

Quartic Force Fields for All of the Spectroscopic Ranges

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Abstract

Quartic force fields (QFFs) are sparse potential energy surfaces applied to computing anharmonic vibrational frequencies and rotational constants. Our group has worked to make QFF construction less computationally expensive without sacrificing accuracy and has extended application of QFFs into UV-visible spectroscopy, as well.

The most accurate QFFs today rely upon coupled cluster singles, doubles, and perturbative triples [CCSD(T)] computations involving complete basis set (CBS) extrapolations, core electron correlation, scalar relativity treatment, and, often, higher-order electron correlation. While composite schema like the CcCR QFF can reduce this total cost, the molecules studied with such approaches are still of six atoms or less. Explicitly correlated CCSD(T)-F12b QFFs have been able to stretch into larger molecules. While CCSD(T)-F12b/cc-pVTZ-F12 QFFs retain CcCR-level accuracy for anharmonic frequencies, the rotational constants often suffer. However, CCSD(T)-F12b/cc-pCVTZ-F12 computations including explicit core electron correlation coupled to a scalar relativity correction (the so-called F12-cCR-TZ QFF) are equally accurate for computing anharmonic frequencies, are *more* accurate for rotational constants, and cost less than 5% of the computational time as CcCR QFFs.

Additionally, our group has developed a new methodology for computing QFFs of electronically excited states. Since CCSD(T) generates a perturbative energy, a true wave function is not created at this same level precluding construction of a standardized, non-iterative, approximate triples methods for coupled cluster excited state theory. This work has shown that an approximate, triples-including, excited state approach can be applied to QFFs by taking the (T) energy along with the EOM-CCSD energy and adding this to the ground state CCSD energy. This (T)+EOM QFF is shown to produce vibrational frequencies to within 1.6 cm^{-1} in some cases of established benchmarks for variationally-accessible electronic states.