

Towards a realistic prediction of the dynamics of complex quantum systems and their spectroscopic signatures

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Modern advances in ultrafast spectroscopy, with wavelengths spanning the infrared to the X-ray regime, enable the investigation of chemical dynamics with unprecedented spatial and temporal resolution. This progress requires equally advanced theoretical tools, not only to interpret existing measurements but also to predict new experiments. The challenge lies in combining different areas of theoretical chemistry and physics, including quantum chemistry, molecular dynamics, and the theory of light–matter interaction [1].

This talk provides an overview of the computational methodologies we are developing to investigate a range of dynamical phenomena in chemical systems, from small gas-phase molecules to complex biological photosystems.

I will begin by illustrating the use of advanced electronic structure calculations to analyse time-resolved X-ray photoelectron spectroscopy measurements of UV-excited gas-phase 2-thiouracil performed at the FLASH2 beamline at DESY. The simulations enabled the identification of the spectroscopic signature of the intersystem crossing between a singlet $\pi\pi^*$ state and a triplet $n\pi^*$ state, as well as the determination of the timescale of this process [2].

Next, I will discuss the simulation of a symmetry-breaking charge-transfer process in a quadrupolar dye using multimode, multistate quantum wave-packet dynamics implemented in our in-house codes. The fully first-principles quantum mechanical simulations allow the prediction of transient absorption spectra and reveal the molecular vibrational modes driving charge separation, together with the role of solvent relaxation [3].

The second part of the talk focuses on novel approaches currently under development to model decoherence in condensed-phase molecular systems arising from dissipation into the surrounding environment. Decoherence marks the

transition from a quantum coherent regime, where well-defined phase relationships exist between different wave-packet components, to incoherent, classical-like dynamics. To describe this process while retaining a quantum mechanical treatment of many vibrational degrees of freedom, we introduce a framework in which the open quantum system is represented as a statistical mixture of high-dimensional, time-dependent wave packets governed by coupled Schrödinger equations [4], while the environment is described by a multicomponent quantum master equation [5].

The methodology is validated on a surface-science problem involving the vibrational relaxation of D–Si bending modes on a deuterium-covered silicon surface. The resulting approach quantitatively predicts vibrational relaxation rates at a modest computational cost [5].

Finally, I will present its application to exciton transport in the Fenna–Matthews–Olson pigment–protein complex, demonstrating the possibility of quantitatively simulating exciton dynamics in complex systems while explicitly accounting for environmental fluctuations.

The talk concludes with a brief outlook on future methodological developments and prospective applications.

[1] S. Faraji, D. Picconi & E. Palacino-Gonzalez, WIREs Comput. Mol. Sci. e1731 (2024)

[2] D. Mayer, F. Lever, D. Picconi, ..., M. Gühr, Nat. Commun. 13, 198 (2022)

[3] D. Picconi, J. Chem. Phys. 156, 184105 (2022)

[4] D. Picconi & I. Burghardt, J. Chem. Phys. 150, 224106 (2019)

[5] D. Picconi, J. Chem. Phys. 161, 164108 (2024)