
Dynamics of electrons and nuclei in molecules: Beyond the Born-Oppenheimer approximation

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Résumé

Excited-state dynamics is at the heart of Photophysics and Photochemistry. Nonadiabatic transitions are induced by the strong coupling between electronic dynamics and the ultrafast motion of the nuclei, and are observed in phenomena such as photosynthesis, photovoltaics, and exciton transport in pi-conjugated complexes. An essential part of the research efforts in these fields is directed towards developing theoretical and computational approaches to describe conformational changes, energy dissipation, or quantum decoherence, i.e., the signature aspects of excited-state processes. In this context, among the most successful frameworks for molecular dynamics simulations of excited-state processes stand trajectory-based quantum-classical methods, as they give access to the study of complex molecular systems. Trajectory-based approaches combine a classical description of nuclear dynamics with a quantum-mechanical description of electronic dynamics. However, the approximations underlying quantum-classical methods are sometimes severe, and are at the origin of controversies as well as of continuous developments.

In this talk I will introduce the problem in general, and I will present a recently-developed trajectory-based approach to nonadiabatic dynamics [1,2]. The actual numerical scheme has been derived from the exact factorization of the electron-nuclear wavefunction [3], a new framework proposed to investigate, interpret and approximate the coupled dynamics of electrons and nuclei beyond the Born-Oppenheimer approximation. The exact factorization provides a new perspective to analyze nonadiabatic processes: (i) it proposes an alternative [4] to the standard Born-Oppenheimer framework, that pictures excited-state processes in terms of wavepackets moving on and transferring between static potential energy surfaces; (ii) it suggests new interpretations [5] of molecular geometric-phase effects, related to conical intersections; (iii) it provides guidelines for developing simulation algorithms in different [6] nonadiabatic regimes.

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