Analytic calculations of anharmonic effects in vibrational spectra

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Anharmonic effects are small, but can make important contributions to a wide range of vibrational spectroscopies. With the advent of nonlinear vibrational spectroscopies, these anharmonic effects can be directly probed [1,2].

Computationally, the calculation of anharmonic corrections to vibrational spectra and nonlinear vibrational spectroscopies is complicated due to the need for calculating higher-order energy derivatives with respect to geometrical perturbations. Calculations of anharmonic effects are almost exclusively done in a mixed analytical-numerical scheme [3,4], although an analytic implementation including up to quartic force constants was presented at the Hartree–Fock level of theory by Handy and coworkers twenty years ago [5].

In this talk, I will present our recent efforts in obtaining an analytic approach for calculating the necessary energy derivatives analytically, both at relativistic and non-relativistic levels of theory [6]. In addition to a brief presentation of the theoretical framework, I will present sample calculations of anharmonic effects in various linear and nonlinear vibrational spectroscopies.

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