

Numerical Models for Accurate DFT Energetics

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Abstract

Despite the progress in DFT, Becke's three-parameter hybrid functional (B3LYP) is by far the most popular density functional in chemistry.^[1] It has been widely recognized as a cost-effective method and has been successfully applied to many chemically interesting systems. However, there are increasing evidences, showing that B3LYP degrades rapidly with the increase of the molecular size. Previously, we have put forward the X1 method^[2-5] that combines B3LYP with a neural network correction for an accurate yet efficient prediction of thermochemistry. Without paying additional computational cost, X1 reduces B3LYP's mean absolute deviation (MAD) for a set of 92 bond dissociation energies (BDEs) from 5.5 to 2.4 kcal/mol. Recently, we extended X1 to propose the X1s method^[6] by including further the spin change from molecules to atoms during atomization as a new descriptor. X1s further reduces the MAD for BDEs to 1.4 kcal/mol, thus showing substantial improvement. Both B3LYP and the X1/X1s methods fail to give reliable energy differences for large hydrocarbon isomers.^[7] In order to alleviate this problem, environmental correction term for single bond, ESBC,^[8] is introduced into the X1s method as another new descriptor, which brings about the X1se method. The results show that X1se greatly reduces MAD of isomerization energies from 6.02 to 2.87 kcal/mol, approaching to the accuracy of the generally acknowledged G3 theory. In this presentation, we will introduce the methods of the X1 series in detail, and will present their performances on prediction of heats of formation, bond dissociation energies, heats of reaction and reaction barriers of large sets of molecules.

References:

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