Coupled electron-nuclear dynamics in non-adiabatic process: The exact factorization approach

Federica Agostini¹, Ali Abedi², Seung Kyu Min³, Yasumitsu Suzuki⁴, Neepa T. Maitra⁵, E. K. U. Gross¹

¹) Max-Planck-Institute of Microstructure Physics, Halle - Germany
²) Centro Joxe Mari Korta, Nano-bio Spectroscopy Group, San Sebastian - Spain
³) Department of Chemistry, School of Natural Science, Ulsan National Institute of Science and Technology - Korea
⁴) Tokyo University of Science - Japan
⁵) Department of Physics and Astronomy, Hunter College of the City University of New York - USA

Corresponding author: Federica Agostini (agostini@mpi-halle.mpg.de)

The quantum-classical modelling of non-adiabatic processes in large molecular systems is among the major challenges in Theoretical Chemistry and Condensed Matter Physics. Beyond the Born-Oppenheimer (BO) approximation a molecule cannot be visualised as a set of nuclei moving on a single electronic potential energy surface (PES). The excited states dynamics has to be taken into account and coupled to a classical description of the nuclear motion. But how is such classical motion generated, if the problem does not allow to uniquely identify the force as the gradient of a PES? In fact several BO-PESs and their couplings have to be considered when dealing with non-adiabatic processes. This question is answered by introducing the exact factorization of the electron-nuclear wave function [1], which allows to define uniquely the time-dependent potential responsible for the nuclear dynamics coupled to the non-adiabatic electronic motion. The theory provides two exact coupled equations, one for the electrons and one for the nuclei. In order to transform this idea into a useful computational scheme, we investigate the properties of the potential, we analyse the quality of the classical approximation [2] and we develop a quantum-classical algorithm by treating classically the nuclear dynamics [3,4].

(Semi-)Classical dynamics on the time-dependent potential energy surface