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Development of a Composite Method Based Exclusively on The Density Functional Theory

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Abstract: Composite methods tend to combine different ab initio calculations with different basis functions at different level of electron correlation effects, in addition to other important effects[1-4]. On the other side, Density Functional Theory (DFT) has been widely used for the calculation of different properties in large molecular systems containing hundreds of atoms. One of the great difficulty in choosing the appropriate DFT method is the diversity of the exchange-correlation functional.[5-6]

The most used functional in the literature is the B3LYP hybrid functional, which includes semi-empirical parameters optimized from thermochemical properties, such as atomization energy, ionization potential and proton affinity.[7]

A thermochemical property not well described by the B3LYP functional is the enthalpy of formation. In this work, basis functions, exchange-correlation parameters of the functional and atomization energies were optimized to achieve results close to the experimental values. The theoretical method combines the principles of the composite method, but considering additional corrections takin the B3LYP/6-31G(2df,p) calculations as reference (E_{ref}). The fundamental corrections considered in this work are:

$$E_{new} = E_{ref} + \Delta E_{xc} + E_{SO} + E_{ZPE} + E_{therm} + E_{HLC}$$

Where the corrections are: ΔE_{xc} for the exchange-correlation, E_{SO} for spin-orbit, E_{ZPE} for zero point energy, E_{therm} for thermal and E_{HLC} for a "higher level correction" which take into account the number of valence α and β electrons.

Three different methods were teste: a) the first one considered only the optimization of the exchange-correlation functional, b) the second method, in addition to the exchange-correlation parameters, considered the optimization of the basis functions of the atoms: aluminum, bromine, fluorine, phosphorus, nitrogen, carbon, chlorine, sulfur and oxygen, c) the third and fourth methods are direct use of the adjusted parameters from (a) and (b)

as original parameters yielding two different functionals. An additional adaptation of the experimental atomization energies of the elements used in the calculation of the enthalpies of formation was also tested in all cases. This adjustment proved to be necessary to achieve a remarkable accuracy.

The second composite method is the best alternative with the optimization of 10 basis set and the exchange-correlation functional, achieving a mean absolute error of less than 2 kcal mol^{-1} for a set of 254 enthalpies of formation of compounds in gas phase. The direct use of the parameterization in two original functionals present a quantitative behavior not far from methods (a) and (b), indicating that they can be considered as acceptable to provide reliable enthalpies of formation. All the attempts made in this work provide significantly better enthalpies of formation regarding the original B3LYP functional.

Key-words: **Composite Method, DFT, B3LYP, Enthalpy of formation.**

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