

# **Perturbation theory for vibronic structure and dynamics: non-adiabatic and vibrationally unbound molecules**

Bryan Changala

Center for Astrophysics | Harvard & Smithsonian

This poster summarizes recent work on perturbative methods for two general vibronic problems: non-adiabatic Jahn-Teller (and pseudo-Jahn-Teller) molecules, and systems with vertical excitation geometries in regions of negative vibrational curvature, e.g. transition state spectroscopy.

(i) For the Jahn-Teller problem, we have implemented a generalized vibronic mean-field theory to describe the zeroth-order structure of molecules exhibiting strong non-adiabatic coupling. By accounting for the essential electronic-vibrational correlation at the zeroth-order level, a qualitatively accurate picture is obtained for both weak and strong coupling regimes. The remaining vibronic interactions can be accounted for with simple second-order perturbation theory, resulting in highly accurate vibronic energy levels. Certain phenomena not usually encountered in the pure vibrational problem include artificial symmetry breaking, which is characterized as a pseudo-phase transition using a finite-temperature variant of the theory.

(ii) Franck-Condon simulations are an ubiquitous tool for interpreting the vibronic spectra of ion, radicals, and excited electronic states. When the vertical excitation geometry lies far from an equilibrium well or near a transition state, the local potential energy surface has negative curvature, making eigenstate-based Franck-Condon methods inapplicable. We have developed a time-dependent correlation function approach that resolves two key technical issues that appear in the harmonic problem: branch-cut discontinuities associated with bound (real frequency) modes and exponentially unstable arithmetic associated with unbound (imaginary frequency) modes. This zeroth-order result forms the foundation for a time-dependent perturbation theory of anharmonic Franck-Condon simulations for both bound and unbound systems.