

AB INITIO EFFECTIVE ROVIBRATIONAL HAMILTONIANS FOR NON-RIGID MOLECULES VIA CURVILINEAR VMP2

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Accurate predictions of spectroscopic constants for non-rigid molecules are particularly challenging for *ab initio* theory. For all but the smallest systems, “brute force” diagonalization of the full rovibrational Hamiltonian is computationally prohibitive, leaving us at the mercy of perturbative approaches. However, standard perturbative techniques, such as second order vibrational perturbation theory (VPT2), are based on the approximation that a molecule makes small amplitude vibrations about a well defined equilibrium structure. Such assumptions are physically inappropriate for non-rigid systems. In this talk, we will describe extensions to curvilinear vibrational Møller-Plesset perturbation theory (VMP2) that account for rotational and rovibrational effects in the molecular Hamiltonian. Through several examples, we will show that this approach provides predictions to nearly microwave accuracy of molecular constants including rotational and centrifugal distortion parameters, Coriolis coupling constants, and anharmonic vibrational and tunneling frequencies.