

A reactivity index based on orbital energies

Takao Tsuneda

Fuel Cell Nanomaterials Center, University of Yamanashi, Japan

ttsuneda@yamanashi.ac.jp

A reaction analysis method based on the orbital energies, which are accurately given by the long-range corrected (LC) DFT[1, 2] calculations, is presented. Although there are several methods using orbital energies in reaction analyses, these methods have used hypothetical orbital energies instead of the calculated ones in reaction diagrams. This is because there is no conventional method giving accurate orbital energies. Surprisingly, it was recently found that LC-DFT quantitatively reproduces valence orbital energies including LUMO energies for the first time.[3]

Based on the quantitative orbital energies of LC-DFT, we have developed a new reaction analysis method based on orbital energies for gas-phase reactions. To make clear the relation between reactivities and orbital energies, we have exhaustively explored the orbital energy variance on the intrinsic reaction coordinates (IRCs) for the major reactions of small light molecules. Consequently, we proposed a reactivity index using the LC-DFT orbital energies. Using this reactivity index, we found that forward reactions initially proceed through electron transfers associated with no intramolecular geometrical change except for the S_N2 , symmetric, and other several reactions. By investigating these exceptional reactions, we have found that several reactions including the S_N2 and symmetric reactions are questioned about their reaction paths. We have, therefore, explored reaction paths, which are not located on the IRCs, for these reactions. As a result, we have found plausible reaction paths obeying the reactivity index, which are also consistent with experimental results, for these reactions.

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[3] T. Tsuneda, J.-W. Song, S. Suzuki, and K. Hirao. *J. Chem. Phys.*, 133:174101(1-9), 2010.