Density Based Reactivity Descriptors: Relation to Molecular Properties and the Strength of Chemical Interactions

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CERTIFICATE

This is to certify that the work presented in this thesis entitled, "**Density Based Reactivity Descriptors: Relation to Molecular Properties and the Strength of Chemical Interactions**" by **Akhilesh Tanwar**, for the degree of Doctor of Philosophy, was carried out by the candidate under my supervision in the Physical Chemistry Division, National Chemical Laboratory, Pune, India. Any material that has been obtained from other sources has been duly acknowledged in the thesis.

Date: Dr. Sourav Pal

Place: Pune.   (Research Guide)

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Abstract

Understanding molecular interactions has been a great challenge from both experimental and theoretical points of view.[1] Many theoretical models based on molecular orbital density, charge on atoms, bond order, etc., have been extensively used in correlating the reactivity of the systems.[2] In particular, density-based descriptors are known to play key role in determining the stability and reactivity of chemical species. There have been recent studies on the qualitative and quantitative description of these concepts and use of these in the selectivity of reactions in catalysis, adsorption and molecular recognition.

Global reactivity descriptors (GRD), like softness, hardness and chemical potential along with the concept of hard soft acid base (HSAB) principle, are widely used in describing the reactivity and the stability of chemical systems.[3, 4] On the other hand, local reactivity descriptors (LRD), e.g. Fukui function (FF), local softness[5, 6] etc. have been studied extensively in recent years for characterizing the reactivity and site-selectivity in chemical reactions. These descriptors have been used qualitatively to characterize reactivity of a molecule in chemical reaction. Reactivity to specific agents, e.g. electrophilic, nucleophilic or radical can be described qualitatively using the above descriptors.[5]

The general objective of the thesis is to critically analyze some aspects of the density derived reactivity descriptors. In addition, new descriptors and principle are proposed to study molecular interactions with in the framework of Conceptual Density Functional Theory (DFT).[4, 5] Specific objectives of the proposed work are as follows:

1. Derivation of analytical results for study of size extensivity or intensivity of LRD and to verify the results using *ab-initio* calculations.

2. Description of red shift in OH stretching frequencies[7] of water using LRD. The shift in stretching frequencies is believed to be arising due to the local polarizations in water.

3. Extending the domain of applicability of the conceptual DFT in explaining the magnetic interactions and magnetochemistry.

The organizations of the dissertation work is as follows

Chapter 1

In chapter 1, we review the earlier theoretical developments made towards the area of chemical reactivity using quantum chemical methods. We will describe how the conceptual DFT has been developed. Based on the idea that the electron density is the fundamental quantity for describing atomic and molecular ground states, conceptual DFT provided sharp definitions of different chemical concepts like electronegativity, chemical potential, hardness etc. We discuss the developments in the area of both global and local HSAB principle, maximum hardness principle. We also discuss that the softness and polarizability link. In the end we discuss the applicability of the both GRDs and LRDs in describing various aspects of reactivity.

Chapter 2

In chapter 2, we study the extensivity of the local reactivity descriptors. We present the analytical results for the same. We study size dependence of LRDs in two cases viz. *AB* type of complex and Dimer A_2. We show that in the non-interacting

regime, the Condensed fukui functions, [9] local softness and local philicity[10] of dimer separate out as half of the monomer values, while relative electrophilicity and relative nucleophilicity[11] of dimer approach its corresponding monomer values. For AB type complex, the non-interacting values of the LRD approach those of the fragmented species for complex anion or cation respectively.

Chapter 3

In chapter 3, we verify our hypothesis regarding the separability of local reactivity descriptors (presented in chapter 1) through *ab-initio* calculations. For *AB* type complex we study *BXX'X"NH₃ (X, X', X" = H, F)* while for A_2 type complex we study dimer of *BH₃NH₃*. We discuss the behavior of local reactivity descriptors along the reaction path during complexation.

Chapter 4

In chapter 4, we present a first-principle theory of interaction induced shifts in the *O-H* stretching frequency in clusters. It is well-known that because of the elongation of the *OH* bond due to hydrogen bonding, the *O-H* frequencies show red shift with respect to average symmetric and asymmetric stretch[7]. We propose two new descriptors viz. Normalised Atom Condensed Fukui Functions (NFF) and Bond Deformation Kernel (BDK). We extend their applicability to study *OH* frequency shifts in the Flouride ion-water clusters. We show that the BDK provides microscopic description of the bond elongation in the systems where local polarization effects are quite important. BDK correlates well with the corresponding shifts in *OH* stretching frequencies obtained by normal mode analysis.

Chapter 5

Though, the effect of external electric field has been studied by various authors on the stability of chemical species, there have been very few studies on the effect of external magnetic field. In chapter 5, we propose and also verify through *ab initio* calculations a new electronic structure principle, viz. the Minimum Magnetizability Principle (MMP), to extend the domain of applicability of the conceptual DFT in explaining the magnetic interactions and magnetochemistry. The principle states that, "A stable configuration/conformation of a molecule or a favorable chemical process is associated with a minimum value of the magnetizability". In order to verify our prognosis we study the asymmetric and symmetric stretching of H_2O.

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General Introduction to Reactivity Theory

1-I. Introduction

Ever since its inception, the focal activity of theoretical chemistry has been to formulate the concepts to explain the vast phenomenology of chemical reactions and ultimately to predict their natural course to product formation. Over the years, these concepts have transformed from empirical notions into a rich multifaceted theory known as chemical-reactivity theory. Theoretical models in correlating the reactivity of molecular systems based on different quantities, such as molecular orbital density, charge on atoms, bond order, etc., have been used extensively. Of many important contributions to the reactivity theory, the skeleton of reactivity theory lies mainly with two major works. The first is the Fukui's introduction of the concept of frontier molecular orbitals.[1] The second one is from Parr and collaborators, [2-9] on how the concepts of frontier orbitals and other closely related ideas could be given a rigorous foundation, within the framework of Density Functional Theory (DFT). [2, 10, 11]

In this context, the concepts of density based descriptors, like chemical potential, hardness and softness have been used to provide a simple model for describing

reactivity and interactions between the species.[2, 12] The global hardness and softness, along with the concept of hard-soft-acid-base (HSAB) principle and maximum hardness principle, have been studied to describe the reactivity of acids and bases and the stability of chemical systems.[2, 12-14] The HSAB principle has systematized the reactivity of the acids and bases in terms of softness and hardness indices, based on the experimental observations.[13(c)] The nature of these basic chemical concepts, hardness and softness, called Global reactivity descriptors (GRD), has been theoretically justified within the framework of DFT.[2,3,14] Many groups have attempted to validate and prove the HSAB principle using the GRDs and Local Reactivity Descriptors (LRDs).[15] These studies have led to some important insights about the nature of the reactivity and the stability of molecular systems in terms of η /S parameters.[9-13,14-19]

However, these global descriptors cannot describe the reactivity of a particular site in a molecule. The LRDs , such as Fukui-function (FF) and local softness, were proposed to rationalize the problem and identify reactive sets in molecules.[4,5,16,17] Electrophilic and nucleophilic FFs have been used as indications of reactivity to nucleophilic and electrophilic reagents, respectively.[18-20] In addition, Pal and co-workers, used the local softness as well as local hardness to probe both the intra- and intermolecular reactivity of a nucleophilic attack on carbonyl compounds and introduced concepts of relative electrophilicity and relative nucleophilicity which were shown to be reliable descriptors for intramolecular reactivity.[21] Several other reactivity descriptors have been proposed. Parr *et al.*,[22] with the idea similar to the equation of power ($W=V^2/R$) in classical electricity, proposed electrophilicity index (*W*) as μ^2/η.

Taking cue from this, Chattaraj *et al.* [23] proposed the existence of local electrophilicity index $w(r)$ such that $w(r)$ integrates to global (W).

The LRD and GRD have been used to formulate local version of HSAB principle for interaction energy between two molecules.[12 (b), 17, 24, 25] The local HSAB principle, proposed by Gazquez and Mendez, [24] is an alternative description of reactivity using local descriptors. However, it involves the descriptors of both of the reacting systems for prediction of reactive sites. In general, the local HSAB principle states that the interaction between any two molecules will occur not necessarily through their softest atoms, but rather through those atoms of the two systems, whose FFs are the same. Different forms of local HSAB principle have been used successfully in recent years.[24, 25] The elaborate discussion about the reactivity descriptors and the principles will be made in subsequent sections.

The present thesis deals with some aspects of the reactivity of molecular systems using density based reactivity descriptors. In particular, we critically analyze some characteristics of these descriptors. In addition, new descriptors and principles are proposed to study molecular interactions within the framework of Conceptual DFT. We analyze the validity and applicability of these descriptors and principles. The advantages and limitations of the models are also addressed.

1-II. Introduction to DFT (from wavefunction based theory to DFT)

According to the elementary quantum mechanics, all information about a state of a given system is contained in the wave function, ψ, of the state. The nuclear degrees of freedom (e.g., the crystal lattice in a solid) appear only in the form of potential $v(r)$

acting on the electrons, so that the wave function depends only on the electronic coordinates.[26] Non-relativistically, this wave function is calculated from the Schrödinger's equation, which, for a single electron moving in a potential v(r) reads as

$$\left[-\frac{\hbar^2\nabla^2}{2m}+v(r)\right]\Psi(r)=\varepsilon\Psi(r) \tag{1.1}$$

If there is more than one electron (i.e., one has a many-body problem) Schrödinger's equation becomes,

$$\left[\sum_{i}^{N}\left(-\frac{\hbar^2\nabla_i^2}{2m}+v(r_i)\right)+\sum_{i<j}U(x_i,x_j)\right]\Psi(x_1,x_2,x_3,...,x_N)=E\Psi(x_1,x_2,x_3,...,x_N) \tag{1.2}$$

where, x_i represents the electronic coordinates which are composed of spatial coordinate (r_i) and a spin coordinate (ω_i) of ith electron. $v(r_i)$ represents the potential due to atomic nuclei. $U(x_i,x_j)$ is electron-electron interaction term. Or, in other words,

$$(\hat{T}+\hat{V}+\hat{U})|\psi\rangle=E|\psi\rangle \tag{1.3}$$

where, $\hat{T}$, $\hat{V}$ and $\hat{U}$ are kinetic energy operator, potential energy (due to nuclei) and electon-electron interaction energy operators, respectively. Hartree-Fock approximation simplifies this many electron problem to a single electron problem by treating the electron-electron repulsion term in an average way.

In short, the usual quantum-mechanical approach to the Schrödinger's equation (SE) can be summarized by the following sequence,

$$v(r_i)\xrightarrow{\ SE\ }\Psi(x_1,x_2,x_3,...,x_N)\xrightarrow{\ \langle\Psi|...|\Psi\rangle\ }observables$$

i.e., one specifies the system by choosing $v(r)$, plugs it into the Schrödinger's equation, solves that equation for the wave function, and then calculates the observables by taking

expectation values of operators with this wave function. One of the observables that are calculated in this way is the particle density.

$$\rho(r) = N \int ds \int d^3r_2 \int d^3r_3 \dots \int d^3r_N \Psi^*(x, x_2, \dots, x_N) \Psi(x, x_2, \dots, x_N) \tag{1.4}$$

For more accurate treatment (which involves correlation between electrons), post-Hartee-Fock methods such as many-body perturbation theory, configuration interaction and coupled cluster method etc. have been extensively used these days for small systems. The problem with these methods is the great demand they place on the computational resources. It is simply impossible to apply them efficiently to large and complex systems.

DFT provides a viable alternative to this, though less accurate it is much more versatile. DFT explicitly recognizes that non-relativistic coulombic systems differ only by their potential v(r) and supplies a prescription for dealing with the universal operators, $\hat{T}$ and $\hat{U}$, once and for all. Furthermore, DFT provides a way to systematically map the many-body problem onto a single-body problem in the similar fashion as Hartree-Fock method does. The essence of DFT lies in promoting electron density form, just one among the observables, to a key variable on which calculation of the other observables is based. Kohn and Hohenberg[10], in 1964, proved that the information content in the electron density function ρ(r), depending on only three variables,[27] determines all ground state properties, thus replacing the crucial position of the complex wavefunction based approach which is functional of 4N variables (three spatial and one spin coordinate, N is number of electrons). According to Hohenberg-Kohn (HK) theorem, energy as a functional of density ρ(r) can be written as

$$E[\rho] = \int \rho(r)v(r)dr + F_{HK}[\rho] \tag{1.5}$$

With

$$F_{HK}[\rho] = T[\rho] + V_{ee}[\rho] \tag{1.6}$$

where, $v(r)$ is external potential and F_{HK} is universal Hohenberg-Kohn functional comprising of electronic kinetic energy functional, $T[\rho]$, and the electron-electron interaction functional, $V_{ee}[\rho]$. Kohn and Sham in 1965, provided a convenient way to calculate optimum $\rho(r)$ by introducing orbitals, whose squares sum up to the electron density.[11] A variational procedure yields a pseudo-one electron equation, the analogue of the Hartree-Fock equation, which is written as:

$$\left(-\frac{1}{2}\nabla^2 - v_{eff}(r) \right)\Psi_i = \varepsilon_i \Psi_i \tag{1.7}$$

where,

$$v_{eff}(r) = v(r) + \int \frac{\rho(r)}{|r-r'|}dr' + v_{xc}(r) \tag{1.8}$$

The form of exchange correlation term v_{xc} is unknown. In principle, DFT is an exact theory subject to the knowledge of the exact functionals. The present day DFT, mainly deals with the search for best performing exchange correlation functionals.[28] Though, there have been many functionals available in literature, there is no principle that decides which functional is the best. In recent years, there has been significant progress in the area with the use of hybrid functions[29] in evaluating various properties with accuracy comparable to much accurate *ab inito* wavefunction based theories. Parr and Yang termed this branch of DFT as "computational DFT" [28]. We would not go into details of this, but, we will confine the discussion in this thesis, mainly, to the other branch of DFT which provided the quantitative descriptions of various chemical concepts which were already known (like electonegativity, hardness etc). Same authors

coined the term "conceptual DFT" for this branch.[28] As stated earlier also, the reactivity theory is wholly supported on the foundations of conceptual DFT. We shall discuss this in detail in the further sections.

1-III. Conceptual DFT

1-III(A). A journey to Global Reactivity Descriptors

As already mentioned, electron density $\rho(r)$ is the fundamental variable in DFT. It contains all the information about the system. $\rho(r)$ determines external potential (due to nuclei), $v(r)$. Determination of $v(r)$ implies fixing of the Hamiltonian H of the system. It also determines N, the total number of electrons, via its normalization.

$$\int \rho(r)dr = N \tag{1.9}$$

Since, it determines number of electrons, it follows that $\rho(r)$ also determines the wavefunction and all other electronic properties. This theorem is also known as first Hohenberg-Kohn theorem. [10]

$$\rho(r) \longrightarrow v(r) \longrightarrow H \qquad N \longrightarrow \psi \longrightarrow E$$
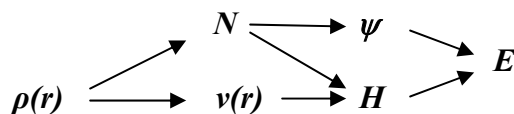
Scheme 1.1: Interdependence of basic variables in DFT

Scheme 1 clearly shows that energy is functional of electron density.

$$E=E_v(\rho) \tag{1.10}$$

The second HK theorem provides the energy variational principle i.e. looking for $\rho(r)$ what minimizes the energy functional $E_v(\rho)$.

For optimal $\rho(r)$ the energy doesn't change with variation of $\rho(r)$, provided the $\rho(r)$ integrates to N. This constraint can be introduced by method of Lagrangian multipliers, yielding the variational condition:

$$\delta\left\{E - \mu\left(\int \rho(r)dr - N\right)\right\} = 0 \qquad (1.11)$$

where, μ is the corresponding Lagrangian multiplier.

One finally obtains Euler-Lagrange equation:

$$\mu = \frac{\delta E_v[\rho]}{\delta\rho(r)} = v(r) + \frac{\delta F_{HK}}{\delta\rho(r)} \qquad (1.12)$$

F_{HK} is universal Hohenberg-Kohn functional (now onwards we will use notation F instead of F_{HK}) comprising of electronic kinetic energy functional, $T[\rho]$ and the electron-electron interaction functional, $V_{ee}[\rho]$.

In the landmark paper by Parr and coworkers[14], they provided interpretation of Lagrangian multiplier μ. They showed that under "N representability assumption"[30] and "V representability assumption"[31] if the density is derived from anti-symmetric wavefunctions, the following stationary principle holds.

$$\delta\left\{E[\rho'] - \mu N[\rho']\right\} = 0 \qquad (1.13)$$

where, ρ' is some approximation to exact ground state density ρ, normalized to total number of electrons, $N[\rho']=N$. The Lagrangian multiplier μ associated with Eq. (1.13) is the derivative $w.r.t.$ the value of constraint, N, of the minimum of the functional $E_v[\rho']$
[32]

$$\mu = \left(\frac{\partial E}{\partial N}\right)_{v(r)} \tag{1.14}$$

In analogy to thermodynamic chemical potential

$$\mu_{therm} = \left(\frac{\partial G}{\partial n}\right)_{P,T} \tag{1.15}$$

where, G represents Gibb's free energy and n the number of moles, μ is commonly termed as electronic chemical potential and measures the escaping tendency of the electrons from the molecule. Based on Iczkowski and Margrave[33] formulation of electronegativity formula $\chi = -\left(\frac{\partial E}{\partial n}\right)_{n=0}$, where n=N-Z, Z being atomic number of the nucleus; they made identification of this abstract Lagrange multiplier as

$$\chi = -\mu = -\left(\frac{\partial E}{\partial N}\right)_{v(r)} \tag{1.16}$$

The Mulliken's definition of electronegativity, which is given by,

$$\chi_M = \frac{I+A}{2} \tag{1.17}$$

where, I and A are the ionization potential and electron affinity respectively, which are nothing but the finite difference approximation to the Eq. (1.16)

Parr and Pearson[3] demonstrated the importance of second derivative of the energy with respect to number of electrons and termed it as absolute hardness (η).

$$\eta = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_{v(r)} = \frac{1}{2}\left(\frac{\partial \mu}{\partial N}\right)_{v(r)} \tag{1.18}$$

From Eq. (1.18), chemical hardness can be interpreted as resistance of chemical potential to the change in number of electrons. The operational definition of the same

was provided by the finite difference approximation to the above equation and can be expressed as,

$$\eta = \frac{I - A}{2} \qquad (1.19)$$

They further theoretically deduced the HSAB principle (section 1-IV(A)), later, using concept of hardness and electronegativity equalization principle.[34]

Another molecular property, softness (S), is also defined as,

$$S = \frac{1}{2\eta} = \left(\frac{\partial N}{\partial \mu}\right)_{v(r)} \qquad (1.20)$$

In view of hardness-polarizability link in Pearson's original and defining approach to the introduction of HSAB principles, it is worth mentioning that softness is the indicator of polarizability of the system. Various studies relating softness to polarizability strengthen this view (sec. 1-V).

Recently Parr, Von Szentpaly and Liu, introduced another reactivity descriptor viz. electrophilicity index by combining electronegativity and hardness. To propose an electrophilicity index, Parr *et al.* [22] assumed electrophile immersed in a sea of free electron gas at zero temperature and zero chemical potential. For calculation of change in binding energy due to partial electron transfer from the sea to the electrophile, energy change to the second order at constant external potential is considered.

$$\Delta E = \mu \Delta N + \frac{1}{2}\eta \Delta N^2 \qquad (1.21)$$

The saturation point of the ligand for electron inflow was characterized by putting,

$$\frac{\Delta E}{\Delta N} = 0 \qquad (1.22)$$

Combining Eqs. (1.21) and (1.22) yields the amount of partial electron transfer as,

$$\Delta N = -\frac{\mu}{\eta} \qquad (1.23)$$

and corresponding stabilization energy as,

$$\Delta E = -\frac{\mu^2}{2\eta} \qquad (1.24)$$

The quantity μ^2/η, is described as electrophilicity index (W) and considered to be a measure of electrophilicity of the ligand. In analogy to the equation of power ($W = V^2/R$) in classical electricity, it is also considered to be measure of "electrophilic power". Under finite difference approximation, electrophilicity index can be written as,

$$W = \frac{\mu^2}{2\eta} = \frac{(I+A)^2}{8(I-A)} \qquad (1.25)$$

The above descriptors can also be related to frontier orbital energies by making use of Koopman's approximation within the molecular orbital theory, where in I and A can be expressed in terms of HOMO and LUMO energies.[13(b), 35,36]

$$I = -\varepsilon_{HOMO} \qquad (1.26a)$$

$$A = -\varepsilon_{LUMO} \qquad (1.26b)$$

Since, all these parameters (chemical potential, hardness, softness and electrophilicity index) are obtained by averaging over molecular space these are called GRDs. Though, they are quite capable of describing overall reactivity of the system, they do not have any information about the nature of active atoms or group that constitutes the molecule.

1-III(B). Local Reactivity Descriptors

The most chemical reactions are generally associated with the expressed properties of the atoms or groups of atoms in the molecule and not to the molecule itself. Inability of the GRDs in identifying the reactive site in the molecule that has high

proclivity to undergo chemical reaction is a matter of concern for understanding of reactivity in such systems. Concerning chemical reactivity, an important aspect is how the charge or density fluctuations in chemical systems affect, and are related to the observed reactivity trends. Since the electron density distribution, $\rho(r)$, contains all of the information on the system in its ground state, it is thought that the chemical reactivity should be reflected in its sensitivity to perturbations. These facts have necessitated or demanded the proposition of some descriptors that are local or non-local in nature, so called LRDs.

The concept of using electron density for description of reactivity was initiated by Fukui [1(a)-(b)], when he introduced the role of frontier orbitals in describing reactivity of aromatic systems leading to three principles. He proposed that the site of attack is described by the highest electron density of two electrons in the frontier-orbitals. For electrophilic attack, the frontier orbitals are considered to be HOMO, for nucleophilic attack, the frontier orbitals are considered to be LUMO, whereas, for radical attack, one electron is assumed to be in HOMO and other in LUMO.

Parr and collaborators [2-5, 9] showed how Fukui's frontier-orbitals concept could be grounded in DFT. They used ensemble formulation of DFT to introduce the expectation value N of total electron number as continuous variable and defined FFs (or the frontier function) as,

$$f(r) = \left(\frac{\delta \mu}{\delta v(r)} \right)_N = \left(\frac{\partial \rho(r)}{\partial N} \right)_{v(r)} \tag{1.27}$$

Considering the Fundamental equations for change in energy,

$$dE = \mu dN + \int \rho(\vec{r}) dv(\vec{r}) dr \tag{1.28a}$$

$$d\mu = 2\eta dN + \int f(\vec{r})dv(\vec{r})dr \tag{1.28b}$$

The quantity dμ in Eq. (1.28) measures the extent of the reaction. The preferred direction is the one for which the initial |dμ| for the species is a maximum. The first term on the right side of Eq (1.28b) involves only global quantities and at large distances, is ordinarily less direction sensitive than the second term. The preferred direction is the one with largest f(r) at the reaction site.[4]

Like E(N), ρ(r) being function of N, also has discontinuity at integral N[37]; Eq. (1.27) in fact provides two reaction indices as left- and right-hand-side derivatives, to be considered at a given number of electrons, $N = N_0$.

$$f^-(r) = \left(\frac{\partial \rho(r)}{\partial N}\right)^-_{v(r)} \tag{1.29a}$$

for an electrophilic attack, provoking an electron increase in the system, and

$$f^+(r) = \left(\frac{\partial \rho(r)}{\partial N}\right)^+_{v(r)} \tag{1.29b}$$

for a nucleophilic attack, provoking an electron decrease in the system.

Under the frozen core approximation $d\rho = d\rho_{valence}$ in each case and therefore governing electrophilic attack,

$$f^-(r) = \rho_{HOMO} \tag{1.30a}$$

governing nucleophilic attack,

$$f^+(r) = \rho_{LUMO} \tag{1.30b}$$

and the third function governing radical attack, as arithmetic mean of the above two.

$$f^0(r) = \frac{1}{2}\left(\rho_{HOMO} + \rho_{LUMO}\right) \tag{1.30c}$$

These are nothing but the rules of the classical frontier orbital theory.

FF is normalized to unity,

$$\int f^a(r)dr = 1 \quad \forall a = +, -, 0 \tag{1.31}$$

Thus, FF contains the relative information about different regions in a given molecule; it doesn't describe the local intensity of the response. When comparing across different molecules, local softness s(r), defined by Yang and Parr[5] turns out to describe the intensity of the response:

$$s(r) = \left(\frac{\partial \rho(r)}{\partial \mu}\right)_{v(r)} \tag{1.32}$$

s(r) is local analogous to global softness S (see Eq. 1.20). By applying chain rule, local softness can be written as the product of total softness and the FF,

$$s(r) = \left(\frac{\partial \rho(r)}{\partial \mu}\right)_{v(r)} = \left(\frac{\partial \rho(r)}{\partial N}\right)_{v(r)}\left(\frac{\partial N}{\partial \mu}\right)_{v(r)} = f(r)S \tag{1.33}$$

indicating that f(r) redistributes the global softness among different parts of molecules, and that s(r) integrates to S. The above equation can also be written as following to explicitly describe the electrophilicity, nucleophilicity or radical type attack.

$$s^a(r) = f^a(r)S \quad \forall a = +, -, 0 \tag{1.34}$$

$$S = \int s^a(r)dr \quad \forall a = +, -, 0 \tag{1.35}$$

Ghosh, Berkowitz and Parr [6-8] also defined the local hardness η(r).

$$2\eta(r) = \frac{1}{N}\int \frac{\delta^2 F}{\delta\rho(r)\delta\rho(r')}\rho(r')dr' = \left(\frac{\partial \mu}{\partial \rho(r)}\right)_{v(r)} \tag{1.36}$$

$$\eta = \int \eta(r)f(r)dr \tag{1.37}$$

Berokowitz and Parr [8] have given a derivation of local softness that reveals its relation to its reciprocal property, local hardness. They established a coherent quantitative language of hardness and softness on hierarchy of local and non local functions. Non local functions are called kernels.

$$\eta(r,r') = \frac{\delta^2 F}{\delta\rho(r)\delta\rho(r')} = -\frac{\delta u(r)}{\delta\rho(r')} = -\frac{\delta u(r')}{\delta\rho(r)} \tag{1.38}$$

$$s(r,r') = -\frac{\delta\rho(r)}{\delta u(r')} = -\frac{\delta\rho(r')}{\delta u(r)} \tag{1.39}$$

where $\eta(r,r')$ and $s(r,r')$ are hardness and softness kernels respectively. u(r) is the modified potential, given by,

$$u(r) = v(r) - \mu \tag{1.40}$$

The hardness and softness kernels are reciprocal to each other in the sense that,

$$\int s(r,r'')\eta(r'',r')dr'' = \delta(r-r') \tag{1.41}$$

Local softness can be obtained by integrating over softness kernel over one of the variables. Local hardness is difficult to define unequivocally, in terms of hardness kernels.[7,38,39]. The most convenient form is given by Harbola [38].

$$\eta(r) = \int \eta(r,r')f(r')dr' \tag{1.42}$$

It is now easy to interpret that,

$$\int s(r)\eta(r) = 1 \tag{1.43}$$

Chattaraj et al. [23] provided a local descriptor viz. "philicity", w(r) that redistributes the global philicity (W). w(r) integrates to global philicity. (Discussed later)

$$w(r) = Wf(r) \tag{1.45}$$

1-III(B.1). Atom Condensed Local Descriptors

The formal definition of the FF as introduced by Parr and Yang, [4] is a function of position r in the given molecular space, varying from one position to another. By plotting these functions one can get idea about the reactive centers. However, to describe reactivity quantitatively, with reference to atomic centers, is difficult to interpret. Hence, it is necessary, to condense the values of f(r) and s(r) around each atomic site into a single value that characterizes the atomic contribution in molecule to describe the site selectivity or site reactivity of an atom in a molecule. Yang and Mortier [18] introduced Atom condensed FFs, based on the idea of electronic population over atomic regions, similar to procedure followed in population analysis technique.

$$f_A^+ = q_{A,N_0+1} - q_{A,N_0} \tag{1.46a}$$

$$f_A^- = q_{A,N_0} - q_{A,N_0-1} \tag{1.46b}$$

$$f_A^0 = (q_{A,N_0+1} - q_{A,N_0-1})/2 \tag{1.46c}$$

where, $q_{A,N}$ denotes the electronic population of atom A of a system with N-electrons. They used Mulliken's population scheme[40] to describe the reactivity associated with the respective atoms. Other population schemes, such as, Löwdin population[41], natural population analysis[42], Bader's atoms-in-molecules (AIM) partitioning method[43], the charges derived from molecular electrostatic potential[44] and electronegativity equalization methods,[45] are also employed for calculation of atom condensed FFs.

Using Eqs. (1.34) and (1.46(a)-(c)), various condensed local softnesses of an atom can be defined.

$$s_A^a = f_A^a S \quad \forall a = +,-,0 \tag{1.47}$$

where, +, - and 0 indicate electrophilicity, nucleophilicity and tendency for radical attack respectively.

Pal and co-workers, introduced concepts of "relative electrophilicity" (R.E.) and "relative nucleophilicity" (R.N.) [21]. These descriptors were shown to be reliable descriptors for intramolecular reactivity as they contain information about both electrophilic and nucleophilic character. They defined these descriptors as

$$R.E. = s_A^+ / s_A^- \tag{1.48a}$$

$$R.N. = s_A^- / s_A^+ \tag{1.48b}$$

Based on additive rule, $S = \Sigma s_A^+$ and Eq. (1.25), local electrophilicity (w_A^+) was introduced

$$W = \frac{\mu^2}{2\eta} = \frac{\mu^2}{2} S = \frac{\mu^2}{2} \sum s_A^+ = \sum w_A \tag{1.49}$$

From this, Perez et al. [46] proposed a regional electrophilicity power condensed value on atom A.

$$w_A = \frac{\mu^2}{2} s_A^+ \tag{1.50}$$

Considering the existence of some function $w(r)$ that integrates to the global philicity (W), Chattaraj and co-workers,[23] presented a generalized version of above equation through the resolution of the identity associated with FFs, as,

$$W = W \int f(r) = \int W f(r) = \int w(r) \tag{1.51}$$

They argued that w(r) contains information about both $f(r)$ and W (which in turn also provide information of chemical potential and softness), thereby, it is the most powerful concept of reactivity and selectivity when compared to other descriptors. This was, later

criticized by Roy and others by numerically testing the reliability of philicity.[47] Their argument is that the philicity index does not provide any extra reliability over other descriptors as the main contribution comes from FFs. Atom condensed philicity can be written as:

$$w_A{}^a = W f_A{}^a \qquad \forall a = +, -, 0 \tag{1.52}$$

1-IV. Principles

In this section, we will discuss some of the electronic structure principles based on DFT. In particular, these principles are based on definitions of both global and local descriptors of reactivity. We shall mainly discuss the HSAB principle and MHP.

1-IV(A). Hard Soft Acid Base principle (HSAB)

Pearson in his landmark paper, [13(c)] formulated HSAB principle on basis of experimental data. He classified the molecular systems in terms of the hard-soft acid-base in a general way as follows:

(a) Hard acid (acceptors or nucleophiles): High positive charge, low polarizability and small in size. e.g. H^+, Ca^{2+}, BF_3, etc.

(b) Soft acid: Low positive charge, high polarizability and larger in size e.g. Hg^{2+}, BH_3, I^+

(c) Hard base (donors or electrophiles): High electronegativity, difficult to oxidize and low polarizability. e.g. F^-, NH_3, OH^-

(d) Soft base: Low electronegativity, easily oxidizable and higher polarizability. e.g. H^-, I^-, C_2H_4, CN^-

HSAB principle says that there is an extra stabilization if hard acids bind to hard bases and soft acids bind to soft bases. This concept, which found its first applications in rationalizing inorganic stability constants, was shown to be useful even in organic chemistry.

Klopman attempted to give a theoretical basis for HSAB principle using the quantum mechanical theory based perturbation method.[48,49] He assumed that when two reactants approach each other, a mutual perturbation of the molecular orbitals of both reactants occurs and the resulting change in energy can be estimated from molecular orbital calculations. The total perturbation energy is produced by two distinct effects: (a) the neighboring effect, which accounts for the interaction due to the formation of an ion pair without any charge or electron transfer, and (b) the partial charge transfer usually accompanied by covalent bonding.

As said earlier, the Pearson's original formulation of HSAB lacks the sharp definitions of the hardness and softness. Parr and Pearson's introduction of hardness as second derivative of energy of atomic or molecular system with respect to number of electrons, paved the way for formal proof of HSAB principle.[3] They made use of the Taylor series energy expansion in terms of the number of electron (N) as a perturbation variable. Assuming the systems A and B are the interacting systems, the energy expression for each system is expressed as,

$$E_A = E_A^{\,o} + \mu_A (N_A - N_A^{\,o}) + \eta_A (N_A - N_A^{\,o})^2 + ... \tag{1.53a}$$

$$E_B = E_B^{\,o} + \mu_B (N_B - N_B^{\,o}) + \eta_B (N_B - N_B^{\,o})^2 + ... \tag{1.53b}$$

If one ignores all other effects, except, the second order, the total change in energy will have the form as,

$$\Delta E = (\mu_A - \mu_B)\Delta N + (\eta_A - \eta_B)\Delta N^2 \tag{1.54}$$

where, $\Delta N = N_B{}^o - N_B = N_A - N_A{}^o$ (1.55)

In a molecule μ_A and μ_B are equal. Thus ΔN is such that $\mu_A = \mu_A{}^o + 2\eta_A\Delta N = \mu_B$

$= \mu_B{}^o + 2\eta_B\Delta N$

or

$$\Delta N = \frac{\mu_B - \mu_A}{2(\eta_A + \eta_B)} \tag{1.56}$$

On substituting the expression for ΔN, the interaction energy can be expressed as,

$$\Delta E_{AB} = -\frac{(\mu_B - \mu_A)^2}{4(\eta_A + \eta_B)} \tag{1.57}$$

It can be observed from the Eq. (1.57), that the energy lowering results from electron transfer and the differences in electronegativity or chemical potential drive the electron transfer. This process is assumed to take place continuously till the equilibrium is attained and it is referred as the chemical potential or electronegativity equalization process. If both acid and base are soft, $(\eta_A + \eta_B)$ is a small number, and for a reasonable difference in electronegativity, ΔE is substantial and stabilizing. This explains the HSAB principle, in part: soft prefers soft. It does not explain, however, the hard-hard preference (large denominator).

Chattaraj, Lee, and Parr gave two proofs for HSAB principle.[15] [a] In the first proof, the interaction process between an acid A and a base B is dissected into two steps: a charge-transfer process, resulting in a common chemical potential at a fixed external potential, and a reshuffling process at a fixed chemical potential. While the energy

change transfer process is taken as provided by Eq. (1.57), MHP[50] was invoked in qualitative sense for reshuffling of charge at constant chemical potential.

If the above Eq. (1.57) is rewritten in terms of softness parameter, the expression for ΔE becomes,

$$\Delta E_{AB} = -\frac{(\Delta\mu)^2 S_A S_B}{2(S_A + S_B)}$$ (1.58)

This implies that for a given S_A, larger value of S_B is better. While MHP implies exactly reverse. Opposing tendencies in two steps are reconciled by compromise

$$S_A = S_B$$ (1.59)

In the second proof, one casts Eq. (1.57) into the form,

$$\Delta E_{AB} = \Delta\Omega_A + \Delta\Omega_B$$ (1.60)

introducing the grand potentials, Ω_A and Ω_B, of the interacting systems as the natural "thermodynamic" quantities for an atom, functional group, or any other sub-unit of the molecule due to their "open" nature. $\Delta\Omega_A$ is given as,

$$\Delta\Omega_A = \frac{(\mu_B - \mu_A)^2 \eta_A}{4(\eta_A + \eta_B)^2}$$ (1.61)

with an analogous expression for $\Delta\Omega_B$. For a given $\mu_A - \mu_B$ and η_B, minimization of $\Delta\Omega_A$ with respect to η_A yields

$$\eta_A = \eta_B$$ (1.62)

The same result is obtained when $\Delta\Omega_B$ is minimized with respect to η_B, for a given η_A, yielding HSAB principle.

If one considers the general molecular interaction case, where A interacts with B to give third species AB,

$$A + B \rightarrow AB$$
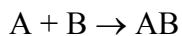
Energy change associated with the process can be written as,

$$\Delta E_{\text{int}} = E[\rho_{AB}] - E[\rho_A] - E[\rho_B]$$ (1.63)

where, $\rho_{AB}(r)$ is the electron density of the system AB at equilibrium and $\rho_A(r)$ and $\rho_B(r)$ are the electronic densities of the isolated systems.

Gazguez [39] tried to validate the HSAB principle based on the old assumption that the interaction can be divided into two steps. In the first step, when A and B are located far apart from each other, their chemical potentials, μ_A and μ_B, change to reach a common value of μ_{AB} at constant external potential. The energy change associated with this step can be written as,

$$\Delta E_v = \Delta E_v(A) + \Delta E_v(B)$$ (1.64)

where,

$$\Delta E_v(A) = E[\rho_A^*] - E[\rho_A^0]$$ (1.65)

and

$$\Delta E_v(B) = E[\rho_B^*] - E[\rho_B^0]$$ (1.66)

Here $\rho_A^*(r)$ corresponds to system A with v_A and μ_{AB} and $\rho_B^*(r)$ corresponds to system B with v_B and $\mu_{AB.}$

In the second step, A and B evolve towards the equilibrium state through changes in the electronic density of the global system AB produced by changes in the external potential v_{AB}. This step occurs under conditions of constant chemical potential, and can be expressed in the form,

$$\Delta E_\mu = E[\rho_{AB}] - E[\rho_{AB}^*]$$ (1.67)

where, $\rho_{AB}{}^*(r) = \rho_A{}^*(r)+\rho_B{}^*(r)$ is the electronic density of the system AB with $\mu_{AB,}$ when A and B are far away from each other. Adding Eqs. (1.64)–(1.68), one can find that,

$$\Delta E_{int} = \Delta E_v + \Delta E_\mu \tag{1.68}$$

expression for ΔE_v can be presented in the form as given by Eqs. (1.57) and (1.58).

$$\Delta E_v = -\frac{(\mu_B - \mu_A)^2}{4(\eta_A + \eta_B)} = -\frac{(\mu_B - \mu_A)^2}{2(S_A + S_B)} S_A S_B \tag{1.69}$$

Since, much of the work presented in the thesis is based on working at constant chemical potential, we will not go much into the details on discussion of ΔE_v. What is of our interest is in the step, which involves reshuffling of density at constant chemical potential. We shall now derive the expression of ΔE_μ..

1-IV(A.1). Expression for ΔE_μ [51]

From Hohenberg-Kohn Equation (Eq. 1.5) and its corresponding Euler-Lagrange equation (Eq. 1.12), one can write

$$E[\rho] = F[\rho] + \mu N - \int dr \frac{\delta F[\rho]}{\delta \rho(r)} \rho(r) \tag{1.70}$$

The energy difference between a ground state characterized by μ_i, $\rho_i(r)$, N_i, $v_i(r)$ and another ground state characterized by μ_f, $\rho_f(r)$, N_f, $v_f(r)$, may be expressed by, from the expression (1.70),

$$Let, \Delta E = E[\rho_f] - E[\rho_i] \tag{1.71}$$

$$\Delta E = N_f \mu_f - N_i \mu_i - F[\rho_f] - F[\rho_i] + \int \rho_i(r) \frac{\delta F}{\delta \rho(r)}\bigg|_{\rho_i(r)} + \int \rho_f(r) \frac{\delta F}{\delta \rho(r)}\bigg|_{\rho_f(r)} \tag{1.72}$$

Now, if one performs a Taylor series functional expansion of $F[\rho_f]$ around $F[\rho_i]$, and of $\delta F/\delta\rho(r)\,|\rho_f(r)$ around $\delta E/\delta\rho(r)|\rho_i(r)$, the above expression for ΔE can be written as,

$$\Delta E = \left(N_f \mu_f - N_i \mu_i\right) - \frac{1}{2}\iint dr dr' \eta_f(r,r')\rho_f(r)\rho_f(r) + \frac{1}{2}\iint dr dr' \eta(r,r')\rho_i(r)\rho_i(r')$$

(1.73)

where, the expression for $\eta(r,r')$ is used, and in the first integral $\eta_i(r,r')$ has been replaced by $\eta_f(r,r')$, and the higher order terms are neglected.

If electronic densities of anion and cation are approximated as renormalized N-electron system density, and FF under a finite difference approximation can be shown as $f(r) \approx \rho(r)$, one can relate the above integral to global hardness as defined in the Eqs. (1.36) and (1.37). Hence,

$$\Delta E \approx (N_f \mu_f - N_i \mu_i) - \frac{1}{2}N_f^2 \eta_f + \frac{1}{2}N_i^2 \eta_i$$

(1.74)

Now, if we assume that the total number of electrons are not changing, i.e. $N_i = N_f = N$ and if the two ground states have the same chemical potential, $\mu_i = \mu_f$, then Eq. (1.74) becomes,

$$\Delta E_\mu \approx -\frac{1}{2}N^2 \Delta\eta$$

(1.75)

from Eqs. (1.68), (1.69) and (1.75) [39]

$$\Delta E_{int} \approx -\frac{\left(\mu_B - \mu_A\right)^2}{2\left(S_A + S_B\right)}S_A S_B - \frac{1}{2}N^2 \Delta\eta$$

(1.76)

Here second term is actually manifestation of principle of maximum hardness. We will discuss this in detail in the next section.

Gazquez *et al.*[24] put forward another equation which is widely used to study HSAB and lays foundations of Local HSAB principle.

$$\Delta E_{AB} \approx -\frac{\left(\mu_B - \mu_A\right)^2}{2\left(S_A + S_B\right)} S_A S_B - \frac{1}{2}\frac{\lambda}{\left(S_A + S_B\right)} \quad (1.76b)$$

where, λ is constant related to effective number of valence electrons.

1-IV(A.2). Local HSAB Principle

Local version of HSAB was put forward by Mendez and Gazquez,[24(a)] in which A interacts with B via its kth atom and thus transforming Eq. (1.76b)

$$\Delta E_{AB,k} \approx -\frac{\left(\mu_B - \mu_A\right)^2}{2\left(S_A f_{Ak} + S_B\right)} S_A S_B f_{Ak} - \frac{1}{2}\frac{\lambda}{\left(S_A f_{Ak} + S_B\right)} \quad (1.77)$$

where, authors introduced FF f_{ak} for atom k in acid A. Further, if interaction from B is considered to be from lth atom of B. S_B can be replaced by $S_B f_{Bl}$, leading to the situation similar to HSAB principle.[52] Here, one infers that the interaction is more favored from the sites whose local softnesses are similar.

1-IV(B). The Maximum Hardness Principle

"Maximum hardness principle" (MHP) proposed by Pearson [13(b)] in 1987 has received considerable attention over the past few years.[53] The MHP states that there seems to be rule of nature, that molecules arrange themselves to be as hard as possible. This idea was supported by Parr, Zhou and co-workers,[54] by the series of studies on relationship between hardness and aromaticity of hydrocarbons. Parr and Chattaraj gave proof of MHP based on combination of fluctuation-dissipation theorem of statistical mechanics and DFT.[50] They have shown that the hardness of a system has maximum at

equilibrium nuclear configuration, under conditions of constant chemical potential and temperature. This proof rests on the assumption, that, all non-equilibrium states near the equilibrium can be generated by small perturbations of the equilibrium state. However, relaxation of these constraints seems to be permissible, and in particular, it has been found that MHP still holds even though the electronic chemical potential varies along the reaction coordinate.[51, 55-64] Chattaraj *et al.*[58(b)] compared the isomers HCN and HNC, and found a higher hardness for the more stable isomer (HCN), the μ values, however, not being identical. MHP has been numerically studied and its validity has been shown by several groups. In the period from 1992 to 1993, the directionality of inorganic reactions[15(c)] and the stability of metallic clusters (Li_n, n = 2-67)[65] were also found to obey the MHP. Datta has shown that the exchange reaction always went into the direction that produced the hardest molecule or the product with highest average hardness, where, μ and $v(r)$ are not constant. The variation of hardness along reaction path has been studied to validate maximum hardness criterion in the chemical reactions and this has been referred as "hardness profile". Datta has first studied the hardness profiles for the inversion of ammonia and the intra-molecular proton transfer in malonaldehyde.[57] From these hardness profiles, he observed that the profile goes through a minimum at the transition state. The maximum hardness criterion complements the minimum energy criterion for stability. Since a chemical species is most reactive at the transition state, its hardness value is minimum there, on the reaction profile, i.e., at the transition state a species becomes most soft. Although, the above observations have further validated MHP for a variety of cases such as the molecular inversion, internal rotation, rearrangement cases, etc. and for various types of simple

reaction, there are cases where the hardness does not pass through a minimum near or at the transition state. [66]

Pearson and Palke observed that the totally symmetric distortions do not show any sign of a maximum or minimum hardness near the equilibrium geometry and the hardness keeps increasing steadily as the nuclei approach each other.[56] However, the condition of constant chemical potential is observed for small asymmetric vibrations about a symmetric equilibrium position and this is in agreement with the formulation of Parr and Chattaraj.[50] Pal *et al.* also obtained similar results while testing the MHP using the highly correlated wave function method by considering the symmetric and asymmetric variations around the equilibrium geometry of water molecule.[59] These results confirm the Pearson and Palke's observations. Makov has further demonstrated that all the invariants (e.g., energy, chemical potential, hardness) will be extremal with respect to asymmetric variations about a symmetric nuclear configuration.[67] This has been derived by employing group theoretical symmetry arguments within the framework of "pure-state" DFT. The above statement holds to be true whether the asymmetric distortions are carried out around symmetric equilibrium or non-equilibrium geometries. It should be noted that the symmetry principles derived by Makov, do not determine by themselves, whether such extrema will be minima or maxima.

Although many groups have studied MHP, the principle still lacks from the exact formal proof and it is still not well understood. Sebastian questioned the validity of the formal statistical-mechanical proof [68(a)]. He however, later reported errors in his numerical counter examples. [68(b)] Despite all criticisms, it has generally been observed

that the variation of hardness along a chemical reaction is found to be useful in understanding the chemical reactions.

Recently, Liu and Parr have demonstrated the MHP with several constraints and it states that at fixed electron number, external potential and chemical potential, the global hardness should go to a maximum as the total energy approaches a minimum.[69] Using functional expansion methods up to second order, they obtained the following expression for $E[N,v]$,

$$E[N,v] = N\mu - \frac{1}{2}N^2\eta + \int v(r)[\rho(r) - Nf(r)]dr - \frac{1}{2}\iint \rho(r)\rho(r')\omega(r,r')drdr' \qquad (1.78)$$

connecting the total energy, chemical potential, hardness, FF and response function $\omega(r,r')$. If one neglects the contribution from last two terms, one finds that larger the hardness, lower is the energy.

In the previous section we discussed derivation of approximated form of energy change at constant chemical potential. On looking at Eq. 1.75, since $\eta > 0$, implies that $\Delta E > 0$ when $\Delta\eta < 0$ and $\Delta E < 0$ when $\Delta\eta > 0$. Thus, one can see that when a system evolves toward a state of greater hardness ($\Delta\eta > 0$), under conditions of constant chemical potential, its stability increases. Thus, this relation also leads to the MHP.

1-V. Polarizability and Softness link

Since softness and polarizability are often assumed to be linked, there have been lots of studies on this subject. The link between hardness and polarizability first appeared in the works of Pearson when he presented his HSAB approach.[13(c)] There have been extensive studies for describing this link. The relationship between

Polarizability and softness was first put forward by Politzer in 1987.[70] Vela and Gazquez used local approximation to softness kernel to derive expression for linear response functions.[71] He made use of exact Berkowitz-Parr relation,[8]

$$\left(\frac{\delta \rho(r)}{\delta v(r')} \right)_N = -s(r,r') + Sf(r)f(r')$$

(1.79)

and then made an approximation to softness kernel as,

$$s(r,r') \approx Sf(r)\delta(r-r')$$

(1.80)

which led him to express energy change up to second order in $\delta v(r)$ as,

$$dE = \rho(r)\delta v(r)dr + \frac{1}{2} S\left[\left(\int f(r)\delta v(r)dr \right)^2 - \int f(r)(\delta v(r))^2 dr \right]$$

(1.81)

When static polarizability is considered, the change in external potential is given by,

$$\delta v(r) = \vec{r} \cdot \hat{\in}$$

(1.82)

where, $\hat{\in}$ represents a uniform electric field of unit amplitude. The second order correction to the energy in this case, is given by,

$$E^{(2)} = -\frac{1}{2} \hat{\in} \cdot \alpha \cdot \hat{\in}$$

(1.83)

where, α is polarizability tensor.

One finally ends up with,

$$\alpha = -S\left[\int \left(rf(r)dr \right)^2 - \int rrf(r)dr \right]$$

(1.84)

for atomic systems, this equation, can be further simplified to,

$$\alpha = S\int f(r)\cos\theta dr = \int s(r)\cos\theta dr$$

(1.85)

The above expression indicates the polarizability to be proportional to global softness. This also indicates the link between local softness and local polarizability. This is further strengthened by similarities in local polarizability plots of Stott and Zaremba and the atomic FFs.[72]

In the framework of molecules absorbed in cages, Langenaeker, De Proft, Tielens, and Geerlings also derived similar expressions,[73] also relating softness and polarizability. Correlations between the polarizability and S^3 were also presented on a less rigorous basis by various authors. For atomic systems, Nagle demonstrated a proportionality between the softness and $(\alpha/n)^{1/3}$, where, n represents the number of valence electrons.[74] Ghanty and Ghosh found, on an empirical basis, that the softness linearly correlates with $\alpha^{1/3}$ for a number of atoms and sodium clusters.[75] In a study of the relationship between the atomic softness and the electric dipole polarizability, Fuentealba and Reyes concluded that, in the case of both atoms and ions with one or two valence electrons, a good relationship exists between the latter property and the third power of the softness.[76] Hatti and Datta derived following expression using classical equations of energy to charge a conducting sphere,[77]

$$\eta = \frac{1}{2}\left(\frac{C}{\alpha}\right)^{\frac{1}{3}} \tag{1.86}$$

where, the value of C yields to closest reproduction of experimental hardness. This was further strengthened by analytic derivation by Simon-Manso and Fuentealba using local functional model for hardness kernel.[78]

Pal and co-workers have studied the variation of polarizability and hardness with bond distortion in polyatomic systems.[67] They demonstrated the linear relation

between η and $\alpha^{1/3}$. On the basis of inverse relationship between hardness and polarizability, minimum polarizability principle (MPP) has been postulated to complement MHP[61(a),79] This will be discussed later in chapter 5.

1-VI. Applicability of Reactivity descriptors

The objective for introduction of these reactivity descriptors is to quantify and analyze the conceptually important quantities such as chemical reactivity, selectivity and the stability of molecular systems from general theoretical view. The numerous works in terms of monographs and reviews in this field, brings out the utility of these descriptors in generalizing the chemical reactivity within the framework of DFT.[2, 12, 13, 28, 80-86] Based on proposition that both hardness and aromaticity are measures of high stability and low reactivity, Zhou, Parr and Garst put forward the absolute and relative hardness as a measure of aromaticity. [54] Parr and co-workers have successfully correlated resonance energy per Π electron, which is conventional valence-bond measure of aromaticity, with absolute hardness or relative hardness. [54(a)] It has been shown that in electrophilic substitution reactions, the change in the hardness from reactant to the transition state, is the measure of activation energy of the system. They also argued that the absolute hardness is generally the most useful quantitative index for marking the closing of electronic shells and the closing of shells can be seen as consequence of MHP; the hardness of fully filled s- shells and half filled p- shells are seen to be local minima. Hardness has been shown as successful candidate in predicting the stability of different types of metal clusters. [87, 88]

As we have already discussed earlier in section 1-III(B) about the information contained in *f(r)* and *s(r)*, these are extensively used to study intramolecular reactivity from local perspective. [12, 86, 89] Langenaeker et [90] all have shown that more reliable reactivity order for intermolecular reactivity can be obtained by making use of local hardness, rather than FFs or local softness. Intermolecular interactions being charge controlled (hard-hard) interactions, are therefore, better described by hardness related descriptors, while the intramolecular interactions, being covalent, are better described by orbital related descriptors (like FF and s(r)). [86, 89]

Based on local HSAB principle, interpretation of orientation in organic reactions has also been studied in detail by various groups. [12, 84, 86] LRDs have been reasonably successful in interpreting both regio-selectivity and mechanism of the Diels-Alder reactions. [62, 86, 91-95] In addition these have been extensively applied for problems of regio-selection in substituted benzynes and hexarynes and α,β- unsaturated aldehydes and ketones; and the nucleophilic and electrophilic substitution reactions of mono substituted benzenes. [17, 90, 96-103] Recently, region-slelectivity in fullerenes chemistry has been adequately rationalized by means of local softness. [97] The local hardness, in one or another approximate form, has also been studied on inter-molecular reactivity sequences, acidity of substituted acetic acids, hydrides, zeolites, alkyl alcohols and reactivity of mono-substituted benzenes. [90, 98, 99]

There have been reported cases, where, these descriptors have failed in describing the experimentally observed reactivity trends. [106-108] Study by Mineva *et al.* has claimed that orbital FFs do not provide correct reactivity pattern for protonation sites of aniline in gas phase. [66(d)] Roy *et al.* have reported some mismatches for α,β-

unsaturated ketones on basis of local softness and FFs.[21] They proposed relative electrophilicity and relative nucleophilicity as a more reliable descriptors over the condensed FFs.[21, 108, 109] Krishnamurty *et al.* studied intermolecular reactivity using concept of group softness, where, the group consists of reacting atoms and nearest neighbors of that atom.[107]

Contreas *et al.* [46,110] examined the usefulness of philicity in predicting region-selective isomers in Diels-Alder reaction. Importance of philicity in describing global electrophilicity has been also discussed by few authors.   Numerically, philicity has been tested to perform better than FFs in describing intermolecular reactivity.

As we have seen that there has been considerable success in describing the reactivity of the simple organic molecules, using the reactivity descriptors, the applicability of these descriptors has also been extended to more complex systems like zeolites. The acidity and basicity of different sites in zeolites lattice are the two important properties that determine the catalytic activity of zeolite. These properties have been extensively studied using these LRDs. [108,111-114] Recently, the influence of changes in the average framework electronegativity, (by the variations in the composition of the zeolites or by the isomorphous substitution of Si and Al atoms by other atoms), on the acidity of the bridging hydroxyl groups has been investigated using the reactivity descriptors by Geerlings *et al.*, Pal and co-workers, Deka *et al.* and Chatterjee *et al.*[108, 109, 112, 114]

In addition to ground state description of reactivity, Chattaraj and co-workers also focused on extending the scope of these conceptual DFT tools of ground state to exited state.[116] These studies have led to significant understanding of excited state

chemistry. They showed that hardness values for excited stated are lower than those for the ground state. On the other hand, the surface plots of local quantities FFs, charge density etc. show increase in reactivity for the excited states. They also revealed the linear relation between the $\alpha^{1/3}$ and the softness of the system even for the excited states.

1-VII. Conceptual DFT at work

The most important aspect in the application of conceptual DFT has been the calculation of the density. The density may be derived from basic DFT as well as wavefunction based techniques as described in scheme 2. This point should be stressed that in early 1990s the assessment of DFT has not been performed up to the level of wavefunction based techniques, leading to uncertainty in testing the concepts using the DFT computational techniques that themselves have not been sufficiently tested. Though in the later years, DFT methods using different hybrid functionals have led to the extensive testing yielding sufficient basis for applying purely DFT. However, with the many exchange correlation functionals (like B3LYP, SLYP, GVWN, PBEVWN, etc. to name a few) available today, adds to the confusion in choosing the correct functional for the study as some of these functionals suit evaluation of some kind of properties and others for other kinds. DFT has not been standardized till now despite considerable success in testing of the functionals to reproduce similar accuracy as that of wave function based techniques. In this thesis, we have used second order Moller-Plesset (MP2) densities for evaluation of various descriptors.
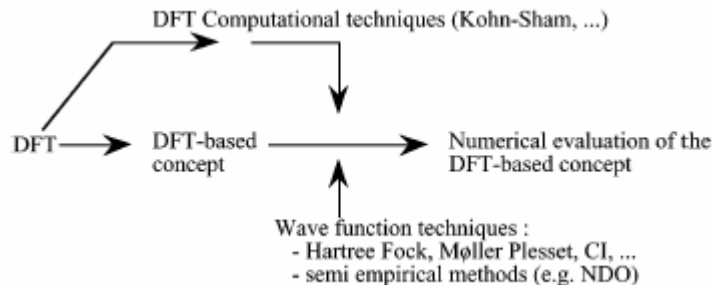
Scheme 1.2: Conceptual DFT at work [12(b)]

1-VIII. Organization of the thesis

The thesis is focused on analysis of some aspects of the density reactivity descriptors. In addition, the thesis deals with the formulation of new concepts under the framework of DFT based concepts. We also test these new concepts using *ab-initio* calculations to validate our prognosis.

In chapter 2, we study the separability of the LRDs. We present the analytical results for the same. We study size dependence of LRD in two cases, viz. *AB* type of complex and Dimer A_2. We show that in the non-interacting regime, the Condensed FF, local softness and local philicity of dimer separate out as half of the monomer values, while relative electrophilicity and relative nucleophilicity of dimer approach its corresponding monomer values. For AB type complex, the non-interacting values of the LRD approach those of the fragmented species for complex anion or cation respectively.

In chapter 3, we verify our hypothesis regarding the separability of LRDs (presented in chapter 2) through *ab initio* calculations. For *AB* type complex, we

study $BXX'X''NH_3$ (X, X', X'' = H, F), while for A_2 type complex, we study dimer of BH_3NH_3. We discuss the behavior of LRDs along the reaction path during complexation.

In chapter 4, we present a first-principle theory of interaction induced shifts in the O-H stretching frequency in clusters. It is well-known, that because of the elongation of the OH bond due to hydrogen bonding, the O-H frequencies show red shift with respect to average symmetric and asymmetric stretch. We propose two new descriptors, viz. Normalized-Atom-Condensed-Fukui-Functions (NFF) and Bond Deformation Kernel (BDK). We extend their applicability to study OH frequency shifts in the Fluoride-ion water clusters. We show that the BDK provides microscopic description of the bond elongation in the systems, where, local polarization effects are quite important. BDK correlates well with the corresponding shifts in OH stretching frequencies obtained by normal mode analysis.

Though, the effect of external electric field has been studied by various authors on the stability of chemical species, there have been very few studies on the effect of external magnetic field. In chapter 5, we propose and also verify through *ab initio* calculations, a new electronic structure principle, viz. the minimum magnetizability principle (MMP), to extend the domain of applicability of the conceptual DFT in explaining the magnetic interactions and magnetochemistry. The principle states that, "A stable configuration/conformation of a molecule or a favorable chemical process is associated with a minimum value of the magnetizability". In order to verify our prognosis, we study the asymmetric and symmetric stretching of H_2O.

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$Chapter$-2

Separability of Local Reactivity Descriptors

2-I. Introduction

Separability has a special significance in quantum mechanics. If one considers a quantum system composed of N monomers, in absence of entanglement i.e. in the absence of any quantum correlations between the subsystems, the state is called separable. Physically, it is clear that the energy of such system will be N times the energy of the monomer. An approximation scheme for calculating energy of such a system that has this property is said to be size-consistent.[1,2] In electronic structure calculations, size consistency plays an important role. Imagine, for instance, a system is broken into many fragments. The computation methods must be size-consistent to describe the breakup of system into the fragments. Hartree-Fock, full configuration-interactions (CI), Perturbation theory and coupled-cluster methods are size consistent methods while truncated CI is not size consistent.[2-4]

Though it is a priori clear that energies of non-interacting fragments are additive to describe the total energy of the system and the electronic densities of the fragments should separate out, it is not clear what happens to the Local Reactivity

Descriptors (LRDs)[5] (see sec. 1-III(B)). Earlier, Pal and co-workers had discussed the evaluation of chemical potential and hardness at the non-interacting limit.[6] In this chapter, we discuss the size-dependence of LRDs. The central quantity of interest among the local descriptors is the Fukui-function (FF). Based on the separability of FFs we will discuss the behavior of some other local descriptors. In the next section, we present a brief theoretical background defining the local descriptors and how these have been used in the study of reactivity and selectivity. In section 2-III, the separability problem of local descriptors will be studied. The standard finite difference forms, as well as, the condensed values in these standard forms will be discussed. The conclusions of the study are presented in section 2-IV.

2-II. Theoretical Background

In the previous chapter, the detailed account on reactivity descriptors has already been presented. However, a brief summary of reactivity descriptors would be helpful in exploring these descriptors for their size dependence.

According to Hohenberg-Kohn (HK) theorem, ground state energy of atom or molecule is written as a function of electron density (ρ).[7]

$$E[\rho] = \int \rho(r)v(r)dr + F_{HK}[\rho] \tag{2.1}$$

With

$$F_{HK}[\rho] = T[\rho] + V_{ee}[\rho] \tag{2.2}$$

Where $v(r)$ is external potential and F_{HK} is universal Hohenberg-Kohn functional comprising of electronic kinetic energy functional, $T[\rho]$ and the electron-electron interaction functional, $V[\rho]$.

The first and second partial derivatives of $E[\rho]$ with respect to the number of electrons, N, under the constant external potential $v(r)$ are defined as the chemical potential (μ) and the global hardness (η) of the system, respectively.[8-10] The global softness (S) is the half inverse of the hardness. The global descriptor of hardness has been known as an indicator of overall stability of the system. It has been customary to use a finite difference approximation for the computation of μ and η[11]

$$\mu = -\frac{(I + A)}{2} \tag{2.3}$$

$$\eta = \frac{1}{2}(I - A) \tag{2.4}$$

The site-selectivity of a chemical system, cannot, however, be studied using the global descriptors of reactivity. For this, appropriate local descriptors need to be defined. An appropriate definition of local softness $s(r)$ is given by[12]

$$s(r) = \left(\frac{\partial \rho(r)}{\partial N}\right)_{v(r)} \left(\frac{\partial N}{\partial \mu}\right)_{v(r)}$$

$$= f(r)S \tag{2.5}$$

such that

$$\int s(r)d(r) = S \tag{2.6}$$

where, $f(r)$ is defined as the FF.[12] It can be interpreted (cf. the use of Maxwell's relation in this scheme) either as the change of the electron density $\rho(r)$ at each point r when the total number of electrons is changed or as the sensitivity of chemical potential of a system to an external perturbation at a particular point r.

$$f(r) = \left(\frac{\partial \rho(r)}{\partial N}\right)_{v(r)} = \left(\frac{\partial \mu}{\partial v(r)}\right)_{N} \tag{2.7}$$

The latter point of view, by far the most prominent in literature, faces the N-discontinuity problem of atoms and molecules,[13,14] leading to the introduction[12(a)] of both right- and left-hand-side derivatives, to be considered at a given number of electrons, $N = N_0$,

$$f^+(r) = \left(\frac{\partial \rho(r)}{\partial N}\right)^+_{v(r)} \tag{2.8}$$

for a nucleophilic attack provoking an electron increase in the system, and

$$f^-(r) = \left(\frac{\partial \rho(r)}{\partial N}\right)^-_{v(r)} \tag{2.9}$$

for an electrophilic attack provoking an electron decrease in the system.

The finite difference method, using the electron densities of N_0, N_0+1, N_0-1, one can define

$$f^+(r) \approx \rho_{N_0+1}(r) - \rho_{N_0}(r) \tag{2.10}$$

and

$$f^-(r) \approx \rho_{N_0}(r) - \rho_{N_0-1}(r) \tag{2.11}$$

A third function describing radical attack, $f^0(r)$, is then obtained as the arithmetic average of $f^+(r)$ and $f^-(r)$.

$$f^0(r) \approx \left(\rho_{N_0+1}(r) - \rho_{N_0-1}(r)\right)/2 \tag{2.12}$$

Atom condensed FFs were first introduced by Yang et al.[15], based on the idea of electronic population over atomic regions, similar to procedure followed in population analysis technique.[16] Combined with finite difference approximation, this yields working equations of the type

$$f_A^+ = q_{A,N_0+1} - q_{A,N_0}$$
$$f_A^- = q_{A,N_0} - q_{A,N_0-1} \qquad (2.13)$$
$$f_A^0 = (q_{A,N_0+1} - q_{A,N_0-1})/2$$

Where, $q_{A,N}$ denotes the electronic population of atom A of a system with N-electrons.

Using Eqs. (2.5) and (2.13), various condensed local softnesses of an atom can be defined.

$$s_A^a = f_A^a S \qquad \forall a = +, -, 0 \qquad (2.14)$$

where +, - and 0 indicate electrophilicity, nucleophilicity and tendency for radical attack respectively.

Several other reactivity descriptors have been proposed. 'Relative electrophilicity' (*R.E.*) and 'relative nucleophilicity' (*R.N.*) defined as (f^+ / f^-) and (f^- / f^+) respectively have been used successfully by Roy *et al.*[17] for describing intra-molecular reactivity. Attempts to use these for inter-molecular reactivity have also been made in recent years. Parr *et al.*[18] proposed a global philicity (*W*) as $\mu^2/2\eta$. Using this, Chattaraj *et al.*[19] proposed the existence of local philicity index *w(r)* as *Wf(r)*, such that, *w(r)* integrates to global *W*. The condensed philicity w_A^a in the definition is given by,

$$w_A^a = W f_A^a \qquad \forall a = +, -, 0 \qquad (2.15)$$

2-III. Separability of LRDs

2-III(A). Separability of FFs

First, we discuss the separation of FF, which is the most important quantity among the LRDs. We shall discuss two different types of systems viz. AB and dimer A_2.

2-III(A.1). Separability in AB type system

Let us consider a complex AB composed of two subsystems A and B, which dissociates into fragments A and B. Electron density $\rho^{AB}(r)$ at point r can be written as sum of electron densities of A and B.

$$\rho^{AB}(r) = \rho^{A}(r) + \rho^{B}(r) \tag{2.16}$$

where $\rho^{A}(r)$ is the density at r due to atom A. Similarly, $\rho^{B}(r)$ is the electron density at point r due to atom B.

From definition of FF in Eq. (2.7)

$$f_{AB}(r) = \left(\frac{\partial \rho^{AB}(r)}{\partial N}\right)_{v(r)} = \left(\frac{\partial \rho^{A}(r)}{\partial N}\right)_{v(r)} + \left(\frac{\partial \rho^{B}(r)}{\partial N}\right)_{v(r)} \tag{2.17a}$$

$$\neq f_{A}(r) + f_{B}(r) \tag{2.17b}$$

as $N = N_A + N_B$ where N_A is number of electrons in A and N_B is number of electrons in B. One can interpret $f_A(r)$ as the FF of atom A in the molecular complex AB at point r.

The inequality (2.17b) implies that, the FF of complex AB can not be expressed as sum of FF of the isolated fragments and hence FF is not size-extensive.

Let us assume that (N_0+1) electronic state of AB at the geometry of AB i.e. vertical (AB)⁻ fragments as :

(AB)⁻ ⟶ A⁻ + B
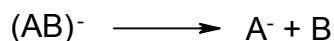
Therefore,

$$\rho^{AB}_{N_0+1}(r) = \rho^{A}_{N_0+1}(r) + \rho^{B}_{N_0}(r) \tag{2.18}$$

Using finite difference method for differentiation with respect to N at the non-interacting limit, we obtain,

$$f^+_{AB}(r) \approx \rho^{AB}_{N_0+1}(r) - \rho^{AB}_{N_0}(r)$$

$$= \left(\rho^A_{N_0+1}(r) + \rho^B_{N_0}(r)\right) - \left(\rho^A_{N_0}(r) + \rho^B_{N_0}(r)\right)$$

$$= \rho^A_{N_0+1}(r) - \rho^A_{N_0}(r)$$

$$= f^+_A(r) \qquad\qquad (2.19)$$

Assuming the vertical (N_0-1) electronic state of AB i.e. $(AB)^+$ to fragments as,

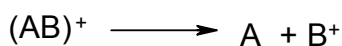$$(AB)^+ \longrightarrow A + B^+$$

$$\rho^{AB}_{N_0-1}(r) = \rho^A_{N_0}(r) + \rho^B_{N_0-1}(r) \qquad\qquad (2.20)$$

Again, using finite difference method of differentiation, we obtain at the non-interacting limit,

$$f^-_{AB}(r) \approx \rho^{AB}_{N_0}(r) - \rho^{AB}_{N_0-1}(r)$$

$$= \left(\rho^A_{N_0}(r) + \rho^B_{N_0}(r)\right) - \left(\rho^A_{N_0}(r) + \rho^B_{N_0-1}(r)\right)$$

$$= \rho^B_{N_0}(r) - \rho^B_{N_0-1}(r)$$

$$= f^-_B(r) \qquad\qquad (2.21)$$

The third function describing radical attack is $f^0_{AB}(r)$, which is the arithmetic average of $f^+_{AB}(r)$ and $f^-_{AB}(r)$, is then obtained at the non-interacting limit as,

$$f^0_{AB}(r) = \left(f^+_A(r) + f^-_B(r)\right)/2 \qquad\qquad (2.22)$$

From Eqs. (2.19) and (2.21), it can be seen that, as the complex dissociates, the FF of the complex reduces to the FF of individual fragment depending on whose cation or anion is more stable. Electrophilic FF of complex at dissociation is the electrophilic

FF of the fragment whose anion is more stable while the nucleophilic FF at dissociation is the nucleophilic FF of the fragment whose cation is more stable.

From Eqs. (2.19) and (2.21), the following can be seen

$$\sum_{k=1}^{a_k} f^{+}{}_{A_k,AB} + \sum_{k=1}^{b_k} f^{+}{}_{B_k,AB} = \sum_{k=1}^{a_k} f^{+}{}_{A_k} \tag{2.23a}$$

$$\sum_{k=1}^{a_k} f^{-}{}_{A_k,AB} + \sum_{k=1}^{b_k} f^{-}{}_{B_k,AB} = \sum_{k=1}^{b_k} f^{-}{}_{B_k} \tag{2.23b}$$

Where, A_k and B_k are k th atoms of fragments A and B, respectively and a_k and b_k are total number of atoms in systems A and B respectively.

One can thus write for condensed FF,

$$
\begin{aligned}
f^{+}{}_{A_k,AB} &= f^{+}{}_{A_k} \\
f^{+}{}_{B_k,AB} &= 0 \\
f^{-}{}_{A_k,AB} &= 0 \\
f^{-}{}_{B_k,AB} &= f^{-}{}_{B_k}
\end{aligned} \tag{2.24}
$$

Hence, as the complex dissociates, the condensed electrophilic FF of the atoms of the fragment for which, anion is formed, goes towards the condensed electrophilic FF of isolated fragment, while, for other atoms it goes towards zero. The condensed nucleophilic FF of the atoms of the fragment for which, cation is formed, goes towards the condensed nucleophilic FF of isolated fragment, while, for the atoms of the other fragment these values go to zero.

From Eq. 2.22, one can write the following

$$\sum_{k=1}^{a_k} f^{0}{}_{A_k,AB} + \sum_{k=1}^{b_k} f^{0}{}_{B_k,AB} = \frac{1}{2}\left[\sum_{k=1}^{a_k} f^{+}{}_{A_k} + \sum_{k=1}^{b_k} f^{-}{}_{B_k} \right] \tag{2.25}$$

One can conclude about the condensed FF for radical attack,

$$f^0{}_{A_k,AB} = f^+{}_{A_k}/2 \neq f^0{}_{A_k}$$
$$f^0{}_{B_k,AB} = f^-{}_{B_k}/2 \neq f^0{}_{B_k}$$

(2.26)

Though, the electrophilic and nucleophilic condensed FFs of complex at isolated limit separate out as those of isolated fragments depending on the fragmentation of cation or anion of the complex, it is interesting to note that the condensed FFs describing radical attack have different behavior.

2-III(A.2). Separability of FFs of dimer (A_2 type system)

Let us consider the non-interacting dimer A_2 of system A as a special case. The electron density $\rho_{A_2}(r)$ at point r can be written as

$$\rho^{A_2}(r) = \rho^{A(R_1)}(r) + \rho^{A(R_2)}(r)$$

(2.27)

where, $A(R_1)$ and $A(R_2)$ are the monomers A at different positions R_1 and R_2

Let us assume that (N_0+1) electronic state of A_2 at the geometry of A i.e. vertical A_2^- fragments as,

$$A_2^- \longrightarrow A(R_1)^- + A(R_2)$$

therefore,

$$\rho^{A_2}{}_{N_0+1}(r) = \rho^{A(R_1)}{}_{N_0+1}(r) + \rho^{A(R_2)}{}_{N_0}(r)$$

(2.28a)

since, $A(R_1)$ and $A(R_2)$ are indistinguishable, therefore there exist another degenerate pathway for the fragmentation.

$$A_2^- \longrightarrow A(R_1) + A(R_2)^-$$
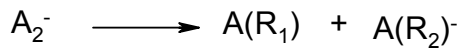
therefore,

$$\rho^{A_2}{}_{N_0+1}(r) = \rho^{A(R_1)}{}_{N_0}(r) + \rho^{A(R_2)}{}_{N_0+1}(r)$$ (2.28b)

we can now write them as an average.

$$\rho^{A_2}{}_{N_0+1}(r) = \frac{1}{2}\left([\rho^{A(R_1)}{}_{N_0+1}(r) + \rho^{A(R_2)}{}_{N_0}(r)] + [\rho^{A(R_1)}{}_{N_0}(r) + \rho^{A(R_2)}{}_{N_0+1}(r)] \right)$$

$$= \frac{1}{2}\left([\rho^{A(R_1)}{}_{N_0+1}(r) + \rho^{A(R_1)}{}_{N_0}(r)] + [\rho^{A(R_2)}{}_{N_0+1}(r) + \rho^{A(R_2)}{}_{N_0}(r)] \right)$$ (2.28c)

differentiating with respect to N, using finite difference method,

$$f^{+}{}_{A_2}(r) \approx \rho^{A_2}{}_{N_0+1}(r) - \rho^{A_2}{}_{N_0}(r)$$

$$= \frac{1}{2}\left([\rho^{A(R_1)}{}_{N_0+1}(r) + \rho^{A(R_1)}{}_{N_0}(r)] + [\rho^{A(R_2)}{}_{N_0+1}(r) + \rho^{A(R_2)}{}_{N_0}(r)] \right) - \left(\rho^{A(R_1)}(r) + \rho^{A(R_2)}(r) \right)$$

$$= \frac{1}{2}\left([\rho^{A(R_1)}{}_{N_0+1}(r) - \rho^{A(R_1)}{}_{N_0}(r)] + [\rho^{A(R_2)}{}_{N_0+1}(r) - \rho^{A(R_2)}{}_{N_0}(r)] \right)$$

$$= \frac{1}{2}\left(f^{+}{}_{A(R_1)}(r) + f^{+}{}_{A(R_2)}(r) \right)$$ (2.29)

on the similar lines, the following can be shown.

$$f^{-}{}_{A_2}(r) = \frac{1}{2}\left(f^{-}{}_{A(R_1)}(r) + f^{-}{}_{A(R_2)}(r) \right)$$ (2.30)

and,

$$f^{0}{}_{A_2}(r) = \frac{1}{2}\left(f^{+}{}_{A_2}(r) + f^{-}{}_{A_2}(r) \right)$$

$$= \frac{1}{2}\left[\frac{1}{2}\left(f^{+}{}_{A(R_1)}(r) + f^{+}{}_{A(R_2)}(r) \right) + \frac{1}{2}\left(f^{-}{}_{A(R_1)}(r) + f^{-}{}_{A(R_2)}(r) \right) \right]$$

$$= \frac{1}{2}\left[\frac{1}{2}\left(f^{+}{}_{A(R_1)}(r) + f^{-}{}_{A(R_1)}(r) \right) + \frac{1}{2}\left(f^{+}{}_{A(R_2)}(r) + f^{-}{}_{A(R_2)}(r) \right) \right]$$

$$= \frac{1}{2}\left(f^{0}{}_{A(R_1)}(r) + f^{0}{}_{A(R_2)}(r) \right)$$ (2.31)

According to Eqs. (2.29-2.31), it can be seen that the FF of the dimer at dissociation is nothing but the sum of the half of FFs of the monomer. The results can be generalized to the non-interacting associations of n systems of A i.e. A_n.

It would be interesting to study the behavior of the condensed FF of the atoms for the non interacting dimer. From Eqs. (2.29-2.31), the following can be written

$$\int f^a{}_{A_2}(r)d(r) = \frac{1}{2}\int \left(f^a{}_{A(R_1)}(r) + f^a{}_{A(R_2)}(r) \right)d^3r$$

$$= \frac{1}{2}\left(\int f^a{}_{A(R_1)}(r)d^3r + \int f^a{}_{A(R_2)}(r)d^3r \right) \qquad (2.32a)$$

$$= \int f^a{}_A(r)d^3r \qquad \forall a = +,-,0$$

The above integral can be written as the sum of atom condensed FFs. Since the system of A_2 consists of two identical systems A, every atom i, of monomer A, is represented twice in identical manner

$$\sum_{i=1}^{k} 2f^a{}_{A_i,A_2} = \sum_{i=1}^{k} f^a{}_{A_i,A} \qquad \forall a = +,-,0 \ \ and \ \ i = 1,2....k \qquad (2.32b)$$

where, k is number of atoms in the monomer. $f^a{}_{A_i,A_2}$ and $f^a{}_{A_i,A}$ denotes the atom condensed FF of atom A_i of dimer and monomer, respectively. The following can be deduced from Eq. 2.32b

$$f^a{}_{A_i,A_2} = f^a{}_{A_i,A}/2 \qquad \forall a = +,-,0 \ \ and \ \ i = 1,2....k \qquad (2.33)$$

It may be interesting to note that while the FF of non-interacting dimer, at a point r, is the sum of the half of FF of the monomer, the atom condensed FFs of the atoms of the non-interacting dimer would be half as that of the monomer. Similarly, for non-interacting A_n, the condensed FF of ith atom in a system A, is n times less than that of the atom k in isolated A itself.

$$f^a_{A_i,A_n} = f^a_{A_i,A}/n \quad \forall a = +,-,0 \ \ and \ \ i = 1,2....k \tag{2.34}$$

Let us analyze the behavior of some other reactivity descriptors. Since both electrophilic and nucleophilic condensed FF of an atom in a dimer are half as that of the corresponding atom in a monomer, by definition, *R.E.* and *R.N.* of the atoms of dimer, are same as those of the corresponding atoms of the monomer. From Eq. 2.33, *R.E.* and *R.N.* at isolated limit can be derived as,

$$R.E._{A_i,A_2} = \frac{\left(f^+_{A_i}/2\right)}{\left(f^-_{A_i}/2\right)} = R.E._{A_i,A} \ \ \forall \ \ i = 1,2....k$$

$$R.N._{A_i,A_2} = \frac{\left(f^-_{A_i}/2\right)}{\left(f^+_{A_i}/2\right)} = R.N._{A_i,A} \ \ \forall \ \ i = 1,2....k \tag{2.35}$$

Contrary to atom condensed FFs, it may be noted that the condensed *R.E.* and *R.N.* are size-intensive. Eqs. (2.33) and (2.34) resulted due to the artifact of summation of condensed FF being unity. However, the sum of the condensed *R.E.* and *R.N.* of all atoms in a system is not a fixed quantity Eq. (2.350 implies that the sum of *R.E.* or *R.N.* for non interacting dimer is twice that of the sum for all atoms of monomer. On the similar lines, results can be generalized for non interacting A_n.

2-III(B) Separability of other LRDs

Earlier, Pal *et al.* [6] had shown that for hetero diatomic molecules or in general a system composed of two sub-systems A and B, the hardness of system in the limit of separation of A and B, can be written as the difference of the ionization potential of more electropositive atom and the electron affinity of the electronegative atom and the chemical potential as average of ionization potential of more electropositive atom and

the electron affinity of the electronegative atom. On the other hand, for homo-diatomic molecules, hardness and chemical potential is same as that of isolated atoms[6]. Thus, we can write for total softness of AB and dimer of A,

$$S_{AB} = \frac{1}{I_B - A_A} \tag{2.36a}$$

$$S_{A_2} = S_A \tag{2.36b}$$

From Eqs. (2.14), (2.24), (2.26) and (2.36a), the expressions for local softness of the complex AB can be written. In particular, we write the expressions for condensed local softness as follows.

$$
\begin{aligned}
s^+_{A_k,AB} &= f^+_{A_k} S_{AB} \neq s^+_{A_k} \\
s^+_{B_k,AB} &= 0 \\
s^-_{A_k,AB} &= 0 \\
s^-_{B_k,AB} &= f^-_{B_k} S_{AB} \neq s^-_{B_k} \\
s^0_{A_k,AB} &= f^+_{A_k} S_{AB} / 2 \neq s^0_{A_k} \\
s^0_{B_k,AB} &= f^-_{B_k} S_{AB} / 2 \neq s^0_{B_k}
\end{aligned}
\tag{2.37}
$$

Though, the electrophilic and nucleophilic FFs at dissociation limits separate out as those of isolated fragments, depending on the fragmentation of cation or anion of complex fragments, it can be seen from the above relations that the local softness does not separate out as that of the fragment, because, the global descriptors have different behavior.

Similarly, using Eqs. (2.14), (2.33) and (2.36b), local softness of dimer can be derived as,

$$s^a_{A_k,A_2} = s^a_{A_k} / 2 \qquad \forall a = +,-,0 \tag{2.38}$$

From above relations, it can be seen that local softness of dimer does behave the same way as the atom condensed FFs behaves for the dimer. Both atom condensed FFs and local softness of the dimer becomes the half of the corresponding values of monomer for all three reactions *viz.* electrophilic, nucleophilic and radical. On the similar lines, local softness of atoms of A_n can shown to be the nth part of local softness of isolated monomer.

Along the similar lines as of (2.36a) and (2.36b) and using definition of global philicity $(W)^{18}$ the following can be written.

$$W_{AB} = \frac{(I_B + A_A)^2}{4(I_B - A_A)} \tag{2.39a}$$

$$W_{A_2} = W_A \tag{2.39b}$$

using Eqs. (2.15), (2.24), (2.26) and (2.39a) the following relations about local philicity of complex AB can be derived.

$$
\begin{aligned}
w^+_{A_k,AB} &= f^+_{A_k} W_{AB} \neq w^+_{A_k} \\
w^+_{B_k,AB} &= 0 \\
w^-_{A_k,AB} &= 0 \\
w^-_{B_k,AB} &= f^-_{B_k} W_{AB} \neq w^-_{B_k} \\
w^0_{A_k,AB} &= f^+_{A_k} W_{AB}/2 \neq w^0_{A_k} \\
w^0_{B_k,AB} &= f^-_{B_k} W_{AB}/2 \neq w^0_{B_k}
\end{aligned}
\tag{2.40}
$$

Similarly, by using Eqs. (2.15), (2.33) and (2.39b), local philicity of dimer can be derived as

$$
\begin{aligned}
w^a_{A_k,A_2} &= w^a_{A_k}/2 \quad \forall a = +,-,0 \\
w^a_{A_k,A_n} &= w^a_{A_k}/n \quad \forall a = +,-,0
\end{aligned}
\tag{2.41}
$$

On comparing relations (2.37), (2.38), (2.40) and (2.41) it can be seen that both local philicity and local softness behave in same manner.

It should be noted that throughout the paper anions or cations referred are the vertical anions or cations, since the definition of FF demands that external potential be kept constant while calculating the derivatives.

2-IV. Conclusions

In this chapter we studied the separation behavior of some LRDs that have been used extensively in the literature. These descriptors play very important role in describing the reactivity and site-selectivity in chemical reactions. In general, the local descriptors are not size-extensive. We showed, that, for a general system AB, the electrophilic FF at a point reduces to the FF of the more stable vertical anion in the regime of no interaction between AB. Similarly, the nucleophilic FF reduces to the FF of the more stable vertical cation in this non-interacting regime. The radical FF becomes the average of the above two, as expected. We also discussed the size-intensive nature of this general result for a dimer of A. Further, we explored the behavior of the condensed FF of atoms and show the difference in their behavior. Along similar lines, we studied separation of *R.E.*, *R.N.*, local softnesses and philicity.

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Chapter-3

Behavior of the Local Reactivity Descriptors during Complexation

3-I. Introduction

The study of molecular interactions has been a great challenge from the experimental and theoretical point of view.[1] Theoretical models in correlating the reactivity of molecular systems based on different quantities, like molecular orbital density, charge on atoms, bond order, etc. have been extensively used.[2] These models provide simpler theoretical perspectives compared to the more rigorous quantitative calculations of interaction energies and reactivity. In the chapter-1, we had presented a detailed overview on how the global and the local descriptors of reactivity provide for the interpretation of the preferred direction of a reaction. The LRDs in particular have been used to predict the specific site of interaction in a molecule.[3-5] Electrophilic and nucleophilic FFs have been used as indicators of reactivity for nucleophilic and electrophilic reagents, respectively.[6-8] More recently Parr and co-workers have defined a new concept of global philicity[9] from which, Chattaraj and co-workers have defined local philicity indices[10], which have been the subjects of recent studies.

It is well known that an atom with the highest condensed FF is the most reactive atom. The 'relative-electrophilicity' (*R.E.*) and 'relative-nucleophilicity' (*R.N.*), in general, are more reliable to characterize the most reactive atom in a molecule. For example, in BH_3, it is shown that the boron atom is the most electrophilic in character either from *R.E.* of boron atom or by simply looking at the electrophilic FF of atoms in the BH_3 molecule. Similarly, the nitrogen atom behaves as the most nucleophilic atom in ammonia. However, it is important to know what happens to these descriptors of atoms as the reaction takes place. The objective of this chapter is to study the relative changes in different descriptors as the reaction takes place. In the previous chapter we had discussed the separability of the LRDs and provided the analytical description for LRDs at the non-interacting limit based on fragmentation pattern of the complex. It is not a priori clear if the descriptors undergo monotonic change or go through an extremum during the reaction paths. We study the same using the example of interaction of BH_3 or fluorine substituted boranes and NH_3 as an example for AB type of complex. For A_2 type of system, we also study the behavior of LRDs during dimerisation of BH_3NH_3, which has been extensively studied by many groups owing to formation of unusual "dihydrogen bond".[11] In our example, we vary the distance between the reactive sites as the reactive species approach each other. We also verify the separability behavior (as discussed in chapter-2) of the LRDs using *ab initio* calculations.

The chapter has been organized as follows. In section 3-II, the methodology and computational details are presented. In section 3-III, we will present our results and discuss the reactivity behavior of atomic sites. In particular, we study the heterocomplex

aminobarones and dimer of BH_3NH_3. In section 3-IV, we will present the conclusions.

3-II. Methodology and Computational Details

(a) *Study of AB type of complex:* Geometry optimization of individual BH_3 and NH_3 as well as constrained optimization of BH_3NH_3, BH_2FNH_3, BHF_2NH_3 and BF_3NH_3 complexes were carried out. We have also computed the local descriptors for fluorine and hydrogen (H^B) connected to boron, and for hydrogen (H^N) connected to nitrogen and their average values are reported.

For obtaining limiting values of the FF of atoms of the complex, calculations were performed on isolated BH_3, BH_2F, BHF_2, BF_3 and NH_3 molecules.

(b) *Study of A_2 type of complex:* For simplicity, symmetrical (C_2) closed shell system $(BH_3NH_3)_2$ is chosen, which, on fragmentation, will also yield closed shell monomer BH_3NH_3. Geometry optimization of individual BH_3NH_3, as well as, constrained optimization of $(BH_3NH_3)_2$ were carried out. The average values are reported for dihydrogen bonded hydrogen connected to boron H^B_{bonded} and free hydrogen connected to nitrogen H^N_{free}.

For limiting values of the FF of atoms of the complex, results for equilibrium geometry of BH_3NH_3 molecules are used.

All calculations were done at *ab initio* Moller-Plesset perturbation (MP2) level using 6-31++G(d,p) basis set. Chemical potential and global softness were calculated via Eqs. (2.3) and (2.4). Condensed FFs were calculated via Eqs. (2.12) and (2.13) using Lowdin population analysis (LPA).[12(a),(b)] The calculations were performed using the GAMESS system of programs.[13]

3-III. Results and Discussions

3-III(A). Heterocomplex of boranes and ammonia.

Fig. 3.1 represents basic geometries of the complexes used for the calculations. Staggered conformations of $BXX'X''NH_3$ were used for study. Various structural parameters for equilibrium geometries are shown in Table 3.1. The equilibrium geometries of the complexes corresponding to r^0 are the unconstrained optimized geometries. The geometries for different B-N bond length were optimized by freezing B and N atoms while the optimum coordinates of other atoms were calculated. As the B-N distance increases, $BXX'X''$ flatten to planar geometry, while the NH_3 approaches its tetrahedron geometry. At small B-N distances B-X and N-H bonds elongate and XBX' and HNH angles decrease.
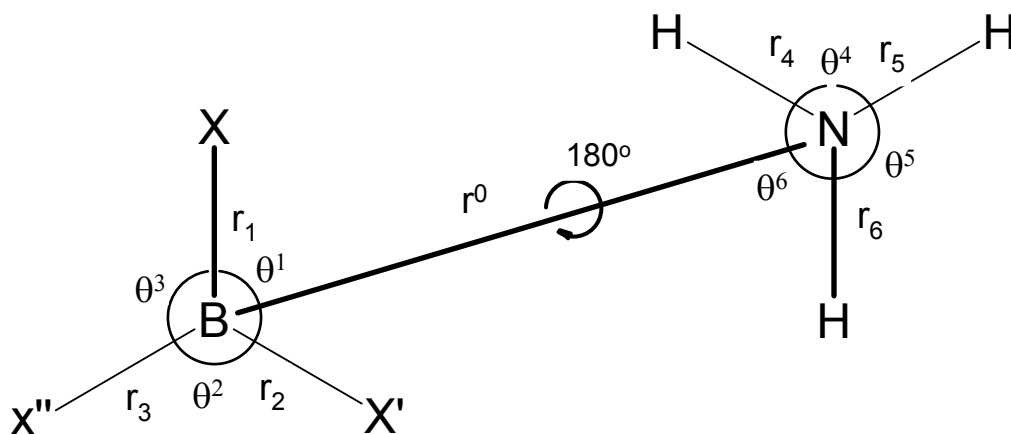
Figure 3.1: Basic geometry of complexes studied. X,X',X''=H or F

Table 3.2 presents the variation of global softness and chemical potential with B-N distance in complexes. It is observed that the global softness first decreases as

distance increases from 0.9 Å to 2.3 Å, and then again increases. Though it is not minimum at equilibrium geometry, it cannot be seen as violation of Maximum-Hardness-Principle, [14] since, the chemical potential of the complex is not constant as the complexes are dissociated along the *B-N* bond. Similar behavior of monotonic change of hardness/softness along a large part of the potential energy surface was earlier seen for diatomic molecules.[15]

Table 3.1: Structural parameters for equilibrium geometry for the *BXX'X"NH₃* complexes.

Parameter	BH_3NH_3 X=X'=X"=H	BH_2FNH_3 X=F and X'=X"=H	BHF_2NH_3 X=H and X'=X"=F	BF_3NH_3 X=X'=X"=F
	Bond Distance (Å)			
r^0	1.6604	1.6644	1.6691	1.6612
r_1	1.2053	1.4260	1.2005	1.3878
r_2	1.2053	1.2051	1.4033	1.3878
r_3	1.2053	1.2051	1.4033	1.3878
r_4	1.0157	1.0167	1.0163	1.0169
r_5	1.0157	1.0167	1.0163	1.0169
r_6	1.0157	1.0163	1.0181	1.0169
	Bond Angle (deg.)			
θ^1	113.90	113.70	115.02	114.18
θ^2	113.90	115.92	112.93	114.18
θ^3	113.90	113.70	115.02	114.18
θ^4	107.78	107.94	108.97	108.56
θ^5	107.78	108.54	108.45	108.56
θ^6	107.78	108.54	108.45	108.56

Table 3.3 presents condensed FF values of different atoms of isolated *BH₃* or fluoro-boranes and *NH₃*. Since the complex is formed by donation of electrons from nitrogen atom of *NH₃* to boron atom of *BH₃*, or fluoro-boranes, the electrophilic descriptor of *B* atom and nucleophilic descriptor of *N* atom are expected to be the highest in the isolated case. This is evidenced by the highest value for f^+ of boron

Table 3.2: Variation of Global softness and Chemical potential with B-N distance.

Distance (Å)	Global softness				Chemical potential			
	BH_3NH_3	BH_2FNH_3	BHF_2NH_3	BF_3NH_3	BH_3NH_3	BH_2FNH_3	BHF_2NH_3	BF_3NH_3
0.9	2.95705	2.88920	2.49534	2.01477	-0.16138	-0.17135	-0.20328	-0.25649
1.2	2.70404	2.66700	2.37529	1.95210	-0.17501	-0.18011	-0.20612	-0.25661
1.5	2.54695	2.54766	2.31296	1.94838	-0.18387	-0.18507	-0.20696	-0.25165
r^{0a}	2.47461	2.48737	2.27714	1.93676	-0.18767	-0.18729	-0.20718	-0.24979
1.8	2.41330	2.43532	2.24891	1.96423	-0.19077	-0.18910	-0.20711	-0.24288
2.0	2.33267	2.35801	2.16949	2.04210	-0.19473	-0.19188	-0.21063	-0.22807
2.3	2.22860	2.23065	2.21316	2.15301	-0.20024	-0.19853	-0.19986	-0.20863
2.6	2.28374	2.27293	2.25608	2.22239	-0.19155	-0.19070	-0.19165	-0.19729
3.0	2.32128	2.30506	2.29203	2.27598	-0.18568	-0.18517	-0.18585	-0.18968
3.5	2.34625	2.32886	2.31985	2.31445	-0.18237	-0.18179	-0.18233	-0.18499
4.0	2.36137	2.34290	2.33616	2.33619	-0.18107	-0.18025	-0.18072	-0.18253
4.5	2.37343	2.35166	2.34594	2.34879	-0.18071	-0.17984	-0.18022	-0.18108
5.5	2.41997	2.36178	2.35748	2.36171	-0.18316	-0.17891	-0.17915	-0.17945
6.0	2.42986	2.36470	2.36082	2.36515	-0.18351	-0.17860	-0.17880	-0.17894
7.0	2.44398	2.36760	2.36439	2.36812	-0.18406	-0.17790	-0.17825	-0.17819
non-interacting	2.47853	2.35959	2.35959	2.35959	-0.18604	-0.17587	-0.17587	-0.17587

[a] r^0 is B-N distance at fully optimized geometries of complexes.

Table 3.3: Condensed FFs at non-interacting limit.

Atom	f^+					f^-				
	BH_3	BH_2F	BHF_2	BF_3	NH_3	BH_3	BH_2F	BHF_2	BF_3	NH_3
B	0.86542	0.82868	0.85197	0.88859		0.38263	0.22888	0.17784	0.04782	
H^B	0.04487	0.03588	0.01866			0.20579	0.23688	0.31274		
F		0.09956	0.06468	0.03714			0.29737	0.25471	0.31739	
N					0.06214					0.76410
H^N					0.31262					0.07863

Table 3.4: *R.E.* and *R.N.* at non-interacting limit.

Atom	R.E.					R.N.				
	BH_3	BH_2F	BHF_2	BF_3	NH_3	BH_3	BH_2F	BHF_2	BF_3	NH_3
B	2.26177	3.62059	4.79065	18.58197		0.44213	0.27620	0.20874	0.05382	
H^B	0.21803	0.15147	0.05967			4.58663	6.60201	16.75991		
F		0.33480	0.25394	0.11703			2.98684	3.93800	8.54492	
N					0.08132					12.29643
H^N					3.97563					0.25153

Among, f^+ of atoms of BH_3 (B and H^B) and fluoro-boranes (B, H^B and F) and f^- for nitrogen atom among f^- of atoms of NH_3 (N and H^N). Recently $R.E.$ (f^+/f^-) and $R.N.$ (f^-/f^+) of atomic centers have been shown to be better indicators of intramolecular reactivity. Table 3.4 presents $R.E.$ and $R.N.$ values of different atoms of isolated BH_3, fluoro-boranes and NH_3. In fact, the trend of the most reactive atom, being associated with the highest value of reactivity descriptor, comes out even more clearly with these descriptors, with values 12.29643 for $R.N.$ values of nitrogen atom and 2.26177, 3.62059, 4.79065 and 18.58197 for $R.E.$ values of boron atom in BH_3, BH_2F, BHF_2 and BF_3, respectively.

Local softness is not a reliable index for comparing reactivity as the B-N distance changes due to the artifact of change in global softness with the change of B-N distance. However, f^+ and f^- values can be used for comparison owing to the sum of these descriptors of all atoms of the complex being normalized to unity. Similarly, $R.E.$ and $R.N.$ can also serve as appropriate indices for comparison of reactivity since these are also independent of global softness.

As we have discussed in the previous chapter, the non interacting values of f^+ or f^- are, however, correctly approached only for atoms of fragmented species for complex anion or cation respectively. The possible schemes for fission of N_0+1 and N_0-1 electronic states of $BXX'X''NH_3$ complex along the B-N bond are shown in Fig. 3.2. Table 3.5 presents the energies of the complexes at non-interacting limits according to different fragmentation schemes. In case of $(BH_3NH_3)^-$, its dissociation as BH_3^- and NH_3 (scheme I in Fig. 3.2), is energetically favorable route. Hence, f^+ of atoms of BH_3 in BH_3NH_3 complex reach the correct isolated limit values. On the other hand, f^+ of the

atoms of NH_3 remain zero. For the systems $(BHF_2NH_3)^-$, $(BHF_2NH_3)^-$ and $(BF_3NH_3)^-$, the dissociation products are neutral BH_2F, BHF_2, BF_3 and NH_3^- (scheme II). The planer geometry of BH_3 or fluoro-boranes is required for compatibility with dissociation process, which is as expected from Table 3.5. It is well known that in fluoro-boranes, boron is less electron deficient as compared to BH_3, due to back donation of the

$$(BXX'X''NH_3)^- \longrightarrow \begin{cases} (BXX'X'')^- + NH_3 & \textbf{Scheme I} \\ BXX'X'' + NH_3^- & \textbf{Scheme II} \end{cases}$$

$$(BXX'X''NH_3)^+ \longrightarrow \begin{cases} (BXX'X'')^+ + NH_3 & \textbf{Scheme III} \\ BXX'X'' + NH_3^+ & \textbf{Scheme IV} \end{cases}$$
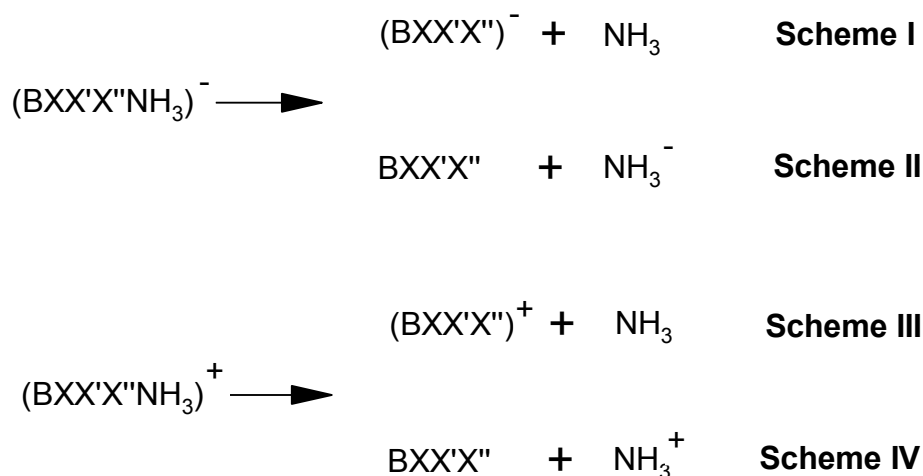
Figure 3.2: Possible fragmentation schemes for fission of complexes along B-N bond (X,X',X''=H or F)

Table 3.5: Energies of complexes at non-interacting limits according to different fragmentation schemes.

|	Energy (hartree)			
	Scheme I	**Scheme II**	**Scheme III**	**Scheme IV**
BH_3NH_3	-82.864125	-82.843787	-82.398364	-82.492054
BH_2FNH_3	-181.949566	-181.949998	-181.519133	-181.598264
BHF_2NH_3	-281.043453	-281.061437	-280.568188	-280.709704
BF_3NH_3	-380.131436	-380.161476	-379.580880	-379.809742

p-electrons of the fluorine atom into the vacant *p*-orbital on the boron atom. Here, we have considered only the vertical electron affinity. (In reality, the acceptance of extra electron would be facilitated by pyramidalization,[16] which is not appropriate for limit considered here, as the calculations are to be done under constant external potential.) Hence, for these fluoro-borane-*NH₃* complexes, f^+ values of atoms of ammonia atom go to the isolated limit of *NH₃* and the f^+ values of boron and H^B or fluorine atoms go to zero. In the case of all $(BXX'X''NH_3)^+$ systems, the dissociation leads to *BXX'X''* and NH_3^+ (scheme IV). Hence, f^- of all atoms of *NH₃* leads to the isolated case at non-interacting limits and f^- of *B* and H^B or *F* attached to boron becomes zero. Hence, the isolated limit results are obtained at the non-interacting limit preferentially only for one fragment, depending on the fragmentation of the anion or cation, as the case may be. At the non-interacting limit, the values for the other fragment approach zero. This manifests in very large *R.E.* or *R.N.* values of that fragment, which is due to the artifact of separation limit values of the FF of that particular fragment.

In addition to the above, the condensed FFs of atoms often become negative, when computed using Lowdin/Mulliken population analysis[12] technique. The problem of negative condensed FF has been analyzed in detail[13] and it has been realized that the problem originates from the population analysis used. While the above analyses are quite standard, they lead to the negative FF values in some cases as has been observed by many workers.[17,18] However, among these two, LPA is more reliable and hence has been used in this thesis.

Fig. 3.3 presents variation of condensed nucleophilic FF for the nitrogen atom of different complexes with *B-N* distance. f^- (*N*) falls to much lower values at interacting distances. The results reveal the loss of nucleophilicity of *N* as the reaction proceeds. This is due to the electron donation from nitrogen atom to *BH₃* or fluoro-boranes. Nitrogen which had a surplus lone pair of electrons in isolated *NH₃*, is no longer electron rich, as it reaches near equilibrium geometry. Fig. 3.4 presents variation of *R.N.* of nitrogen atom with *B-N* distance which also shows the similar trend.

Variations of condensed electrophilic FF and R.E. for nitrogen atom with *B-N* distance are shown in Fig. 3.5 and 3.6 respectively. The electrophilic descriptors
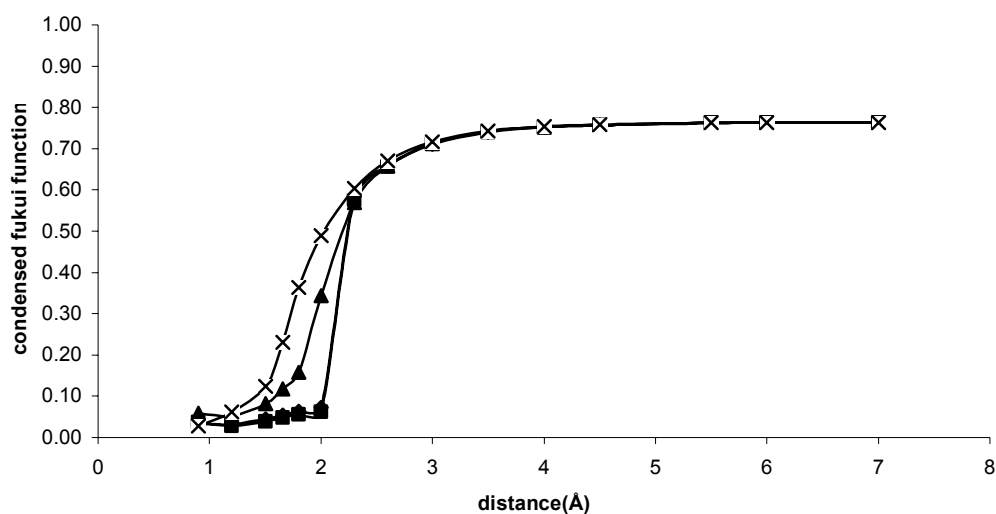
Figure 3.3: Variation of condensed nucleophilic FFs for nitrogen atom of different complexes with *B-N* distance

—◆— *BH₃NH₃*   —■— *BH₂FNH₃*   —▲— *BHF₂NH₃*   —×— *BF₃NH₃*
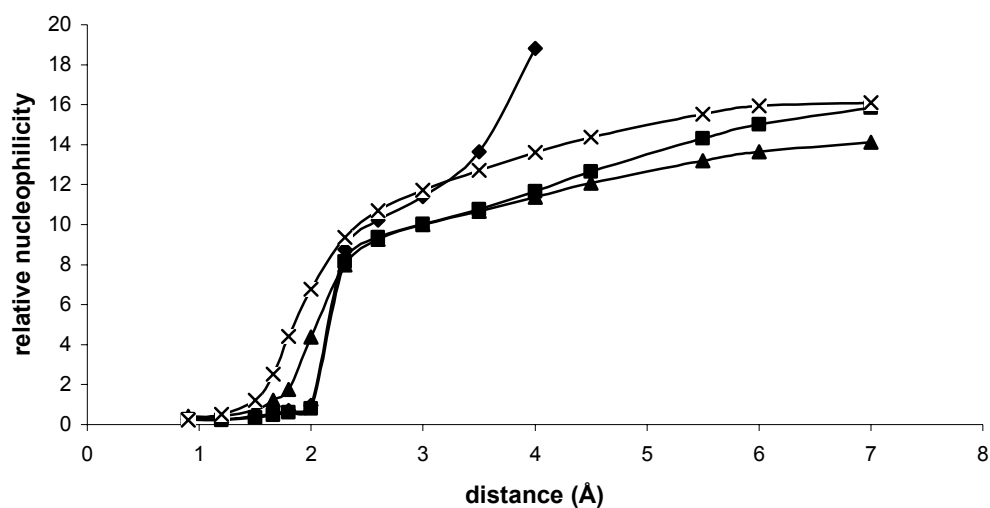
Figure 3.4: Variation of *R.N.* of nitrogen atom of different complexes with *B-N* distance

—◆— *BH₃NH₃*   —■— *BH₂FNH₃*   —▲— *BHF₂NH₃*   —×— *BF₃NH₃*
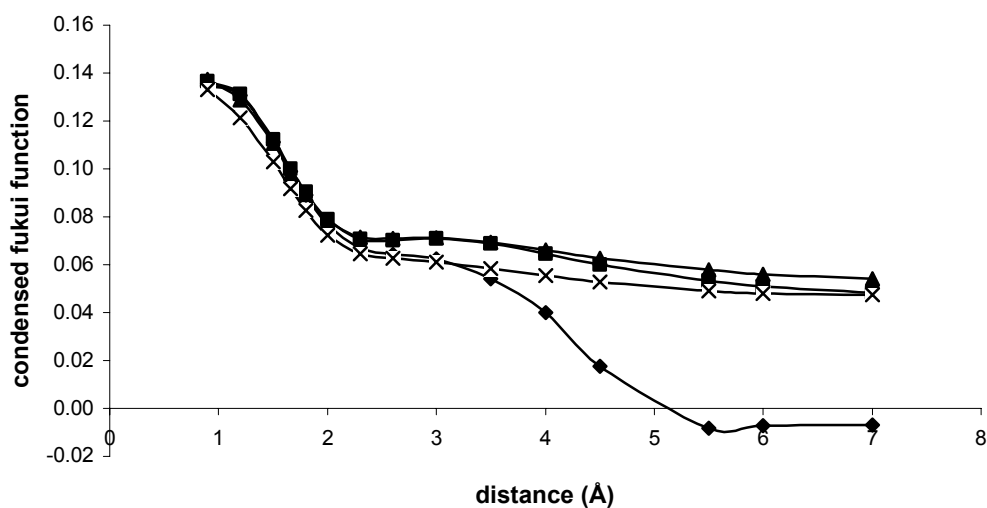
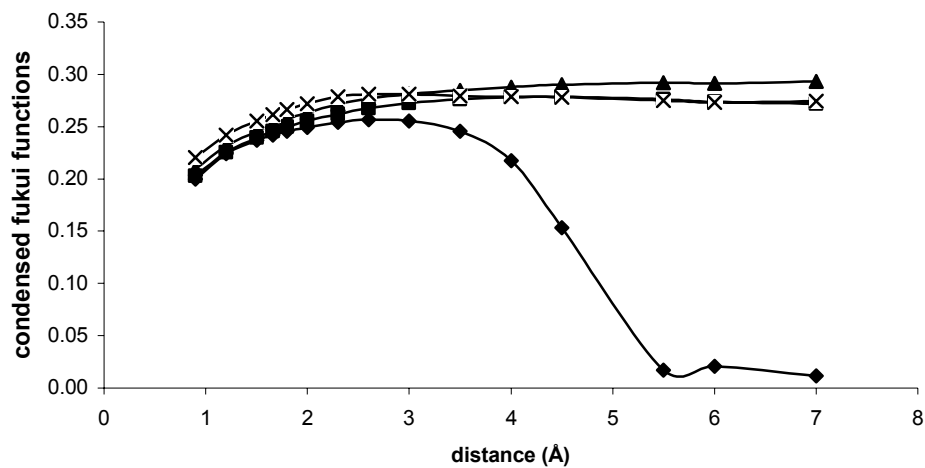**Figure 3.5:** Variation of condensed electrophilic FFs for nitrogen atom of different complexes with *B-N* distance

—◆— *BH₃NH₃*   —■— *BH₂FNH₃*   —▲— *BHF₂NH₃*   —×— *BF₃NH₃*
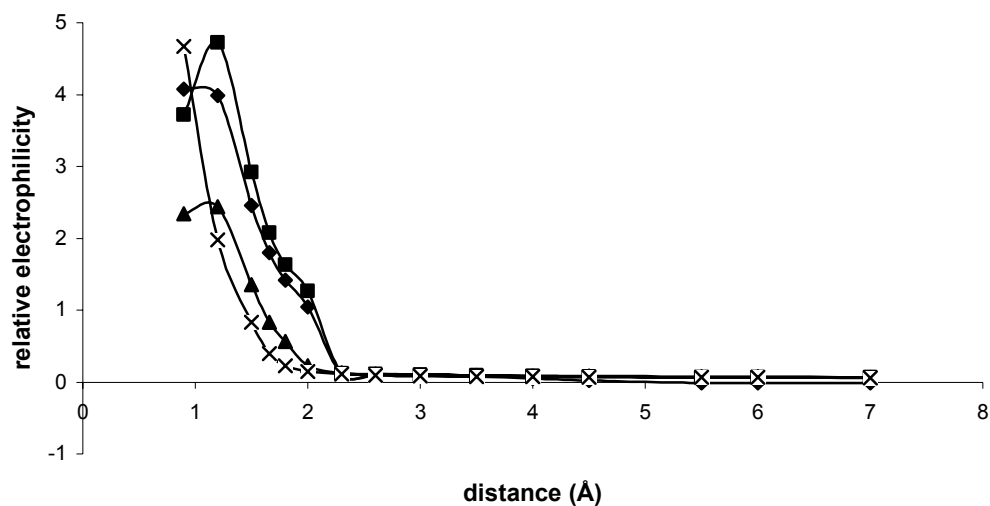
Figure 3.6: Variation of *R.E.* of nitrogen atom of different complexes with *B-N* distance

—◆— *BH₃NH₃*   —■— *BH₂FNH₃*   —▲— *BHF₂NH₃*   —×— *BF₃NH₃*

of nitrogen atoms increase monotonically as the reaction proceeds. This, is the artifact of donation of electrons by nitrogen atom, as a result of which, electron density around nitrogen decreases and the nucleus is somewhat less shielded and which in turn marginally increases its affinity for electrons.

Electrophilic descriptors for any hydrogen atom connected to nitrogen should show increasing values as the reaction proceeds. This is because; the nitrogen becomes more electronegative at interacting distances as a consequence of its loss of electrons to boron, thereby, reducing electron density on hydrogen. Fig. 3.7 presents variation of condensed electrophilic FF for H^N with *B-N* distance. Though the expected trend is not seen with these values, except, for *BH₃NH₃* the trend is clearly seen in Fig. 3.8 which presents variation of *R.E.* of H^N with *B-N* distances. The variation of condensed

Figure 3.7: Variation of condensed electrophilic FFs for H^N of different complexes with *B-N* distance
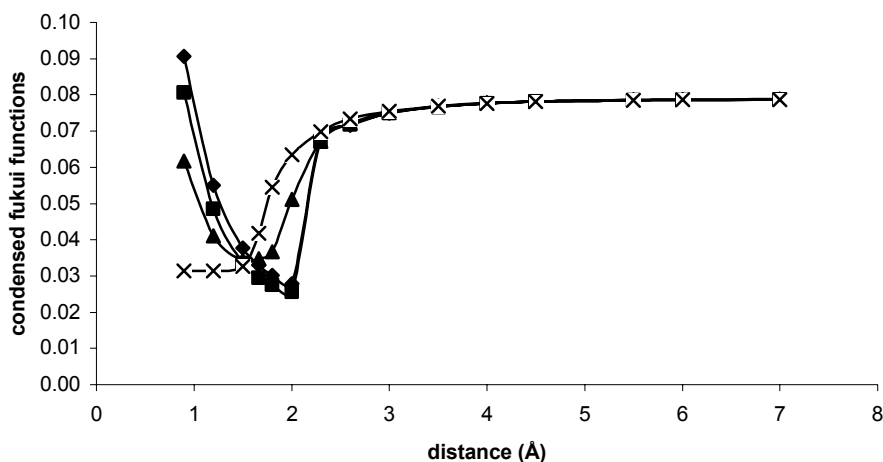
    ◆   *BH₃NH₃*   ■   *BH₂FNH₃*   ▲   *BHF₂NH₃*   ─×─   *BF₃NH₃*
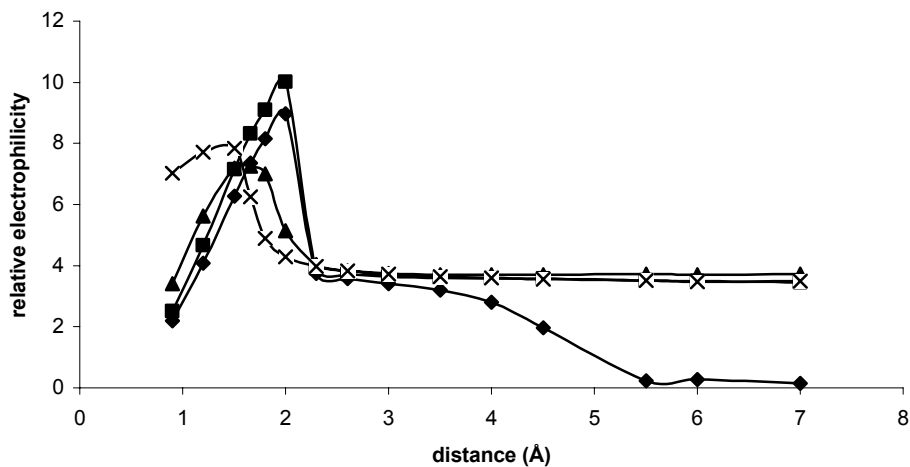
Figure 3.8: Variation of *R.E.* of H^N of different complexes with *B-N* distance
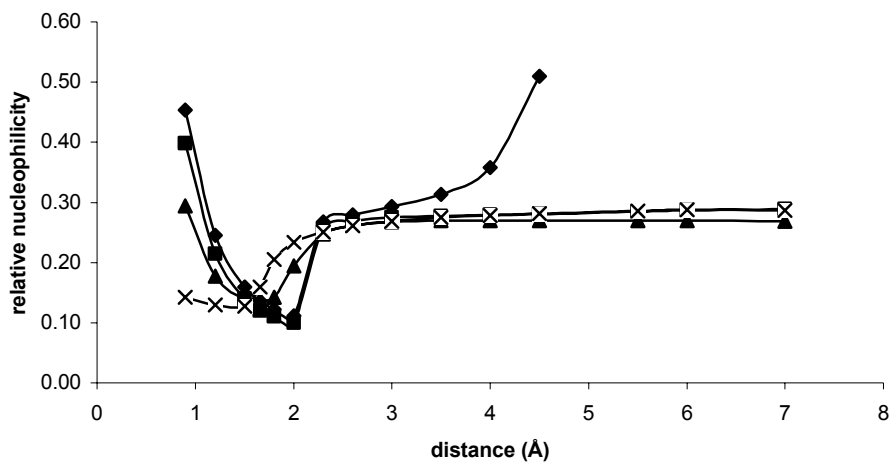
    ◆   *BH₃NH₃*   ■   *BH₂FNH₃*   ▲   *BHF₂NH₃*   ─×─   *BF₃NH₃*

nucleophilic FF and *R.N.* values for H^N with *B-N* distance is shown in Fig. 3.9 and 3.10, which shows the expected trend of losing nucleophilicity as reaction proceeds because of the same reason above.

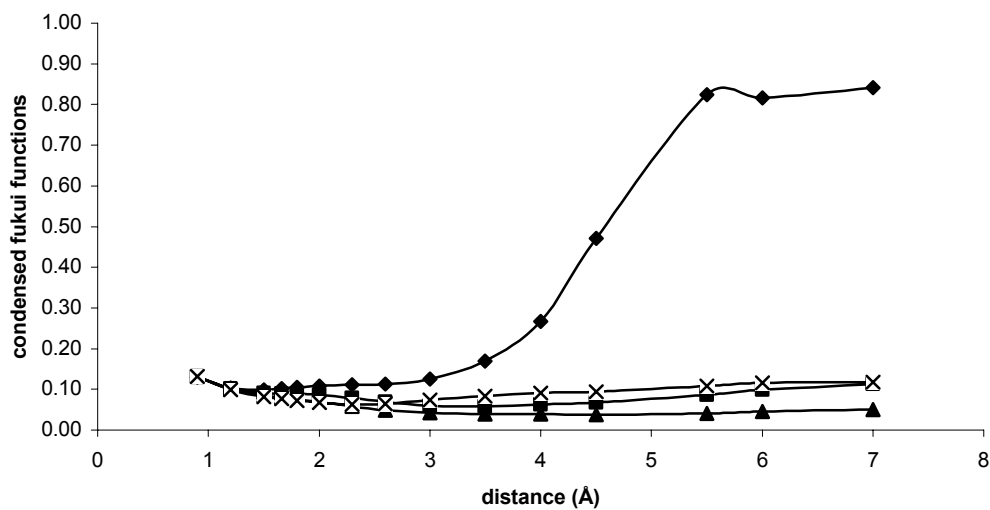**Figure 3.9:** Variation of condensed nucleophilic FFs for H^N of different complexes with *B-N* distance

━◆━ *BH₃NH₃*   ━■━ *BH₂FNH₃*   ━▲━ *BHF₂NH₃*   ─×─ *BF₃NH₃*

Fig. 3.11 presents variation of condensed electrophilic FF for the boron atom with *B-N* distance. Results show how loss of electrophilicity accompanies the reaction, starting from its limiting value, which was initially very high (> 0.8) and now falling to very low values (~0.1) at equilibrium geometry. This is attributed to gain of electron by boron atom. The variations of condensed nucleophilic FF and *R.N.* of *B* with *B-N* distance are shown in Fig. 3.12 and 3.13, respectively. The nucleophilic descriptors of boron atoms increase considerably as reaction proceeds.
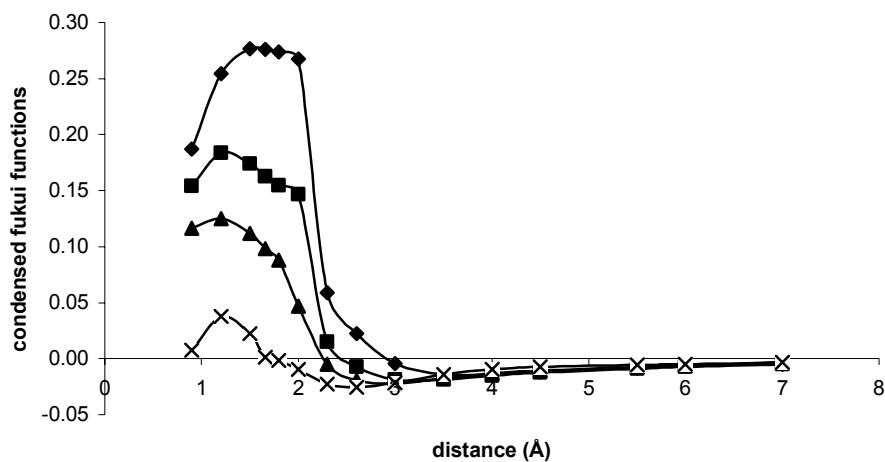
Figure 3.10: Variation of *R.N.* of H^N of different complexes with *B-N* distance

$\blacklozenge$ *BH$_3$NH$_3$* $\blacksquare$ *BH$_2$FNH$_3$* $\blacktriangle$ *BHF$_2$NH$_3$* $-\times-$ *BF$_3$NH$_3$*
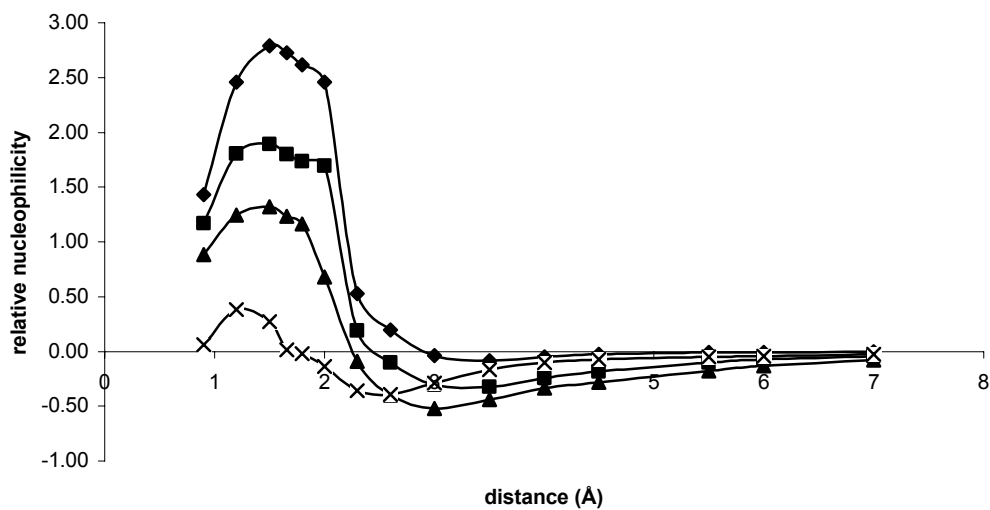

Figure 3.11: Variation of condensed electrophilic FFs for boron atom of different complexes with *B-N* distance

$\blacklozenge$ *BH$_3$NH$_3$* $\blacksquare$ *BH$_2$FNH$_3$* $\blacktriangle$ *BHF$_2$NH$_3$* $-\times-$ *BF$_3$NH$_3$*

Figure 3.12: Variation of condensed nucleophilic FFs for boron atom of different complexes with *B-N* distance

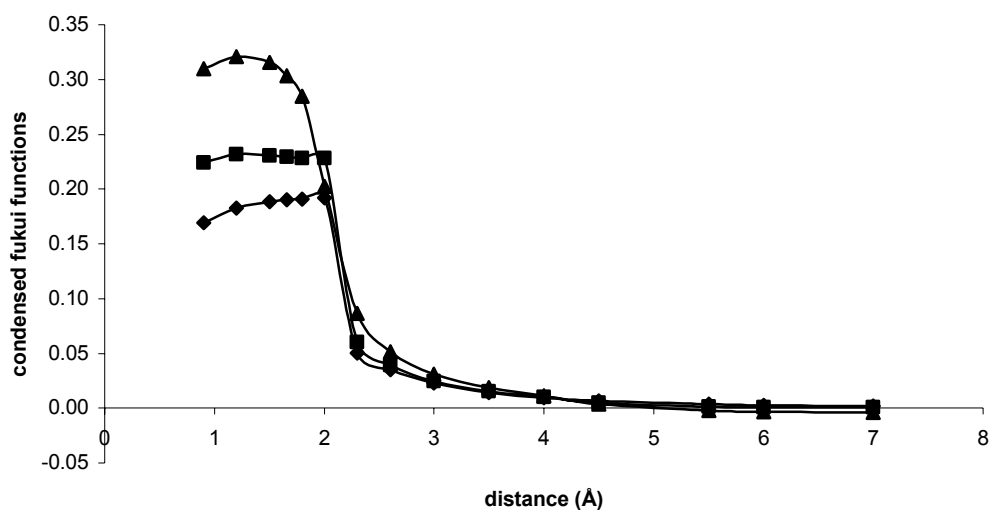$\rightarrow$ *BH₃NH₃* $\rightarrow$ *BH₂FNH₃* $\rightarrow$ *BHF₂NH₃* $-\times-$ *BF₃NH₃*

Figure 3.13: Variation of *R.N.* of boron atom of different complexes with *B-N* distance

$\rightarrow$ *BH₃NH₃* $\rightarrow$ *BH₂FNH₃* $\rightarrow$ *BHF₂NH₃* $-\times-$ *BF₃NH₃*

Figure 3.14: Variation of condensed nucleophilic FFs for H^B of different complexes with *B-N* distance

$\rightarrow\!\!\blacklozenge\!-$ *BH₃NH₃* $\quad\rightarrow\!\!\blacksquare\!-$ *BH₂FNH₃* $\quad\rightarrow\!\!\blacktriangle\!-$ *BHF₂NH₃*
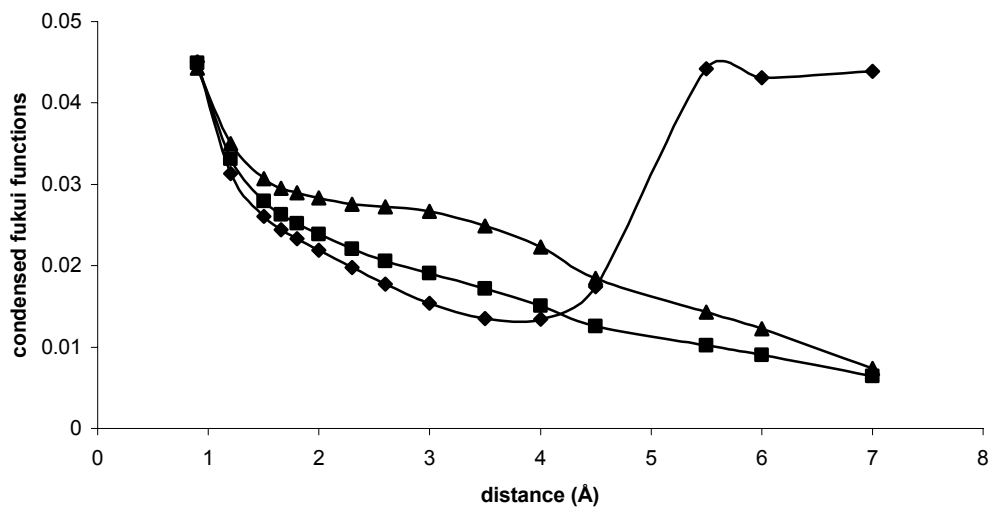
The variation of condensed nucleophilic FF for H^B with *B-N* distance is shown in Fig 3.14. As the reaction proceeds, f^- of hydrogen connected with boron should increase, since the boron atom after gaining electron from nitrogen becomes less electronegative, and thereby H^B and *F* have more electron density around. This is evidenced by gained values of f^- for H^B. The same trend is seen in Fig. 3.15 which presents variation of 'relative- nucleophilicity' of H^B with *B-N* distance. The variation of electrophilic descriptors of H^B with *B-N* distance is shown in Figs. 3.16 and 3.17. As expected, the electrophilic descriptors of H^B show monotonic decrease as the complex is formed because of similar reason.

The variation of reactivity descriptors of *F* are shown in Figs. 3.18-3.21. The fluorine atom behaves in similar fashion as that of H^B which is quite expected.
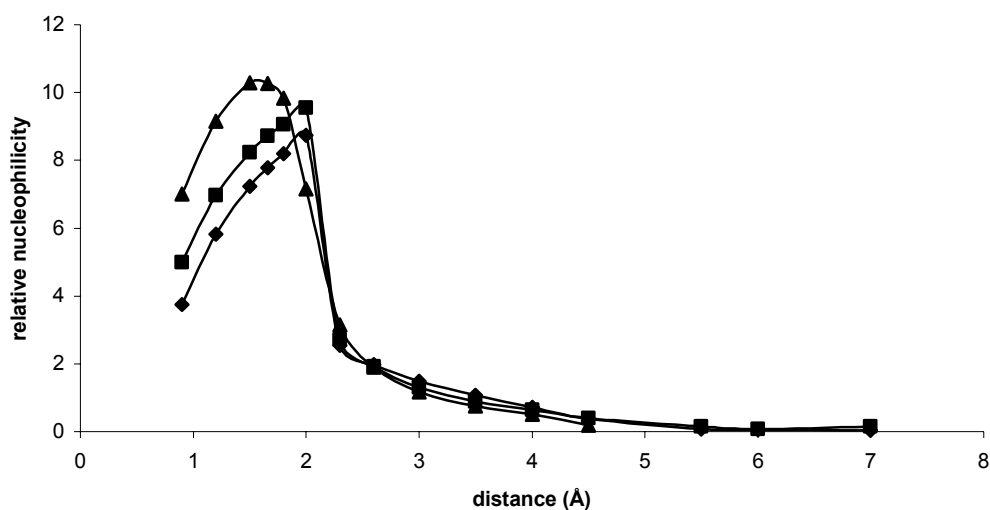
Figure 3.15: Variation of *R.N.* of H^B of different complexes with *B-N* distance

$\longrightarrow$ *BH₃NH₃* $\longrightarrow$ *BH₂FNH₃* $\longrightarrow$ *BHF₂NH₃*

Figure 3.16: Variation of condensed electrophilic FFs for H^B of different complexes with *B-N* distance

$\longrightarrow$ *BH₃NH₃* $\longrightarrow$ *BH₂FNH₃* $\longrightarrow$ *BHF₂NH₃*
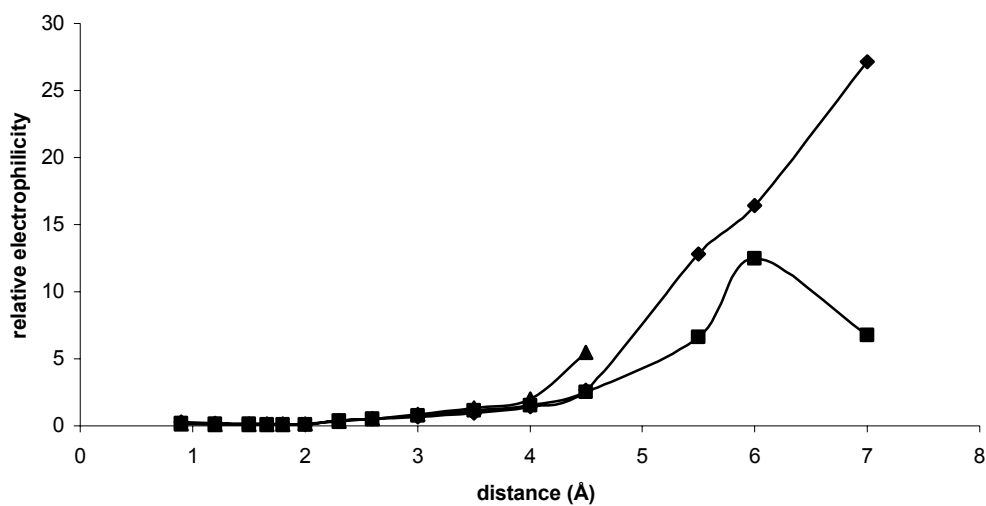
Figure 3.17: Variation of *R.E.* of H^B of different complexes with *B-N* distance

   ♦   *BH₃NH₃*   ■   *BH₂FNH₃*   ▲   *BHF₂NH₃*
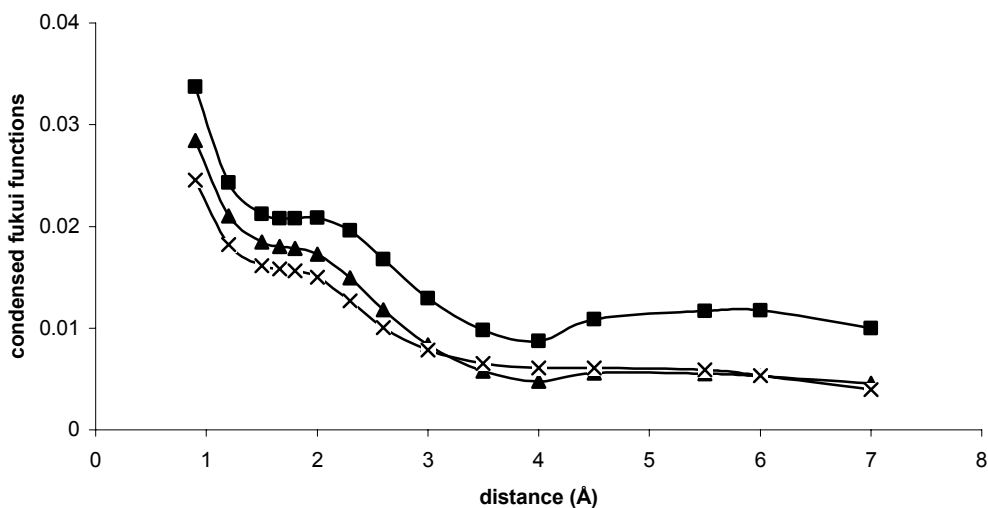
Figure 3.18: Variation of condensed electrophilic FFs for fluorine atom of different complexes with *B-N* distance

   ■   *BH₂FNH₃*   ▲   *BHF₂NH₃*   −×−   *BF₃NH₃*

Figure 3.19: Variation of *R.E.* of fluorine atom of different complexes with *B-N* distance
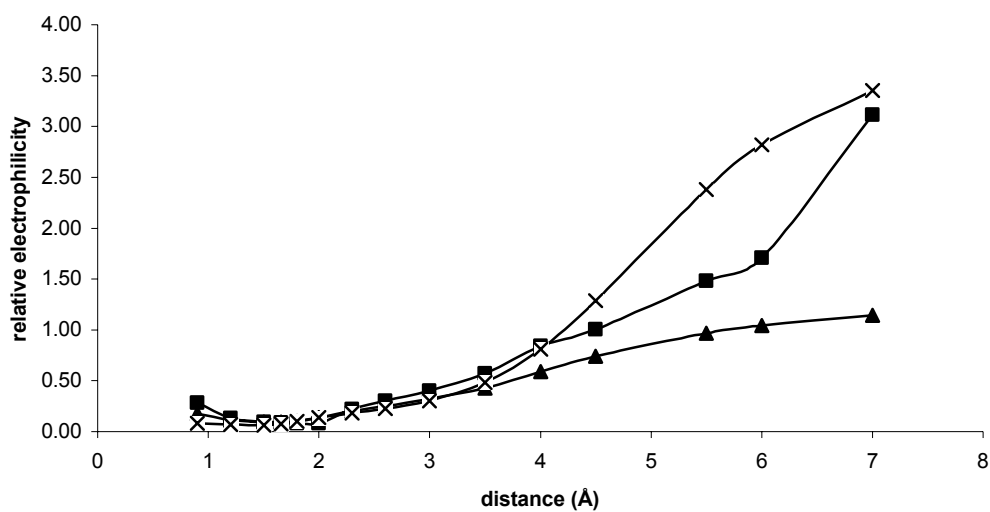
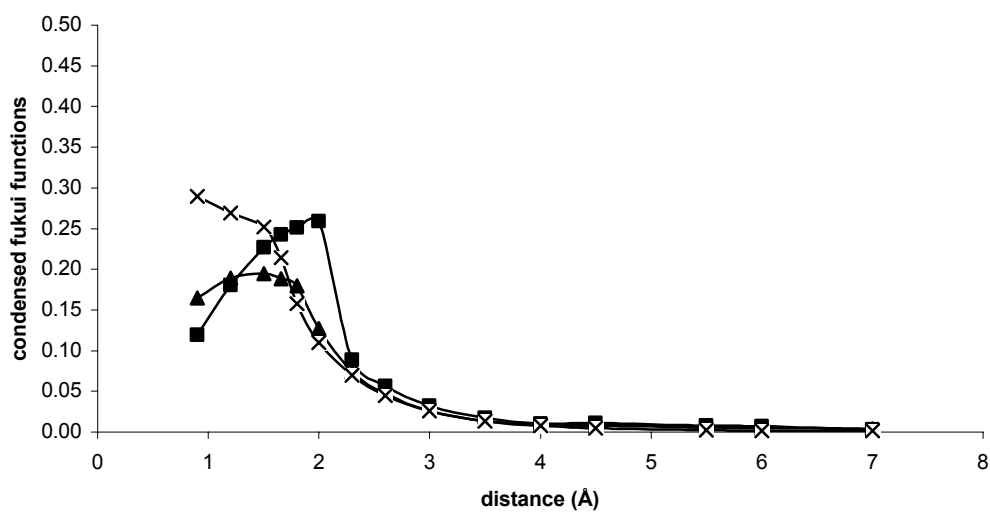■— BH_2FNH_3 ▲— BHF_2NH_3 —×— BF_3NH_3

Figure 3.20: Variation of condensed nucleophilic FFs for fluorine atom of different complexes with *B-N* distance
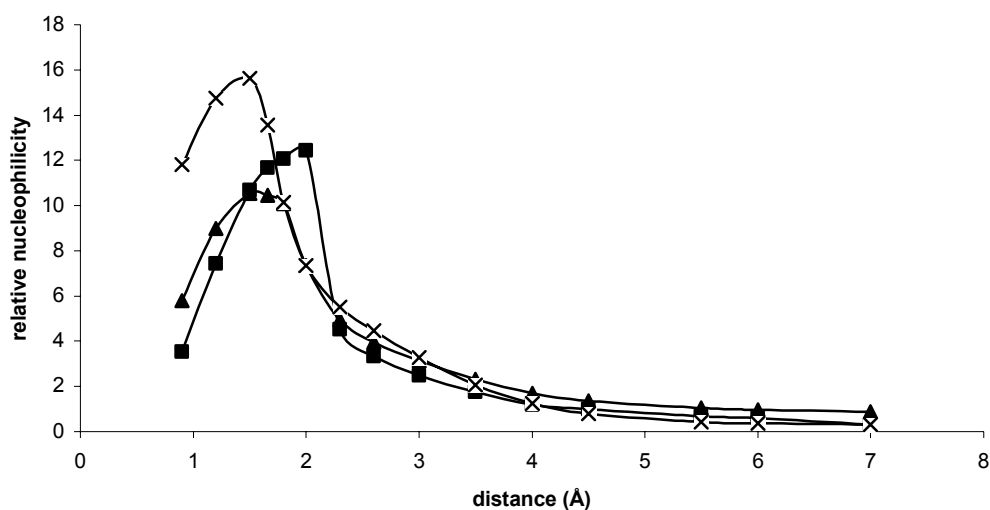
■— BH_2FNH_3 ▲— BHF_2NH_3 —×— BF_3NH_3

Figure 3.21: Variation of *R.N.* of fluorine atom of different complexes with *B-N* distance

—■— BH_2FNH_3 —▲— BHF_2NH_3 —×— BF_3NH_3

3-III(B). BH_3NH_3 Dimer

Hydrogen connected to nitrogen (H^N) and hydrogen connected to boron (H^B) which do not have good affinity at non-interacting limits are having larger values of $f^+(H^N)$ and $f^-(H^B)$ [Figs. 3.7 and 3.14] at equilibrium geometry. Also the *R.E.* of H^N and *R.N.* of H^B are maximum [Fig. 3.8 and 3.15] among all atoms at equilibrium geometry, which clearly justifies the formation of the dihydrogen bond (*N-H...H-B*) in BH_3NH_3 dimer.[11] It also justifies H^N as site for nucleophilic attack by oxygen in the adduct between 2, 3,11,12-Tetra-anisyl- 18-crown-6 and ammonia-borane.[19]

Fig. 3.22 presents the structure of the BH_3NH_3 dimer. The structure corresponds to the fully optimized structure of BH_3NH_3 dimer and the *B-N'* distance is 3.314 Å.
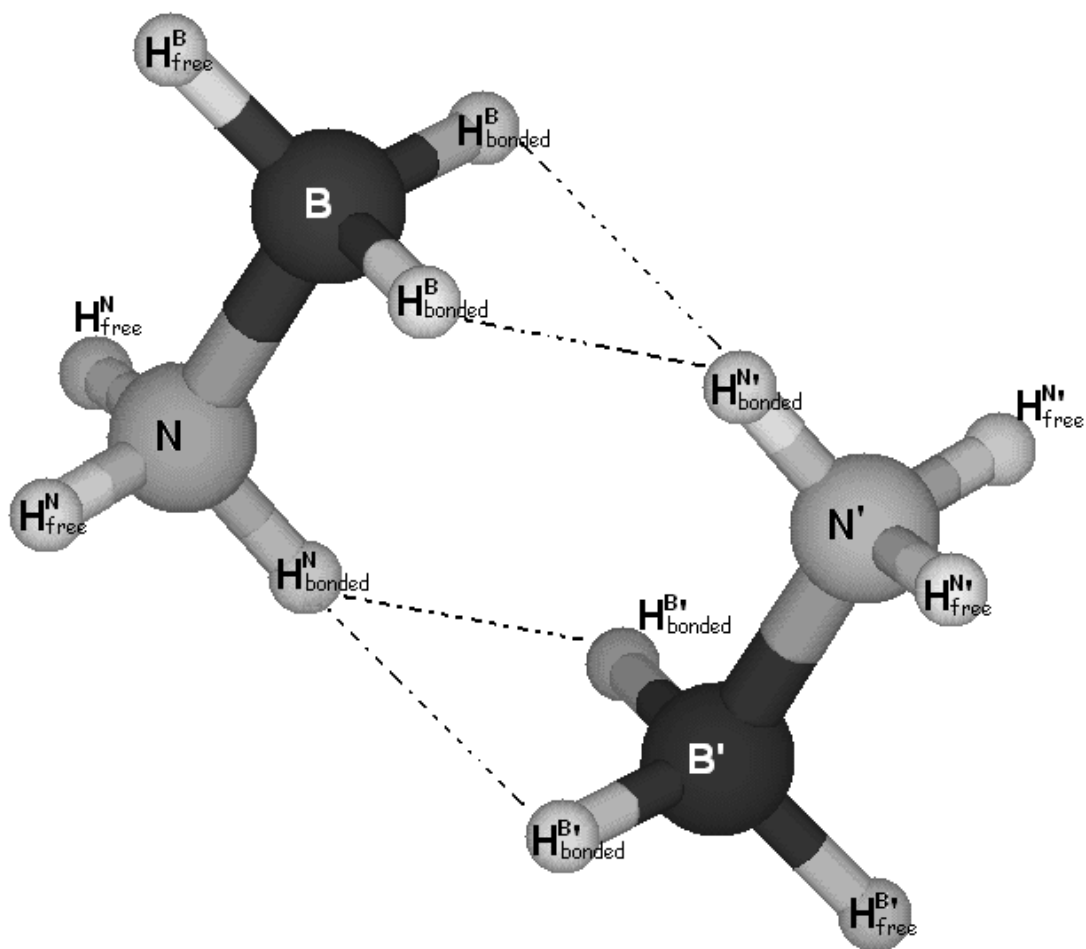
Figure 3.22: Structure of *BH₃NH₃* dimer.

Fig. 3.23 presents the LRDs of H^B_{bonded}. As the *BH₃NH₃* approach each other the nucleophilicity of H^B_{bonded} decreases and its electrophilicity increases. Fig. 3.24 present the LRDs of H^B_{free}. It may be noted that, after dimerisation, the nucleophilicity of H^B_{free} increases a lot. Fig. 3.25 presents the LRDs for boron atom. The local philicity values are scaled up ten times and values for *R.E.* and *R.N.* are scaled down by factor of 40, so that they could be presented on the same figure.
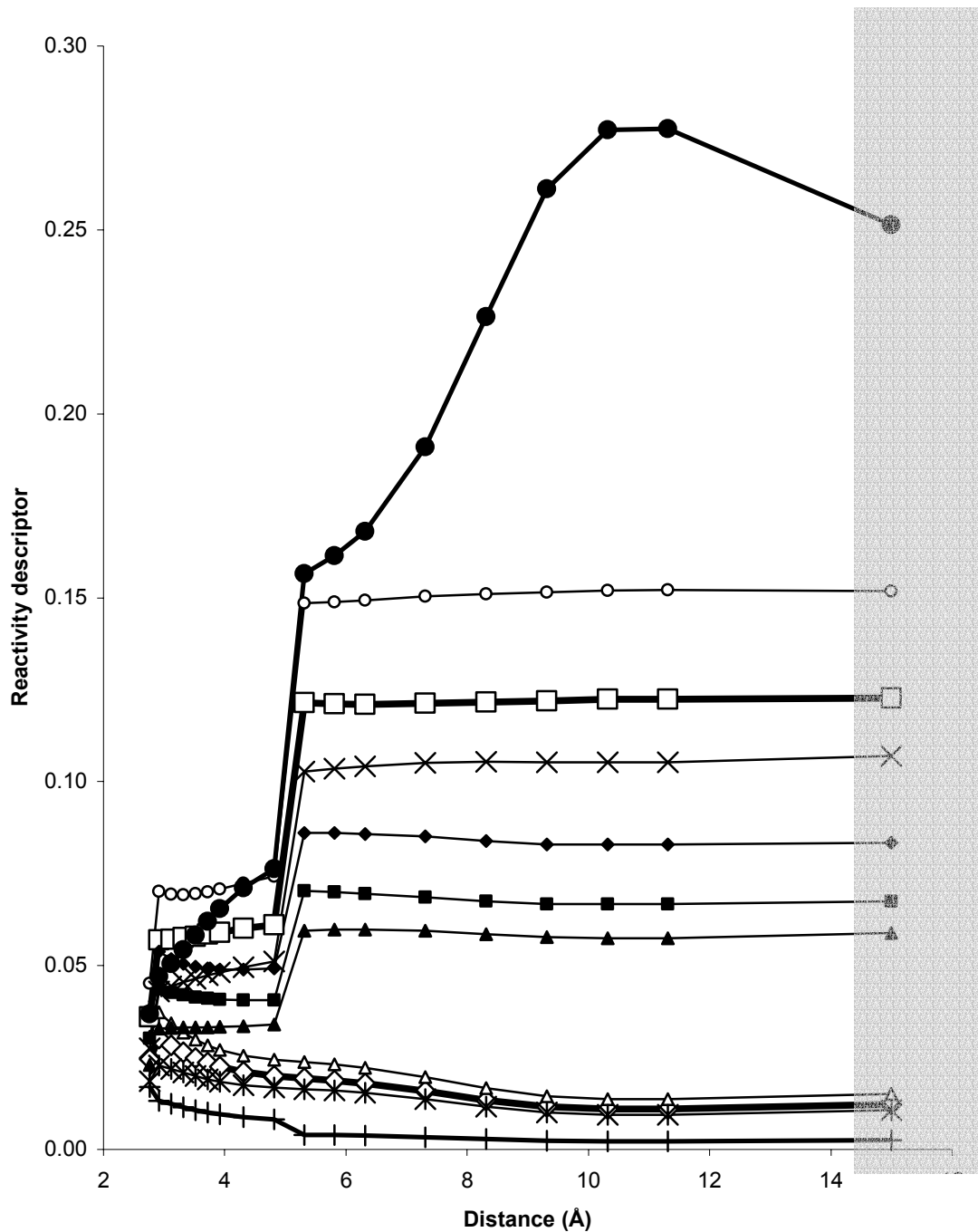
Figure 3.23: Variation of LRDs of H^B_{bonded} in $(BH_3NH_3)_2$ with $B\text{-}N'$ distance
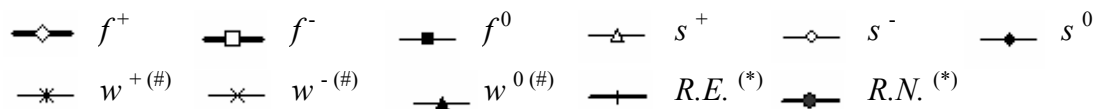
Legend:
- f^+
- f^-
- f^0
- s^+
- s^-
- s^0
- $w^{+\,(\#)}$
- $w^{-\,(\#)}$
- $w^{0\,(\#)}$
- $R.E.^{\,(*)}$
- $R.N.^{\,(*)}$

scaled up by factor of 10. * scaled down by factor of 40. Shaded area corresponds to half value of monomers except for *R.E.* and *R.N.* where it corresponds to the full value.
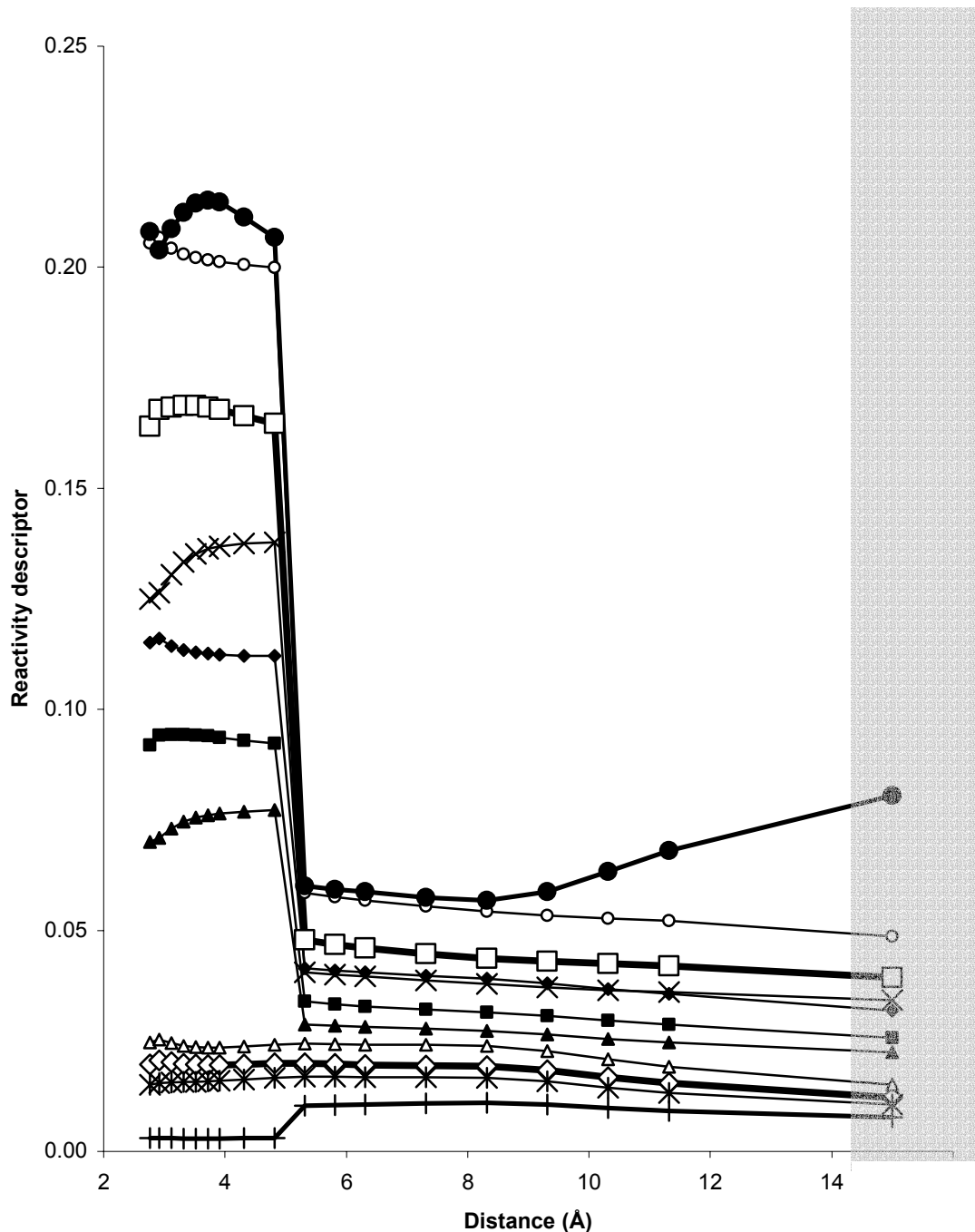
Figure 3.24: Variation of LRDs of H^B_{free} in $(BH_3NH_3)_2$ with B-N' distance
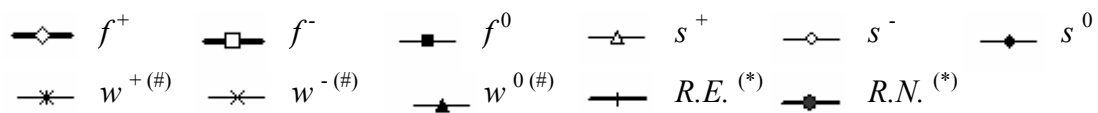
Legend:
f^+, f^-, f^0, s^+, s^-, s^0, $w^{+(\#)}$, $w^{-(\#)}$, $w^{0(\#)}$, R.E. $^{(*)}$, R.N. $^{(*)}$

scaled up by factor of 10. * scaled down by factor of 40. Shaded area corresponds to half value of monomers except for *R.E.* and *R.N.* where it corresponds to the full value.

Figure 3.25: Variation of LRDs of Boron in $(BH_3NH_3)_2$ with $B\text{-}N'$ distance

◇	f^+	☐	f^-	■	f^0	△ s^+
◇	s^-	◆	s^0			
✳	$w^{+\,(\#)}$	✳	$w^{-\,(\#)}$	▲	$w^{0\,(\#)}$	+ $R.E.^{(*)}$ ● $R.N.^{(*)}$

\# scaled up by factor of 10. * scaled down by factor of 40. Shaded area corresponds to half value of monomers except for *R.E.* and *R.N.* where it corresponds to the full value.

Fig. 3.26 presents the variation of different reactivity descriptors of H^{N}_{bonded}. Fig. 3.27 presents LRDs of H^{N}_{free}. Electrophilic character of H^{N}_{bonded} decreases as the dimer is formed. On the other hand, it increases for H^{N}_{free}. Fig. 3.28 presents LRDs for Boron atom. The local philicity values are scaled up ten times and values for $R.E.$ and $R.N.$ are scaled down by factor of 40, except, in Fig. 3.26 where $R.E.$ is scaled down by factor of 100.

Points under the shaded region in the Figs. 3.23-3.28 correspond to the half values of the reactivity descriptors of the monomer BH_3NH_3, except, for the relative-electrophilicity and relative-nucleophilicity, where they correspond to the values for monomer. From Figs. 3.23-3.28 it can be seen that the reactivity descriptors of dimer, do behave as described in the previous chapter. Condensed FFs, local softness and local philicity of dimer separate out as half of the monomer values, while the $R.E.$ and $R.N.$ approach their corresponding monomer values.

3-V. Conclusions

In this chapter we studied the separation behavior of some LRDs during complexation. We numerically test the analytical results obtained in previous chapter. It is interesting to observe that condensed LRDs of the systems discussed in this chapter behave in the same manner as described in chapter 2.

Figure 3.26: Variation of LRDs of H^N_{bonded} in $(BH_3NH_3)_2$ with $B\text{-}N'$ distance

f^+ f^- f^0 s^+ s^- s^0 $w^{+\,(\#)}$ $w^{-\,(\#)}$ $w^{0\,(\#)}$ $R.E.^{(*)}$ $R.N.^{(\%)}$
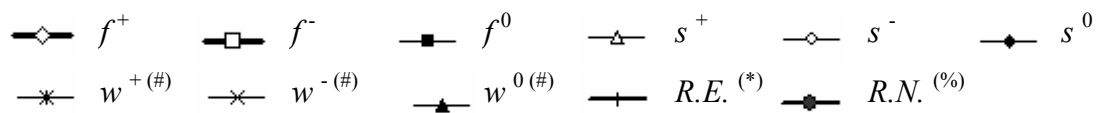
scaled up by factor of 10.; * scaled down by factor of 100; $^{\%}$scaled down by factor of 40. Shaded area corresponds to half value of monomers except for *R.E.* and *R.N.* where it corresponds to the full value.
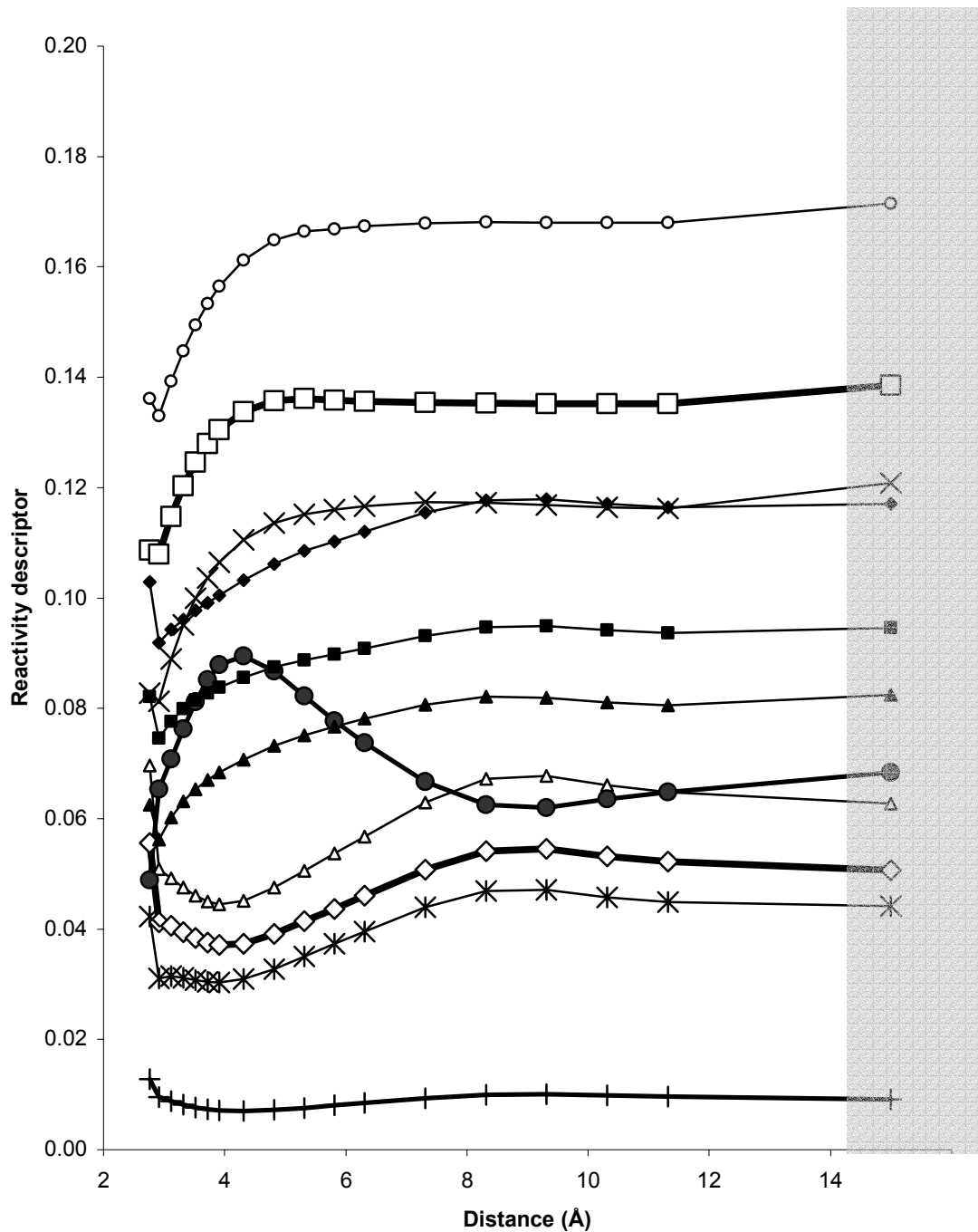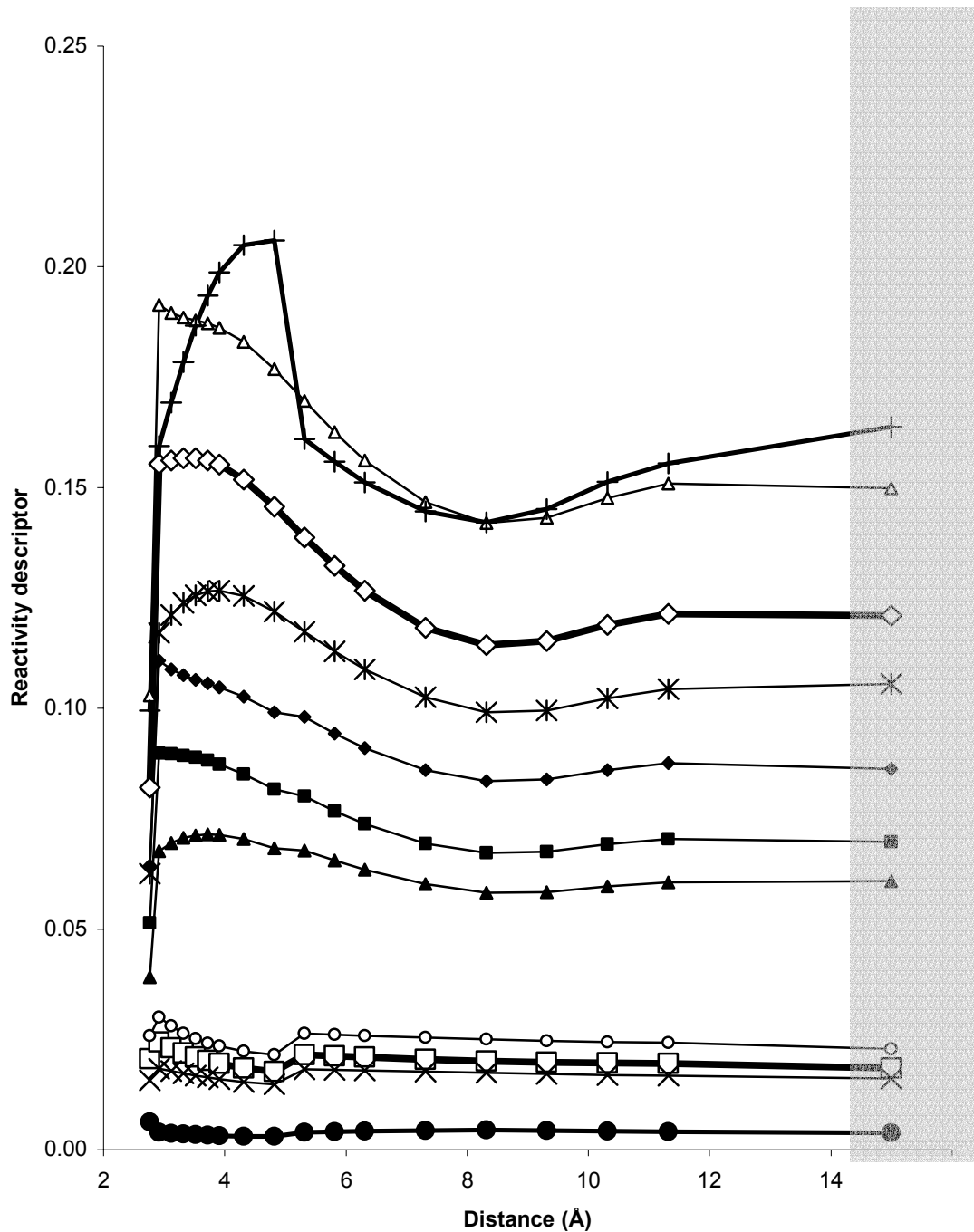
Figure 3.27: Variation of LRDs of H^N_{free} in $(BH_3NH_3)_2$ with B-N' distance
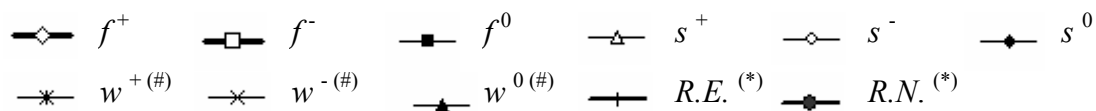
Legend:
- f^+
- f^-
- f^0
- s^+
- s^-
- s^0
- $w^{+ (\#)}$
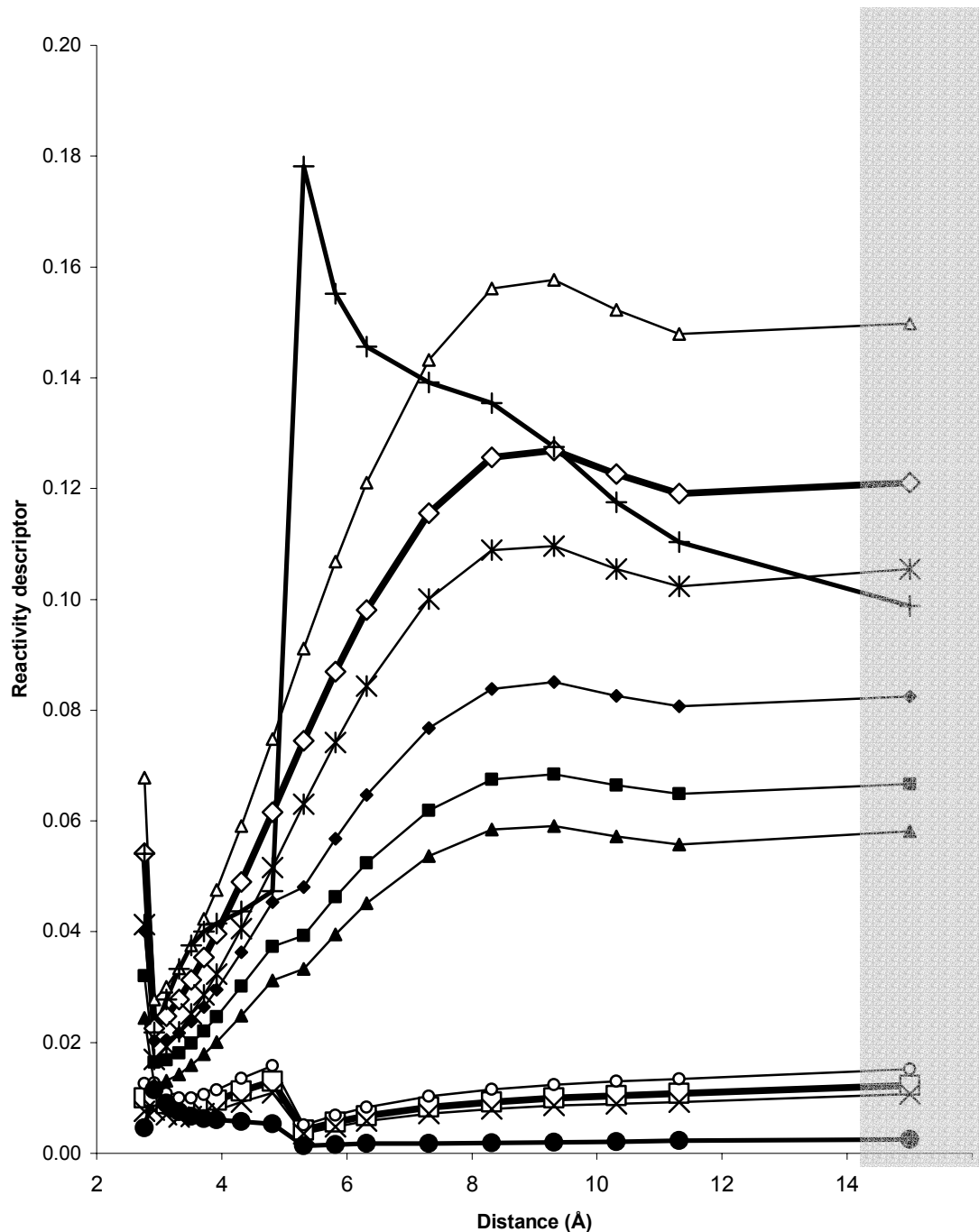- $w^{- (\#)}$
- $w^{0 (\#)}$
- $R.E.^{(*)}$
- $R.N.^{(*)}$

scaled up by factor of 10. * scaled down by factor of 40. Shaded area corresponds to half value of monomers except for *R.E.* and *R.N.* where it corresponds to the full value.
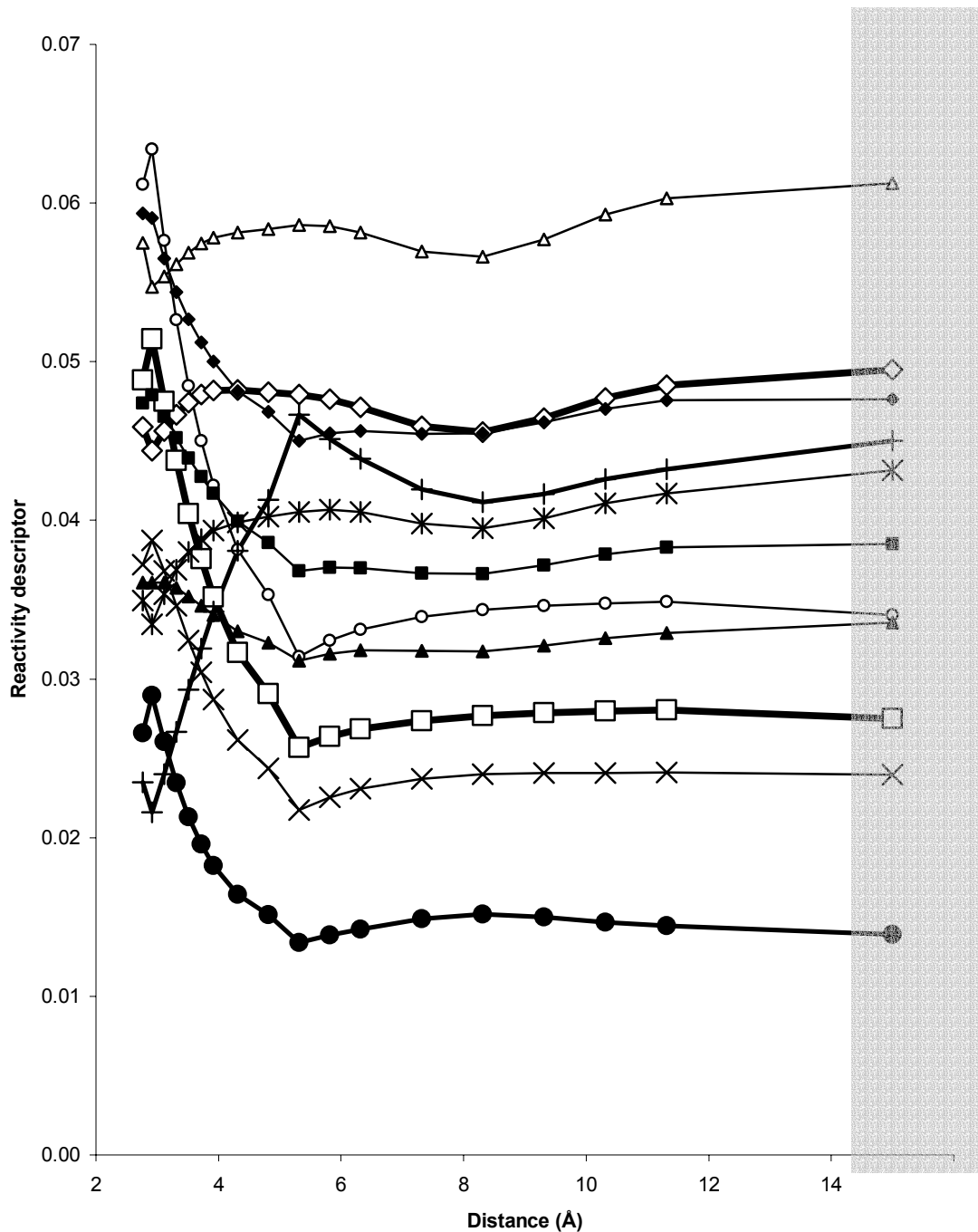
Figure 3.28: Variation of LRDs of Nitrogen in $(BH_3NH_3)_2$ with $B\text{-}N'$ distance

$\diamond$ f^+ $\square$ f^- $\blacksquare$ f^0 $\triangle$ s^+ $\diamond$ s^- $\blacklozenge$ s^0

$*$ $w^{+\,(\#)}$ $\times$ $w^{-\,(\#)}$ $\blacktriangle$ $w^{0\,(\#)}$ $+$ $R.E.^{(*)}$ $\bullet$ $R.N.^{(*)}$

\# scaled up by factor of 10. * scaled down by factor of 40. Shaded area corresponds to

half value of monomers except for *R.E.* and *R.N.* where it corresponds to the full value.

3-V. References

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*C*hapter-4

Interaction induced shifts in *O-H* stretching frequency of water in halide-ion water clusters: A microscopic approach with a bond descriptor

4-I. Introduction

Water halide clusters, owing to their unique spectroscopic and thermodynamic properties have been drawing a lot of interest of both experimentalists[1-11] and theorists.[12-27] The most widely studied properties of these clusters are thermodynamics,[1-5] charge-transfer-to-solvent (CTTS) [11, 17-18] properties and vibrational spectroscopy.[6-10,15-16] It is well-known that *O-H* bond elongates due to hydrogen bonding and the *O-H* frequencies show red shift with respect to average symmetric and asymmetric stretch[15]. In halide-water clusters, these shifts are mainly attributed to the polarization of water by the halide ion. However, coulombic interactions ($1/r^2$) alone cannot explain this huge red shift. [28(a)]

Over the years, attention has been drawn to the understanding of the molecular interactions[29]. Many theoretical concepts and models based on *ab initio* molecular orbital calculations are powerful tools for providing information regarding structure, energetics and reactivity of the molecular systems[30]. In particular, the density based

descriptors are known to play important role in determining the stability and reactivity of the systems. Global reactivity descriptors (GRD), like softness, hardness and chemical potential along with concept of hard soft acid base (HSAB) principle are widely used in describing the reactivity and the stability of chemical systems.[31-32] Several authors have showed that the polarizabilty of system correlates well with cube of global softness.[33] On the other hand, local reactivity descriptors (LRD), e.g. Fukui function (FF), local softness, relative electro/nucleo-philicity [34-40] etc. have been studied extensively in recent years for characterizing the reactivity and site-selectivity in chemical reactions. LRDs and GRDs have been used to formulate the local HSAB principle for interaction energy between two molecules[34, 37, 41-43]. While studying Lewis acidity of alkali cation-exchanged zeolites with adsorbed carbon monoxide, Deka et $al.$[44(a)] have shown that the blue shift of CO stretching frequency varies linearly with "relative electrophilicity" [44(b)] values of exchanged alkali cations.

Kim[15(a)] and co-workers have studied in detail the vibrational spectra of $F^-(H_2O)_n$, with cluster size n. Vibrational spectra for $O\text{-}H$ stretch can be mainly classified as (i) hydrogen bonded to halide atom $[\bar{v}(O-H_x)]$ (ii) hydrogen bonded to water $[\bar{v}(O-H_w)]$ and (iii) non-bonded free $[\bar{v}(O-H_n)]$. They showed the huge red shift in $\bar{v}(O-H_f)$ (from ~1600 cm^{-1} for n=1 to ~500 cm^{-1} for n=4) while very little shift in $\bar{v}(O-H_n)$. Recently, the dependence of O-H stretching frequency on hydrogen bond length has been widely used to obtain a measure of hydrogen bond strength and dynamics. [45] Recent femtosecond IR spectroscopy has successfully used this shift to study ultrafast vibrational dynamics.[46] Vibrational Self-Consistent Field (VCSF) method has been quite successful in describing vibrational spectra.[28] In this chapter we

present a first principle theory of interaction induced shifts in the *O-H* stretching frequency in clusters. We introduce a new descriptor "Bond Deformation Kernel" based on conceptual density functional theory[34] for describing shifts in *O-H* stretching frequencies of fluoride-ion water clusters. Central to our model is the use of local reactivity descriptors to include polarization effects.

The present chapter has been organized as follows. In section 4-II, we give a brief theoretical background of GRDs and LRDs. In section 4-III, methodology and computational details are presented. In section 4-IV, we will present our model and discuss results justifying the validity of the model to describe shifts in *O-H* stretching frequencies in fluoride-ion water clusters. In section 4-V we will present conclusions and the scope of the work for future exploration.

4-II. Theoretical Background

We have already discussed in detail, the local and global descriptors of reactivity in the previous chapters. These have been used to formulate local HSAB principle to study molecular interactions. As we have discussed earlier in chapter 1 (Sec. 1-IV(A)), the interaction between A and B can be assumed to be taken in two steps. In the first step, the interaction takes place at constant external potential through chemical potential equalization and in the second step, A and B evolve to equilibrium state by the reshuffling of the electron density by changes in external potential at constant chemical potential. Hence the total interaction energy between A and B can be given as,

$$\Delta E_{\text{int}} = \Delta E_{\nu} + \Delta E_{\mu} \tag{4.1}$$

Following Gazquez *et al*, [41, 47] the expression for the each term in Eq. (4.1) can be written,

$$\Delta E_v \approx -\frac{1}{4}\frac{(\mu_A - \mu_B)^2}{(\eta_A + \eta_B)} = -\frac{(\mu_B - \mu_A)^2}{2(S_A + S_B)}S_A S_B \tag{4.2}$$

and,

$$\Delta E_\mu \approx -\frac{1}{2}N^2(\eta_{AB} - \eta^*_{AB}) \tag{4.3}$$

where, η_{AB} is the hardness of the system AB at equilibrium and η^*_{AB} is the hardness of the system when the constituents of the system are far away from each other. Making use of approximate additivity of the softness of constitutive parts, [48, 49] softness of system AB can be written as,

$$S_{AB} = k'(S_A + S_B) \tag{4.4}$$

Where, k is the proportionality constant, S_A and S_B are the softness of the isolated systems A and B. It has been shown by Yang *et al*[49] that the molecular softness of a system at equilibrium can be replaced by the average of the softness of each constituent of the molecular system implying k'=1/2. In the limit of separation or dissociation of the molecule into its constituents, the proportionality constant can be approximated as 1 and in the interacting limit, the total softness decreases (conforming to the principle of maximum hardness) and thus k attains a value less than 1. As the total molecular softness is insensitive to the number of electrons,[50] one may consider the softness values of constitutive parts either before or after the charge transfer has occurred, and therefore S^*_{AB} may be approximated with another proportionality constant k'. The difference in the hardness (η_{AB} - η^*_{AB}) can be approximated by,

$$(\eta_{AB} - \eta*_{AB}) = \left(\frac{1}{S_{AB}} - \frac{1}{S*_{AB}} \right) = \left(\frac{1}{k'(S_A + S_B)} - \frac{1}{k''(S_A + S_B)} \right)$$

$$= \frac{K}{(S_A + S_B)} \tag{4.5}$$

where, K is another proportionality constant. By applying Eq. (4.5) in Eq. (4.3),

$$\Delta E_\mu \approx -\frac{1}{2} N^2 K \left(\frac{1}{S_A + S_B} \right) \tag{4.6}$$

where, N_{AB} is the total number of electrons of the system AB. The product of the terms N^2 and K, known as λ,[41] can be related physically to the effective number of valence electrons that have participated in the interaction between A and B.

$$\Delta E_{int} \approx -\frac{1}{2} \frac{(\mu_A - \mu_B)^2}{S_A + S_B} - \frac{1}{2} \frac{\lambda}{S_A + S_B} \tag{4.7}$$

Pal *et al*. provided for the quantitative description of λ as the change in the electron densities of the systems before and after the interaction process. This change gives the effective number of valence electrons participating in the interaction process.

From a local point of view, if the interaction between two chemical systems A and B occurs through the kth atom of A, one can express the interaction at the kth atom by replacing global softness of A by the local softness of the site k in A.

$$\left(\Delta E_{int} \right)_{Ak} \approx -\frac{(\mu_B - \mu_A)^2}{2(S_A f_{Ak} + S_B)} S_A S_B f_{Ak} - \frac{1}{2} \frac{\lambda}{(S_A f_{Ak} + S_B)} \tag{4.8}$$

Further, if the interaction from B is considered to from lth atom of B. S_B can be replaced by $S_B f_{Bl}$.

$$\left(\Delta E_{\text{int}}\right)_{Ak,Bl} \approx -\frac{\left(\mu_B - \mu_A\right)^2}{2\left(S_A f_{Ak} + S_B f_{Bl}\right)} S_A S_B f_{Ak} f_{Bl} - \frac{1}{2}\frac{\lambda}{\left(S_A f_{Ak} + S_B f_{Bl}\right)} \qquad (4.9)$$

The above expression is similar to the situation in HSAB, here one can infer that the interaction is more favored from the sites whose local softnesses are similar. This is also known as local HSAB principle.

4-III. Methodology and Computational details

Geometry optimization of water and different fluoride-ion water clusters were carried out at second order Moller-Plesset (MP2) level 6-31++G(d,p) basis set. *O-H* stretching frequencies of different clusters were calculated at the same level. Global softness and atom condensed FFs were calculated as described in earlier chapter (via Eq. 2.4 and 2.13), using Lowdin[51] population analysis. The atomic populations of (N_0+1) electronic state were calculated by freezing molecular orbitals of N_0 electronic state of the cluster at SCF. The FFs are obtained under finite difference approximation. Ideally, the change in the electrons for such calculations should be kept minimum ($\Delta N \rightarrow 0$). The change of one electron introduces too large relaxation. To avoid occurrence of this it is desirable to freeze the core [35(a)]. The calculations were performed using the GAMESS system of programs[52].

4-IV. Results and discussions

Fig. 1 presents the structures of different fluoride-ion water clusters. Table 1 presents the averaged *O-H* vibration frequency of different fluoride-ion water clusters and their shifts with respect to averaged *O-H* stretching frequency of water (3910.859 cm^{-1}). Our results are in agreement with the results obtained earlier. [15(a)] It should be noted that the shift in vibrational frequency of *O-H$_f$* bond correlates with the halide-ion distance ($r_{(O-F)}$), which also is in agreement with the earlier studies.
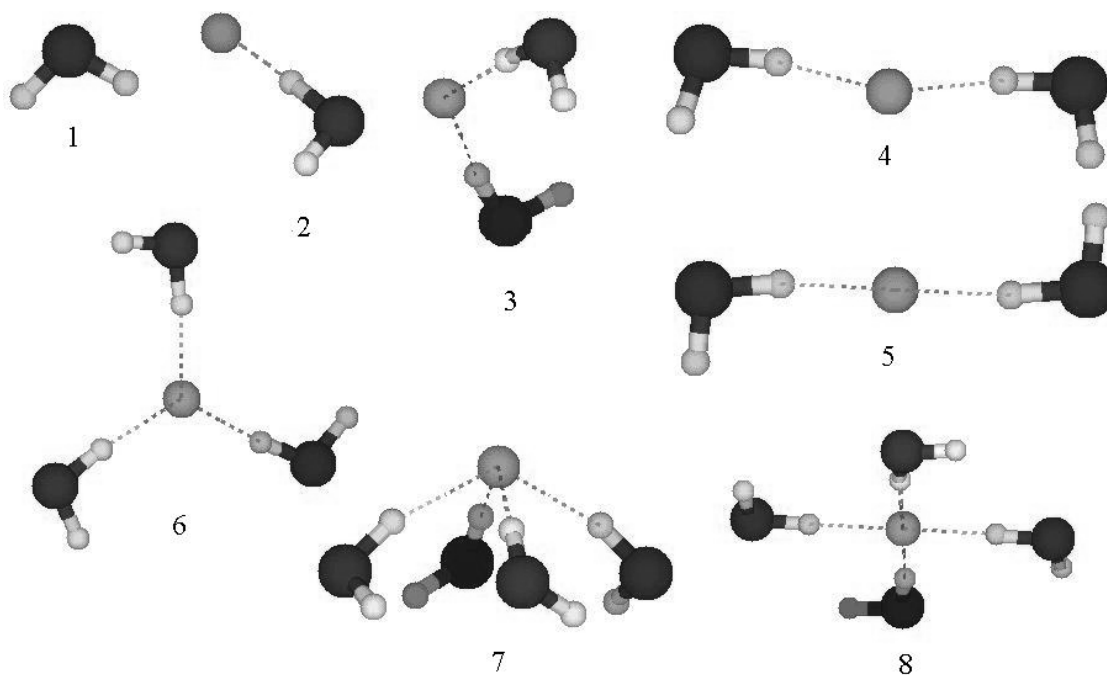
Figure 4.1: Structures of fluoride-ion water clusters

Table 4.1: *O-H* vibration frequency of different fluoride-ion water clusters and its average shifts with respect to average *O-H* stretching frequency of water. [MP2/6-31++G**]

N	Structure	$r_{(O-F)}$ [a]	($O-H_f$)		($O-H_n$)	
			$\bar{\nu}$ [b]	$\Delta\bar{\nu}$ [b]	$\bar{\nu}$ [b]	$\Delta\bar{\nu}$ [b]
0	1				3910.859	0
1	2(Cs)	2.46230	2377.986	-1532.873	3901.881	-8.97758
2	3(C2)	2.54395	2992.457	-918.4024	3920.914	10.0548
	4(C2v)	2.54870	3051.640	-859.2201	3914.607	3.74815
	5(C2h)	2.54728	3050.479	-860.3799	3913.481	2.62239
3	6(C3)	2.60091	3282.242	-628.6168	3915.394	4.53529
4	7(C4)	2.69247	3503.688	-407.1715	3875.072	-35.78718
	8(C4h)	2.66277	3479.698	-431.1605	3913.829	2.96977

[a] in Å

[b] in cm^{-1}

It has been shown that the softness of the system is related to polarizability. More polarizable a system, softer it is. However, the vibrational frequencies cannot be correlated to the GRDs, but they depend on local polarizability. These must be related to appropriately defined local descriptors, such as FFs, local softness etc. Interestingly, the Stott and Zaremba[53] plots of local polarizability and the atomic FFs are similar.

The condensed local reactivity descriptors, as defined earlier, describe the effect of addition or removal of one electron, on the electronic population on an atom. These are used for reactivity studies of systems of similar number of atoms. However, these become inappropriate for comparison across the systems, where the number of atoms is not constant. If the number of atoms increases (as in case of our system), the additional

electron is distributed over a larger number of atoms. Thus this distribution is not an appropriate description for system with different number of atoms.

In this chapter, we propose a new descriptor, the Normalized-Atom-Condensed-Fukui-Functions (NFF) (ς_A), as an appropriate indicator of local polarizability for making comparisons between system of different number of atoms and hence, we propose this to model the change in vibrational frequency. We define this as,

$$\varsigma_A{}^a = N \times f_A{}^a \qquad \forall a = +, - \tag{4.10}$$

where, N is number of atoms in the system.

Table 4.2 presents the normalized atom condensed electrophilic FFs for atoms of water in the different fluoride-ion water clusters. It is interesting to observe that NFF values of H_f, give correct qualitative idea about the corresponding O-H stretch but same does not hold for H_n.

Table 4.2: Normalized Atom Condensed electrophilic Fukui-functions for atoms of water in the different fluoride-ion water clusters. [MP2/6-31++G**]

N	Structure	Softness	Atoms		
			H_f	O	H_n
0	1	1.953352		0.20391	1.39805
1	2(Cs)	2.559131	0.14456	0.29724	3.47116
2	3(C2)	2.383431	0.21147	0.28525	2.95869
	4(C2v)	2.421854	0.23429	0.30527	2.95421
	5(C2h)	2.407542	0.28644	0.27741	2.92789
3	6(C3)	2.477269	0.33133	0.25020	2.74873
4	7(C4)	2.322732	0.34814	0.33787	2.53019
	8(C4h)	2.409723	0.35022	0.28158	2.61391

Taking cue from Eq. (4.9), while dealing with our system, we propose a new descriptor, the "Bond Deformation Kernel" (BDK) to model the interaction between O and H atom of water molecule in the cluster. BDK, as the name suggests, describes the deformation of the O-H bond of water due to addition of fluoride-ion. Addition of fluoride-ion to neutral water leads to elongation of one of the OH bonds, which is reflected by a huge red shift in stretching frequency of that bond [45(a)]. We define BDK as:

$$\mho_{O-H} = \frac{\Lambda}{S(\varsigma_O^+ + \varsigma_H^+)} \tag{4.11}$$

Where, $\mho_{O-H}$ is BDK of O-H bond, Λ is charge transferred to the water from fluoride-ion and S is global softness of the fluoride-ion water cluster. A careful examination of BDK shows that it actually arises out of Eq. 4.9 as both O and H have the same chemical potential as that of the cluster, rendering the first term zero. NFF has been used in lieu of FFs to include effects of polarizations. Λ is calculated as:

$$\Lambda = (\rho_{H_f} + \rho_O + \rho_{H_n} - \rho_{water}^0)$$
$$= (\rho_{H_f} + \rho_O + \rho_{H_n} - 10.0) \tag{4.12}$$

Table 4.3 presents, the BDK of different O-H bonds of different halide-ion water clusters. It is interesting to note that the correlation of BDK of the O-H_f bond with $r_{(O-F)}$ is similar to that of the shift in vibrational frequency of O-H_f bond with $r_{(O-F)}$. Fig. 4.2 presents the plots of the shift in O-H stretch with BDK. From Fig. 4.2, it can be seen

Table 4.3: BDK of O-H bonds for different halide-ion water clusters.[MP2/6-31++G**]

n	Structure	$\mho_{O-H_f}$ [a]	$\mho_{O-H_n}$ [a]
0	1	0.00000	0.00000
1	2(Cs)	0.13738	0.01611
2	3(C2)	0.08652	0.01325
	4(C2v)	0.07435	0.01231
	5(C2h)	0.07199	0.01266
3	6(C3)	0.05282	0.01024
4	7(C4)	0.03297	0.00808
	8(C4h)	0.03701	0.00789

(a) in a.u.
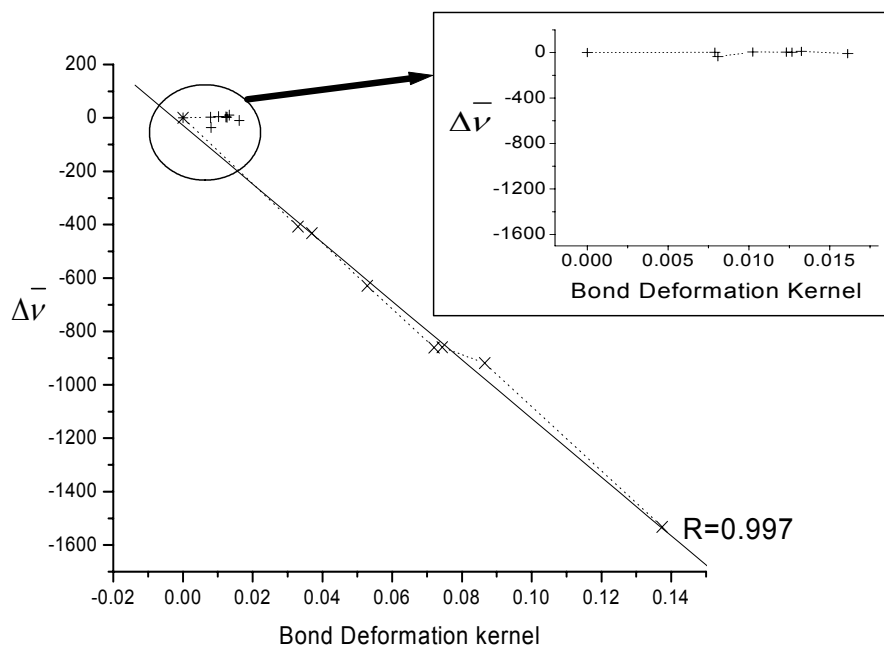
Figure 4.2: Plots of shift in *O-H* stretch vs the Bond Deformation Kernel. ⋯✗⋯(O-H_f) ⋯+⋯(O-H_n). $\Delta\bar{\nu}$ in cm^{-1} and BDK in a.u.

that BDK correlates linearly with the change in *O-H* stretching frequency (BDK varies

linearly with $\Delta \bar{v}(O-H_f)$. Though the correlation seen is not that good with (*O-Hn*), it

gives very low values of BDK, which is consistent with very low shift in (*O-Hn*) stretch.

Looking at the results obtained, BDK appears to be an important tool to describe local

polarizations in the system and, in particular, to describe the shift in vibrational spectra

arising due to polarization in the system.

4-V. Conclusions and Future Scope

In summary, we propose here two new descriptors, the NFF (ς_A), as an

appropriate measure of local polarizability and BDK (υ) as a measure of bond

elongation. We show that NFF along with BDK can be successfully used to describe

interactions between different atoms especially in the cases where simple coulombic

interactions are not sufficient to describe it. Though our model does not provide

distribution of frequencies as seen in the IR spectra, combining our approach with other

empirical models (force fields) in computer simulations should provide better

description of IR spectroscopy and electrostatic interactions.

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Chapter-5

Minimum Magnetizability Principle

5-I Introduction

The prediction of the preferred direction of a reaction and the product formation is the major question connected with the problem of reactivity of molecules in different environmental conditions. Pearson proposed the "Maximum Hardness Principle" (MHP) which states that "There seems to be a rule of nature that molecules arrange themselves so as to be as hard as possible".[1] This principle in general has invoked a considerable attention over the years in the understanding of molecular interactions.[2] We have discussed MHP in detail in section 1-IV. Original proof of MHP given by Chattaraj and Parr is based on assumption that the chemical potential remains constant.[3] Pearson and Palke tested the formulation of MHP by Chattaraj et. al. and observed that the condition of constant chemical potential is observed for small asymmetric vibrations about a symmetric equilibrium position while the same does not hold for symmetric vibrations.[4] The same was verified by Pal et al using the highly correlated wave function method by considering the symmetric and asymmetric variations around the equilibrium geometry of water molecule.[5]

The linear response of the electronic cloud of a chemical species to weak external electric field is measured in terms of polarizability (α). Polarizability and softness are closely related (see section 1-V). Several authors demonstrated the linear relation between cube root of polarizability and softness for ground stated.[6] Analytic derivation by Simon-Manso and Fuentealba using local functional model for hardness kernel further strengthened this view.[7] Chattaraj et. al. showed the linear relationship also observed even for excited states.[8] This linear relationship give rise to the minimum polarizability principle (MPP)[9] which states that, "The natural direction of evolution of any system is towards a state of minimum polarizability". Though, the effect of external electric field has been studied by various authors on the stability of chemical species, there have been very few studies on the effect of external magnetic field.

The response of the chemical species to external magnetic field, which is measured in terms of magnetizability (ξ), is of special interest in this chapter. The understanding of the same will help in extending the scope of the conceptual density functional theory (DFT) [10] to explain the magnetic interactions and magnetochemistry of the species. In this chapter we propose and also verify through *ab initio* calculations a new electronic structure principle of stability, viz. the minimum magnetizability principle (MMP), as a companion to MHP and MPP. MMP may formally be stated as "*A stable configuration/conformation of a molecule or a favorable chemical process is associated with a minimum value of the magnetizability*"

5-II. Theoretical Background and Insights

The linear responses of the electronic cloud of a chemical species to weak external electric and magnetic fields are measured in terms of polarizability (α) and magnetizability (ξ) respectively[11], as follows:

$$P = \alpha \in \quad ; \quad \alpha = -\frac{\partial^2 E(\in)}{\partial \in^2}\Big|_{\in=0} \tag{5.1}$$

and

$$m = \xi B \quad ; \quad \xi = -\frac{\partial^2 E(B)}{\partial B^2}\Big|_{B=0} \tag{5.2}$$

where P and m refer to induced dipole moment and magnetic moment respectively. $\in$ and B refer to the external electric and magnetic fields respectively.

The presence of perturbation gives rise to extra terms in Hamiltonian. While considering terms up to quadratic terms, Hamiltonian may be written as

$$H = H_0 + \lambda P_1 + \lambda^2 P_2 \tag{5.3}$$

where H_0 is normal electronic Hamiltonian operator, and the perturbations are defined by operator P_1 and P_2 with λ determining the strength. Based on an expansion in exact wavefunctions, perturbation theory gives the first and second-order corrections as

$$W_1 = \lambda \langle \psi_0 | P_1 | \psi_0 \rangle \tag{5.4}$$

$$W_2 = \lambda^2 \left[\langle \psi_0 | P_2 | \psi_0 \rangle + \sum_{i \neq 0} \frac{\langle \psi_0 | P_1 | \psi_i \rangle \langle \psi_i | P_1 | \psi_0 \rangle}{E_0 - E_i} \right] \tag{5.5}$$

In general, the second order response of energy with respect to any perturbation can be derived from second order perturbation theory and may be written as[11(a)].

$$\delta^2 E_{xy} = -\sum_{j=1}^{\infty} \frac{\langle \psi_0 | \hat{\delta}_x | \psi_j \rangle \langle \psi_j | \hat{\delta}_y | \psi_0 \rangle + \langle \psi_0 | \hat{\delta}_y | \psi_j \rangle \langle \psi_0 | \hat{\delta}_x | \psi_j \rangle}{E_j - E_0} \tag{5.6}$$

On looking at the above expression for second order response, one can conclude that the most dominating term is the one which involves first excitation energy leading to above mentioned principles.

The Hamiltonian in presence of magnetic field is given as

$$H = \frac{1}{2}(p+A)^2 + V \tag{5.7}$$

where, A is the vector potential associated with magnetic field

$$B = \nabla \times A \tag{5.8}$$

Equation 5.7 can be deduced to the following form

$$H = \frac{1}{2}p^2 + A \cdot P + \frac{1}{2}A^2 + V \tag{5.9}$$

The vector potential is not uniquely defined. It is convention to select it as

$$A(r) = \frac{1}{2}B \times (r - R_G) \tag{5.10}$$

where R_G is referred to as gauge origin, i.e. the origin of coordinate system.

Inserting expression of vector potential yields in the eq. (5.9), one obtains

$$A \cdot p = \left[\frac{1}{2}B \times (r - R_G)\right] \cdot p = \frac{1}{2}B \cdot (r - R_G) \times p = \frac{1}{2}B \cdot L \tag{5.11a}$$

where, L is angular momentum operator.

$$\frac{1}{2}A2 = \frac{1}{2}\left[\frac{1}{2}B \times (r - R_G)\right] \cdot \left[\frac{1}{2}B \times (r - R_G)\right] = \frac{1}{8}\left\{B^2 \cdot (r - R_G)^2 - \left[B \cdot (r - R_G)\right]^2\right\} \tag{5.11b}$$

The presence of magnetic field introduces two terms both linear and quadratic in the field to the Hamiltonian. The second order property is magnetizability which according to eqs (5.3) and (5.5) contains both linear and quadratic perturbation operator. The P_1^ξ operator is half angular momentum operator (L), while P_2^ξ may be written as

$$P_2^\xi = \frac{1}{8}\left[(r-R_G)^t (r-R_G) - (r-R_G)(r-R_G)^t \right] \qquad (5.12)$$

from second order perturbation theory eq. (5.5) yields

$$\xi = 2\langle \psi_0 | P_2^\xi | \psi_0 \rangle + \sum_{i=1}^{\infty} \frac{\left| \langle \psi_0 | L | \psi_i \rangle \right|^2}{E_0 - E_i} \qquad (5.13)$$

where, the first term refers to as diamagnetic component (ξ_{dm}) of magnetizability while the later is paramagnetic component (ξ_{pm}). ξ_{dm} is negative.

$$\xi_{Total} = \xi_{dm} + \xi_{pm} \qquad (5.14)$$

5-III. Methodology and Computational details

In order to verify our prognosis we study the asymmetric and symmetric stretching of H_2O. Calculations were performed using DALTON[12] system of programs. MP2 level properties are calculated using second-order-perturbation-propagation-approximation (SOPPA) [13] method. Hardness and chemical potential were calculated using finite difference approximation as done in previous chapters.

5-IV. Results and discussions

Figure 1 presents the variations in $\alpha^{1/3}$, $|\xi_{dm}|^{1/3}$ and $|\xi_{pm}|^{1/3}$ with 2S during the stretching of H_2O. Like polarizability, the magnetizability also shows linear behavior with the softness. This implies that magnetizability would show similar nature as that of
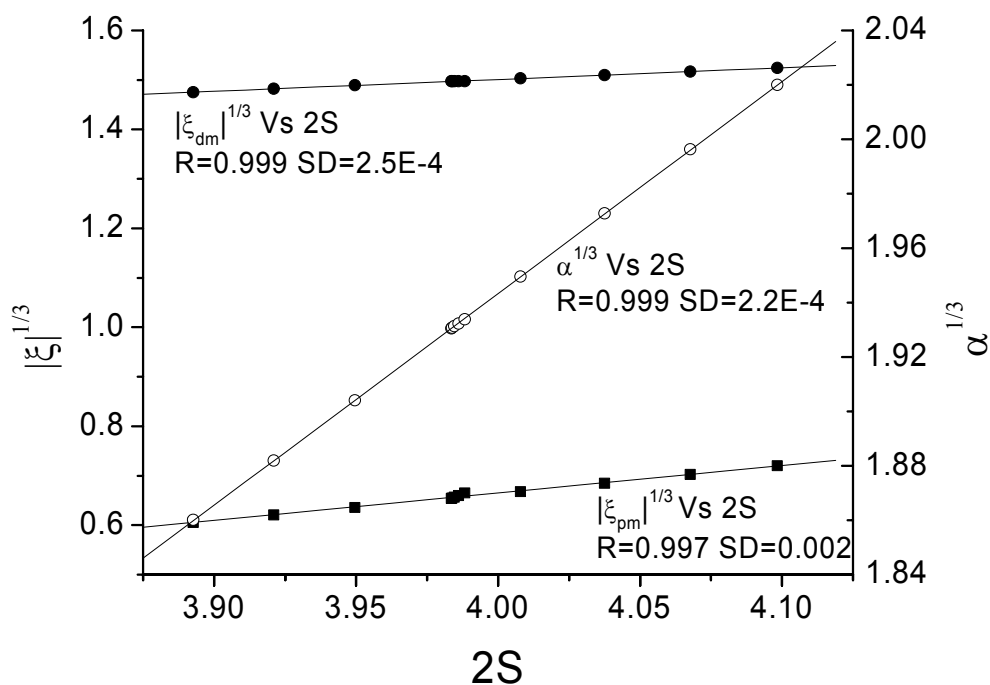
Figure 5.1: Plots of $|\xi|^{1/3}$ and $\alpha^{1/3}$ vs 2S calculated during the stretching of water [MP2/6-31++G**]. ξ, α in a.u. and S in hartree^{-1}.

polarizability at equilibrium position.

Figure 2 presents the related variations in η, α and ω with respect to (*O-H*) bond length during asymmetric stretch. As expected from the MHP and MPP, η attains its maximum value and α attains its minimum value for the equilibrium bond length where ω is also a minimum. The chemical potential remains constant[5,14] in the sense of Pearson-Palke[4] and Makov.[15] Table 1 presents the variation in μ, η, α, ξ and ω with respect to (O-H) bond length during symmetric stretch of water. During symmetric stretch no maximum in η is observed near equilibrium geometry as chemical potential itself is not constant. Hence the principle cannot be tested in this case. This is also in agreement with earlier works on PMH.[4,5, 14]
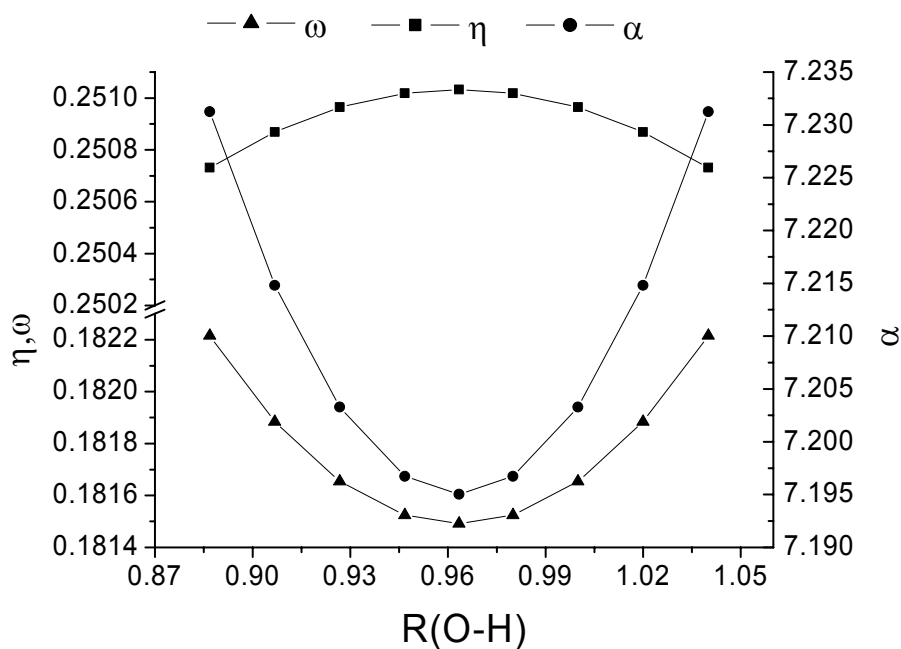
Figure 5.2: Profiles of η, α, and ω during the asymmetric stretching of water [MP2/6-31++G**]. η,ω,α in a.u. and R(O-H) in Å

Table 5.1: Variation of ξ, η, μ, α, and ω with respect to (O-H) bond length during symmetric stretch [MP2/6-31++G**]

O-H Distance	ξ	η	μ	α	Ω
0.9000	-2.9884	0.256893	-0.216809	6.4359	0.18298
0.9200	-3.0172	0.255036	-0.215689	6.6649	0.182412
0.9400	-3.0450	0.253188	-0.214623	6.9035	0.181932
0.9634[a]	-3.0761	0.251032	-0.213448	7.1950	0.181491
0.9800	-3.0973	0.249508	-0.212665	7.4098	0.181262
1.0000	-3.1216	0.247672	-0.211777	7.6776	0.181085
1.0200	-3.1446	0.245837	-0.210955	7.9553	0.181022
1.0400	-3.1663	0.243999	-0.210200	8.2427	0.181083

(a) Equilibrium geometry (MP2 optimized)

Figure 3 presents the variation in magnetizability of water during asymmetric stretch. It is heartening to note that in concurrence with MMP stated earlier, total magnetizability indeed shows its minimum at equilibrium geometry. What is of interest is to note that minimum in the total magnetizability is driven by the minimum observed by the paramagnetic component. This can be however be seen as artifact of equation 5.13 where, the difference of excitation energies comes in denominator for term involving paramagnetic component. The diamagnetic component, however, does not change much during the asymmetric stretch.
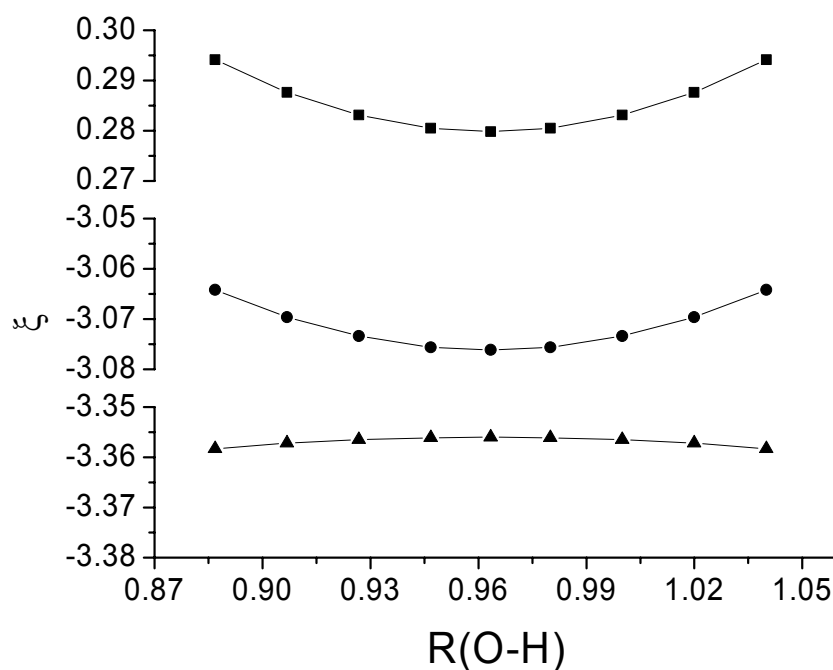
Figure 5.3: Plot of ξ during asymmetric stretching of water [MP2/6-31++G**]. ξ in a.u. and R(O-H) in Å. $-\blacksquare-$ Paramagnetic $-\blacktriangle-$ Diamagnetic $-\bullet-$ Total

5-V. Conclusions

A new electronic structure principle, viz. the minimum magnetizability principle (MMP) has been proposed to extend the domain of applicability of the conceptual density functional theory (DFT) in explaining the magnetic interactions and magnetochemistry. This principle may be stated as, "A stable configuration/conformation of a molecule or a favorable chemical process is associated with a minimum value of the magnetizability".

The variants of HSAB principle and MHP in terms of magnetizability would be helpful in analyzing chemical reactions especially when they are associated with changes in magnetic properties.

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List of Publications

1. Akhilesh Tanwar and Sourav Pal "Behavior of the Local Reactivity Descriptors during Complexation: A Case Study of $BXX'X''NH_3$(X, X', X'' = H, F)" *J. Phys. Chem. A* **2004**, 108, 11838.

2. Akhilesh Tanwar and Sourav Pal "Separability of local reactivity descriptors" *J. Chem. Sci.* **2005**, 117, 497.

3. Akhilesh Tanwar, Debesh Ranjan Roy, Sourav Pal, and Pratim Kumar Chattaraj, "Minimum magnetizability principle" *J. Chem. Phys.* **2006**, 125, 056101 (2 pages).

4. Akhilesh Tnawar, Biman Bagchi and Sourav Pal, "Interaction induced shifts in O-H stretching frequency of water in halide-ion water clusters: A microscopic approach with a bond descriptor" *J. Chem. Phys.* **2006** (accepted for publication).