

SIMULATING FRANCK-CONDON SPECTRA WITH IMAGINARY-FREQUENCY VIBRATIONS

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Vibronic spectra simulated under the harmonic Franck-Condon approximation are an ubiquitous tool for interpreting the structure of optical, photoelectron, and photoionization spectra. For transitions to bound final states located in a well on their potential energy surface, it is straightforward to calculate overlap integrals between discrete vibrational eigenstates, but this approach breaks down when the surface has locally negative curvature, such as near transition states. Time-dependent methods based on the vibrational autocorrelation function alleviate many of these difficulties, but suffer from certain analytical and technical deficiencies, including branch-cut discontinuities (associated with bound, periodic vibrations) and unstable finite-precision arithmetic (associated with unbound, imaginary-frequency modes). In this talk, we present a new derivation of the multidimensional, harmonic autocorrelation function that resolves these issues. An application is illustrated with the cyclopropyl radical, $c\text{-C}_3\text{H}_5$, which undergoes prompt ring-opening to allyl upon photoionization. We will also discuss progress towards perturbative anharmonic corrections within the time-dependent approach.