

Diabatic Strategies for Molecular and Macromolecular Photodynamics

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Quantum dynamics simulations applied to ultrafast photoinduced processes often require an adiabatic-to-diabatic transformation (diabatization) of the data produced from quantum chemistry calculations. The vibronic coupling Hamiltonian (VCH) quasidiabatic model developed by Köppel and coworkers is a fruitful strategy that has been used for calculating photoabsorption and photoelectron spectra with the multiconfiguration time-dependent Hartree (MCTDH) method. We present here an example of strategy whereby a generalised VCH approach was applied to the description of the excited-state intramolecular proton-transfer (ESIPT) process in 3-hydroxychromone simulated with the multilayer formulation of MCTDH termed ML-MCTDH.^[1]

Alternatively, the direct dynamics variational multiconfiguration Gaussian (DD-vMCG) wavepacket method frees simulations from this preliminary step by calculating the potential energy and its derivatives on the fly. Various diabatization procedures for generating quasidiabatic Hamiltonians on-the-fly have been implemented in the current code and are being tested at the moment. This is illustrated with simulations of internal conversion in fulvene.^[2,3]

Finally, we will expose some recent methodological developments aimed at describing excitation-energy transfer within conjugated macromolecules such as the building blocks of poly(phenylene ethynylene) dendrimers.^[4]

References:

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