

# Nonadiabatic Decay of Photoexcited Nucleobases in Water Studied by Mixed Quantum/Classical Dynamical Approaches.

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Quantum nuclear effects can play a major role in determining the fate of the photoexcited dynamics in molecular systems. Recent advancements in quantum-dynamical (QD) approaches, like those provided by multilayer extension [1, 2] of the MCTDH method [3], allow an efficient description of such effects, even in large systems, if they are rigid (harmonic) and in gas phase. Systems embedded in solvents, or in heterogeneous media, possibly establishing with them specific interactions, represent a challenge for QD treatments. In most of the cases, the effects of the environment are represented through the interaction with a spectral density. On the other side, the inclusion of these effects in semiclassical trajectory-based approaches is much more straightforward. However, one has to pay the cost to neglect quantum effects in the motion of the nuclei.

In this contribution, we present a recently proposed Mixed Quantum Classical (MQC) approach to introduce environmental dynamical effects in QD simulations [4]. The solute degrees of freedom are represented by a wavepacket moving according to nonadiabatic quantum dynamics, while the motion of an explicit solvent model is described by a classical trajectory. The core idea is to describe the mutual coupling of the solute and solvent dynamics within a mean-field framework, solving the quantum and classical equations of motions simultaneously. The computations are performed interfacing Quantics [6] (ML-MCTDH propagations), with Gromacs [7] (classical MD), and Gaussian (electronic computations) [8]. The method is currently suitable for systems with coupled potential surfaces (and couplings) amenable of a description in terms of a quadratic local expansion (linear vibronic, quadratic vibronic models) [4]. Although necessarily approximate, it is attractive because it merges a full QD description of the solute decay with an explicit description of the motion of a molecular model of the solvent. It is therefore possible to exploit all the standard MD analysis tools for investigating the solvent effect on the solute dynamics. With this method we studied the quantum dynamics of the  $\pi\pi^*$  internal conversion of thymine and other nucleobases in explicit water models. These decay processes are involved in DNA photo-damage and its prevention [5]. In this way, we were able to evidence a correlation between the time evolution of the radial distribution functions of solute/water H-bonds and the rate and quantum yield of internal conversions [4].

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