

Diabatic Strategies for Photochemical Quantum Dynamics

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Quantum dynamics simulations applied to ultrafast photoinduced processes often require an adiabatic-to-diabatic transformation (diabatisation) 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) quantum dynamics approach. We present here a set of strategies to generalise the VCH model to the treatment of photochemical reactions whereby large-amplitude nuclear motions occur along complicated reaction pathways connecting several potential energy wells through transition barriers.

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. The quasidiabatic Hamiltonian is currently generated from a regularisation method, and work is in progress to implement a local diabatisation procedure.