Eliminating Systematic DFT Errors via Connectivity-Based Hierarchy:

Towards Accurate Prediction of Reaction Enthalpies

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Over the last decade, several studies have raised questions about the accuracy of DFT calculated reaction enthalpies of common organic reactions. While newly developed dispersion corrected and long-range corrected density functionals offer improved results, the errors are still greater than 2 kcal/mol for many reactions, often exceeding 5 kcal/mol. Moreover, the lack of a universal DFT or a generic protocol to assess DFT errors has also been a source of confusion in quantum chemistry. Herein, we demonstrate the application of our generalized Connectivity-Based Hierarchy (CBH) schemes to calculate accurate reaction enthalpies. The well-defined and reliable error-canceling thermochemical hierarchy can derive accurate thermochemical properties for both open and closed shell organic molecules using DFT and wave function-based methods in conjunction with modest basis-sets.¹⁻³ A benchmark set of 25 organic reactions of medium and large molecules (consisting of 17 to 81 atoms) has been composed to evaluate the performance of conventional DFT methods against G4 method. The isoatomic CBH-2 corrections results in dramatic improvement for all the DFT and WFT methods and thus offers a unique protocol consistent with different methods and different reaction types to obtain accurate reaction enthalpies. The CBH-2 corrections in B2PLYP, BMK, B3LYP-D3, B2PLYP-D3, and B3LYP-NL resulted in mean absolute errors of < 1.5 kcal/mol.

References:

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