

Mathematical questions of quantum dynamics

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10:30 – Federica Agostini

Title: Excited-state dynamics with trajectories

Abstract: 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.

In this talk I will present a recently-developed trajectory-based approach to nonadiabatic dynamics. The actual numerical scheme has been derived from the exact factorization of the electron-nuclear wavefunction, 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 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 of molecular geometric-phase effects, related to conical intersections; (iii) it provides guidelines for developing simulation algorithms in different nonadiabatic regimes. These points will be discussed during the talk and illustrated on low-dimensional models and molecular systems.