In pursuit of sub-20 cm^{-1} computational thermochemistry

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Enthalpies of formation (and related total atomization energies) are one of the most fundamental quantities used in chemical sciences. Their estimation via computational model chemistries has been of long-standing interest in the thermochemical community, and a number of "families" of these methods have been developed to calculate said quantities to within sub-chemical accuracy (+/- 1 kJ mol−1), including HEAT[1], Wn[2], FPD[3], FPA[4], ANLn[5], to name a few. The achievement of sub-chemical accuracy marked a roughly four-fold improvement over the goal of chemical accuracy (+/- 1 kcal mol−1) previously proposed by Pople[6], and these methods have had significant impact in the field of high-accuracy thermochemistry, especially when used in combination with experimental studies to provide quality data to the Active Thermochemical Tables (ATcT)[7].

This presentation focuses on a similar four-fold increment from sub-chemical accuracy to what we provisionally term "semi-spectroscopic" accuracy; routine prediction of enthalpies of formation within +/- 20 cm^{-1} of ATcT values. The challenges of this process are discussed, and the resulting model chemistries, which feature up to nonuple basis sets, correlated wavefunctions up to CCSDTQ(P)$_\Lambda$, and composite vibrational zero-point energies, are presented. These methods are used to examine some cases where the added accuracy (and expense) is important in removing errors from the computational prediction of thermochemical properties, and to shed some light on what remaining challenges exist on the road to extending these methods to systems of more than a few atoms.

References

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