Intitulé du Sujet de Thèse : Coherences and Decoherences in Excited-State Dynamics of Realistic Molecular Systems [CohDec]

Laboratoire : Institut de Chimie Radicalaire

Equipe : Chimie théorique

Directeur de thèse : Mario BARBATTI

Encadrant (éventuellement) : -

Co-encadrant (éventuellement) : -

email : mario.barbatti@univ-amu.fr | www.barbatti.org

Contexte de l'étude

Excited-state dynamics simulations have become the leading methodology to describe light-induced processes in molecular and supramolecular systems. These simulations are often based on mixed-quantum-classical approximations that aim to reduce the harsh computational costs when dealing with realistic molecules.[1] The currently most employed method is surface hopping, which propagates a swarm of independent classical trajectories that can switch states during the run, following a stochastic algorithm called fewest switches surface hopping. Our group in Marseille specializes in this type of simulation. It is responsible for developing Newton-X (www.newtonx.org), one of the most used software in the field.[2]

Although surface hopping has been successfully applied to many physical-chemical problems, it holds many conceptual challenges. It cannot be derived from first principles, suffers from over-coherence issues due to the independent-trajectory approximation, and has an unbalanced treatment of electronic and nuclear systems. As a result, it has been difficult to apply such a method to situations where quantum coherences play a significant role, such as in exciton transport.

The CohDec project aims to develop the underlying theory, propose new methodologies, and implement algorithms to overcome these obstacles.

Descriptif du projet

Although decoherence has been exhaustively investigated,[3] it has often been dealt with in large dimensionality systems employing continuum spectral densities. CohDec will return to the fundamentals of quantum mechanics to clarify the status of electronic coherence and decoherence in low-dimensionality systems like molecules.

Independent-trajectory approaches such as surface hopping already count with decoherence correction methods. However, these methods are not well anchored on the quantum mechanical fundamentals and fail under situations where re-coherences are relevant. CohDec will propose new decoherence dynamics models for use in independent-trajectories excited-state dynamics.

Part of the problems with surface hopping arises from a simultaneous time propagation of entangled electrons and classical nuclei. Such a situation occurs in regions of nonadiabatic interactions, creating inconsistent electronic-nuclear dynamics. CohDec will fix this problem by moving from standard surface hopping to decoherence-corrected mean-field propagation.

CohDec will make all these new developments available to the entire theoretical-chemistry community by implementing them in the Newton-X software platform.

Références Bibliographiques

[1] Crespo-Otero; Barbatti. *Chem Rev* **2018,** *118*, 7026. DOI: 10.1021/acs.chemrev.7b00577
[2] Barbatti *et al. J Chem Theory Comput* **2022,** *18*, 6851. DOI: 10.1021/acs.jctc.2c00804
[3] Shu; Truhlar. *J Chem Theory Comput* **2023,** *19*, 380. DOI: 10.1021/acs.jctc.2c00988