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Surface-hopping excited-state dynamics

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Semiempirical quantum-chemical methods are well-established tools for computational studies of large molecules [1]. Methods with explicit orthogonalization corrections (OM1, OM2, OM3) offer better overall accuracy in standard statistical evaluations of ground-state properties as well as qualitative improvements for hydrogen bonding and conformational properties [2,3]. OMx-based studies of electronically excited states employ a general implementation of the GUGACI approach in a semiempirical framework which provides analytic gradients and nonadiabatic couplings. Comparisons with high-level ab initio benchmark data show that OMx/MRCI methods describe electronically excited states reasonably well [4]. They can thus be used in mixed quantum-classical dynamics to investigate fast nonradiative relaxation processes after photoexcitation. Numerous such surface-hopping dynamics studies have been carried out at the OM2/MRCI level in recent years [1], for example simulations on DNA bases in different environments, azobenzenes, molecular motors [5] and switches, GFP chromophores [6], and Schiff bases, covering both photophysical and photochemical processes.

The lecture will address the theoretical background of the OMx/MRCI surface-hopping methodology and present selected OM2/MRCI applications. Time permitting, it will also cover a nonadiabatic excited-state dynamics study on the bithiophene dimer using time-dependent density functional theory (TDDFT) to describe time-dependent excitonic effects in molecular aggregates [7,8]. The lowest excited states are found to be localized and unproductive in terms of charge separation. Productive high-energy charge-transfer (CT) states are populated within 50 fs during exciton deactivation, but they are short-lived (∼100 fs) and quickly transfer their population to lower states. The TDDFT simulations offer molecular-level insights into ultrafast photoinduced charge separation potentially triggered by hot CT states in solid-state organic materials. They allow us to suggest design rules to increase hot exciton lifetimes, favoring the population of CT states as gateways for direct charge generation.

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