Predicting Electrophilicity, Nucleophilicity and Regioselectivity with Density Functional Reactivity Theory

Shubin Liu

Research Computing Center, University of North Carolina, Chapel Hill, North Carolina 27599-3420, U.S.A.

Abstract

Density functional reactivity theory (DFRT) employs the electron density and its derivatives to describe structure, bonding and reactivity properties of a molecular system. Quantities from information theory such as Shannon entropy, Fisher information, and Ghosh-Berkowitz-Parr entropy are natural descriptors within the DFRT framework because these quantities employ electron density and its derivatives only. We have previously illustrated their strong correlations among these quantities.[1-3] Fisher information was also used as a measure of the steric effect.[4-5] In this work, based on the early work by Nalewajski and Parr,[6] we demonstrate that information gain, also called Kullback–Leibler divergence, together with Hirshfeld charge, can be used to quantify electrophilicity, nucleophilicity and simultaneously determine regioselectivity.[7,8] In addition, we examine their scaling properties with respect to the total number of electrons. We considered their representations with both electron density and shape function for isolated atoms and neutral molecules. We also investigate their atomic behaviors in different molecules with three partition schemes, Bader's zero-flux, Becke's fuzzy atom, and Hirshfeld's stockholder partitioning.[9-11]

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