Chapter 5
DFT Correlation of the Site Selectivity of Donor–Acceptor Chemical Interaction

Dulal C Ghosh
University of Kalyani, India

Soma Bhattacharyya
University of Kalyani, India

ABSTRACT

In this study, the time evolution of concept local HSAB principle as a necessary prelude to our jargon of the trade Correlation of the Site Selectivity of Donor–Acceptor Chemical Interaction in terms of the Local Density Functional Descriptors is discussed at length. The authors try to correlate the known facts relating to the formations of some donor acceptor supermolecules such as HCN–BF$_3$, HNC–BF$_3$, H$_3$C–CN–BF$_3$, and H$_3$C–NC–BF$_3$ by the chemical interaction of a well known Lewis acid, BF$_3$ and various donor ligands/Lewis bases like HCN, HNC, H$_3$C–CN, H$_3$C–NC which are inherently structural isomers having multiple donating sites, in terms of the local DFT descriptors like the local softness (s) and fukui functions (f) of such chemical systems. It is also noted that the dynamic chemico-physical process of site selectivity is found to have a very nice correlation in terms of the computed values of the local descriptors namely the fukui functions and the local softnesses. Thus, the authors find that the theoretical descriptors of the local HSAB principle can be efficiently exploited to study the mechanism of site selectivity in a chemical reaction.

DOI: 10.4018/978-1-4666-1607-3.ch005
INTRODUCTION

In terms of the computed numerical values of the local descriptors, it has been observed that BF$_3$ always attaches with the ligands through the B– end and never through the F– end – which is a well established experimental fact. The electronegativity and the chemical hardness are the two old but very important conceptual constructs of chemistry and physics from the early days of science. These conceptual constructs have been so important and indispensable that, without the concept and operational significance of hardness and electronegativity, chemistry and many aspects of condensed matter physics become chaotic and the long established unique order in chemico-physical world would be heavily disturbed. But these descriptors are fundamentally conundrums and are not the objects of the real world. We must make the position distinctly clear that these descriptors –the electronegativity and the hardness are not observables and according to the rules of quantum mechanics have no quantum mechanical operator to make their quantum mechanical evaluation feasible. Thus, these descriptors are qualitative per se and the possibility of their quantum mechanical evaluation is ruled out (Ghosh et al. 2009, 2010, 2011; Ghosh & Islam, 2010, 2011). One may find the resemblance between the appearance and significance of heuristically developed concepts of electronegativity and hardness in chemistry and physics and the unicorns of mythical saga (Frenking et al. 2007). They exist but never seen. We may refer to the opinion of Parr et al. (2005) who seem to have connected the reality of the hardness and the electronegativity with the noumenon of Kantian philosophy. The noumenon is an object knowable by the mind or intellect, not by the senses. Thus both the hardness and electronegativity are objects of purely intellectual intuition.

In order to mathematise these abstract concepts, it is required that these descriptors be reified goaded by their physico-chemical behavior. After the modeling, some algorithm has to be developed and some mathematical formulae be suggested for their evaluation. We feel it pertinent to recall the opinion of Ayers (2007) that before any algorithm of computing the hardness and the electronegativity is developed, the reification of abstract concept into things of the real world is absolutely necessary.

The current scenario of theoretical research in the domain of the density functional theory has basically three directions, namely, theoretical, conceptual, and computational (Kohn, Becke, & Parr, 1996; Liu & Parr, 1997; Parr & Yang, 1989; Parr & Yang,1995). The conceptual density functional theory has demonstrated its amazing power to quantify the qualitative theoretical principles and conceptual structure used for the understanding and rationalizing the relationship between molecular structure and reactivity for long time (Parr, Donnelly, Levy, & Palke, 1978; Parr, & Pearson, 1983; Sanderson, 1976; Ziegler, 1991). There is a paradigm shift in the realm of conceptual chemistry due to the density functional underpinning of Parr and co-workers. The useful qualitative entities like hardness and electronegativity which were abstract semiotic representations are now considered as theoretical quantities of cognitive representations.

Many new chemical concepts are also suggested, conceived and theoretically introduced within the scope of density functional theory (Chandrakumar & Pal, 2002; Martier Ghosh, S.K. & Sarkar, 1986; Pearson, 1988). Some potential density functional reactivity descriptors are chemical potential ($\mu$), global hardness ($\eta$), the local softness ($s$) and fukui functions ($f$). The entire gamut of current descriptors – global and local, have been introduced by Parr and coworkers (Parr & Yang, 1989). Ghosh et al have already discussed (Ghosh & Bhattacharyya, 2006) the role of global DFT parameters viz. chemical potential ($\mu$) and global hardness ($\eta$) in the formation of donor-acceptor supermolecules formed by the well known Lewis acid BF$_3$ and some Lewis
Related Content

Nanomaterials in Medical Devices: Regulations' Review and Future Perspectives

Antimycotic Activity of Nanoparticles of MgO, FeO and ZnO on some Pathogenic Fungi
[www.igi-global.com/chapter/antimycotic-activity-of-nanoparticles-of-mgo-feo-and-zno-on-some-pathogenic-fungi/102068?camid=4v1a](www.igi-global.com/chapter/antimycotic-activity-of-nanoparticles-of-mgo-feo-and-zno-on-some-pathogenic-fungi/102068?camid=4v1a)

Nanocomposites and Hybrid Materials for Adsorptive Desulfurization
[www.igi-global.com/chapter/nanocomposites-and-hybrid-materials-for-adsorptive-desulfurization/139159?camid=4v1a](www.igi-global.com/chapter/nanocomposites-and-hybrid-materials-for-adsorptive-desulfurization/139159?camid=4v1a)

A Formal Model of Universal Algorithmic Assembly and Molecular Computation
[www.igi-global.com/article/formal-model-universal-algorithmic-assembly/52089?camid=4v1a](www.igi-global.com/article/formal-model-universal-algorithmic-assembly/52089?camid=4v1a)