

A FLEXIBLE APPROACH TO VIBRATIONAL PERTURBATION THEORY

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Vibrational perturbation theory is a commonly-used method for obtaining anharmonic corrections to harmonic zero-order wave functions and energies. Traditional approaches use analytic expressions for second order corrections derived from the Watson Hamiltonian expressed in normal modes constructed from displacements of Cartesian coordinates. Given that in the absence of resonances internal and Cartesian coordinates provide identical corrections to the energies and other properties, Cartesian coordinates provide a convenient choice. However, when the Hamiltonian is expressed in Cartesian coordinates, the corrections to the energies result from large cancellations of positive and negative contributions from cubic and quartic terms in the expansion of the Hamiltonian. In internal coordinates the amount of cancellation is significantly smaller.

We present a recently-developed implementation of perturbation theory that allows for flexibility in coordinate choice, order of correction, and handling of degeneracies.¹ This approach is straightforward and provides a route to obtain insights into the origins of spectral intensities among other applications. We apply this method to a fully *ab initio* potential energy surfaces for several polyatomic molecules as well as model systems.

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