T. J. Martínez, *J. Phys. Chem. A* **104**, 5161–5175 (2000).

[2] B.F.E. Curchod, I. Tavernelli, *J. Chem. Phys.* **138**, 184112 (2013); I. Tavernelli, *Phys. Rev. A*, **87**, 042501 (2013).

[3] A. Abedi, F. Agostini, E.K.U. Gross, *Europhysics Letters* **106**, 33001 (2014).

[4] S.K. Min, F. Agostini, I. Tavernelli, E. K. U. Gross, *J. Phys. Chem. Lett.*, *accepted.*