Effective Estimation of Formation Enthalpies for Organic Compounds with Local Coupled-Cluster Methods

Eugene Paulechka [C, S] and Andrei Kazakov
Applied Chemicals and Materials Division, NIST, Boulder, CO, U.S.A.
yauheni.paulechka@nist.gov

An accurate and cost-efficient methodology for the estimation of the enthalpies of formation for closed-shell compounds composed of C, H, O, and N atoms is presented. The simulations were validated against critically evaluated experimental data. The computational efficiency was achieved through the use of the resolution-of-identity (RI) and localized orbital coupled cluster approximations, which resulted in a drastic reduction in both the computational cost and the number of necessary steps for a composite quantum chemical method. The approximations implemented in the Orca, MRCC, and Psi4 packages were compared. In all cases, an expanded uncertainty of about 3 kJ·mol^{-1} was achieved with a data set of 45 thoroughly vetted experimental values for molecules containing up to 12 heavy atoms, competitive with those of typical calorimetric measurements. Accurate calculation of the anharmonic zero-point vibrational energy (ZPVE) was found to limit the accuracy of the considered methods for large molecules. Lack of additivity of the post-CCSD(T) contributions was important for some groups of compounds. A procedure is proposed to indirectly estimate deficiencies in ZPVE and post-CCSD(T) contributions. With this procedure, an expanded uncertainty well below 3 kJ·mol^{-1} was achieved.