Vibronic effects in the photophysics of complex systems. Mixed quantum classical schemes in combination with adiabatic and nonadiabatic approaches

Fabrizio Santoro
Istituto dei Composti OrganoMetallici, Consiglio Nazionale delle Ricerche, Pisa, Italy.

The shape of molecular electronic spectra, as well as the dynamics of photophysical processes like internal conversions, or charge and energy transfers in multichromophoric systems are all affected by the quantum nature of molecular vibrations. In spectroscopy, it explains vibronic resolution and contributes to spectral shape and width, whereas in dynamics it lies at the heart of the same idea of nonadiabatic transitions and rules features like coherences.

Recent advances have made full quantum (vibronic) calculations rather standard for stiff (harmonic) molecules in gas-phase for both adiabatic and non-adiabatic systems. The current challenge in this research field is the development of suitable non-phenomenological methods to compute the spectra and to study the photoexcited dynamics of flexible molecules interacting with an environment, preserving as much as possible a description of the relevant quantum nuclear effects.

In this talk we will discuss what we have been doing in the last years along this research line, exploiting the general idea of mixed quantum-classical approaches for the nuclear motion.

For adiabatic systems we recently proposed a method that we call Adiabatic Molecular Dynamics-generalized Vertical Hessian (Ad-MD|gVH), to compute electronic spectra of flexible dyes in solution [1]. It is based on a partition of the solute+environment nuclear degrees of freedom in stiff (quantum) and soft (classical) modes and an adiabatic hypothesis in which stiff modes instantaneously rearrange to movements along soft modes. The partition is enforced through iterative projectors in curvilinear coordinates which separate soft and stiff modes. The approach couples Molecular Dynamics techniques (driven by quantum-mechanically derived force fields) to accurately sample the molecular flexibility of the solute and the effect of solvent fluctuations, and quantum vibronic calculations for stiff modes. The latter are performed within the harmonic vertical Hessian (VH) model, through the analytical computation of the necessary time-correlations functions. The spectrum arises as the configurational average of individual quantum spectra obtained for reduced-dimensionality models along the stiff modes, which are specific for each configuration of the soft modes.

We are currently working to generalize this approach to non-adiabatic systems, essentially replacing the adiabatic VH model with the Linear Vibronic Coupling (LVC) model and replacing the computation of analytical correlation functions with effective numerical wavepacket propagations with the MCTDH method. To that end we worked out effective schemes to parametrize LVC Hamiltonians [2]. Moreover, combining the LVC model with a fragment-based diabatization [3], we are now also ready to study the spectra of exciton-coupled dimers, including also the effect of possible charge transfers and of the solvent.   This same approach allows also automatically to study the effect of the static disorder of the soft modes on the photoexcited dynamics of wavepackets describing the quantum modes. We will show our preliminary results for the spectroscopy and energy/charge transfer dynamics of the dimer of perylene diimides.

The most challenging step toward the development of a complete mixed quantum classical approach for photoexcited dynamics remains how to account for cases in which the motion of soft and stiff modes take place on the same timescale and are coupled. We will briefly present our first attempt based on a mean-field coupling scheme and its application to the study of the effect of a water solution on the pipi*/npi* decay of Thymine in water [4].

References
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