Harmonic and anharmonic vibrational frequency calculations with the double-hybrid B2PLYP method: analytic second derivatives and benchmark studies.

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Streszczenie

This work aims to provide reliable benchmark data on the accuracy of harmonic and anharmonic vibrational frequencies computed with the B2PLYP double-hybrid density functional method. The exchange-correlation contributions required for the B2PLYP analytical second derivatives are presented here, which allow for the effective calculation of harmonic frequency as well as cubic and semidiagonal quartic force fields. The latter, in turn, are necessary to compute the anharmonic vibrational frequencies with the perturbative approach (VPT2). The quality of harmonic vibrational frequencies computed in conjunction with basis sets of double- to quadruple-ζ quality has been checked against reference data from the F38 benchmark set. Then, for an additional set of small closed- and open-shell systems, both harmonic frequencies and anharmonic contributions computed at the B2PLYP/N07D and the B2PLYP/aug-cc-pVTZ levels have been compared to their CCSD(T) counterparts. Moreover, for selected medium-size molecules (furan, pyrrole, thiophene, uracil, anisole, phenol, and pyridine), anharmonic frequencies have been compared to well established experimental results. Such benchmark studies have shown that the B2PLYP/N07D model provides good quality harmonic frequencies and describes correctly anharmonic contributions, the latter being of similar accuracy to their B3LYP/N07D counterparts, but obtained at significantly larger computational cost. Additionally, increased accuracy can be obtained by adopting hybrid models where the B2PLYP/N07D anharmonic contributions are combined with harmonic frequencies computed with more accurate quantum mechanical (QM) approaches or by B2PLYP with larger basis sets. This work confirmed also that most of the recently developed density functionals are significantly less suited for vibrational computations, while the B2PLYP method can be recommended for spectroscopic studies where a good accuracy of vibrational properties is required.

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