Franck-Condon spectra of vibrationally unbound molecules

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The vibronic features of optical, photoelectron, and photoionization spectra encode a wealth of information about the structure and dynamics of radicals, ions, and electronically excited molecules. In systems where the vertical excitation geometry lies far from an equilibrium well or near a transition state, the potential energy surface has "unbound" vibrational modes of local negative curvature, which renders eigenstate-based Franck-Condon methods inapplicable. In this talk, I will present a time-dependent approach to the harmonic problem using Lie-algebraic tools that resolves two important technical issues associated with bound and unbound modes, respectively: branch-cut discontinuities in the correlation function and stable finite-precision arithmetic. I will conclude by outlining progress towards an anharmonic time-dependent perturbation theory based on these results.