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"Semiclassical Modelling of the Non-Adiabatic Photodynamics of Molecular Systems in Gas and Condensed Phases"

Femtosecond-laser pulse driven non-adiabatic spectroscopy and dynamics in molecular and condensed phase systems continues to be a challenge for theoretical modelling. One of the main obstacles is the "curse of dimensionality" encountered in non-adiabatic, exact wavepacket propagation. A possible route towards treating complex molecular systems is via semiclassical surface-hopping schemes, in particular if they account not only for non-adiabatic post-excitation dynamics but also for the initial optical excitation. As a simple test case which can be compared with exact wavepacket dynamics, we investigate the influence of the different parameters determining the shape of a laser pulse (e.g., its finite width and a possible chirp) on the predissociation dynamics of a NaI molecule, upon photoexcitation of the A(0+) state. The finite-pulse effects are mapped into the initial conditions for semiclassical surface-hopping simulations. The branching ratios between the bound and the dissociative reaction channels and the time-evolution of the molecular wavepacket predicted by the semiclassical method agree with those computed using quantum wavepacket propagation.

Applications of semiclassical schemes to more challenging molecular systems, namely the photoisomerization dynamics using model and realistic Hamiltonians, and the photoinduced reorganization of lithium-doped rare gas matrices, are presented. The models enable the microscopic description of the isomerization yields and non-radiative excited-state lifetimes, as well as the time evolution of the configurational rearrangement and the internal energy redistribution. On the other hand, the absorption band of lithium-doped rare gas matrices exhibit a three-fold structure, as a consequence of dynamic Jahn-Teller effect, the splitting being in close correspondence with available experimental results for this system. Lattice reorganization is found to be sensitive to the shallow long-range tail of the interatomic potentials, pointing to the feasibility to employ many-body response of doped matrices upon photoexcitation as a tool to study the topology of the excited electronic states of alkali-rare gas systems.