

Excited-State Dynamics with the Exact Factorization: A Novel Approach to the Ultrafast Dynamics of Molecular Systems

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Excited-state dynamics in molecules: Light absorption in molecular systems triggers a highly nonequilibrium ultrafast dynamics, most of the time combined with the appearance of nonadiabatic effects attesting from the breakdown of the Born-Oppenheimer (BO) approximation. Studies in this field focus on achieving a comprehensive understanding of ultrafast photo-activated phenomena (Fig. 1) such as conformational changes of irradiated molecules [2], conversion of light energy into electric current [3] or chemical energy [4], and quantum decoherence [5], intimately related to the effect of electronic excited states on nuclear motion. To this end, theoretical works are mainly directed towards developing an adequate framework able to capture the highly non-trivial coupling of electronic and nuclear dynamics in nonadiabatic condition [6]. Motivation is indeed provided by the advances, for instance, in ultrafast spectroscopy techniques [2, 3], that have made possible the observation and control of dynamical processes at the molecular time and length scales, which are readily available by numerical simulations.

From theoretical and computational perspectives, the major bottleneck is the exponential scaling of the numerical cost with the number of degrees of freedom to solve the quantum-mechanical problem exactly. Therefore, approximations to quantum dynamics based on (semi)classical molecular dynamics are needed to study realistic molecular systems.

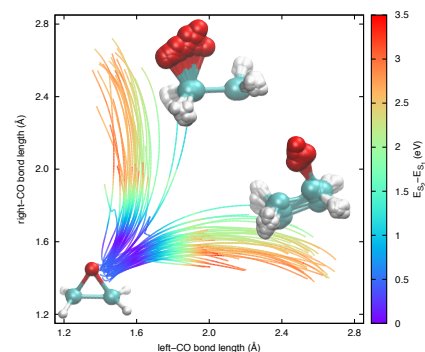


FIG. 1: Photoinduced ring-opening in oxirane: classical trajectories (colored curves) are represented in reduced (2D) configuration space, i.e., CO bonds length. Colors indicate the S_1/S_2 energy gap, which reduces to zero (violet) at the conical intersection. Figure from Ref. [1].

Objectives: Within this project we propose to investigate photo-activated processes based on a recently developed approach to excited-state dynamics, the exact factorization of the electron-nuclear wavefunction [7], where the full (molecular) wavefunction is rigorously expressed as a single product of an electronic and a nuclear contribution. The exact factorization represents a change of perspective in comparison to the conventional BO framework, usually adopted to rationalize excited-state phenomena: it has successfully been employed (i) to propose new tools [8, 9] for interpreting excited-state processes, (ii) to analyze conical-intersection [10], and related geometric-phase, effects on nuclear dynamics, (iii) to develop algorithms [1, 11] for quantum molecular dynamics simulations. The work mentioned here only represents preliminary and promising investigation routes, but an overall understanding of the capabilities (and limitations) of each research line is far from being exhaustively addressed. Therefore, we propose to further develop these points

- by applying the tools that the exact factorization puts at our disposal, for interpreting photo-activated processes affected by the presence of conical intersections. So far, only low-dimensional model systems [8, 10] have been investigated, thus systematic studies of more involved phenomena still remain unexplored territory;
- by developing/improving the quantum-classical algorithm [1, 11] derived from the exact factorization, by refining the underlying approximations, for instance toward a more accurate description of nuclear dynamics beyond purely classical trajectories, and by proposing new challenging applications.

We aim at answering questions such as

How do the geometric-phase effect on the ground-state dissociation process of CH_2OH [12] translate into the exact-factorization perspective?

How can the photo-dissociation of phenol [13] be analyzed [14, 15] based on the tools that the exact factorization puts at our disposal?

Can an algorithm for excited-state dynamics be designed, to capture, in general, the most elusive phenomena that are signature of excited-state processes, such as quantum decoherence or interferences?

Research team: The PhD position will be available from October 1st, 2018 for a duration of three years at the Laboratoire de Chimie Physique (LCP) of the University Paris-Sud (Orsay, south of Paris, France), in the group ThéoSim (Theory and Simulations, <http://www.lcp.u-psud.fr/spip.php?rubrique158&lang=fr>). The work will be supervised by Dr. Federica Agostini, in collaboration with Dr. David Lauvergnat, experts in quantum molecular dynamics simulations, quantum chemistry, exact factorization, and quantum-classical approaches for excited-state dynamics. A list of publications in their research domains is provided below.

Profile of the candidate: The objectives presented above require both theoretical and numerical developments. We expect the candidate to have a Master degree in Theoretical/Chemical Physics, or Theoretical/Quantum Chemistry, a solid background in quantum mechanics and/or theoretical chemistry, as well as knowledge of programming languages (Fortran, C, Python, ...). Knowledge of English is required, knowledge of French will be considered a plus. The project places itself in an ongoing collaboration with Prof. B. F. E. Curchod (Durham University, UK) and Dr. I. Tavernelli (IBM Research Laboratory, Zurich, Switzerland), therefore we are looking for candidates willing to work in a dynamic and international environment.

Interested applicants shall submit CV and at least one recommendation letter at the email address indicated below by **March 31st, 2018**.

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