Semiclassical methods for photodynamics simulations

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This talk will be concerned with semiclassical simulations of photochemical dynamics using the coherent switches with decay of mixing method and energy-based decoherence. When semiclassical electronically nonadiabatic dynamics is carried out in the electronically adiabatic representation, the coupling of electronic states is due to the nonadiabatic coupling vectors (NACs), which are the off-diagonal electronic matrix elements of the nuclear momentum operator. When the system has N atoms, these are $3N$- dimensional vectors that become singular on $(3N - 8)$-dimensional conical intersection seams. Their treatment is cumbersome because of these singularities and because of the phases of the NACs, and NACs are not readily available for all electronic structure methods. Furthermore, NACs are origin-dependent, they do not account for momentum of electrons moving with nuclei, they lead to spurious long-range coupling, and they do not conserve the momentum of the center of mass or the nuclear angular momentum. We have developed curvature-driven approximations to the NACs that allow semiclassical nonadiabatic dynamics calculations –including decoherence – with only the adiabatic potential energy surfaces and their gradients. We have employed these algorithms successfully for several applications using both trajectory surface hopping and the more accurate coherent switching with decay of mixing method. This talk will review the methods and recent applications.

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