Editorial foreword

Special Issue on Application of Density Functional Theory in Chemical Reactions

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Rapid advances are taking place in the application of density functional theory (DFT) to describe complex chemical reactions. Researchers in different fields working in the domain of quantum chemistry tend to have different perspectives and to use different computational approaches. DFT owes its popularity to recent developments in predictive powers for physical and chemical properties, and its ability to accurately treat large systems.

Both theoretical content and computational methodology are developing at a pace which offers scientists working in diverse fields of quantum chemistry, cluster science and solid state physics, new opportunities. A major goal of this special issue is to draw together contributors from different fields to spread knowledge of current capabilities and new possibilities, and to stimulate the exchange of information between apparently disparate disciplines. The current issue aims to extract the current scenario of application of DFT on chemical problems based on two broad headings: (1) The chemical reactivity theory, approach and its application resolving chemical issues of importance within the helm of DFT and (2) Application of DFT on resolving structure property relationship in catalysis, reactions and small molecules.

The first section consists of few very distinctive Review articles. The section starts the first theme with a scintillating review on applications of the information theoretic concepts to molecular systems from Roman F. Nalewajski. This survey covers the information theory basis of the Hirshfeld partitioning of molecular electron densities, its generalization to many electron probabilities, the local information distance analysis of molecular charge distributions, the charge transfer descriptors of the donor-acceptor reactive systems, the elements of a "thermodynamic" description of molecular charge displacements, both "vertical" (between molecular fragments for the fixed overall density) and "horizontal" (involving different molecular densities), with the entropic representation description provided by the information theory.

Then the next study in this series is on basic concepts of DFT as applied to materials modeling in the microscopic, mesoscopic and macroscopic length scales by Swapan K. Ghosh. The picture that

emerges is that of a single unified framework for the study of both quantum and classical systems. This study illustrates the current approach and proposes the future challenges of DFT.

This brings us to two contemporary reviews and one article based on reactivity index theory, approach and its applications. The first one in this series is from P. Geerlings which covers a broad spectrum of chemical reactivity as described by quantum chemical methods with a special emphasis on DFT. An overview is given of the most important reactivity descriptors and the principles from which they have been generated. A whole set of examples have been provided to rationalize an understanding of this area. The second review in this series deals with the exciting reactivity parameters derived locally in the helm of DFT. Here Chandra & Nguyen deals with use of local softness to interpret and predict various complicated organic reactions The article in the series by Pal et al tried to give a quantitative flavor on the reactivity descriptors, They made a sincere effort to explain the theoretical basis for the empirical hardness/softness concepts to address the reactivity of molecular complexes in a semi-quantitative way within the framework of density functional theory.

Finally theme 1 ends with a very exciting article on Dynamical behavior of chemical reactivity indices like electronegativity, hardness, polarizability, electrophilicity and nucleophilicity indices are studied within a quantum fluid density functional framework for the interactions of a hydrogen atom in its ground electronic state (n = 1) and excited electronic state (n = 20) with monochromatic and bichromatic laser pulses. by Chattaraj et al. A tug – of – war between the spherically symmetric nuclear coulomb field and cylindrically symmetric external electric field to govern the electron density distribution is delineated through the dynamical profiles of various reactivity indices like electronegativity, hardness, polarizability, electrophilicity, nucleophilicity and phase volume for the external field and in different electronic states.

This brings us to a second section. This section deals with applications of DFT on different molecular set with different targets to achieve ranging from electronic structures to organic reactions. The first study in this series is with a conceptual question on the usage of unrestricted DFT by Cremer et al. They proposed that UDFT could be used for the description of open shell singlet biradicals provided a number of precautions are considered.

The second study in this theme is on recent first principles molecular dynamics simulations within the Becke-Lee-Yang-Parr gradient-corrected density functional approach to study the Ti-based Ziegler-Natta supported heterogeneous catalysis of α-olefins by Boero, Terakura and Parinello. Comparison with the few experimental data available has shown that simulation can reproduce activation barriers and the overall energetics of the reaction with sufficient accuracy.

Next in this theme is a study by Chandra & Uchimaru, where the correlations of Hammett's substituent constants with the bond dissociation enthalpies of the O-H bonds of phenols and proton affinities of phenoxide ions have been explored. Elucidation of the relationship between structure and reactivity has long been a chief goal of physical organic chemistry. Attempts have been made in this paper to find out such correlation from the results of BDE (O-H) and PA calculations.

Next in this study is with a series consisting two papers with application of DFT on catalytic materials with an emphasis to zeolites. The first study by Govind et al is on detailed density functional theory (DFT) calculations of important mechanisms in the methanol to gasoline (MTG) process in a zeolite catalyst. This study shows the impotance of DFT in resolving industrially important issues. This study is followed by a study of Broclawik et al, which has a goal set to devise the model of

CuZSM-5 capable of describing geometrical and electronic properties of metal sites and adsorption complexes with small molecules. Electron donor/acceptor properties of the sites combined with electronic properties of adsorbed molecules led to the proposal for the mechanism of NO activation by Cu^+ZSM-5: transfer of electrons from copper d orbitals to antibonding states of NO should cause large weakening of the bond, which was evidenced also by IR measurements. This study as well compares available experimental results to validate the utility of DFT in resolving chemical problems.

I wish to express my sincere thanks to each of the authors for their contributions. The DFT community is much wider and even more diverse even in this smallest domain of this issue what we have been able to put up here. Yet we have brought together a set of viewpoints and benchmarks in our respective fields, which will be of immense service to the community.