

Vibronic effects on electronic spectra and nonadiabatic photophysics. A quantum/classical dynamical approach.

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Quantum vibronic effects have a remarkable impact on the lineshape of electronic spectra.¹ They can also play an important role in the dynamics of photophysical processes like internal conversions at Conical Intersections or charge and energy transfer in multichromophoric systems.

Recent advancements allow a fair description of such effects in rigid (harmonic) molecules in gas phase.¹⁻⁴ However, in biology and in material science the photoexcited chromophores are usually embedded in a solvent, possibly establishing with them specific interactions, or even in more complex and heterogeneous environments. Moreover, many systems with interesting optical properties are flexible, i.e. the optical transition triggers large-amplitude curvilinear distortions, and this challenges the applicability of harmonic approximation. Trajectory based approaches are very suitable to deal with these scenarios but they neglect quantum nuclear effects.

We are currently working with the hope to devise robust hybrid quantum/classical (QC) approaches to merge the potentialities of trajectory based methods and those of the quantum vibronic methods developed for rigid systems in gas phase or implicit solvents.^{1,5-6} The system is partitioned in two subsystems: a quantum core (the chromophore or just its high-frequency modes) and an environment (which can include also large amplitude motions of the system itself and is treated at a more approximate classical level) and the challenge is the reliable description of their mutual couplings. We will illustrate our recent results with a number of examples ranging from the chiro-optical properties of flexible conjugated systems (e.g. oligothiophenes) to the nonadiabatic decay of photoexcited DNA nucleobases⁷ in aqueous solution.⁸⁻¹²

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