

Conical intersections and nonadiabatic dynamics

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Conical intersections, where two potential-energy surfaces cross to each other, play one of central roles in photochemistry. At intersections, strong interstate couplings can induce the transitions from one state to the other, namely “nonadiabatic transitions”, which can quench fluoresces, lead to internal conversions, and open new reaction channels.

The theoretical investigation of conical intersections involve the characterization of intersections, the construction of relevant reaction paths and the calculation of nonadiabatic dynamics. To investigate the real-time nonadiabatic dynamics of interesting systems with full dimensionality, on-the-fly surface-hopping methods have been implemented in our QM and QM/MM codes (MNDO and ChemShell, respectively). This allows us to study nonadiabatic dynamics in gas and condensed phases with different QM (OM2, CASSCF, ...) and different QM/MM (OM2/CHARMM, ...) Hamiltonian, respectively. Particularly, the semiempirical OM2 Hamiltonian [1] with GUGA-CI approach [2] provides reasonably accurate excitation energies and excited-state geometries, both for minima and conical intersections [3]. Therefore, the employment of OM2/MRCI surface-hopping simulations are efficient and practical since they allow the computation of a large number of the trajectories.

For gas-phase problems, the nonadiabatic dynamics of for several test molecules (ethylene, methaniminium ion, methanimine, retinal) [4] and nucleobases [5-7]. have been investigated at the OM2/MRCI CASSCF level. For condensed-phase problems, the nonadiabatic dynamics of nucleobases in aqueous solution have been investigated at the QM/MM level. The surface-hopping simulations provide insight into the role of different conical intersections during the nonadiabatic dynamics of these interesting molecules in the gas phase and in aqueous solution.

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