Non-Born-Oppenheimer Electronic-Vibrational Structure Applied to Vibronic Spectra Prediction

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The Born-Oppenheimer (BO) potential energy surface has been a central quantity in the understanding of chemical dynamics for over 80 years, allowing the adiabatic separation of electronic and nuclear degrees of freedom. The breakdown of the BO approximation occurs in many chemically important circumstances, with many current difficulties arising from the coupling of many nuclear degrees of freedom within a potential energy surface.

By employing harmonic approximations to vibrational degrees of freedom and linear electronic-vibrational couplings, we treat electronic and vibrational degrees of freedom quantum mechanically and simultaneously.

We apply these approximations to both model and chemical Hamiltonians to efficiently predict gas phase vibronic spectra and condensed phase optical spectra using time-dependent mean-field theory.