Study of a Rational Model of Gas Phase Molecules in External Electric Field and in Solvents Using Local Reactivity Descriptors

A THESIS SUBMITTED TO THE
UNIVERSITY OF PUNE

FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
(IN CHEMISTRY)

BY
RAHUL KAR

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(Research Guide)

Physical Chemistry Division
National Chemical Laboratory
Pune-411008
INDIA

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CERTIFICATE

CERTIFIED that the work incorporated in the thesis **Study of a Rational Model of Gas Phase Molecules in External Electric Field and in Solvents Using Local Reactivity Descriptors** submitted by **Rahul Kar** for the degree of Doctor of Philosophy to the University of Pune, was carried out by the candidate under my supervision in the Physical Chemistry Division, National Chemical Laboratory, Pune-411008, India. Such material as has been obtained from other sources has been duly acknowledged in the thesis.

Date: Dr. Sourav Pal
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DECLARATION

I declare that the thesis entitled **Study of a Rational Model of Gas Phase Molecules in External Electric Field and in Solvents Using Local Reactivity Descriptors** submitted by me for the degree of Doctor of Philosophy is the record of work carried out by me at the Physical Chemistry Division, National Chemical Laboratory, Pune from August, 2004 to May, 2009 under the supervision of Dr. Sourav Pal and has not formed the basis of award of any degree or diploma.

I further declare that the material obtained from other sources has been duly acknowledged in the thesis.

Date: Rahul Kar

Place: Physical Chemistry Division
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Dedicated to
my parents

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Pune Rahul Kar

Abstract

A study on the behavior of electron density and its variation with respect to the small perturbations can reveal many interesting aspects concerning the reactivity pattern of the atomic and molecular systems.[1-4] Due to the small perturbations, the electron density of the interacting systems will be redistributed. Moreover, it will also throw some light on the application of these reactivity descriptors for some gas phase molecules i.e. the reactivity of are studied and their application. The reactivity descriptors, such as chemical potential,[5] chemical hardness,[6] Fukui function[7] etc., are the concepts developed from the knowledge of energy and electron density and primarily represent the area of conceptual density functional theory (DFT).[8] The concepts involved are, in general, quantified in terms of the global and local reactivity descriptors.

The main objectives of the present thesis are as follows:

- To study the influence of external perturbations, mainly the effect of external electric field on reactivity descriptors.
- To throw some insight on how the reactivity of gas phase molecules change in the presence of solvent with different dielectric constant.
- To propose a new reactivity descriptor to understand the group reactivity in metalloaromatic and metalloantiaromatic compounds.

The organization of the thesis will be as follows:

Chapter 1

In chapter 1, we review the earlier theoretical developments made towards the area of chemical reactivity using the quantum chemical methods. We will describe how the area of conceptual density functional theory has grown over the years. Considering electron density as a basic variable, conceptual DFT provided sharp definition of different chemical concepts like chemical potential, electronegativity, chemical hardness, etc. We would also enlighten the concepts developed to understand the local behavior i.e.,

the site selectivity and site reactivity.[9] The success and failure of these descriptors in predicting the reactivity of molecular systems will be discussed. In addition, we will discuss the developments carried out in the area of the semi-quantitative model based local Hard-Soft Acid-Base (HSAB) principle.[10]

Chapter 2

In chapter 2, we study the response of the global and local reactivity descriptors in the presence of external electric field for some of the simple prototype linear molecular systems such as HF, CO, HCN and C_2H_2 molecules. In addition to the analysis on the reactivity of these systems, the influence of the electric field on the interaction energy of the complexes formed by these systems has also been studied using the recently proposed semi-quantitative model based on the local HSAB principle. The complexes formed by the above molecules such as FH---CO, FH----OC, NCH----CO, NCH---OC, and HCCH---CO, HCCH---OC, and HCCH---NCH were considered in analyzing the semi-quantitative model based on the local HSAB principle. The external electric field is varied from 0.000 au to 0.012 au. Using the inverse relationship between the global hardness and softness parameters, a simple relationship is obtained for the variation of hardness in terms of the Fukui function under the external electric field. It is shown that the increase in the hardness values for a particular system in the presence of external field does not necessarily imply that the reactivity of the system would be deactivated or vice versa.

Chapter 3

Chapter 3 includes two parts. This chapter will study the consequences of the effect of external electric field on changing the symmetry of molecules. The first part of our study mainly involves the application of weak electric field (electric field varied from 0.000 au to 0.006 au) in a direction along the principal axis and in perpendicular directions of some nonlinear planar C_{2v} symmetry molecules such as H_2O, HCHO, CH_2S, SO_2 and O_3. We also discuss the strength of the electric field studied in this work in terms of the strength of the molecular interaction. The work is expected to throw light on the effect of interactions within the above range on reactivity descriptors. In addition, the nonlinearity in the variation of condensed Fukui function is explained by a perturbative analysis. In the second part, conceptual DFT has been used to understand the reactivity of biologically important molecule, deoxyribonucleic acid (DNA) bases under the influence of external electric field. The four bases found in DNA are adenine, cytosine, guanine and thymine and the double helix are stabilized by the hydrogen bonds between the bases formed by the reactive atoms. The electric field (electric field varied from 0.000 au to 0.006 au) is applied towards the atoms forming the hydrogen bonds (i.e. parallel to the hydrogen bonds) as well as towards its perpendicular directions. The reactivity of the atoms forming the hydrogen bonds is only analyzed. Moreover, the influence of the electric field on the interaction energy of the base pairs (adenine-thymine and guanine-cytosine) has also been studied using the semi-quantitative model based on the local Hard-Soft Acid-Base (HSAB) principle. The calculated local HSAB stabilization energy is compared with the stabilization energy calculated by quantum chemical method. All the calculation was performed using the GAMESS software with 6-31++G (d, p) basis set and B3LYP hybrid functional.

Chapter 4

In chapter 4, conceptual DFT is exploited to understand the reactivity of molecules in a medium of solvent with increasing dielectric constant. Aprotic as well as protic solvents are used for the present study. The effect of solvation, with different solvents, on the reactivity and stability of CH_3CHO and CH_3CH_2CHO are analyzed. The solvents chosen for the present study are n-hexane (1.89), diethyl ether (4.335), pyridine (12.3), ethanol (24.3), methanol (32.63) and water (78.54); dielectric constants are shown in parenthesis. It is found that the global parameter, such as chemical potential and hardness, decrease from gas phase to solvent phase with increasing dielectric constant. However, it is observed that the Fukui function of the reactive atoms increases significantly with the dielectric constant of the aprotic solvents while for the protic solvents the variation of the reactivity indices is insignificant. The local reactivity parameters are calculated using the Hirshfeld population scheme as implemented in $DMol^3$ software. The COSMO (COnductor-like Solvatiob MOdel is a continuum solvation model in which the solute molecule forms a cavity within the dielectric continuum of permittivity that represents the solvent) solvation model as employed in $DMOL^3$ is utilized to compute the global as well as the local parameters in the different solvent surroundings. The consistent of the results were confirmed using different functionals like BLYP, PW91 and PBE.

Chapter 5

In chapter 5, local reactivity descriptors such as the condensed local softness and Fukui function have been employed to investigate the inter-cluster reactivity of the metalloaromatic (Al_4Li^- and Al_4Na^-) and antiaromatic (Al_4Li_4 and Al_4Na_4) compounds. We have proposed the concept of group Fukui function which is defined as group softness divided by global softness. It is useful when the reaction does not take place through a single atom, but through neighbouring atoms in a cooperative manner. This concept is used along with group softness to characterize the strength of the nucleophilicity of the Al_4 unit in these compounds. The aim of this work is to understand the enhanced efficiency of the electron injection of the Al-Li cathode in the organic light emitting diode due to the formation of Al-Li clusters at the interface. The calculations were done using 6-31+G* basis set at the MP2 level. Our analysis shows that the Al_4 unit of the Al_4Li^- cluster has the highest nucleophilicity compared to the other clusters. The trend of the above compounds on the basis of the strength of nucleophilicity of the Al_4 unit is as follows $Al_4Li^- < Al_4Na^- < Al_4Li_4 < Al_4Na_4$. Hence, we believe that the formation of Al_4Li^- kind of metalloaromatic clusters would be favorable for the increase in the efficiency of the electron injection of the Al-Li cathode.

Chapter 6

In chapter 6, we would like to study the reaction involving a ketene and a double bond via a [2+2] cycloaddition reaction where the final product is a cyclobutanone. Local reactivity descriptor such as local softness is used to understand the facts. In addition, local HSAB principle is exploited which states, interaction between any two molecules occur not necessarily through their softest atoms, but rather through those atoms which have similar local softness. Hence, our study suggests that the local hard-soft acid-base principle may be a guide line for predicting the feasibility of these types of reactions. The consistency of the results are tested using different basis set, 6-31++G (d, p) and 6-311++G (d, p) and different functionals like B3LYP, BHHLYP and BLYP.

Chapter 1

General Introduction

1.1 Introduction and Motivation

The study of molecular interaction has been a challenge to the community of theoretical and computational chemists. Even though the quantum chemical methods provide basic framework to study these interactions in an accurate way, the applicability of the methods was limited to small systems. Several concepts or indices such as, valency, orbital symmetry, molecular electrostatic potential, etc. have been extensively used to explain the reactivity of molecular systems.[1-5] Apart from these concepts, the initiative taken by Fukui in developing the concept of frontier molecular orbital (FMO) was another path breaking achievement in elucidating the chemical reactions.[6] However, Parr and his coworkers correlated the chemically relevant concepts from the framework of density functional theory (DFT).[7-11] This branch of DFT, termed as conceptual DFT, by one of its protagonists Robert G Parr, mainly deals with concepts and principles derived from the density functional theory.

Over the recent years, conceptual DFT has offered a perspective for the prediction and interpretation of many theoretical and experimental results. The quantification of the widely used concepts, such as chemical potential,[11] hardness,[8] Fukui Function[9] etc., within the framework of density functional theory is one of the accomplishments in the area of quantum chemistry in the past few decades. The reactivity indices are grouped as global reactivity descriptors (GRD) and local reactivity descriptors (LRD). These descriptors along with the hard-soft acid-base (HSAB) principle and maximum hardness principle (MHP) lay the foundation of chemical reactivity theory.[12-14]

The reactivity descriptors have been used as simple models for describing the reactivity and interactions of chemical species along with the above two principles.[7, 15] Several research groups have contributed to this area. The contributions are in the form of proposing new descriptors to its applications in chemical problems. It started with the definition of chemical potential (its equivalence to electronegativity), absolute hardness (its inverse softness) which together form GRD. In terms of hardness and softness parameters, these studies have led to some important insights about the nature of reactivity and stability of molecular systems.[11-12, 14, 21-25] Soon after, Parr and Yang correlated the FMO concept of Fukui within the density functional framework as Fukui function, a local reactivity descriptor.[9] An elaborate discussion on these descriptors will be made in the subsequent sections.

Gazquez and Mendez used the GRD and LRD to formulate the semi quantitative model based on local HSAB principle for calculating the interaction energy between two molecules.[15b, 23, 26-27] The local HSAB principle states that the interaction between two molecular systems is favored, when it occurs through those atoms whose local softnesses are approximately equal.[26] An elaborate discussion on the HSAB principle will be made in the subsequent sections.

In this present thesis, we explore the effect of the external perturbations on these reactivity descriptors. Since the basic reactivity descriptors are derivatives of energy and electron density with respect to the number of electrons, the effect of external field on these descriptors can be understood by a perturbative analysis of energy and electron density with respect to the number of electrons and external field. For this purpose, we choose external electric field and solvents having different dielectric constants. In particular, we would like to discuss the influence of external electric field on reactivity descriptors for linear as well as general classes of molecules. In addition, we dedicate one chapter to throw some insight on how the reactivity of gas phase molecules change in the presence of solvent with different dielectric constant. Later, we would propose a new reactivity descriptor called group Fukui function which is used to understand the group reactivity in metalloaromatic and metalloantiaromatic compounds.

1.2 A Journey from Wave function theory to DFT

1.2.1 Wave function based theory[28-29]

The electronic structure of atoms and molecules can be studied by solving the time-independent Schrödinger equation,

$$\left(-\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2-\sum_{i,A=1}^{N}\frac{Z_A}{r_{iA}}+\sum_{i<j}^{N}\frac{1}{r_{ij}}\right)\psi=E\psi \qquad 1.1$$

where the term in the bracket is the time-independent non-relativistic electronic Hamiltonian, under the Born-Oppenheimer approximation. All the information of a state in a system is contained in the wave function, $\psi\left(x_1,x_2,......x_N\right)$. The first term in the Hamiltonian is the kinetic energy operator ($\hat{T}$) and the second term represents the electron-nuclear attraction. The crux of the problem lies in the last term i.e., the repulsive electron-electron interaction. Hartree-Fock approximation models the many electron problem to a many one-electron problem in an average way by introducing the model Hartree-Fock potential. Hartree-Fock method takes into account the correlation between electrons of parallel spins, called as Fermi hole. However, it does not take care of the correlation of electrons of opposite spins, which is called as Coulomb hole. Hence, the correlation energy is defined as the difference between the exact energy and the Hartree-

Fock energy obtained with completeness in basis set. Although, the corrections are very small compared to the total energy of the system, these are significant in calculating energy differences, e.g., spectroscopic energies etc.

On the other hand, post Hartree-Fock methods such as configuration interaction (CI), many-body perturbation theory (MBPT), and coupled cluster (CC) theory are used quite extensively to take into account the correlation effects.[29] However, the main disadvantage of these correlated methods is the computational costs for large and complex systems.

We will discuss the Rayleigh-Schrödinger perturbation theory (RSPT) as our studies require its knowledge. In general, the Hamiltonian is partitioned into two parts H_0+V, where the eigenfunctions and the eigenvalues of H_0 (zeroth order Hamiltonian) are known to us and V is called the perturbation. This method is size consistent at each order.[29] At this point, it is necessary to mention that a method is said to be size-consistent if the energy of a system at non-interacting limit is same as the sum of the energies of its fragments. When calculating the correlation energy, Hartree-Fock Hamiltonian can be chosen as the zeroth order Hamiltonian. Such a choice of H_0 is called as Møller-Plesset Perturbation theory (MPPT). If one wishes to solve the eigenvalue problem,

$$H\left|\phi_i\right\rangle=(H_0+V)\left|\phi_i\right\rangle=\varepsilon_i\left|\phi_i\right\rangle \qquad 1.2$$

one has to know the eigenfunctions and eigenvalues of H_0. Let ψ_i^0 and E_i^0 are eigenfunction and eigenvalue of H_0, respectively. Now, if V is small, we expect ϕ_i and ε_i to be close to ψ_i^0 and E_i^0, respectively. Hence, to expand the eigenfunction and eigenvalue of the ground state of H in the orders of perturbation, an ordering parameter λ is introduced. The expansion of exact eigenfunctions and eigenvalues in a Taylor series in λ can be written as,

$$\left|\phi_0\right\rangle = \left|\psi_0^0\right\rangle + \lambda\left|\psi_0^1\right\rangle + \lambda^2\left|\psi_0^2\right\rangle + \dots\dots\dots \qquad 1.3$$

$$\varepsilon_0 = E_0^0 + \lambda E_0^1 + \lambda^2 E_0^2 + \dots\dots\dots \qquad 1.4$$

Now, equating the coefficient of λ and using the normalization conditions we get the first, second, higher order energies. The first and second order corrections to the ground state energy are given as,

$$E_0^1 = \left\langle \psi_0^0 \middle| V \middle| \psi_0^0 \right\rangle \qquad 1.5$$

$$E_0^2 = \sum_{n\neq 0} \frac{\left|\left\langle \psi_0^0 \middle| V \middle| \psi_0^n \right\rangle\right|^2}{E_0^0 - E_n^0} \qquad 1.6$$

It is to be mentioned that the correlation energy corrections appear from second order. The second order energy in MPPT is given as,

$$E_0^2 = \sum_{\substack{a<b\\ r<s}} \frac{\left|\left\langle \psi_0^0 \middle| \sum_{i<j} \frac{1}{r_{ij}} - \sum_i v_{HF}(i) \middle| \psi_{ab}^{rs} \right\rangle\right|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} \qquad 1.7$$

where ε’s are orbital energies of the respective orbitals and v_{HF} is the Hartree-Fock potential.

The other electron correlated methods are the CI and CC methods. The CI is a linear variational method and, in principle, can provide an exact solution to the many-electron problem in a given basis, if all determinants constructed within that basis are included. However, such a method is impractical even for modest problem. So, CI is implemented by truncating the wave function up to certain order. However, this truncation is no longer size extensive. On the other hand, CC solves an exponential ansatz. These methods provide accurate results however, they can be expensive for larger and complex systems.

1.2.2 Density functional theory

Alternatively, one can even bypass the wave function based theories for dealing the many body problem simply by considering the electron density. i.e. Density Functional Theory.[30, 31] It is capable of handling large systems with comparatively less computational power. The basic variable, here, is the electron density which is defined as,

$$\rho(r_1) = N\int .....\int \psi^*(x_1, x_2, ...x_N)\psi(x_1, x_2, ...x_N)ds_1dx_2...dx_N \qquad 1.8$$

Thus, for a system having N electrons a three variable quantity (electron density) defines all the properties rather than a 4N variable wave function (three spatial coordinate and one spin coordinate). We can rewrite the total energy, using the electron density obtained from the Schrodinger equation as,

$$E = \langle\psi|H|\psi\rangle = \langle\psi|T + V_{ee}|\psi\rangle + \int v_{ext}(r)\rho(r)dr \qquad 1.9$$

Using the above equation with the variation principle, Hohenberg and Kohn (HK) in 1964, showed that there is a one-to-one relationship between the density $\rho(r)$ and the external potential $v(r)$. This is the first HK theorem.[16] Thus, the energy of a system is a functional of electron density $\rho(r)$ and is given as

$$E[\rho] = F_{HK}[\rho] + \int v_{ext}(r)\rho(r)dr \qquad 1.10$$

where, $F_{HK}[\rho]$ is a universal HK functional expressed as the sum of electronic kinetic energy and the electron-electron interaction energy, $F_{HK}[\rho] = T[\rho] + V_{ee}[\rho]$

The second HK theorem provides the energy variational principle. Hence, the ground state density is the density that minimizes E and satisfies the Euler equation

$$\mu = \frac{\delta E_v[\rho]}{\delta\rho(r)} = v(r) + \frac{\delta F}{\delta\rho(r)} \qquad 1.11$$

where μ is the Lagrange multiplier associated with the constraint

$$\int \rho(r)dr = N \qquad 1.12$$

In principle, DFT is an exact theory provided the exact functional is known. However, the implementation of DFT, carried out by Kohn and Sham, by introducing orbitals was a major breakthrough.[20] A variational procedure yields pseudo one-electron equations, analogous to Hartree-Fock equations, as

$$\left(-\frac{1}{2}\nabla^2 + v_{eff}(r)\right)\psi_i = \varepsilon_i\psi_i \qquad 1.13$$

where,

$$v_{eff}(r) = v(r) + \int \frac{\rho(r')}{|r - r'|} dr' + v_{xc}(r) \qquad 1.14$$

where, $v_{eff}(r)$ is the effective potential and $v_{xc}(r)$ is the exchange-correlation potential. The form of exchange-correlation term is unknown. Several functional forms are available and have been used till date.[32] Recently, the hybrid exchange-correlation functionals are used for calculating the properties with comparable accuracies to the *ab initio* wave function based methods.[44] These aspects of DFT, i.e., exploiting DFT as a theory and tool to calculate the energetics and molecular properties, were grouped under "Computational DFT" by Parr and Yang.[32] However, in the present thesis we would mainly focus on the conceptual counterpart of DFT called as "Conceptual DFT" which was developed from late 1970s and early 80s.[32] This branch mainly derives the concepts, which are of chemical relevance (such as chemical potential, electronegativity, hardness etc.), from DFT. From hereon we would discuss the foundation of various concepts of chemical reactivity theory.

1.3 Conceptual DFT

1.3.1 Global Reactivity Descriptors

It was identified by Parr and coworkers that the Lagrange multiplier μ associated with the constraint that $\rho(r)$ integrates to total number of electrons (N), is nothing but the chemical potential of the system.[11]

$$\mu = \left(\frac{\partial E_v[\rho]}{\partial N} \right)_v \qquad 1.15$$

The physical significance of chemical potential is a measure of the escaping tendency of an electron cloud. It is the slope of E versus N curve at constant external potential and is a constant in three-dimensional space for the ground state of an atom, molecule or solid.

It can be noted that the chemical potential is analogous to the thermodynamic chemical potential of a component i at constant temperature T, pressure P and number of moles of jth component n_j

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{P,T,n_{j(j\neq i)}} \qquad 1.16$$

At this point, it is pertinent to mention that the chemical potential is the negative of the electronegativity (χ) concept. According to Iczkowski and Margrave the electronegativity for fixed nuclear charge is defined as[33]

$$\chi = -\left(\frac{\partial E}{\partial N} \right) \qquad 1.17$$

However, Mulliken's definition of electronegativity is also relevant to the present definition of chemical potential.[34] He defined electronegativity as,

$$\chi = \frac{1}{2}(I + A) \qquad 1.18$$

where I and A are ionization potential and electron affinity, respectively. It can be immediately noticed that it is the finite difference approximation to the above definition and is exactly identical to chemical potential.

In 1983, Parr and Pearson defined the second derivative of energy with respect to the number of electrons as absolute hardness, [8]

$$\eta = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_v = \frac{1}{2}\left(\frac{\partial \mu}{\partial N}\right)_v \qquad 1.19$$

It is the resistance to the change in the systems chemical potential with the change in the number of electrons. Finite difference approximation provides an operational definition as

$$\eta = \frac{1}{2}\left(I - A\right) \qquad 1.20$$

Another important global descriptor is the softness, S defined as the inverse of hardness,

$$S = \frac{1}{2\eta} = \left(\frac{\partial N}{\partial \mu}\right)_v \qquad 1.21$$

Very recently, Parr, Szentpaly and Liu proposed electrophilicity index (W) as[35]

$$W = \frac{\mu^2}{2\eta} = \frac{\left(I + A\right)^2}{8\left(I - A\right)} \qquad 1.22$$

where the second equality is due to finite difference approximation. It is considered to be a measure of electrophilicity of the ligand and is analogous to the definition of power ($W=V^2/R$).

Using the Koopmans' approximation, [12, 36-37] one can express I and A in terms of orbital energies of HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) i.e.,

$$\begin{aligned} I &= -\varepsilon_{HOMO} \\ A &= -\varepsilon_{LUMO} \end{aligned} \qquad 1.23$$

All these descriptors, chemical potential, hardness, softness and electrophilicity index, are capable of describing the overall stability and reactivity of a molecule. Hence, they are classified to refer to the whole system, called "global reactivity descriptors" (GRD). However, for predicting the behavior of atoms in a molecule local reactivity descriptors (LRD) are preferred.

1.3.2 Local Reactivity Descriptors

We know that energy is a functional of $v_{ext}(r)$ and N ($E[N,v]$). Now, the second order change in energy due to the changes in N and $v_{ext}(r)$ gives,

$$d\mu = \eta dN + \int \frac{\delta\mu}{\delta v(r)} dr \qquad 1.24$$

The second term in the above expression is known as Fukui function $f(r)$ (FF).[9]

$$f(r) = \left(\frac{\delta\mu}{\delta v(r)}\right)_N = \left(\frac{\partial\rho(r)}{\partial N}\right)_{v(r)} \qquad 1.25$$

The second equality is due to Maxwell's relation. However, the mixed derivative of energy with respect to the number of electrons and external potential can also be identified as the FF, $f(r) = \left(\frac{\delta^2 E}{\delta N \delta v(r)}\right)$ since $\rho(r) = \left(\frac{\delta E}{\delta v(r)}\right)$. The argument provided by Parr and Yang was that large values of $f(r)$ at a site favor reactivity of that site. The physical significance of FF is to measure the response of the systems chemical potential to an external potential at a particular point or the change in the electron density of the system with respect to the change in the number of electrons. Moreover, FF is normalized to unity.

Similar to E (N), $\rho(r)$ has a slope discontinuity,[105] hence three reaction indices at a given number of electrons, N=N$_0$

$$f^{+}(r)=\left(\frac{\partial\rho(r)}{\partial N}\right)^{+}_{v(r)} \quad \text{for a nucleophilic attack} \qquad 1.26$$

$$f^{-}(r)=\left(\frac{\partial\rho(r)}{\partial N}\right)^{-}_{v(r)} \quad \text{for an electrophilic attack} \qquad 1.27$$

and the arithmetic mean

$$f^{0}(r)=\frac{1}{2}\left(f^{+}(r)+f^{-}(r)\right) \quad \text{for an radical attack.} \qquad 1.28$$

Now applying the frontier molecular orbital (FMO) theory, invented by K. Fukui, the FF under the frozen core approximation can be written similarly as,

$$\begin{aligned} f^{+}(r) &\approx \rho_{LUMO} \\ f^{-}(r) &\approx \rho_{HOMO} \end{aligned} \qquad 1.29$$

where ρ_{LUMO} and ρ_{HOMO} are the LUMO and HOMO density, respectively.

The local counterpart of softness, S is the local softness defined as,

$$s(r)=\left(\frac{\partial\rho(r)}{\partial\mu}\right)_{v}=\left(\frac{\partial\rho(r)}{\partial N}\right)_{v}\left(\frac{\partial N}{\partial\mu}\right)_{v}=f(r)S \qquad 1.30$$

From the above expression, one can infer that the FF redistributes the global softness within a molecule. Local softness is normalized to global softness. On similar lines, $s^{a}(r)=f^{a}(r)S$ where $\forall a=+,-.0$ depending on nucleophilic, electrophilic or radical attack.

Ghosh, Berkowitz and Parr defined the local analogue of hardness, local hardness $\eta(r)$[17-19]

$$2\eta(r) = \frac{1}{N}\int \frac{\delta^2 F}{\delta\rho(r)\delta\rho(r')}\rho(r')dr' = \left(\frac{\partial\mu}{\partial\rho(r)}\right)_v \quad 1.31$$

$$\eta = \int \eta(r) f(r) dr \quad 1.32$$

Berkowitz and Parr derived the local softness that reveals its relation to its reciprocal property, local hardness.[19] They established a coherent quantitative language of hardness and softness on hierarchy of local and non local functions. Non local functions are called kernels.

$$\eta(r,r') = \frac{\delta^2 F}{\delta\rho(r)\delta\rho(r')} = -\frac{\partial u(r)}{\partial\rho(r')} = -\frac{\partial u(r')}{\partial\rho(r)} \quad 1.33$$

$$s(r,r') = -\frac{\partial\rho(r)}{\partial u(r')} = -\frac{\partial\rho(r')}{\partial u(r)} \quad 1.34$$

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

$$u(r) = v(r) - \mu \quad 1.35$$

The hardness and softness kernels are reciprocal to each other as

$$\int s(r,r'')\eta(r'',r')dr'' = \delta(r-r') \quad 1.36$$

Integrating softness kernel over one of the variables gives local softness. However, local hardness is difficult to define in terms of hardness kernels.[18, 38-39] Harbola proposed the most convenient form,[38]

$$\eta(r) = \int \eta(r,r') f(r') dr' \quad 1.37$$

Thus,

$$\int \eta(r) s(r) dr = 1 \quad 1.38$$

As can be seen from the equations of local quantities, the local softness is the response of the electron density to a perturbation in chemical potential at constant external potential. In view of the fact that the chemical reactions are considered as a perturbation in the number of electrons, therefore, local softness can be used successfully to predict the course of a reaction. These reactivity indices were successful in explaining the observed intra-molecular reactivity trends. However, based on the condensed local softness, Roy et. al. introduced relative electrophilicity and relative nucleophilicity indices which are shown to describe the intra-molecular reactivity trends in an improved way.[40]

Of late, Chattaraj et. al.[41] proposed another local descriptor, local philicity, w(r) which redistributes the global philicity W as

$$w(r) = f(r)W \qquad 1.39$$

Considering the existence of some function w(r) that integrates to global philicity (W), they presented through the resolution of identity associated with FF as,

$$W = W\int f(r)dr = \int Wf(r)dr = \int w(r)dr \qquad 1.40$$

Another important function, denoted by σ (r), is called shape function[42] defined as the electron density per particle determines all the properties of molecular system.[43]

$$\sigma(r) = \frac{\rho(r)}{N} \qquad 1.41$$

The chemists are, however, interested in properties of atoms or group of atoms rather than the properties associated with points in space (r). The local reactivity indices, described above, are all functions of position r in a given molecule. 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 a molecule to describe the site reactivity and site selectivity of an atom in a molecule. Atom condensed Fukui function (CFF) was introduced by Yang and Mortier.[24] It is based on the idea of electronic population over atomic regions, similar to the procedure followed in population analysis technique. Therefore, the CFF for nucleophilic and electrophilic attack, respectively are

$$f_k^{+} \approx q_k^{N_o+1} - q_k^{N_o} \quad 1.42$$

$$f_k^{-} \approx q_k^{N_o} - q_k^{N_o-1} \quad 1.43$$

where $q_k^{N_o}$ denotes the electronic population of atom k of a system with N_0 electrons. The corresponding condensed local softness of an atom s_k^+, s_k^- and s_k^0 can be defined. Several population schemes such as Mulliken's population scheme,[45] Lowdin population scheme,[46] Hirshfeld partitioning scheme,[47] natural population scheme,[48] Bader's atoms-in-molecules (AIM) partitioning method,[49] charges derived from molecular electrostatic potentials,[50] are used to calculate the CFF values. However, these partitioning schemes are sensitive to the basis sets and the level of calculation. In addition, the main problem lies in the fact that there will always be a change of multiplicity (for computation of charged systems) of the electronic state that may result in convergence problem. Nonetheless, this simplified expression for the CFF and CLS has received overwhelming response in a variety of systems e.g, the intra- and intermolecular reactions, inorganic solid-zeolites and metal oxides, catalysis, metal clusters, biological systems etc., (Discussed in Section 1.9).

Despite the fact that there have been various ways to compute the FF, it should be mentioned that the finite difference approach suggested by Yang and Mortier is considered to be one of the easiest and best ways to calculate the local quantity.[24] However, very recently the calculation of the condensed Fukui function is revisited.[142]

It should be pointed out that there exists some difficulty in analyzing the reactivity of the atomic centers within the molecule when these CFF indices become negative.[40] However, for the first time in the literature, the problem of non-negativity of the CFF was addressed by Pal and co-workers [144-145] Their study reveals that the stockholders charge partitioning technique, as proposed by Hirshfeld, produces non-negative FF.

1.4 Higher Order Derivatives

Since the basic reactivity descriptors are derivatives of energy and electron density with respect to the number of electrons, the effect of external field on these descriptors can be understood by the perturbative analysis of energy and electron density with respect to number of electrons and external field. Such an analysis has been done by Senet, [51] Fuentealba and coworkers.[52] Senet discussed perturbation of these quantities with respect to general local external potential. It can be shown that since $\rho(r)=\frac{\delta E}{\delta v_{ext}}$, Fukui function can be seen either as derivative of chemical potential with respect to the external potential or of electron density with respect to the number of electrons. Further, response of $f(r)$ with N provides same results as response of η with respect to v_{ext}

$$\frac{\delta f(r)}{\delta N}=\frac{\delta^3 E}{\delta v_{ext}\delta N\delta N}=\frac{\delta\eta}{\delta v_{ext}} \qquad 1.44$$

Higher order derivatives with respect to external potential define $\chi_1(r,r')=\frac{\delta\rho(r)}{\delta v_{ext}(r')}$, $\chi_2(r,r',r'')=\frac{\delta^2\rho(r)}{\delta v_{ext}(r')v_{ext}(r'')}$ etc. and their response with N define $\xi_1(r,r')=\frac{\partial\chi_1(r,r')}{\partial N}$, $\xi_2(r,r',r'')=\frac{\partial\chi_2(r,r',r'')}{\partial N}$ etc. This chain of derivatives is diagrammatically depicted in the paper of Senet.[51b] With specific reference to a homogeneous electric field as external potential, one can derive similar response.

Apart from this, Nalewajski obtained different energy and chemical potential derivatives with respect to many parameters.[53] He also derived their inter relationship through Maxwell relation. However, in an interesting paper, Fuentealba and Parr discussed the hardness derivative, γ.[54] It was shown that this value is small for atoms, ions and molecules.

1.5 Hard-Soft Acid-Base Principle

Hard-Soft Acid-Bases (HSAB) was classified on the basis of experimental data by Pearson in 1963 as: [55]

(a) Hard Acids (acceptor or nucleophile) are those which have high positive charge, low polarizability and are small in size, e.g. H^+, Ca^{2+}, BF_3

(b) Soft Acids (donor or electrophile) are those which have low positive charge, high polarizability and are large in size, e.g. Hg^+, I^+, BH_3 etc.

(c) Hard Bases (donor or electrophile) are those which have high electronegativity, low polarizability and are difficult to oxidize, e.g. F^-, OH^-, NH_3

(d) Soft Bases (donor or electrophile) are those which have high polarizability, low electronegativity and are easy to oxidize, e.g. H^-, CN^-, I^-

The HSAB principle states that there is an extra stabilization if hard acids bind to hard bases and soft acids bind to soft bases. It was first applied in rationalizing inorganic stability constants with the concepts being valuable even in organic chemistry.

An interesting conception relates the hard-hard and soft-soft character to ionic and covalent interaction, respectively.[55-60] An explanation for the hard-hard interactions is given by considering them to be primarily electrostatic or ionic interactions. As the electrostatic or Madelung energy of an ion pair is inversely proportional to the interatomic distance, smaller the distance, greater is the attraction between hard acid and base. Since an electrostatic justification cannot explain the soft-soft interactions, it has been suggested that the predominant factor is a covalent one. In this regard, the polarizing power and polarizability become an important factor. Moreover, Π-bonding occurs more readily in those metal ions that have low oxidation states and large number of d electrons and hence, favour soft-soft interactions.

Klopman, on the other hand, tried to give a theoretical basis for HSAB principle using the quantum mechanical theory based perturbation method.[61] He assumed that when the two reactants approach each other, a mutual perturbation of molecular orbitals of both the reactants occur and the resulting change in energy can be estimated from molecular orbital calculations. The total perturbation is produced by two distinct effects (i) 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.

Parr and Pearson, in 1983, proposed the first theoretical proof for HSAB principle and they were partially successful. Their idea was derived on the basis of energy perturbation with respect to the number of electrons.[8] Soon after, Nalewajski employed both the number of electrons and external potential as perturbation variables.[62] Later, Chattaraj et. al. proved the HSAB principle on the basis of minimizing the interaction energy with respect to the softness parameter.[63] Recently, Li and Evans used the softness kernels and other local reactivity descriptors for the purpose and brought out many interesting relationships between the HSAB principle and the FMO theory.[64]

Let us first look into the proof of Parr and Pearson.[8] Here the energy is expanded in Taylor series in terms of the number of electrons (N) as a perturbation variable. Assuming that the systems A and B are interacting,

$$E_A = E_A^0 + \mu_A (N_A - N_A^0) + \eta_A (N_A - N_A^0)^2 + ... \qquad 1.45$$

$$E_B = E_B^0 + \mu_B (N_B - N_B^0) + \eta_B (N_B - N_B^0)^2 + ... \qquad 1.46$$

Ignoring all other effects except second order, total change in energy,

$$\Delta E_{AB} = (\mu_A - \mu_B)\Delta N + (\eta_A - \eta_B)(\Delta N)^2 \qquad 1.47$$

where $\Delta N = N_B^0 - N_B = N_A - N_A^0$ 1.48

The energy stabilization due to such charge transfer is second order in $\mu_B - \mu_A$. On minimizing $(E_A + E_B)$ with respect to ΔN, gives $\mu_A = \mu_B$

where, $\mu_A = \mu_{_A}^0 + 2\eta_A \Delta N + ...$ 1.49

$$\mu_B = \mu_B^0 + 2\eta_B \Delta N + ... \qquad 1.50$$

Consequently, to first order,

$$\Delta N = \frac{\mu_B - \mu_A}{2\left(\eta_A - \eta_B\right)} \qquad 1.51$$

Therefore, the interaction energy can be expressed as

$$\Delta E_{AB} = -\frac{(\mu_B - \mu_A)^2}{4\left(\eta_A - \eta_B\right)} \qquad 1.52$$

This energy lowering results from electron transfer and the differences in electronegativity or chemical potential. This step is assumed to take place continuously till the equilibrium is reached as is referred as the chemical potential or electronegativity equalization process. For soft acid and soft base, $\left(\eta_A + \eta_B\right)$ is small, hence for a reasonable difference in electronegativity, ΔE is substantial and stabilizing. However, it could not explain the hard-hard interaction. Following this, Nalewajski described the hard-hard interaction by the inclusion of the first order contribution due to the perturbing external potential.[62]

Later, Chattaraj et. al. established that among the potential partners of a given electronegativity, hard likes hard and soft likes soft. The expression for ΔE can be rewritten as,[63]

$$\Delta E_{AB} = -\frac{(\mu_B - \mu_A)^2}{4\left(\eta_A - \eta_B\right)} = -\frac{(\Delta\mu)^2}{2}\frac{S_A S_B}{S_A + S_B} \qquad 1.53$$

Assuming for a given S$_A$, $S_B = \alpha S_A$

$$\Delta E_{AB} = -\frac{(\Delta\mu)^2}{2}\frac{\alpha S_A}{1+\alpha} \qquad 1.54$$

where $0 < \frac{\alpha}{1+\alpha} < 1; 0 \le \alpha \le \propto$ 1.55

The supremum value of $\frac{\alpha}{1+\alpha}$ is 1, which corresponds to maximum energy lowering, hence hardness will be minimum. Otherwise, the zero value of α is the case with maximum hardness. Since both the processes simultaneously are not possible, the natural compromise is to take an average value of $\frac{\alpha}{1+\alpha}$ as $\frac{1}{2}$ which implies S$_A$=S$_B$.

The second proof involves the molecular grand potential. Now, the interaction energy can be written as,

$$\Delta E_{AB} = \Omega_A + \Omega_B \qquad 1.56$$

where $\Omega_A = -\frac{(\mu_B - \mu_A)^2}{4}\frac{\eta_A}{\left(\eta_A + \eta_B\right)^2}$ 1.57

$$\Omega_B = -\frac{(\mu_B - \mu_A)^2}{4}\frac{\eta_B}{\left(\eta_A + \eta_B\right)^2} \qquad 1.58$$

Minimizing Ω_A with respect to η_A, for a given $\mu_B - \mu_A$ and η_B gives,

$$\eta_A = \eta_B \qquad 1.59$$

Similar results are obtained when one minimizes Ω_B with respect to η_B, for a given $\mu_B - \mu_A$ and η_A. Hence, the HSAB principle.

An alternative proof for the HSAB principle was derived by Gazquez by approximating the total energy expression in terms of chemical potential and hardness as,[65]

$$E[\rho] = \mu N_e - \frac{1}{2}\eta N_e^2 + E_{core}[\rho] \qquad 1.60$$

where N_e is an effective number of valence electrons and $E_{core}[\rho]$ is the core contribution to the total energy. Using this expression, he has shown that the interaction between species whose softnesses are approximately equal is energetically favored.

1.6 Intermolecular Interactions by Local HSAB Principle

Let us consider the general molecular interaction where the interaction is taking place between the k^th atom of a molecular system A, with the l^th atom of another molecular system B. According to DFT, the interaction energy is given by,[66]

$$\Delta E_{\text{int}} = E[\rho_{AB}] - E[\rho_A] - E[\rho_B] \qquad 1.61$$

where ρ_{AB} , ρ_A and ρ_B are the electron densities of the system AB at equilibrium, and isolated system A and B respectively. [66]

It is assumed that the interaction is divided into two steps:[66] firstly, the chemical potentials of isolated systems A and B attain a common value at constant external potential. Thus, energy change is

$$\Delta E_v = \Delta E_v(A) + \Delta E_v(B) \qquad 1.62$$

where,

$$\Delta E_v(A) = E[\rho_A^*] - E[\rho_A] \qquad 1.63$$

$$\Delta E_v(B) = E[\rho_B^*] - E[\rho_B] \qquad 1.64$$

where ρ_A^* is the electronic density of system A with v_A and μ_{AB} . Similarly, for ρ_B^* .

Secondly, A and B evolve towards the equilibrium state through changes in the electronic density of the global system AB produced by changes in its external potential. This is a constant chemical potential step.

$$\Delta E_{\mu} = E[\rho_{AB}] - E[\rho^{*}_{AB}] \qquad 1.65$$

where, $\rho^{*}_{AB}(r) = \rho^{*}_{A}(r) + \rho^{*}_{B}(r)$ is the electronic density of the system AB with μ_{AB} when A and B are apart. Addition of the above equations, lead to the expression for interaction energy as,[66]

$$\Delta E_{\text{int}} = \Delta E_{v} + \Delta E_{\mu} \qquad 1.66$$

Now, we will derive an expression for each term which will together form the basis of the local HSAB principle.

1.6.1 Expression for ΔE_{v}

As discussed earlier, considering the interaction between system A and B, the total change in energy (up to second order) in terms of softness is given by,

$$\Delta E_{AB} = -\frac{(\mu_B - \mu_A)^2}{4(\eta_A - \eta_B)} = -\frac{(\Delta\mu)^2}{2}\frac{S_A S_B}{S_A + S_B} \qquad 1.67$$

Consider the grand potential,

$$\Omega_A = E_A - \mu_A(N_A - N_A^0) \qquad 1.68$$

$$\Delta\Omega_A = \Delta E_A - \Delta\mu_A \Delta N - \mu_A \Delta N_A \qquad 1.69$$

The systems A and B attain a common chemical potential μ_{AB} (equal to μ_A and μ_B) given as,

$$\mu_{AB} = \frac{\mu_A S_A + \mu_B S_B}{S_A + S_B} \qquad 1.70$$

Using the above equation along with equations 1.48 and 1.49, we get

$$\Delta\mu_A = \mu_{AB} - \mu_A = \eta_A \Delta N_A \qquad 1.71$$

Applying equations 1.50 and 1.70 in 1.68 we get,

$$\Delta\Omega_A = (\mu_A \Delta N_A + \frac{1}{2}\eta_A(\Delta N_A)^2) - \eta_A(\Delta N_A)^2 - \mu_A \Delta N_A = -\frac{1}{2}\eta_A(\Delta N_A)^2 \qquad 1.72$$

$$\Delta\Omega_A = -\frac{\left(\mu_B - \mu_A\right)^2}{2\left(S_A + S_B\right)^2} S_A S_B^2 \qquad 1.73$$

Similarly for system B, the change in grand potential is

$$\Delta\Omega_B = -\frac{\left(\mu_B - \mu_A\right)^2}{2\left(S_A + S_B\right)^2} S_A^2 S_B \qquad 1.74$$

Hence,

$$\Delta\Omega_A + \Delta\Omega_B = -\frac{\left(\mu_B - \mu_A\right)^2}{2\left(S_A + S_B\right)} S_A S_B \qquad 1.75$$

Considering "atoms-in-a-molecule" viewpoint,[26b] the atoms can be seen as an open subsystem leading to a consideration of the grand potential as a natural quantity to describe the interactions in terms of atoms. Now, for a local point of view, i.e., consider the interaction between atom k of molecule A with atom l of molecule B, the expression would be derived the same way as we have described above. Now for the equalization of chemical potential condition,

$$\mu_{AB} = \mu_A + \eta_{Ak}\Delta N_{Ak} = \mu_B + \eta_{Bk}\Delta N_{Bk} \qquad 1.76$$

and, $\Delta N_{Ak} + \Delta N_{Ak} = 0$ 1.77

Therefore,

$$\Delta N_{Ak} = \frac{(\mu_B - \mu_A)}{(S_A + S_B)} S_A S_B f_{Ak} \qquad 1.78$$

Similarly, $\Delta N_{Bl} = \frac{(\mu_B - \mu_A)}{(S_A + S_B)} S_A S_B f_{Bl}$ 1.79

The expression of the change in grand potential for system A and B are,

$$\Delta\Omega_{Ak} = -\frac{(\mu_B - \mu_A)^2}{2(S_A + S_B)^2} S_A S_B^2 f_{Ak} \quad 1.80$$

and, $$\Delta\Omega_{Bl} = -\frac{(\mu_B - \mu_A)^2}{2(S_A + S_B)^2} S_A^2 S_B f_{Bl} \quad 1.81$$

On minimizing the grand potential $\Delta\Omega_{Ak}$ with respect to S_A keeping all other parameter constant, and using the minimum condition,

$$S_A = S_B. \quad 1.82$$

Similarly, minimizing the grand potential $\Delta\Omega_{Bl}$ with respect to S_B keeping all other parameter constant results the same. Thus, the HSAB principle implies that the grand potential of all the atoms in A as well as in B become minimum, when both the system have equal global softness. Hence, the minimum is

$$(\Delta\Omega_{Ak})_{\min} = -\frac{(\mu_B - \mu_A)^2}{8} S_A f_{Ak} \quad 1.83$$

and, $$(\Delta\Omega_{Bl})_{\min} = -\frac{(\mu_B - \mu_A)^2}{8} S_B f_{Bl} \quad 1.84$$

Now, the most favorable situation corresponds to,

$$(\Delta\Omega_{Ak})_{\min} \approx (\Delta\Omega_{Bl})_{\min} \quad 1.85$$

which concludes,

$$f_{Ak} \approx f_{Bl} \quad 1.86$$

Further using equation 1.82 and 1.86, one can get,

$$s_{Ak} \approx s_{Bl} \quad 1.87$$

Thus, the interaction between A and B is favoured when it occurs through those atoms whose softnesses are approximately equal. This proves the local HSAB principle.

When $f_{Ak} \approx f_{Bl}$, the total interaction energy at the minimum is given as,[26]

$$\Delta E_{Ak} + \Delta E_{Bl} = -\frac{\left(\mu_B - \mu_A\right)^2}{2\left(S_A + S_B\right)} S_A S_B f_{Ak} \qquad 1.88$$

It can be observed that the change in energy will be stabilized independent of the values of chemical potentials and softness and greater the FF values, greater the stabilization energy. If we assume that the FF of the reacting atoms are approximately equal, then the interaction between A and B will not necessarily occur through the softer atoms but through those atoms whose FF values are nearly equal.[26]

1.6.2 Expression for ΔE_μ[67]

Combining the HK equation and Euler equation (1.10 & 1.11) we get,

$$E[\rho] = F_{HK}[\rho] + \mu N - \int \frac{\delta F[\rho]}{\delta\rho(r)} \rho(r) dr \qquad 1.89$$

Now, 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

$$\Delta E = E[\rho_f] - E[\rho_i] \qquad 1.90$$

$$E[\rho] = F[\rho_f] - F[\rho_i] + \mu_f N_f - \mu_i N_i - \int \rho_i(r) \left.\frac{\delta F[\rho]}{\delta\rho(r)}\right|_{\rho_i(r)} dr + \int \rho_f(r) \left.\frac{\delta F[\rho]}{\delta\rho(r)}\right|_{\rho_f(r)} dr \qquad 1.91$$

Now, performing a Taylor series functional expansion of F[ρ_f] around F[ρ_i], and of $\left.\frac{\delta F[\rho]}{\delta\rho(r)}\right|_{\rho_f(r)}$ around $\left.\frac{\delta F[\rho]}{\delta\rho(r)}\right|_{\rho_i(r)}$ results in

$$E[\rho] = (\mu_f N_f - \mu_i N_i) - \frac{1}{2}\iint dr dr' \eta_f(r,r') \rho_f(r) \rho_f(r') + \frac{1}{2}\iint dr dr' \eta_i(r,r') \rho_i(r) \rho_i(r') \qquad 1.92$$

If electronic densities of anion and cation are approximated as renormalized N-electron density, and FF under 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 eqn. 1.31 and 1.32. Hence,

$$\Delta E \approx (\mu_f N_f - \mu_i N_i) - \frac{1}{2} N_f^2 \eta_f + \frac{1}{2} N_i^2 \eta_i \qquad 1.93$$

For constant number of electrons and constant chemical potential,

$$\Delta E_\mu \approx -\frac{1}{2} N^2 \Delta\eta \qquad 1.94$$

Since $\Delta\eta > 0$ (system evolving towards greater hardness), its stability ($\Delta E < 0$) increases under constant chemical potential. Thus this step is the manifestation of maximum hardness principle (MHP).

Now, $\Delta\eta = \eta_{AB} - \eta_{AB}^*$ where η_{AB} and η_{AB}^* are the hardness of the system at equilibrium and hardness of the isolated systems A and B,

$$\Delta E_\mu \approx -\frac{1}{2} N^2 (\eta_{AB} - \eta_{AB}^*) \qquad 1.95$$

One has to relate the total hardness of the system AB in terms of the softnesses of the individual systems. In general, the total softness of the system AB at equilibrium can be written as,

$$S_{AB} = k(S_A + S_B) \qquad 1.96$$

where k is the proportionality constant, S_A and S_B are the softnesses of the isolated systems A and B. Yang et. al. showed that the molecular softness of a system at equilibrium can be replaced by the average of the softness of each constituents of the molecular system. In the limit of separation the proportionality constant can be approximated as 1 and in the interacting limit, the total softness decreases and k attains a value less than 1. Lower the value of k, more stable is the system. Thus k has information about the stability of the system AB and can be related to the extent of overlap between the isolated atomic systems. Since the total molecular softness is insensitive to the number of electrons, the difference in the softness ($S_{AB} - S^{*}_{AB}$) can be approximated as

$$\Delta S = S_{AB} - S^{*}_{AB} = k^{'}(S_A + S_B) \qquad 1.97$$

where $k^{'}$ is another proportionality constant.

Equation 1.94 becomes,

$$\Delta E_{\mu} \approx -\frac{1}{2} N^{2}_{AB} K \left(\frac{1}{(S_A + S_B)} \right) \qquad 1.98$$

where N$_{AB}$ is the total number of electrons of the system AB and K is another proportionality constant. The product of the terms N$_{AB}$ and K can be related physically to the effective number of valence electrons that have participated in the interaction between A and B. This term is known as the charge transfer term, λ.

The expression for the interaction energy at constant external potential and constant chemical potential can be written as,.[26]

$$\Delta E_{\text{int}} = -\frac{(\mu_B - \mu_A)^2}{2(S_A + S_B)} S_A S_B - \frac{1}{2} \frac{\lambda}{(S_A + S_B)} \qquad 1.99$$

At this point, it is important to discuss the λ term appearing in the reshuffling term at the constant chemical potential. Several studies considered arbitrary values of λ.[26, 146-147] The formal definition of this charge transfer term was proposed by Pal et. al.[27a] as the change in the electron densities of the systems before and after the interaction process.

$$\lambda_A = \sum_{i=1}^{N} \rho^{eq}_{Ai} - \sum_{i=1}^{N} \rho^{0}_{Ai} \qquad 1.100$$

This change will give the effective number of valence electrons participating in the interaction process. Alternatively, for system B

$$\lambda_B = \sum_{j=1}^{M} \rho^{eq}_{Bj} - \sum_{j=1}^{M} \rho^{0}_{Bj} \qquad 1.101$$

where the first term in both the above equations are the sum of the electron densities of each atom in A and B in the molecule AB at equilibrium and the second term is the sum of the electron densities of each atom in the isolated systems A and B, respectively. In principle, λ_A and λ_B have equal magnitude but opposite sign.[27a]

From a local point of view put forwarded by Mendez and Gazquez,[26] the interaction energy of two chemical systems A and B occurring through the kth atom of A can be expressed as,

$$\Delta E_{\text{int}} = -\frac{(\mu_B - \mu_A)^2}{2(S_A f_{Ak} + S_B)} S_A f_{Ak} S_B - \frac{1}{2}\frac{\lambda}{(S_A f_{Ak} + S_B)} \qquad 1.102$$

Now, if the interaction between the systems occur through the atom x of A with the atom k of the molecular system B, one can express the total interaction energy from the local point of view, as[26, 27]

$$(\Delta E_{\text{int}})_{Ax-Bk} = \frac{-(\mu_A - \mu_B)^2}{2}\left(\frac{S_A f_{Ax} S_B f_{Bk}}{S_A f_{Ax} + S_B f_{Bk}}\right)_v - \frac{1}{4}\left(\frac{\lambda}{S_A f_{Ax} + S_B f_{Bk}}\right)_\mu \qquad 1.103$$

However, for the systems A and B interacting through multiple pair of reactive sites (x-k, y-l, z-m, etc) the net interaction can be written as a logical extension of the single site local HSAB principle to multiple sites, by assuming that the interaction occurs in a decoupled manner and by the additivity of energy[27b]

$$\Delta E_{\text{int}} = \Delta E_{Ax-Bk} + \Delta E_{Ay-Bl} + \Delta E_{Az-Bm} + \ldots.. \qquad 1.104$$

1.7 Maximum Hardness Principle

The MHP (Maximum Hardness Principle) proposed by Pearson[12] states that there is a rule of nature that every system tries to be as hard as possible. This received considerable attention over the past few years.[68] Parr and Chattaraj have proposed a proof based on fluctuation-dissipation theorem of statistical mechanics. [69] Under the condition of constant chemical potential and temperature, they showed that the hardness of a system becomes maximum at equilibrium nuclear configuration. However, it was assumed that all the non-equilibrium states near the equilibrium can be generated by small perturbations of the equilibrium state. It was, however, found that the MHP still holds even though the electronic chemical potential varies along the reaction coordinates.[12, 68, 70-80] Parr, Zhou and coworkers performed a series of studies on the relationship between the hardness and aromaticity of hydrocarbons.[86] MHP has been numerically studied and its validity was shown by several groups. [68, 70-76] On the other hand, Datta has shown that the exchange reactions, μ and v(r) are not constant, always moves in a direction that produces the hardest molecule or the product has highest average hardness.[81]

The variation of hardness along reaction path has been studied to validate maximum hardness criterion in the chemical reactions and this is termed as 'hardness profile'. [72] Datta has first studied the hardness profile for the inversion of ammonia and the intra-molecular proton transfer in malonaldehyde and observed that the profile goes through a minimum in a transition state.[72] However, there are cases where the hardness does not pass through a minimum near or at transition state.[82-85]

Pearson and Palke observed that the totally symmetric distortion do not show any sign of maximum or minimum hardness near the equilibrium geometry while the hardness keeps increasing steadily as the nuclei approach each other.[71] Pal et. al. have made a critical study on the validity of MHP using the highly correlated wave function method by considering the symmetric and asymmetric variations around the equilibrium.[74] They found that for symmetric vibrations neither the chemical potential nor the hardness is at an extremum while for asymmetric vibrations the chemical potential and the hardness were extremum. Further, they noted that among all symmetric configurations with equal chemical potential, hardness at equilibrium geometry is global maximum.[74] These results support the Pearson and Palke's observation. Makov has further demonstrated that all the invariant, such as energy, chemical potential, hardness, will be extremal with respect to asymmetric variations about a symmetric nuclear configuration.[75] This explains and supports the results of Pal et. al. This has been derived by employing group theoretical symmetry arguments within the framework of "pure-state" DFT. The above argument holds to be true whether the asymmetric distortions are carried out around symmetric equilibrium or non-equilibrium geometries. It should also be noted that the symmetry principles derived by Makov do not determine by themselves whether such extrema will be minima or maxima.[75]

Although several groups have studied MHP, the principle still lacks from exact formal proof. One of the difficulties associated with this principle is how the chemical potential and the external potential can be kept constant during a reaction when the hardness varies. Sebestian questioned the validity of the formal statistical-mechanical proof.[87a] He however, later reported errors in his numerical counter examples.[87b] Despite all the criticism, it has been observed that the variation of hardness along a chemical reaction is found to be useful.

Recently, Liu and Parr have demonstrated the MHP with several constraints and it states that at a fixed number of electrons, external potential and chemical potential, the hardness should go to a maximum as the total energy approaches a minimum.[88] They obtained the following expression, using the functional expansion method up to second order as

$$E[N,v]=\mu N-\frac{1}{2}N^2\eta+\int v(r)[\rho(r)-Nf(r)]dr-\frac{1}{2}\iint \rho(r)\rho(r')w(r,r')drdr' \qquad 1.105$$

Very recently, Ayers and Parr discussed the local hardness equalization principle.[143]

1.8 Relationship of Reactivity Descriptors with Physical Properties

Until now, we discussed the developments in the field of Conceptual DFT. Parallelly, efforts have been made to relate these reactivity descriptors with the electronic properties of the chemical system. One of the key interests is to critically rationalize the quantitative definition of these descriptors.[89-92] The link between hardness and polarizability (α) first appeared in the works of Pearson.[55] In a framework of molecules absorbed in cages, Langenaeker, De Proft, Tielens and Geerlings also derived relations between softness and polarizability.[95] A linear correlation between hardness and 1/α for a large number of atoms was shown by Sen et. al. [93] Politzer, on the other hand, showed numerically that the atomic hardness is inversely proportional to the approximated Hartree-Fock atomic polarizability.[94] Since α is directly related to the atomic radius and molar refractivity index, these descriptors have been found to be correlating with the above quantities.[91, 96-98] Ghanty and Ghosh have made a detailed study on the hardness parameter and its relation with the atomic radius, polarizability.[98] Komorowski showed a poor correlation coefficient of 0.77 between polarizability and softness for a collection of neutral molecules.[91] However, in case of polyatomic case, a linear relationship exists between hardness and $\alpha^{1/3}$. Due to the symmetry in atomic systems, these relationships hold. Contrary to this, the molecular systems are not spherical and further distortion would lead to more asymmetry. Pal and coworkers[78] have studied the variation of hardness and polarizability with the bond distortion in polyatomic systems and showed that hardness and $\alpha^{1/3}$ behaves linearly. It may be recalled that the response of chemical hardness with respect to external field was discussed by Pal and Chandra.[92] Using a finite field approximation of η as $E_{N+1} + E_{N-1} - 2E_N$, it can be shown that

$$\frac{\delta\eta}{\delta\vec{F}} = \vec{D}_{N+1} + \vec{D}_{N-1} - 2\vec{D}_N \qquad 1.106$$

By a numerical observation it was found that $\frac{\delta\eta}{\delta\vec{F}}\Big|_{\vec{F}=0}$ is linearly decreasing function of cube root of polarizability, a linear relation between cube root of polarizability of N-electron system with dipole moments of N+1, N-1 and N electron system was derived.[92]

On the basis of the inverse relationship of hardness and polarizability, a minimum polarizability principle (MPP) has been postulated.[77, 99] It states that the natural direction of evolution of any system is toward a state of minimum polarizability. It is supported on the basis of numerical studies.[83, 100-101] Very recently, Tanwar et. al. proposed a principle named minimum magnetizibility principle (MMP),[102] in the line with MPP to extend the domain of application of conceptual DFT to magnetochemistry. It was shown that there is a minimum value of magnetizibility at equilibrium geometry.

There have been relatively few works in relating the local quantities, such as FF with static dipole polarizability. Vela and Gazquez first attempted to derive systematically from DFT an expression for the static-density linear response function in terms of local and nonlocal components that are proportional to the FF and the global softness.[103] Ghanty and Ghosh have also shown connectivity for the above two terms for atomic systems from density functional viewpoint.[98]

In two different works, chemical potential and hardness parameter has been related to the electrostatic potential.[94, 104] Accordingly, hardness is defined as the electrostatic potential at the covalent radius due to Fukui function.[104]

1.9 Chemical Applications of Reactivity Descriptors

Apart from the formal developments of these global and local reactivity descriptors there are subsequent efforts to apply these concepts in understanding and explaining a variety of chemical problems. A vast majority of research has been performed in this area till date. There have been various monographs and reviews bringing out the usefulness of these concepts in quantifying and analyzing the chemical reactivity problems within the framework of DFT.[7, 12-15, 32, 106-108, 130] In this section, a brief discussion on the application of these reactivity descriptors would be focused.

Based on the proposition that both hardness and aromaticity are measures of high stability and low reactivity, Zhou, Parr and Garst put forwarded the absolute and relative hardness as a measure of aromaticity.[86] Parr and coworkers have successfully correlated resonance energy per Π-electron, which is conventional valence bond aromaticity, with absolute hardness or relative hardness.[86a] It has been revealed that for electrophilic aromatic substitution reactions, the change in hardness from reactant to transition state on a potential energy surface is a measure of the activation energy of a reaction. Hardness has been shown to be a successful candidate predicting the stability and reactivity of metal clusters.[109-110]

To understand the intramolecular reactivity, local indices such as FF and local softness are extensively used.[15, 111, 112] However, Langenaeker et. al. have shown that more reliable reactivity order can be obtained by making use of local hardness, rather than FF or local softness.[113] Intermolecular interactions being charge controlled (hard-hard) interactions, and therefore, better described by hardness related descriptors. On the other hand, intramolecular interactions are better described by orbital controlled reactivity descriptors like FF, local softness.[111-112]

The interpretation of orientation in organic reactions, based on both global and local HSAB principle, has also been studied.[15, 106, 112] The local reactivity descriptors have been reasonably successful for interpreting the regioselectivity and mechanism of the Diels-Alder reactions.[113-121] Moreover, these concepts have been applied for studying the regioselectivity of unsaturated aldehydes and ketones, substituted benzynes and hexarynes and the nucleophilic and electrophilic reactions of monosubstituted benzenes.[23, 113, 117, 122-124] Local softness has been adequately rationalized by studying the regioselectivity of fullerenes chemistry.[125] The local hardness, in one or another approximate form, has also been studied on the intermolecular reactivity sequences, acidity of subsequent acetic acids, hydrides, alkyl alcohols, model systems of zeolites, and reactivity of monosubstituted benzenes. [113, 122-124] Very recently, an attempt to evaluate the local hardness has been made by Roy and coworkers. [137]

There have been several studies which point out the failures of these descriptors in explaining the experimental observation.[126-128] A study carried out by Russo et. al. has claimed that the orbital Fukui indices do not offer the correct reactivity pattern for the protonation of aniline in the gas phase.[82] On the basis of local softness and FF, Roy et. al. has reported some mismatch for α, β-unsaturated ketones.[40] The relative electrophilicity and relative nucleophilicity, defined by Roy et. al. are more reliable descriptors than the condensed FF.[40, 127, 129] Krishnamurty et. al. studied the intermolecular interactions by using group softness, where the group consists of the group of reacting atoms or the nearest neighbours.[126]

The applicability of these reactivity descriptors ranges from simple organic molecules to more complex zeolites. For instance, the chemical reactivity of solid surfaces as complicated as the Si (111) surface and zeolites have been analyzed through these descriptors. Particularly, the acidity and basicity of zeolites, the two important factors for determining its catalytic activity, has been analyzed using the local indices.[127, 131-133] Recently, investigations on the influence of changes in the average framework electronegativity (by variations in the composition of the zeolites or by isomorphous substitution of Si and Al atoms by other atoms) on the acidity of the bridging hydroxyl groups have been carried out by Geerlings and coworkers, Pal and coworkers, Deka et. al. and Chatterjee et. al. [127, 129, 131, 133]

The HK theorem is valid for ground states hence, the study of reactivity descriptors for the systems at the excited states are very scarce. Consequently, the extension of ground state DFT formalism for studying the reactivity indices for the excited state poses a difficulty. However, Chattaraj and coworkers have focused on extending the conceptual tools of ground state DFT to excited states.[148] These studies have led to significant understanding of excited state chemistry. In the context of DFT-quantum fluid dynamics, Chattaraj and his coworkers[134] have studied the time evolution of various reactivity parameters such as chemical potential, hardness, polarizability and entropy associated with ion-atom collision process and an atom field interaction process for both the ground and excited electronic states. Moreover, the validity of MHP and electronegativity equalization method has been shown in ground and excited states.

The usefulness of philicity in predicting regioselective isomers in Diels-Alder reaction was examined by Contreras et. al.[135, 136] Numerically, philicity has been tested to perform better than FFs in describing intermolecular reactivity.

Very recently, a new descriptor, multiphilic descriptor (the difference between the nucleophilic and electrophilic condensed philicity function), is used to explain simultaneously the nucleophilicity and electrophilicity of a given atomic site in a molecule.[138] The concept of dual descriptor has been well exploited to understand the Woodward-Hoffmann rules for pericyclic reactions.[139-140] In an another interesting work, an attempt was made to link the density based reactivity descriptors with the redox behavior of a species.[141]

1.10 Organization of the thesis

The main objectives of the present thesis are to study the effect of external perturbations on the reactivity descriptors. Specifically, we would throw some light on the behavior of the reactivity descriptors, using simple prototype molecules, in the presence of external electric field and solvents. We would also present some applications of these reactivity descriptors to understand the reactivity of the mixed metal clusters and study the [2+2] cycloaddition reactions exploiting the local HSAB principle. The organization of the present thesis is as follows:

In chapter 2 of the present thesis, we study the response of the global and local reactivity descriptors in the presence of external electric field for some of the simple prototype linear molecular systems such as HF, CO, HCN and C_2H_2. In addition to the analysis on the reactivity of these systems, the influence of the electric field on the interaction energy of the complexes formed by these systems has also been studied using the recently proposed semi-quantitative model based on the local HSAB principle.

Chapter 3 includes two parts. This chapter will study the consequences of the effect of external electric field on changing the symmetry of molecules. The first part of our study mainly involves the application of weak electric field (electric field varied from 0.000 au to 0.006 au) in a direction along the principal axis and in perpendicular directions of some nonlinear planar C_{2v} symmetry molecules such as H_2O, HCHO, CH_2S, SO_2 and O_3. We also discuss the strength of the electric field studied in this work in terms of the strength of the molecular interaction. The work is expected to throw light on the effect of interactions within the above range on reactivity descriptors. In addition, the nonlinearity in the variation of condensed Fukui function is explained by a perturbative analysis. In the second part, conceptual DFT has been used to understand the reactivity of biologically important molecule, deoxyribonucleic acid (DNA) bases under the influence of external electric field. The four bases found in DNA are adenine, cytosine, guanine and thymine and the double helix are stabilized by the hydrogen bonds between the bases formed by the reactive atoms. The electric field (electric field varied from 0.000 au to 0.006 au) is applied towards the atoms forming the hydrogen bonds (i.e. parallel to the hydrogen bonds) as well as towards its perpendicular directions. The reactivity of the atoms forming the hydrogen bonds is only analyzed. Moreover, the influence of the electric field on the interaction energy of the base pairs (adenine-thymine and guanine-cytosine) has also been studied using the semi-quantitative model based on the local Hard-Soft Acid-Base (HSAB) principle.

In chapter 4, conceptual DFT is exploited to understand the reactivity of molecules in a medium of solvent with increasing dielectric constant. Aprotic as well as protic solvents are used for the present study. The effect of solvation, with different solvents, on the reactivity and stability of CH_3CHO and CH_3CH_2CHO are analyzed. The solvents chosen for the present study are n-hexane (1.89), diethyl ether (4.335), pyridine (12.3), ethanol (24.3), methanol (32.63) and water (78.54); dielectric constants are shown in parenthesis. The COSMO (COnductor-like Solvatiob MOdel is a continuum solvation model in which the solute molecule forms a cavity within the dielectric continuum of permittivity that represents the solvent) solvation model as employed in DMOL^3 is utilized to compute the global as well as the local parameters in the different solvent surroundings.

In chapter 5, local reactivity descriptors such as the condensed local softness and Fukui function have been employed to investigate the inter-cluster reactivity of the metalloaromatic (Al_4Li^- and Al_4Na^-) and antiaromatic (Al_4Li_4 and Al_4Na_4) compounds. We have proposed the concept of group Fukui function which is defined as group softness divided by global softness. It is useful when the reaction does not take place through a single atom, but through neighbouring atoms in a cooperative manner. This concept is used along with group softness to characterize the strength of the nucleophilicity of the Al_4 unit in these compounds. The aim of this work is to understand the enhanced efficiency of the electron injection of the Al-Li cathode in the organic light emitting diode due to the formation of Al-Li clusters at the interface.

In chapter 6, we would like to study the reaction involving a ketene and a double bond via a [2+2] cycloaddition reaction where the final product is a cyclobutanone. Local reactivity descriptor such as local softness is used to understand the facts. In addition, local HSAB principle is exploited which states interaction between any two molecules occur not necessarily through their softest atoms, but rather through those atoms which have similar local softness.

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Chapter 2

Effect of External Electric Field: Reactivity and Stability

2.1 Introduction

The prediction of the changes in reactivity and selectivity of the atom centers within a molecule and the interaction between the molecular systems, in general, can be described by energy-density response functions.[1-4] A study on the behavior of electron density and its variation with respect to the small perturbations can thus reveal many interesting aspects concerning the reactivity pattern of the atomic and molecular systems.[5-8] The electron density of the interacting systems will be redistributed due to small perturbations which can lead to some specific strong, weak or van der Waals bond type interactions. These perturbations can be introduced in many ways. More importantly, the medium in which the reaction is taking place has profound impact in determining many aspects of the reactions.[9] Owing to the importance of the solvent effects, many theoretical efforts have been devoted to study these effects. In addition to the explicit solvent effects, one can also have effects due to introduction of homogeneous and inhomogeneous electric fields. An inhomogeneous electric field can be produced by placing fictitious point charges around the systems. These effects are generally known as environmental effects.[10, 11] These external fields can affect the physical properties and reactivity of the molecular systems. These effects are especially important in ordered crystalline environments such as solid oxides (e.g. zeolites and other metal oxides) and biological macromolecules.[12-15] These local electrostatic fields play an important role in catalytic functions and in governing the stabilization of many bio-molecular systems.[16-18] The environmental effects cause dramatic changes in the reactivity. As a result, the stability of the complexes can become weaker or stronger depending on such effects. Hence, the prediction of the reactivity and stability of molecular systems in the presence of such environmental factors (solvent, electric field or point charges) becomes an important issue.

Our interest in the present chapter is to study these environmental effects on the reactivity of simple molecular systems in gas phase as well as the stability of their complexes in terms of the density based descriptors,[19] namely Fukui function, local softness, hardness and chemical potential. These descriptors have been found to be very useful in rationalizing the reactivity patterns of the molecular systems.[23-30] Geerlings *et. al.* have recently reviewed the theoretical basis for these descriptors and their applications.[31] In general, the descriptors are classified to refer to the whole system, called "global reactivity descriptors" or to a local part of the system, called "local reactivity descriptors". Since most of these descriptors are the derivatives of energy and electron density variables, it is expected that they will provide the modified reactivity information of the molecular systems in the presence of such external effects. A semi-quantitative model based on the energy density perturbation theory, has also been proposed to calculate the interaction energy between the molecular systems and demonstrated its applicability in detail.[32-34] This model also forms the theoretical basis for the local version of the Hard-Soft Acid-Base (HSAB) principle. This model has been critically examined for the general types of molecular interactions[36, 28] and its reliability has been systematically analyzed with respect to several theoretical factors, such as basis set, electron correlation and different electron population methodologies.[37]

The previous studies have dealt with the interactions in vacuum (or in the gas phase) where the system is completely independent of its surroundings.[33,34,36,37] However, if one is interested in the features of the chemical process in condensed media such as aqueous solution or in the presence of other external fields, it is important to include such external effects. Such studies, in particular, the change in the reactivity and stability of different complexes due to applied electric field in terms of the reactivity descriptors are very scarce in the literature. Using energy-density perturbation methods, Fuentealba and Cedillo have derived an expression for the variation of Kohn-Sham Fukui function under the external fields involving the Unsöld approximation.[38] Senet has recently generalized the higher order derivatives of global and local reactivity descriptors in terms of different perturbation variables and included the linear and nonlinear response functions within the framework of DFT.[39] Apart from these few works, there have been other studies, which take into account the solvent effect explicitly, on investigation of the reactivity of molecular systems by the reactivity descriptors using the continuum dielectric model, Born-Onsager approach and effective fragment potential approach.[40-45]

Accordingly, in this chapter we will study the response of the global and local reactivity descriptors (hardness and Fukui function) in the presence of an external perturbation. In addition, an attempt has also been made to study the stability of the model systems using these descriptors. Using a simple relationship between the hardness and softness parameters, the variation of these descriptors in the presence of external electric field has also been explained.

The present chapter is organized as follows: In Section 2.2, we give a brief theoretical background of the global and local reactivity descriptors and describe the local HSAB principle for calculating interaction energy. In section 2.3, the methodology and computational details are presented. In section 2.4, we will present our results for the systematic description of the reactivity and stability of the molecular systems in the presence of external field in terms of these reactivity descriptors.

2.2 Theoretical Background

The detailed description on the reactivity descriptors has already been presented in the previous chapter. However, a brief outline of the reactivity descriptors would be helpful.

2.2.1 Global and Local Reactivity Descriptors

The ground state energy of an atom or a molecule, in density functional theory, can be expressed in terms of electron density, ρ(r) as [35]

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

where, $v(r)$ is the external potential and $F_{HK}[\rho]$ is universal Hohenberg-Kohn functional expressed as sum of electronic kinetic energy and the electron-electron interaction energy.

The first and second partial derivative of E [ρ] with respect to the number of electron N under constant external potential $v(r)$ are defined as chemical potential, μ and the hardness, η for a system[21]

$$\mu = \left(\frac{\partial E[\rho]}{\partial N}\right)_{v(r)} \qquad 2.2$$

$$\eta = \frac{1}{2}\left(\frac{\partial^2 E[\rho]}{\partial N^2}\right)_{v(r)} = \frac{1}{2}\left(\frac{\partial \mu}{\partial N}\right)_{v(r)} \qquad 2.3$$

Global softness, S defined as the inverse of hardness, can be written as

$$S = \frac{1}{2\eta} = \left(\frac{\partial N}{\partial \mu}\right)_{v(r)} \qquad 2.4$$

It has been customary to use the finite difference approximation to compute μ and η using the energies of N, N+1 and N-1 electron systems as [19]

$$\mu \approx \frac{-I-A}{2} \tag{2.5}$$

$$\eta \approx \frac{I-A}{2} \tag{2.6}$$

where, I and A are ionization potential and electron affinity of a chemical species, respectively.

The principle of maximum hardness was proposed by Pearson [46] relating the hardness and stability of a system at constant chemical potential and later proved by Parr and Chattaraj.[47] The global hardness reflects the overall stability of a system.

However, the site selectivity and reactivity can only be studied using the local reactivity descriptors, such as local softness [20b] s(r), which is defined as

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

and

$$\int s(r)dr = S \tag{2.8}$$

where, f(r) is the Fukui function(FF),[20a]

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

Thus, Fukui function can be interpreted either as the change of electron density at 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.

The N discontinuity problem of atoms and molecules [48] in equation (2.9) leads to the introduction[20a] of both right and left hand side derivatives at a given number of electrons, N_0(=N)

$$f^{+}(r) = \left(\frac{\partial \rho(r)}{\partial N}\right)^{+}_{v(r)} \qquad \text{for nucleophilic attack,} \qquad 2.10$$

and $$f^{-}(r) = \left(\frac{\partial \rho(r)}{\partial N}\right)^{-}_{v(r)} \qquad \text{for electrophilic attack} \qquad 2.11$$

By finite difference method using the electron densities of N_0, N_0+1, N_0-1 electron systems, Fukui functions for the nucleophilic and electrophilic attack can be defined respectively, as

$$f^{+}(r) \approx \rho_{N_o+1}(r) - \rho_{N_o}(r) \qquad 2.12a$$

$$f^{-}(r) \approx \rho_{N_o}(r) - \rho_{N_o-1}(r) \qquad 2.12b$$

and for radical attack,

$$f^{o}(r) \approx \frac{1}{2}\left(\rho_{N_o+1}(r) - \rho_{N_o-1}(r)\right) \qquad 2.12c$$

In order to describe the site reactivity or site selectivity, Yang *et al.*[22] proposed atom condensed Fukui function, based on the idea of electronic population around an atom in a molecule, similar to the procedure followed in population analysis technique.[50] The condensed Fukui function for an atom k undergoing nucleophilic, electrophilic or radical attack can be defined respectively as

$$f_k^{+} \approx q_k^{N_o+1} - q_k^{N_o} \qquad 2.13a$$

$$f_k^{-} \approx q_k^{N_o} - q_k^{N_o-1} \qquad 2.13b$$

$$f_k^{o} \approx \frac{1}{2}\left(q_k^{N_o+1} - q_k^{N_o-1}\right) \qquad 2.13c$$

where q_k's are electronic population of the k^th atom of a particular species.

Similarly, the condensed local softness for nueleophilic, electrophilic and radical attack has been defined as,

$$s_k^{a} = f_k^{a} S \qquad a = +, -, 0 \qquad 2.14$$

2.2.2 Local HSAB Principle: Expression for Interaction Energy

Using energy as a functional of number of electrons (N) and the external potential (v), the interaction energy of the two interacting model systems A and B and it is given as,[32,49]

$$\Delta E_{\text{int}} = \frac{-1}{2}\left(\frac{(\mu_A - \mu_B)^2}{\eta_A + \eta_B}\right)_v - \frac{1}{2} N_{AB}^2 \left(\eta_{AB} - \eta_{AB}^*\right)_\mu \qquad 2.15$$

where, η_{AB} and are η_{AB}^* the hardness of the complex at the equilibrium and at the isolated state respectively. For the details of the mathematical part of the derivation for the Eq. (11), one can refer to the work of Gazquez and Mendez[32, 48] and us.[33, 34] In this model, the interaction between the system A and B is assumed to take place in two steps, ΔE_v and ΔE_μ. In the first step, the interaction takes place at constant external potential through the equalization of chemical potential which is referred as ΔE_v.[32] In the second step, A and B evolve toward the equilibrium state through changes in the electron density of the global system produced at constant chemical potential which is referred $\Delta E_{\mu.}$[49] The second step is a manifestation of principle of maximum hardness.[46,47] One can relate the difference in the hardness terms present in the second term of the above Eq.(11) to the softness of system A and B with a proportionality constant (K).[33] Thus, we have shown that, introducing λ as the product of $2N^2_{AB}$ and the proportionality constant K, ΔE_μ can be rewritten in terms of the softness of the systems A and B as,

$$\Delta E_\mu = -\frac{1}{2} N_{AB}^2 K \left(\frac{1}{(S_A + S_B)}\right)_\mu = -\lambda\left[\frac{1}{4(S_A + S_B)}\right]_\mu \qquad 2.16$$

This parameter λ cannot be computed rigorously only through the softness of the molecular complexes. On substituting the expression (2.16) in (2.15), one can get the global model in terms of the softness parameter of the systems A and B.

$$\Delta E_{\text{int}} \approx \frac{-(\mu_A-\mu_B)^2}{2}\left(\frac{S_A S_B}{S_A+S_B}\right)_v - \frac{1}{4}\left(\frac{\lambda}{S_A+S_B}\right)_\mu \qquad 2.17$$

If the interaction between the systems occur through the atom x of A with the atom k of the molecular system B, one can express the total interaction energy from the local point of view, as[32, 33]

$$(\Delta E_{\text{int}})_{Ax-Bk} = \frac{-(\mu_A-\mu_B)^2}{2}\left(\frac{S_A f_{Ax} S_B f_{Bk}}{S_A f_{Ax}+S_B f_{Bk}}\right)_v - \frac{1}{4}\left(\frac{\lambda}{S_A f_{Ax}+S_B f_{Bk}}\right)_\mu \qquad 2.18$$

where S_A, S_B and f_{Ax}, f_{Bk} are the global softness and condensed FF of the atoms x and k in a systems A and B, respectively. We have used the local softness and FF of isolated systems and this approximation is justified for weak to moderately weak interactions. We have related the parameter λ as the change in the electron densities at the interacting site before and after the interaction process.[33] This change will give the effective number of valence electrons that have participated in the interaction process. Thus, an expression for the term λ can be written as the difference in the sum of the atomic charges of the system A before and after the interaction,

$$\lambda_A = \sum_{i=1}^{p} Q_{A_i}^{eq} - \sum_{i=1}^{p} Q_{A_i}^{o} \qquad 2.19$$

Alternately, the term λ can also be defined for the system B as,

$$\lambda_B = \sum_{i=1}^{q} Q_{B_i}^{eq} - \sum_{i=1}^{q} Q_{B_i}^{o} \qquad 2.20$$

The indices p and q are the number of atoms of the systems A and B respectively, and Q^{eq} refers to the condensed electron population of the respective atoms in the equilibrium and Q^{o} refers to the condensed electron population of the respective atoms of the isolated systems.

The interaction energy between systems A and B interacting through multiple pair of reactive sites (x-k, y-l, z-m, etc) can be written as[34]

$$\Delta E_{\text{int}} = \frac{-(\mu_A - \mu_B)^2}{2}\left(\sum_{xk,yl,zm,....}\frac{CSA_x CSA_k}{CSA_x + CSA_k}\right)_v - \frac{\lambda}{4}\left(\sum_{xk,yl,zm,....}\frac{1}{CSA_x + CSA_k}\right)_\mu \qquad 2.21$$

where CSA_x and CSA_k are condensed local softness of the reactive atoms x and k of the systems A and B, respectively. Thus, the net interaction is obtained as a logical extension of the single site local HSAB principle to multiple sites by assuming the interaction occurs in a decoupled manner and by the additivity of energy.

2.3 Methodology and Computational Details

In this study, we have chosen some of the prototype systems HCCH, HF, HCN, and CO and the weakly bonded complexes, namely HCCH---CO, HCCH---OC, FH---CO, FH---OC, NCH---CO, NCH---OC, HCCH---NCH, FH---NCH. All the systems are aligned along the Z-axis of the coordinate system and hence the principle bond axis is the Z-axis. All individual monomers and their complexes were completely optimized at the HF level with zero field using the 6-31G (d,p) basis set and these geometries have been considered for the further study. The minima of all these systems and their complexes have been confirmed by frequency analysis. The electric fields were varied from 0.000au to 0.012au in the steps of 0.002au to calculate the energy of neutral, cationic and anionic species at the DFT level with B3LYP hybrid functional. The electric field has been applied parallel and perpendicular to the principle axis (bond axis) of all the molecular systems. The chemical potential, hardness and condensed FF were calculated from equations (2.5), (2.6), and (2.13), respectively. The effect of change in the orientation of the electric field along the principle axis for all the molecular systems has also been studied. All the calculations were performed using the GAMESS system of programs.[51]

The expression (2.18) is used for the computation of interaction energy of the complexes interacting through single-sites. The parameter λ has been calculated using Eqs. (2.19) or (2.20), through the Lowdin population scheme.[52] In conventional methods, the interaction energy is evaluated by the difference between the energy of the complex AB and sum of the energy of the monomer A and B, $\Delta E = E_{AB} - (E_A + E_B)$.

2.4 Results and Discussions

2.4.1 Effect of External Electric Field on Reactivity Descriptors

In this section, we will first discuss the effect of electric field on the global reactivity descriptors (GRD) and local reactivity descriptors (LRD) for some of the systems, namely, HF, CO, HCN and C_2H_2 and later make an attempt to provide a possible explanation for the observations. The changes in GRD and LRD with respect to zero field for all the monomers against electric field are presented graphically in Figures 2.1-2.4.

When the electric field is applied along the more electronegative atom of HF, CO and HCN, it has been observed that the hardness values for all the molecular systems decrease with the increase of electric field strength from 0.000 au to 0.012 au (Figure 2.2). In case of C_2H_2, due to the symmetrical nature of the molecule, we observe that the hardness is constant in this field range. Further, the global chemical potential is found to decrease as the electric field is applied along the more electronegative atom for all these systems, except in CO, where it follows a reverse trend (Figure2.1).

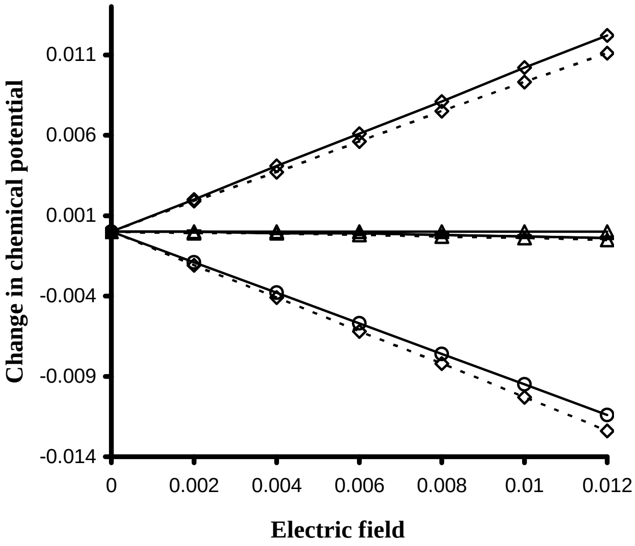

Figure 2.1: Plot of Change in Chemical potential with respect to zero field against applied electric field for the molecular systems HF (—+—), CO (—o—), HCN (—▵—) and C_2H_2 (——). Dashed line represents the values of CP when the field is applied towards electronegative atom while the solid line represents the same when the field is applied in opposite direction.

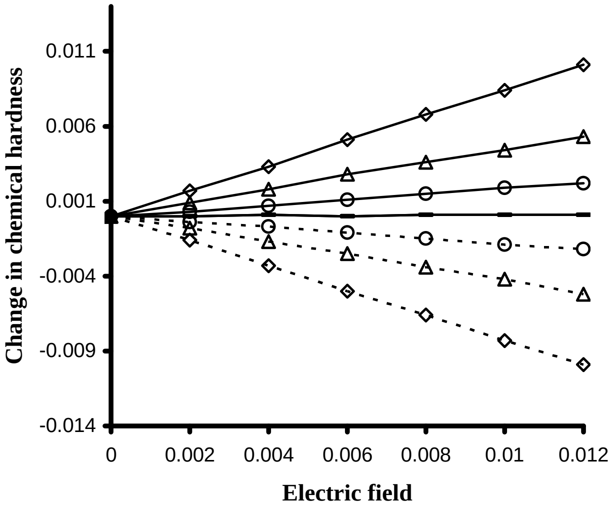

Figure 2.2: Plot of Change in chemical hardness with respect to zero field against applied electric field for the molecular systems HF (—+—), CO (—o—), HCN (—▵—) and C_2H_2 (——). Dashed line represents the values of hardness when the field is applied towards electronegative atom while the solid line represents the same when the field is applied in opposite direction

Table 2.1: Variation of Chemical Potential (CP), Hardness and Condensed Fukui Function (all values are in au) and dipole moment (in Debye) with Electric field for HF molecule

Electric field* (au)	CP	Hardness	f_H^+	f_H^-	f_F^+	f_F^-	Dipole moment
0.000	-0.1911	0.3865	0.8149	0.1293	0.1851	0.8707	1.7972
0.002(H)	-0.1891	0.3882	0.8151	0.1285	0.1849	0.8715	1.8194
0.004(H)	-0.1870	0.3898	0.8153	0.1277	0.1847	0.8723	1.8414
0.006(H)	-0.1850	0.3916	0.8156	0.1269	0.1844	0.8731	1.8634
0.008(H)	-0.1830	0.3933	0.8158	0.1260	0.1842	0.8740	1.8851
0.010(H)	-0.1809	0.3949	0.8161	0.1252	0.1839	0.8748	1.9068
0.012(H)	-0.1789	0.3966	0.8163	0.1245	0.1837	0.8755	1.9282
0.002(F)	-0.1932	0.3849	0.8146	0.1300	0.1854	0.8700	1.7748
0.004(F)	-0.1952	0.3832	0.8143	0.1309	0.1857	0.8691	1.7523
0.006(F)	-0.1973	0.3815	0.8140	0.1318	0.1860	0.8682	1.7297
0.008(F)	-0.1993	0.3799	0.8137	0.1327	0.1863	0.8673	1.7068
0.010(F)	-0.2014	0.3782	0.8134	0.1335	0.1866	0.8665	1.6839
0.012(F)	-0.2035	0.3766	0.8131	0.1345	0.1869	0.8655	1.6607

*Atom(s) along which electric field has been applied is shown in the parenthesis.

The influence of the electric field on the condensed Fukui function of the reactive atoms is observed to be similar to the case of the global descriptors. It is also evident from the Figures 2.3 and 2.4 that a small amount of electric field is sufficient to distort the electron density distribution and hence, it will have a great impact on the reactivity of the systems as well.

Now, from Figure 2.3 and 2.4, we observe that if the electric field is applied towards the more electronegative atom of the systems HF and HCN the value of its condensed Fukui function for electrophilic attack (nucleophilicity) decreases with increasing field strength. For instance, when the field is applied towards N and F atom in HCN and HF, respectively, the nucleophilicity of these atoms decreases.

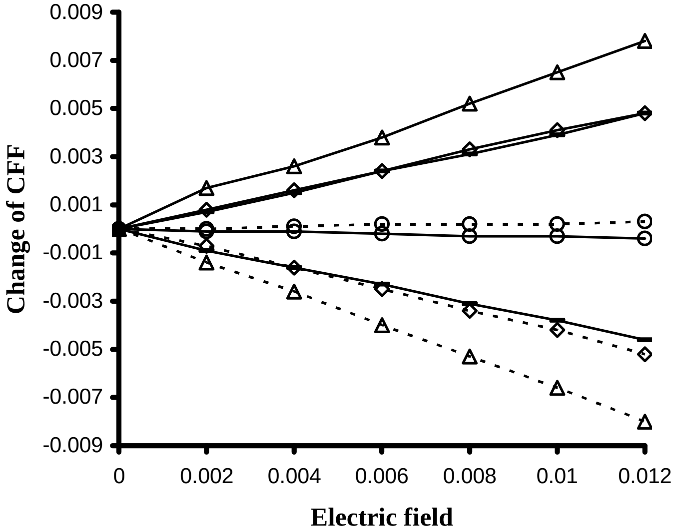

Figure 2.3: Plot of Change in Condensed Fukui Function (CFF) for electrophilic attack with respect to zero field against electric field for the reactive atoms (bolded) H**F** (—◆—), **C**O (—○—), HC**N** (—△—) and HCCH (—▬—). Dashed line represents the values of nucleophilicity when the field is applied towards electronegative atom while the solid line represents the value of that parameter when the field is applied in opposite direction.

Table 2.2: Variation of Chemical potential, Hardness and Condensed Fukui function (all values are in au) and dipole moment (in Debye) with Electric field for CO molecule

Electric field (au)*	CP	Hardness	f_C^+	f_C^-	f_O^+	f_O^-	Dipole moment
0.000	-0.1927	0.3183	0.6865	0.6886	0.3135	0.3114	0.1412
0.002(C)	-0.1908	0.3179	0.6863	0.6886	0.3137	0.3114	0.0793
0.004(C)	-0.1890	0.3176	0.6862	0.6887	0.3138	0.3113	0.0176
0.006(C)	-0.1871	0.3172	0.6859	0.6888	0.3141	0.3112	-0.0440
0.008(C)	-0.1852	0.3168	0.6858	0.6888	0.3142	0.3112	-0.1054
0.010(C)	-0.1834	0.3164	0.6856	0.6888	0.3144	0.3112	-0.1667
0.012(C)	-0.1816	0.3161	0.6854	0.6889	0.3146	0.3111	-0.2278
0.002(O)	-0.1946	0.3186	0.6868	0.6885	0.3132	0.3115	0.2033
0.004(O)	-0.1965	0.3190	0.6869	0.6885	0.3131	0.3115	0.2655
0.006(O)	-0.1984	0.3194	0.6872	0.6884	0.3128	0.3116	0.3279
0.008(O)	-0.2003	0.3198	0.6873	0.6883	0.3127	0.3117	0.3905
0.010(O)	-0.2022	0.3202	0.6876	0.6883	0.3124	0.3117	0.4532
0.012(O)	-0.2041	0.3205	0.6878	0.6882	0.3122	0.3118	0.5161

* Atom(s) along which electric field has been applied is shown in the parenthesis.

Table 2.3: Variation of Chemical Potential (CP), Hardness and Condensed Fukui function (all values are in au) and dipole moment (in Debye) with Electric field for HCN molecule

Electric field(au)*	CP	Hardness	f_N^-	f_N^+	f_C^-	f_C^+	f_H^-	f_H^+	Dipole moment
0.000	-0.1774	0.3305	0.4791	0.3958	0.4059	0.5011	0.1151	0.1030	2.8794
0.002(H)	-0.1774	0.3314	0.4804	0.3966	0.4050	0.5012	0.1146	0.1022	2.9773
0.004(H)	-0.1774	0.3323	0.4817	0.3974	0.4041	0.5013	0.1142	0.1013	3.0750
0.006(H)	-0.1774	0.3333	0.4829	0.3982	0.4033	0.5014	0.1138	0.1004	3.1724
0.008(H)	-0.1774	0.3341	0.4843	0.3989	0.4023	0.5015	0.1134	0.0996	3.2696
0.010(H)	-0.1774	0.3349	0.4856	0.3996	0.4014	0.5016	0.1131	0.0988	3.3666
0.012(H)	-0.1774	0.3358	0.4869	0.4004	0.4005	0.5016	0.1128	0.0980	3.4633
0.002(N)	-0.1775	0.3297	0.4777	0.3951	0.4067	0.5010	0.1156	0.1039	2.7812
0.004(N)	-0.1775	0.3288	0.4765	0.3943	0.4075	0.5009	0.1160	0.1048	2.6827
0.006(N)	-0.1776	0.3280	0.4751	0.3936	0.4083	0.5007	0.1165	0.1058	2.5840
0.008(N)	-0.1777	0.3271	0.4738	0.3927	0.4091	0.5005	0.1171	0.1067	2.4851
0.010(N)	-0.1778	0.3263	0.4725	0.3920	0.4098	0.5004	0.1177	0.1076	2.3858
0.012(N)	-0.1779	0.3253	0.4711	0.3912	0.4105	0.5002	0.1182	0.1087	2.2863

* Atom(s) along which electric field has been applied is shown in the parenthesis.

This is also supported by the fact that the induced dipole moment of these systems decreases when the field is applied along the more electronegative atom (Table 2.1, 2.3). It is interesting to note the exceptional behavior of CO. When the field is applied towards C atom, its nucleophilicity increases marginally. However, the induced dipole moment of C^-O^+ decreases as the field is applied towards C atom **(**Table 2.4**)**. Hence, although the pattern of induced dipole moment of CO is same as HF and HCN, the behavior of the nucleophilicity of C atom is quite different. It is well known that CO exhibits small dipole moment and the value is quite sensitive to the calculation. This probably explains the anomaly. On the other hand, the electrophilicity of the electropositive atom in HF increases when the field is applied towards that atom (Table 2.1).

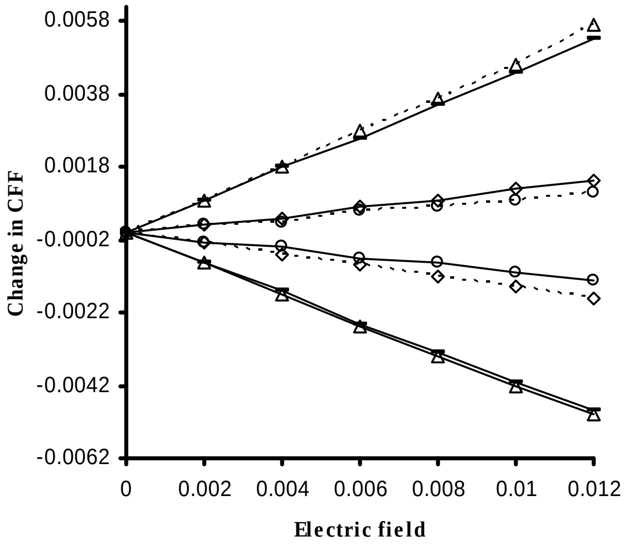

Figure 2.4: Plot of Change in Condensed Fukui Function (CFF) for nucleophilic attack with respect to zero field against electric field for the reactive atoms (bolded) H**F** (—◇—), **C**O (—○—), HC**N** (—△—) and HCCH (—▬—). Dashed line represents the values of electrophilicity when the field is applied towards electronegative atom while the solid line represents the same when the field is applied in opposite direction.

However, when the field is applied towards H and O atom in case of HCN and CO, respectively, its electrophilicity decreases. This behavior of CO is anomalous with the behavior of induced dipole moment. However, in either case, it is interesting to note the marginal change in electrophilicity as well as the nucleophilicity of C and O atoms in CO. This is again expected due to its small dipole moment. The symmetrical molecule C_2H_2 has a different behavior. When the field is applied towards one of the C—H bond, the nucleophilicity as well as the electrophilicity of those atoms decreases, but the decrease in the electrophilicity of C atom is marginal (Table 2.4). Moreover, on comparing across the different systems like HF and HCN, the electrophilicity of H atom in the former is found to be more than that of the latter, at all the field values. In case of CO, the value of the Fukui function for C (f_C^-) is observed to be more than that of O (f_O^-). These results reveal that the nucleophilicity of C atom is more than that of O atom.

It is also pertinent to note that the variation of the GRD and LRD is observed to be almost linear and uniform with respect to the applied electric field except for the case of C_2H_2. In case of C_2H_2, the chemical potential and hardness almost remain constant at the chosen field values.

As can be seen from the Figures 2.1-2.4 that as the field direction is reversed the variation of GRD and LRD are reversed. This important observation reveals that the direction of the external perturbation on the molecular systems will have important role in defining the reactivity of a particular atom. Another interesting observation is that there is no significant change in the value of the global and local reactivity descriptors when the external field is applied perpendicular to the molecular axis of these linear systems. It also means that the polarization induced by the electric field in perpendicular direction is almost negligible for these systems and hence, one cannot expect any change in the reactivity of the descriptors. It should, however, be noted that the change in the reactivity and stability trend for the polyatomic and nonlinear systems can be significant and this is rather difficult to explain.

In earlier part we discussed the change in the hardness and condensed Fukui function parameters due to the external perturbation on the molecular system. It is of particular interest to establish a relation for the variation of these two parameters under the external field. In a recent paper, Fuentealba and Cedillo have shown that the variation of the Kohn-Sham Fukui function with respect to the external perturbation depends on the knowledge on the HOMO density and a mean energy difference of all the occupied and unoccupied orbitals.[38] Here, the quantity, mean energy difference, has been approximately interpreted as hardness. Under this approximation, it has been stated that greater the hardness, the variation of the Fukui function will be smaller under the external perturbation. This statement signifies that the system will become less reactive as the hardness of the systems increases due to the external perturbation.

Contrary to the above statement, in the present study, we have observed that both the hardness and Fukui function decreases when the field is applied along the more electronegative atom of the HF and HCN systems. At the same time, it has also been noticed that the f_k^- value of C in CO increases marginally with the increase of field values and the global hardness value decreases. A similar effect has also been observed for other systems also. These results may probably imply that the decrease of hardness parameters does not necessarily mean that reactivity of the systems increases or vice versa. In what follows, we explain the above using a simple relationship for the variation of the hardness parameters and FF with respect to the electric field. Considering the inverse relationship of hardness with global softness, one can express the variation of hardness with respect to the field (F) as, ($\partial\eta/\partial F$),[53]

$$\partial\eta/\partial F = - 1/S_0^2 \, \partial S/\partial F \qquad 2.22$$

where S_0 is the global softness. The above expression has been used earlier, to exlain a relation between the polarizability and dipole moment as well as to explain the change in hardness values with respect to external field.[53]

At this stage, two comments are pertinent. First, the change in hardness with respect to the electric field is inversely proportional to the square of global softness calculated at the zero fields with a negative sign. The second important point is that the variation of hardness with respect to the external field is directly proportional to the first order variation of softness of the system.

It can be noticed from the above expression (2.22), that the change in hardness parameter with respect to the electric field is actually dependent on the variation of FF of all the atoms present in the molecule. The values of the condensed Fukui function for some of the atoms in a molecule in the presence of the field can become more (or less) than the value of the FF calculated in the isolated state or vice versa. In any case, it should be noted that the net effect would be proportional to $d\eta/dF$. It also signifies that the decrease or increase of hardness of a molecule under the external field does not necessarily imply that the reactivity of a specific site or atom present in the molecule would be enhanced or deactivated due to the variation in the hardness parameter. The variation of the hardness parameter in the presence of external perturbation is actually dependent on the net cooperative effect exhibited by the collection of all the atoms present in the molecule. This is well supported by our earlier discussions. Although the present analysis is not very rigorous, it can, however, explain the present observation in the variation of condensed FF as well as the hardness parameters. A further detailed study should be made in this direction.

2.4.2 Stability of the Complexes under External Electric Field

In the earlier section 2.4.1, the influence of electric field on the determination of global and local parameters has been explained qualitatively. Since the external field influences significantly on both the charge transfer term (λ) and the global and local reactivity descriptors it would be, therefore, interesting to study the stability of the complexes formed by the above systems in the presence of the external field. The stability of the complexes will therefore primarily depend on these two parameters.

Although different complexes can be formed from the above-mentioned systems, we have considered only selected complexes formed by the interaction of CO with C_2H_2, HCN and HF as well as the interaction of HCN with C_2H_2 through N atom in the presence of electric field. As both the atoms C and O in CO can interact with other systems, we have also considered the other possible mode of interaction, CHCH---OC, NCH---OC and FH---OC. The effects of increasing the magnitude of electric field strength on the value of the charge transfer term λ for the above complexes are reported in Table 2.5 and the interaction energy of the above complexes are reported in Table 2.6.

Table 2.4: Variation of Chemical potential, Hardness and Condensed Fukui Function with Electric field for C_2H_2 (all values are in au)

Electric field (au)*	CP	Hardness	$f_{C_1}^-$	$f_{C_1}^+$	$f_{C_2}^-$	$f_{C_2}^+$	$f_{H_3}^-$	$f_{H_3}^+$	$f_{H_4}^-$	$f_{H_4}^+$
0.000	-0.1194	0.2893	0.4118	0.4104	0.4118	0.4104	0.0882	0.0896	0.0882	0.0896
0.002 (C_2--H_3)	-0.1194	0.2893	0.4139	0.4105	0.4098	0.4103	0.0873	0.0888	0.0873	0.0905
0.004 (C_2--H_3)	-0.1195	0.2894	0.4160	0.4106	0.4077	0.4102	0.0866	0.0880	0.0866	0.0914
0.006 (C_2--H_3)	-0.1195	0.2893	0.4180	0.4106	0.4056	0.4100	0.0859	0.0871	0.0859	0.0922
0.008 (C_2--H_3)	-0.1196	0.2894	0.4201	0.4107	0.4035	0.4100	0.0851	0.0863	0.0851	0.0931
0.010 (C_2--H_3)	-0.1197	0.2894	0.4221	0.4107	0.4014	0.4098	0.0844	0.0855	0.0844	0.0940
0.012 (C_2--H_3)	-0.1198	0.2894	0.4241	0.4108	0.3993	0.4096	0.0836	0.0847	0.0836	0.0949

***Variation when the field is applied along one of the C—H bond are given, as the other values will be same.

Table 2.5: Variation of the parameter λ (au) with external electric field for the molecular complexes

Electric field(au)	Values of the parameter λ for the complex							
	FH----CO when field is towards		FH----OC when field is towards		HCCH---CO when field is towards		HCCH---OC when field is towards	
	FH	CO	FH	OC	HCCH	CO	HCCH	OC
0.000	0.0453	0.0453	0.0253	0.0253	0.0128	0.0128	0.0084	0.0084
0.002	0.0435	0.0472	0.0244	0.0262	0.0120	0.0136	0.0080	0.0088
0.004	0.0417	0.0491	0.0236	0.0272	0.0113	0.0145	0.0076	0.0093
0.006	0.0399	0.0510	0.0227	0.0281	0.0105	0.0153	0.0071	0.0098
0.008	0.0383	0.0530	0.0219	0.0291	0.0098	0.0163	0.0068	0.0103
0.010	0.0366	0.0551	0.0211	0.0301	0.0091	0.0173	0.0065	0.0107
0.012	0.0349	0.0572	0.0203	0.0311	0.0084	0.0183	0.0060	0.0113

Table 2.5: Variation of the parameter λ (au) with external electric field for the molecular complexes**.**

Electric field(au)	Values of the parameter λ for the complex							
	NCH----CO when field is towards		NCH----OC when field is towards		HCN---HCCH when field is towards		HCN---HF when field is towards	
	NCH	CO	NCH	OC	HCN	HCCH	HCN	HF
0.000	0.0202	0.0202	0.0142	0.0142	0.0180	0.0180	0.0564	0.0564
0.002	0.0191	0.0212	0.0136	0.0148	0.0190	0.0171	0.0584	0.0544
0.004	0.0181	0.0223	0.0129	0.0154	0.0200	0.0162	0.0604	0.0526
0.006	0.0172	0.0236	0.0124	0.0161	0.0212	0.0153	0.0625	0.0507
0.008	0.0162	0.0248	0.0119	0.0168	0.0223	0.0143	0.0645	0.0489
0.010	0.0153	0.0261	0.0113	0.0174	0.0235	0.0135	0.0667	0.0470
0.012	0.0145	0.0274	0.0108	0.0182	0.0246	0.0126	0.0689	0.0453

It can be seen from Table 2.5 that, when the field is applied towards C_2H_2 for all the above mentioned interactions, the value of the intermolecular charge transfer term λ decreases linearly upon increase in the strength of the electric field. It also shows that the direction of the external field is important for the intermolecular charge transfer, which will eventually affect the mutual interaction between the monomer systems and hence, the stability of the complexes. This field effect is very important in studying the primary electron transfer processes, especially for the electron donor-acceptor systems.

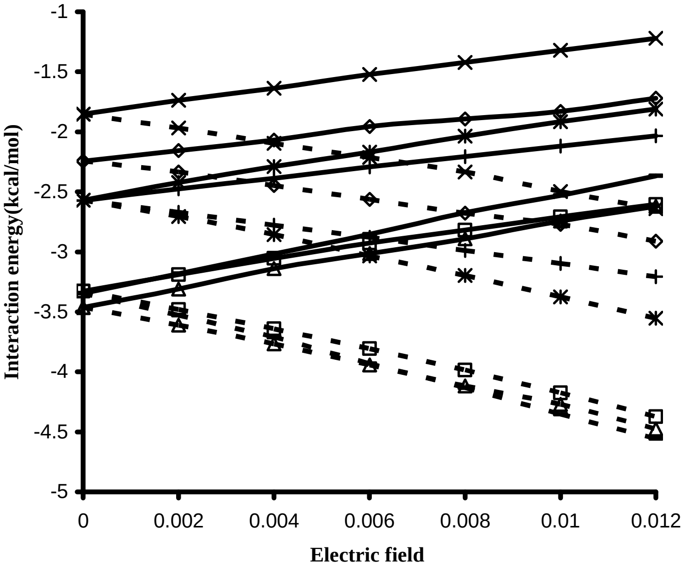

Figure 2.5: Effect of Electric field on the local HSAB Interaction Energy for F**H**---**C**O (—□—), F**H**---**O**C (—+—), NC**H**---**C**O (—✳—), NC**H**---**O**C (—△—), HCC**H**---**C**O (—×—), HCC**H**---**O**C (—◇—), HCC**H**---**N**CH (——) complexes. Dashed lines signify the interaction energy values when the field is applied along CO while solid lines represent the same when the field direction is reversed. For interactions occurring through N atom, dashed lines signify that the field is along HCN while solid lines represent the interaction energy values when the field direction is reversed.

Moreover, when the field direction is towards CO and whether the interaction occurs through C or O atom, the intermolecular charge transfer term $\underset{.}{\lambda}$ always increases. But, HCN has a dual behavior. When the field direction is towards HCN and the interaction occurs through H atom with CO or OC the intermolecular charge transfer term $\underset{.}{\lambda}$ decreases but for the interaction occurring through N atom with C_2H_2 or HF there is an increase in the $\underset{.}{\lambda}$ value with the increase in field strength.

Since the resulting effects in the Fukui function and the term λ are increasing or decreasing linearly at all the field values depending on the field direction, the interaction energies of NCH---CO, NCH---OC, HCCH---CO, HCCH---OC, FH---CO, FH---OC, HCCH---NCH, complexes also increase and decrease approximately linearly with increasing or decreasing the field strength (Figure 2.5). It can also be observed that the stability of the above complexes, formed with CO, increases when the field is applied along the CO direction irrespective of the fact that the interaction may occur either through C or O atom. Since the nucleophilicity of C is stronger than O in CO, the interaction energy of HF with the former is much stronger than that of the later. The actual quantum chemical calculations also show this similar trend. But the local HSAB interaction energy of C_2H_2 and HCN with C in CO is less than that of O atom. This anomaly can be attributed to the combined effect of both the values of charge transfer term and FF of the reactive atoms. But, for the complex HCCH---NCH interacting through the N atom of HCN get stabilized when the field is applied towards HCN, whereas the interaction decreases when the field direction is reversed. The actual quantum chemical calculation for all these complexes also shows this similar trend. Now, if we compare the stability of the above complexes (Figure 2.5) we can conclude that the complexes FH---CO, NCH---OC and HCCH---NCH are more stabilized than the others and their stability increases with the increase in field strength at a particular direction.

It is also evident from the Figure 2.5 that the effect of changing the external field direction on the interaction energy of these complexes is observed to be very significant and these trends show some similarities with the change in the value of global and local reactivity descriptors due to the external field.

In general, the calculated interaction energy for the above complexes shows that these complexes are stabilized more in the presence of external field, in a particular direction, compared to the zero field. It is interesting to observe that although the value of global hardness parameter increases or decreases for all the systems in presence of the electric field, there is a further enhancement or decrease of the bond strength of these complexes at the higher field values. This interesting feature can be attributed with the increase or decrease in the value of the FF indices and the parameter λ due to the applied electric field in a particular direction.

Despite the use of the Lowdin based method of population analysis and medium level basis set, the present model gives an insight about the stability of the complexes in the external field. Thus, this model can be useful for studying other types of complexes in terms of these reactivity descriptors. However, a further study is required to clarify many issues on the variation of the global and local reactivity descriptors due to the external perturbation and its relation with the reactivity of the molecular systems.

Table 2.6: Values of Interaction Energy (kcal/mol) calculated by both local HSAB and Quantum Chemical methods with Electric field

Electric field(au)	Interaction energy(kcal/mol) of							
	F**H**---**C**O complex when field is towards				F**H**----**O**C complex when field is towards			
	FH		CO		FH		OC	
	Local HSAB	Quantum* Chemical	Local HSAB	Quantum Chemical	Local HSAB	Quantum Chemical	Local HSAB	Quantum Chemical
0.000	-3.3277	-4.3499	-3.3277	-4.3499	-2.5715	-2.3513	-2.5715	-2.3513
0.002	-3.1884	-4.0757	-3.4808	-4.6323	-2.4743	-2.1367	-2.6694	-2.5715
0.004	-3.0535	-3.8102	-3.6396	-4.9228	-2.3877	-1.9271	-2.7786	-2.7974
0.006	-2.9255	-3.5517	-3.8058	-5.2221	-2.2904	-1.7225	-2.8784	-3.0290
0.008	-2.8181	-3.3013	-3.9841	-5.5302	-2.2051	-1.5230	-2.9876	-3.2656
0.010	-2.7083	-3.0591	-4.1755	-5.8478	-2.1191	-1.3284	-3.0968	-3.5084
0.012	-2.6054	-2.8238	-4.3719	-6.1741	-2.0338	-1.1389	-3.2078	-3.7575

Electric field(au)	Interaction energy(kcal/mol) of							
	HCC**H**---**C**O complex when field is towards				HCC**H**----**O**C complex when field is towards			
	HCCH		CO		HCCH		OC	
	Local HSAB	Quantum Chemical	Local HSAB	Quantum Chemical	Local HSAB	Quantum Chemical	Local HSAB	Quantum Chemical
0.000	-1.8524	-1.5995	-1.8524	-1.5995	-2.2446	-1.0210	-2.2446	-1.0210
0.002	-1.7376	-1.4458	-1.9672	-1.7633	-2.1549	-0.9080	-2.3331	-1.1414
0.004	-1.6359	-1.3021	-2.0953	-1.9378	-2.0676	-0.8032	-2.4479	-1.2701
0.006	-1.5217	-1.1672	-2.2126	-2.1229	-1.9559	-0.7059	-2.5634	-1.4075
0.008	-1.4213	-1.0423	-2.3350	-2.3193	-1.8932	-0.6166	-2.6782	-1.5525
0.010	-1.3215	-0.9268	-2.4975	-2.5264	-1.8311	-0.5350	-2.7698	-1.7062
0.012	-1.2218	-0.8208	-2.6406	-2.7460	-1.7206	-0.4608	-2.9116	-1.8681

* $\Delta E = E_{AB} - (E_A + E_B)$

Table 2.6: Values of Interaction Energy (kcal/mol) calculated by both local HSAB and Quantum Chemical methods with Electric field

Electric field(au)	Interaction energy(kcal/mol) of							
	HCC**H**---**C**O complex when field is towards				HCC**H**----**O**C complex when field is towards			
	HCCH		CO		HCCH		OC	
	Local HSAB	Quantum Chemical	Local HSAB	Quantum Chemical	Local HSAB	Quantum Chemical	Local HSAB	Quantum Chemical
0.000	-1.8524	-1.5995	-1.8524	-1.5995	-2.2446	-1.0210	-2.2446	-1.0210
0.002	-1.7376	-1.4458	-1.9672	-1.7633	-2.1549	-0.9080	-2.3331	-1.1414
0.004	-1.6359	-1.3021	-2.0953	-1.9378	-2.0676	-0.8032	-2.4479	-1.2701
0.006	-1.5217	-1.1672	-2.2126	-2.1229	-1.9559	-0.7059	-2.5634	-1.4075
0.008	-1.4213	-1.0423	-2.3350	-2.3193	-1.8932	-0.6166	-2.6782	-1.5525
0.010	-1.3215	-0.9268	-2.4975	-2.5264	-1.8311	-0.5350	-2.7698	-1.7062
0.012	-1.2218	-0.8208	-2.6406	-2.7460	-1.7206	-0.4608	-2.9116	-1.8681

Electric field(au)	Interaction energy(kcal/mol) of			
	HCC**H**---**N**CH complex when field is towards			
	HCCH		NCH	
	Local HSAB	Quantum Chemical	Local HSAB	Quantum Chemical
0.000	-3.3446	-2.5929	-3.3446	-2.5929
0.002	-3.1821	-2.3042	-3.5272	-2.8953
0.004	-3.0164	-2.0287	-3.7111	-3.2116
0.006	-2.8545	-1.7671	-3.9326	-3.5423
0.008	-2.6738	-1.5179	-4.1328	-3.8881
0.010	-2.5301	-1.2826	-4.3524	-4.2489
0.012	-2.3670	-1.0599	-4.5557	-4.6247

2.5 Conclusions

The present chapter is focused on the study of the influence of the applied electric field (environmental effects) on the reactivity of some simple prototype systems as well as their complexes using the global and local reactivity descriptors. It is observed that the increase or decrease in the global hardness and the FF of the systems that are considered in the present study depends on the direction in which the electric field is applied along the principle bond axis. Whenever the direction of the field is changed the descriptors shows opposite trend. This unusual trend has been explained by a simple inverse relationship between hardness and Fukui function parameters in the presence of the field. We have also demonstrated that the increase in the value of global hardness in the presence of electric field does not necessarily imply that the reactivity of the molecular systems would be lowered or vice versa. The variation of the hardness parameter in such cases is actually dependent on the net cooperative effect exhibited by the collection of all the atoms present in the molecule. It is also observed that complexes formed by the above simple prototype systems are more stabilized at the higher field applied in a specified direction than at the zero fields.

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Chapter 3

Effect of External Electric Field: Nonlinear Molecules

3.1 Introduction

A systematic study[1] was done to explore the effects of electric field on reactivity descriptors for some linear molecules in the previous chapter. However, it is important to understand the effect of external electric field on the behavior of reactivity descriptors on going from linear to nonlinear molecules. Very recently, the influence of electric field on the hydrogen bond network of methanol has been studied.[2] Parthasarathi *et al* have studied the behavior of the reactivity descriptors in the presence of electric field.[4] In their study, it was observed that the variation of the reactivity descriptors with electric field strength was nonlinear and non uniform.[3] Apart from this, the electric field effects on structures, energetic and transition states of water clusters have been investigated.[4]

In this chapter, however, we will extend our previous study on the response of the GRD and LRD to some planar nonlinear polyatomic molecules with C_{2V} symmetry as well as the DNA bases. In the case of linear molecules, where the electron density is mainly distributed along the molecular axis, one would easily understand the behavior of the descriptors under the application of electric field. This is not the case with nonlinear polyatomic molecules. Therefore, it is important to understand the chemistry of the reactive atoms subjected to external perturbation in the form of external electric field. It is also important to judge the strength of the applied field values in terms of the energies of interaction. This allows us to define the scope of the present chapter in terms of the type of molecular interaction.

The present chapter has been divided into two parts: Section 3.2.1 would present the computational details on C_{2v} symmetry molecules. In Section 3.2.2, we present our results for the stability and reactivity of the molecular systems in the presence of external field in terms of these reactivity descriptors. However, Section 3.3 will focus on the effect of external electric field on the stability and reactivity of DNA bases and their base pairs. In Section 3.3.1, we present the computational details for DNA bases. In subsequent section, we discuss the results. The conclusions are presented in Section 3.4.

3.2 Planar nonlinear molecules with C_{2v} symmetry

3.2.1 Methodology and Computational Details

To study the application of electric field in case of planar nonlinear polyatomic molecules, we consider in the present chapter simple molecules belonging to C_{2v} point group symmetry, such as H_2O, CH_2S, HCHO, SO_2 and O_3. The principal axis of all these molecules is the C_2 axis of symmetry which passes through the central atom(s). First, the above molecules were optimized at DFT level using 6-31++G (d, p) basis set with B3LYP hybrid functional at zero field. These minima were further confirmed by frequency calculations. Then the field was applied along the principal axis from 0.001 au to 0.006 au, increasing by 0.001 au each time, to calculate the energy of the neutral, cationic and anionic systems. Hence, the global and local parameters were calculated at each field value using the equations (2.5), (2.6) and (2.13), respectively. The local parameters such as condensed Fukui function were calculated using the Lowdin[5] based method of population analysis. It should, however, be noted that for higher field values sometimes is unable to converge to the correct state for ($N \pm 1$) systems. This is one of the reasons for choosing such small field values. We also analyzed whether the applied field is strong enough to really mimic the molecular interaction and reaction. To achieve this, we calculated the difference in the energy of the molecule with 0.000 au and 0.006 au field. The effect of change in the orientation of the electric field for all the molecular systems has also been studied. In addition, the electric field was applied perpendicular to the molecular plane as well as in the direction perpendicular to the principal axis in the molecular plane. Similarly, all the global and local parameters were calculated at each field value. All the calculations were performed by GAMESS software.[6]

The theoretical details are presented in the previous chapters, so we avoid repeating it.

3.2.2. Results and Discussion

3.2.2.1. Behavior of Ionization Potential and Electron Affinity in electric field

The ionization potential (IP) and the electron affinity (EA) are presented and analyzed for H_2O and HCHO in the field range of 0.000 to 0.006 au to understand more clearly the behavior of the chemical potential and hardness (Table 3.1a-b). The IP and EA values are calculated using the energies of neutral and charged species.

It can be seen from Table 3.1 that the IP and EA increase on increasing the electric field when the field direction is towards the more electronegative O atom in H_2O and HCHO molecules. Thus, in Koopmans' approximation, the energies of LUMO and HOMO decrease with the increase in field strength. Intuitively, one can predict that the chemical potential and hardness in the context of finite difference approximation as well as Koopmans' approximation. The trend reverses as soon as the direction of the electric field is reversed (Table 3.1).

electric field (in au)*	IP (kcal/mol)	EA (kcal/mol)
0.000	291.416	-17.194
0.001(O)	291.541	-16.190
0.002(O)	291.604	-15.248
0.003(O)	291.729	-14.182
0.004(O)	291.792	-13.178
0.005(O)	291.917	-12.111
0.006(O)	291.980	-11.044
0.001	291.353	-18.198
0.002	291.290	-19.076
0.003	291.227	-20.018
0.004	291.102	-20.896
0.005	291.039	-21.774
0.006	290.976	-22.590

Table 3.1 (a): Variations of IP and EA with electric field applied along the principal axis for H_2O molecule.

* The direction of the electric field is towards that atom as shown in parenthesis.

electric field (in au)*	IP (kcal/mol)	EA (kcal/mol)
0.000	249.309	-19.578
0.001(O)	249.561	-18.762
0.002(O)	249.874	-17.947
0.003(O)	250.125	-17.131
0.004(O)	250.439	-16.253
0.005(O)	250.690	-15.437
0.006(O)	251.004	-14.558
0.001	249.058	-20.394
0.002	248.807	-21.147
0.003	248.556	-21.963
0.004	248.306	-22.716
0.005	248.055	-23.469
0.006	247.804	-24.222

Table 3.1 (b): Variations of IP and EA with electric field applied along the principal axis for HCHO molecule.

3.2.2.2. Behavior of Global and Local Reactivity Descriptors when the electric field is applied along principal axis

The behavior of the global and local reactivity descriptors for planar nonlinear polyatomic molecules, H_2O, CH_2S, HCHO, SO_2 and O_3 in presence of external electric field applied along the principal axis are presented in Tables 3.2-3.3 and Figures 3.1-3.2. In order to avoid repetition, we are presenting the values of GRD and LRD for H_2O molecule in Table 3.2 while results for molecules with similar information, CH_2S and HCHO molecules, are presented in Figure 3.1-3.2.

electric field (in au)*	μ(in au)	η(in au)	f_o^-	f_H^-	f_o^+	f_H^+
0.000	-0.2185	0.2459	0.8368	0.0816	0.0753	0.4623
0.001(O)	-0.2194	0.2452	0.8363	0.0818	0.0766	0.4617
0.002(O)	-0.2202	0.2445	0.8359	0.0821	0.0781	0.4609
0.003(O)	-0.2211	0.2438	0.8354	0.0823	0.0796	0.4602
0.004(O)	-0.2220	0.2430	0.8350	0.0825	0.0812	0.4594
0.005(O)	-0.2229	0.2422	0.8345	0.0828	0.0828	0.4586
0.006(O)	-0.2239	0.2415	0.8340	0.0830	0.0845	0.4577
0.001	-0.2177	0.2467	0.8372	0.0814	0.0741	0.4629
0.002	-0.2169	0.2473	0.8377	0.0812	0.0729	0.4635
0.003	-0.2161	0.2480	0.8381	0.0810	0.0719	0.4640
0.004	-0.2153	0.2486	0.8385	0.0807	0.0711	0.4644
0.005	-0.2146	0.2493	0.8390	0.0805	0.0703	0.4648
0.006	-0.2139	0.2499	0.8394	0.0803	0.0698	0.4651

Table 3.2: Variations of Chemical Potential, Hardness and CFF with electric field applied along the principal axis for H_2O molecule

* Field applied towards O atom is shown in parenthesis alongside the field value.

When the field is applied towards the central atom (say from the line joining the two H atoms to the O atom along the principal axis, in case of H_2O) of all the species, and if the central atom is more electronegative atom the chemical potential and hardness decreases with increasing field values. For instance, when the electric field is applied towards the O and S atom in H_2O, HCHO and CH_2S, respectively, the chemical potential and hardness decreases (Table 3.2; Figure 3.1). On the other hand, if the central atom is more electropositive and if the field is directed towards the central atom, the chemical potential and hardness increase with increasing field. In case of SO_2, the field directed towards the central atom S results in the increase in chemical potential and hardness with increasing field values (Figure 3.1). Interestingly, in case of O_3, when the field is towards the central O atom, the chemical potential decreases, while the hardness remains almost constant with increasing field. But as the field direction is reversed, the chemical potential increases and hardness values decrease marginally with increasing field (Table 3.2). These marginal changes in O_3 may be due to its small dipole moment.

When the direction of the electric field is reversed, the trends in the chemical potential and hardness are also reversed for all the systems except O_3. This signifies that the direction of the field plays a very important role in understanding the stability and reactivity of a system.

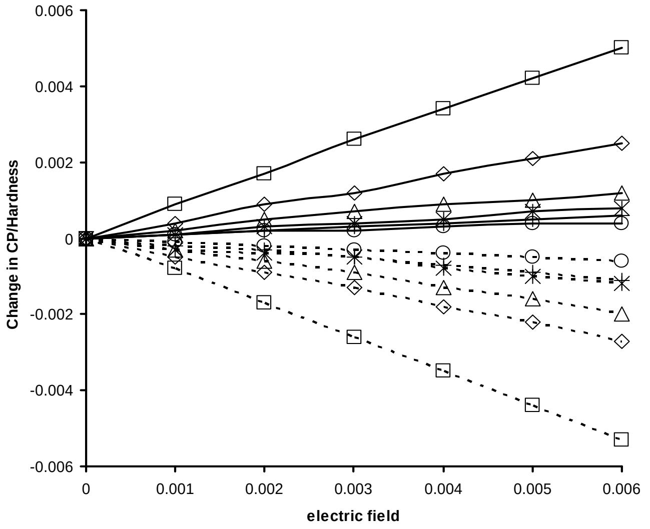

Figure 3.1: Plot of Change in Chemical potential (CP)/Hardness with respect to zero fields against electric field applied along the principal axis for the molecular systems, CH_2S (—△—/—+—), HCHO (—□—/—◇—) and SO_2. (—○—/—✳—). Dashed line represents the values of the parameter when the field is applied towards more electronegative atom while the solid line represents the value of that parameter when the field is applied in opposite direction.

We now turn our attention to the local reactivity descriptors. When the field is applied along the principal axis towards the central atom, the CFF for electrophilic attack (nucleophilicity) decreases for that atom provided the central atom is more electronegative. As an illustration, the nucleophilicity of O in H_2O (Table 3.2**)** and HCHO and S atom in CH_2S (Figure 3.2) decrease, when the electric field is applied towards those atoms. Moreover, the CFF for nucleophilic attack (electrophilicity) of H atoms in H_2O decreases (Table 3.2). At the same time, when the field is applied towards the central atom in CH_2O and CH_2S, the electrophilicity of C atom increases almost linearly with increasing field (Figure 3.2). On the other hand, when the field is towards the electropositive central atom, the electrophilicity for that atom decreases. SO_2 provides an example for this. However, the nucleophilicity of O atoms in SO_2 decreases slowly in this field range (Figure 3.2).

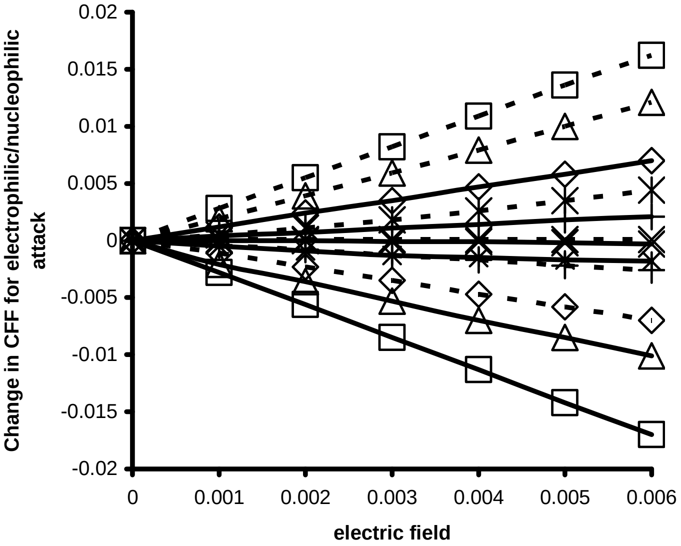

Figure 3.2: Plot of Change in Condensed Fukui Function (CFF) for electrophilic/ nucleophilic attack with respect to zero fields applied along the principal axis for CH_2S (—◇—/—△—), HCHO (—+—/—□—) and SO_2. (—×—/—✳—). Dashed line represents the values of the parameter when the field is applied towards more electronegative atom while the solid line represents the value of that parameter when the field is applied in opposite direction.

Although ozone has a V-shaped structure, it behaves differently. When the field is directed towards the central oxygen atom, its nucleophilicity as well as its electrophilicity decreases while the nucleophilicity and electrophilicity of the other two oxygen atoms increase as the field values increase. This may be due to its resonance structure (Table 3.3).

electric field (in au)*	μ (in au)	η (in au)	f_{O2}^{-}	$f_{O1,3}^{-}$	f_{O2}^{+}	$f_{O1,3}^{+}$
0.000	-0.2803	0.1986	0.2035	0.3983	0.2553	0.3723
0.001(O2)	-0. 2805	0.1987	0.2034	0.3983	0.2550	0.3725
0.002(O2)	-0.2807	0.1987	0.2032	0.3984	0.2548	0.3726
0.003(O2)	-0.2809	0.1987	0.2031	0.3984	0.2545	0.3727
0.004(O2)	-0.2811	0.1987	0.2030	0.3985	0.2543	0.3729
0.005(O2)	-0.2813	0.1987	0.2029	0.3986	0.2540	0.3730
0.006(O2)	-0.2816	0.1987	0.2028	0.3986	0.2538	0.3731
0.001	-0.2801	0.1986	0.2036	0.3982	0.2556	0.3722
0.002	-0.2799	0.1986	0.2037	0.3981	0.2559	0.3721
0.003	-0.2797	0.1986	0.2039	0.3981	0.2561	0.3719
0.004	-0.2795	0.1986	0.2040	0.3980	0.2564	0.3718
0.005	-0.2793	0.1985	0.2041	0.3979	0.2567	0.3717
0.006	-0.2791	0.1985	0.2043	0.3979	0.2570	0.3715

Table 3.3: Variations of Chemical Potential, Hardness and CFF with electric field applied along the principal axis for O_3 molecule

* Field applied towards central O atom is shown in parenthesis alongside the field value.

When the direction of the electric field is reversed, the trends in the nucleophilicity of the reactive atoms in H_2O, CH_2S, HCHO, SO_2 and O_3 as well the electrophilicity reverses (Table 3.2-3.3; Figure 3.2). It should, however, be noted that the global and local reactivity descriptors in case of planar nonlinear polyatomic molecules behave almost similar to those for the linear molecules. Moreover, it is important to observe from Figure 3.1-3.2 that the variations of change in GRD and LRD with respect to zero fields against external electric field are almost linear and uniform. This means that the applied electric field produces small perturbation of the molecular charge distribution.

3.2.2.3. Field applied in perpendicular directions to the principal axis

The behavior of GRD and LRD under the influence of electric field perpendicular to the principal axis for H_2O, CH_2S and SO_2 molecules are presented in Tables 3.4-3.6 and for HCHO and O_3 molecules in Figures 3.3-3.4. When the electric field is applied perpendicular to the molecular plane of the molecules H_2O, CH_2S and SO_2, the hardness and chemical potential decrease with field value increasing from 0.000 to 0.006 au (Table 3.4(b)-3.6(b)) irrespective of the field being applied above or below the plane of the molecule. However, this decrease is much lower than the case in which the field is applied along the principal axis. This implies that there is an induced polarization above and below the plane of the molecule. This induced polarization perpendicular to the axis of the molecules was almost absent for linear molecules, which resulted in constant values of reactivity descriptors, when the field was applied perpendicular to the axis.[1] For O_3 molecule, on the other hand, the hardness and chemical potential remains almost constant with increasing field, regardless of the field directed above or below the molecular plane (Figure 3.3).

Now, when the field is directed perpendicular to the principal axis in the molecular plane i.e., the field is applied in a direction from, say, H_2 atom to H_1 atom in H_2O, CH_2S and HCHO and from O_1 atom to O_2 atom in SO_2. With the increase in the magnitude of field, the chemical potential and hardness for SO_2 (Table 3.6(a)) decrease slowly and for CH_2S (Table 3.5(a)) and HCHO (Figure 3.3**)** these remain almost constant. It should be, however, noted that the decrease is substantial in the case of H_2O (Table 3.4(a)). Although the field direction is reversed, the global parameters do not change. This is mainly due to the symmetry in the molecules.

electric field*(in au)	μ(in au)	η(in au)	f_O^-	f_{H1}^-	f_{H2}^-	f_o^+	f_{H1}^+	f_{H2}^+
0.000	-0.2185	0.2459	0.8368	0.0816	0.0816	0.0753	0.4623	0.4623
0.001	-0.2187	0.2458	0.8368	0.0813	0.0820	0.0756	0.3950	0.5294
0.002	-0.2190	0.2454	0.8368	0.0810	0.0823	0.0765	0.3309	0.5926
0.003	-0.2197	0.2448	0.8367	0.0806	0.0826	0.0780	0.2731	0.6490
0.004	-0.2205	0.2440	0.8367	0.0803	0.0829	0.0797	0.2238	0.6965
0.005	-0.2215	0.2430	0.8367	0.0800	0.0833	0.0815	0.1837	0.7348
0.006	-0.2227	0.2418	0.8367	0.0797	0.0836	0.0832	0.1521	0.7646

*Applying field in opposite direction will change the values CFF of H_1 to H_2

Table 3.4 (a): Variation of Chemical Potential, Hardness and CFF for H_2O molecule when the field is applied from H_2 to H_1 atom.

electric field # (in au)	μ(in au)	η(in au)	f_o^-	f_H^-	f_H^+	f_o^+
0.000	-0.2185	0.2459	0.8368	0.0816	0.4623	0.0753
0.001	-0.2185	0.2460	0.8368	0.0816	0.4623	0.0754
0.002	-0.2186	0.2459	0.8368	0.0816	0.4622	0.0756
0.003	-0.2187	0.2459	0.8368	0.0816	0.4620	0.0759
0.004	-0.2187	0.2458	0.8368	0.0816	0.4618	0.0764
0.005	-0.2187	0.2458	0.8368	0.0816	0.4614	0.0771
0.006	-0.2188	0.2457	0.8368	0.0816	0.4611	0.0778

Same values when the field is reversed

Table 3.4 (b): Variation of Chemical Potential, Hardness and CFF for H_2O molecule when the field is applied perpendicular to the molecular plane.

When the field is directed perpendicular to the principal axis in the molecular plane i.e., say, from H_2 to H_1 atom in H_2O, CH_2S and HCHO, the nucleophilicity of central atoms remains almost constant throughout this field range. For instance, the nucleophilicity of O atom in H_2O, S and O atom in CH_2S and HCHO, respectively, along with C atom remains constant (Table 3.4(a)-3.5(a); Figure 3.4). Moreover, in case of in H_2O, CH_2S and HCHO, the nucleophilicity of the H atom towards which the field is applied decreases (Table 3.4(a)-3.5(a); Figure 3.4). But, in case of SO_2, the nucleophilicity of S atom decreases while the nucleophilicity of O atom towards which the field is applied increases (Table 3.6(a)). This may be due to the presence of more electropositive central atom.

electric field* (in au)	μ(in au)	η(in au)	f_S^-	f_c^-	f_{H1}^-	f_{H2}^-	f_S^+	f_c^+	f_{H1}^+	f_{H2}^+
0.000	-0.1768	0.1633	0.6610	0.1602	0.0894	0.0894	0.5122	0.3824	0.0527	0.0527
0.001	-0.1768	0.1632	0.6610	0.1602	0.0891	0.0897	0.5122	0.3824	0.0525	0.0529
0.002	-0.1769	0.1633	0.6610	0.1602	0.0889	0.0899	0.5122	0.3824	0.0523	0.0531
0.003	-0.1769	0.1633	0.6610	0.1602	0.0886	0.0902	0.5122	0.3824	0.0520	0.0533
0.004	-0.1769	0.1632	0.6610	0.1602	0.0883	0.0905	0.5122	0.3824	0.0518	0.0535
0.005	-0.1770	0.1632	0.6610	0.1602	0.0880	0.0908	0.5122	0.3824	0.0516	0.0537
0.006	-0.1770	0.1632	0.6610	0.1602	0.0878	0.0910	0.5122	0.3824	0.0514	0.0540

Table 3.5(a): Variation of Chemical Potential, Hardness and CFF for CH_2S molecule when the field is applied from H_2 to H_1 atom.

electric field[#] (in au)	μ(in au)	η(in au)	f_S^-	f_C^-	f_H^-	f_S^+	f_C^+	f_H^+
0.000	-0.1768	0.1633	0.6610	0.1602	0.0894	0.5122	0.3824	0.0527
0.001	-0.1768	0.1632	0.6610	0.1602	0.0894	0.5121	0.3824	0.0527
0.002	-0.1769	0.1632	0.6610	0.1602	0.0894	0.5118	0.3825	0.0528
0.003	-0.1769	0.1632	0.6610	0.1602	0.0894	0.5113	0.3826	0.0530
0.004	-0.1770	0.1631	0.6610	0.1602	0.0894	0.5106	0.3827	0.0533
0.005	-0.1771	0.1630	0.6610	0.1602	0.0894	0.5097	0.3829	0.0537
0.006	-0.1772	0.1629	0.6609	0.1603	0.0894	0.5086	0.3830	0.0542

Table 3.5(b): Variation of Chemical Potential, Hardness and CFF for CH_2S molecule when the field is applied perpendicular to the molecular plane.

Surprisingly, the behavior of CFF for nucleophilic attack of central atom varies as the field value is increased. It is observed that the electrophilicity of central atom in H_2O and SO_2 increases with increasing field (Table 3.4(a), 3.6(a)). On contrary, in case of HCHO, the electrophilicity of O and C atoms decreases slowly while the electrophilicity of S, in CH_2S, remains constant with increasing field (Table 3.5(a); Figure 3.4). However, for H_2O, CH_2S and HCHO, the electrophilicity of atom towards which the field is assigned decreases (Table 3.4(a)-3.5(a); Figure 3.4).

When the field is assigned perpendicular to the molecular plane, the nucleophilicity of all the atoms for H_2O, CH_2S and SO_2 molecules remains almost constant with the increase in the field values (Table 3.4(b)-3.6(b)). However, on the other hand, the electrophilicity behavior is quite different. The electrophilicity of the central atom in H_2O and SO_2, i.e., O and S atom, respectively, increases while the S atom in CH_2S decreases (Table 3.4(b)-3.6(b)). This may be due to the nearly equivalent electronegativities of C and S in CH_2S. However, in case of O_3, neither the nucleophilicity nor the electrophilicity of O atoms change in this field range (Figure 3.4).

As the field direction is reversed, there is no change in the behavior of the atoms in terms of their reactivity. This implies that whenever a reagent, either nucleophilic or electrophilic, attacks from above or below the molecular plane would experience similar reactivity on a particular atom.

In our earlier chapter, we inferred that the variation of the hardness parameter in the presence of external electric field is actually dependent on the net cooperative effect exhibited by the collection of all the atoms present in the molecule. The above discussions probably imply the same. Hence, the decrease or increase of hardness of a molecule under the external field does not necessarily mean that the reactivity of a specific site or atom present in the molecule would be enhanced or deactivated.

Apart from the numerical analysis discussed above, we present some of our results using the perturbative analysis. The Fukui function under the presence of electric field (F) can be written as a Taylor series expansion,

$$f(r) = f_0(r) + f'(r)F + \frac{1}{2!} f''(r)F.F + ... \tag{3.1}$$

The first term $f_0(r)$ is the FF at zero field. The second term $f'(r) = \frac{\delta^2 \rho(r)}{\delta N \delta F}$ and the third term $f''(r)$ is equal to $\frac{\delta^3 \rho(r)}{\delta N \delta F \delta F}$ can be related, respectively, to the linear Fukui response and nonlinear Fukui response defined by Senet,[7] who has also made a general perturbative analysis of electron density with respect to number of electrons and external potential. It is clear from the above that the linear trend observed in the present numerical results will breakdown at somewhat stronger fields.

For weak fields, Figure 3.1-3.4 shows the linearity of the reactivity descriptors. To see the effect of breakdown of linearity, we extended our calculations up to larger field values. It is found that, when the field is applied along the principal axis the linearity of GRD breaks after 0.01 au of field value for CH_2S, H_2O, O_3 and SO_2. As an example, to be a linear plot the extrapolated hardness value for CH_2S should be 0.1593 au at a field value of 0.02 au along the C_2 axis, but the calculated hardness at that field is 0.1393 au. This shows a drop in hardness value which is larger than that predicted from the linear plot. Similarly, we have observed the breakdown of linearity of nucleophilicity of S in CH_2S after 0.03 au, O in HCHO after 0.015 au, O in SO_2 after 0.01 au. When the field is perpendicular to the principal axis, the variations of GRD becomes nonlinear after 0.006 au for HCHO and 0.008 au for O_3. On the other hand, the linearity in the variation of nucleophilicity is lost after 0.01 au for O in HCHO, while the variation of electrophilicity is lost after 0.006 au for central O atom in O_3. However, it should be again mentioned that it is often difficult to converge to the correct state for $(N \pm 1)$ systems for higher field values. Thus, it is difficult to demonstrate the nonlinearity at very strong field values.

Moreover, analysis of the energy difference for the above molecular systems in weak field range, applied along the principal axis and in perpendicular direction, clearly suggests that there is a weak interaction with the external electric field. It is found that the difference in the energies of the mentioned systems with and without field along the principal axis ranges from 0.8837 kcal/mol for ozone to 3.9423 kcal/mol for formaldehyde. This energy difference signifies weak interaction of the molecular systems with external electric field applied along the principal axis. The values range from 0.0757 kcal/mol for H_2O to 0.3989 kcal/mol for SO_2 in perpendicular direction. Although the present analysis is not very rigorous, it can, however, explain the present observation in the variation of CFF as well as the hardness parameters.

electric field$^{@}$ (in au)	μ(in au)	η(in au)	f_S^-	f_{O1}^-	f_{O2}^-	f_S^+	f_{O1}^+	f_{O2}^+
0.000	-0.2491	0.2047	0.3131	0.3434	0.3434	0.4830	0.2585	0.2585
0.001	-0.2491	0.2046	0.3130	0.3393	0.3477	0.4830	0.2584	0.2586
0.002	-0.2491	0.2046	0.3129	0.3353	0.3519	0.4831	0.2583	0.2587
0.003	-0.2491	0.2046	0.3126	0.3314	0.3560	0.4832	0.2581	0.2587
0.004	-0.2491	0.2046	0.3122	0.3278	0.3601	0.4834	0.2579	0.2587
0.005	-0.2491	0.2045	0.3117	0.3244	0.3639	0.4836	0.2577	0.2587
0.006	-0.2491	0.2045	0.3112	0.3212	0.3676	0.4839	0.2574	0.2587

Table 3.6 (a): Variation of Chemical Potential, Hardness and CFF for SO_2 molecule when the field is applied from O_1 to O_2 atom

$^{@}$ Applying field in opposite direction will change the values CFF of O2 to O1

electric field$^{\#}$ (in au)	μ(in au)	η(in au)	f_S^-	f_O^-	f_S^+	f_O^+
0.000	-0.2491	0.2047	0.3131	0.3434	0.4830	0.2585
0.001	-0.2491	0.2046	0.3131	0.3434	0.4830	0.2585
0.002	-0.2491	0.2047	0.3131	0.3434	0.4832	0.2584
0.003	-0.2491	0.2046	0.3131	0.3434	0.4836	0.2582
0.004	-0.2492	0.2046	0.3132	0.3434	0.4841	0.2579
0.005	-0.2492	0.2045	0.3132	0.3434	0.4848	0.2576
0.006	-0.2493	0.2045	0.3132	0.3434	0.4857	0.2572

Table 3.6 (b): Variation of Chemical Potential, Hardness and CFF for SO_2 molecule when the field is applied perpendicular to the molecular plane.

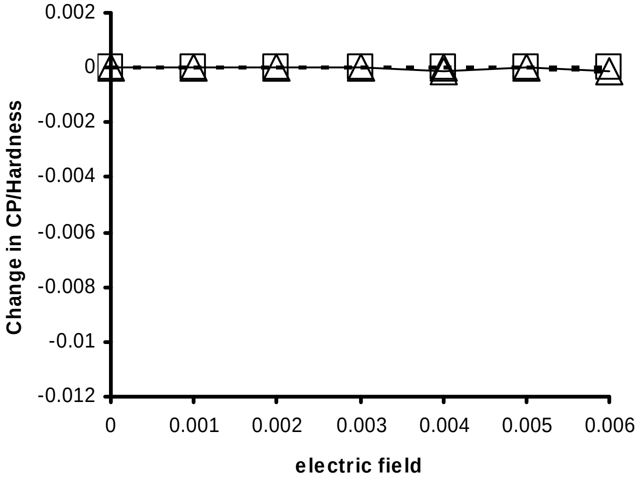

Figure 3.3: Plot of change in CP/Hardness with respect to zero fields against electric field applied perpendicular to the principal axis for HCHO (—△—) and O_3 (—□—) molecules. Dashed line represents the values of hardness while solid line represents the values of CP when the field is applied perpendicular to the principal axis

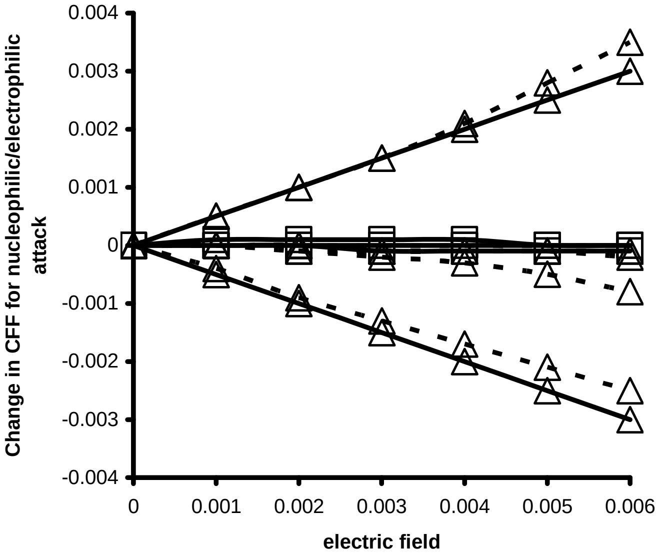

Figure 3.4: Plot of change in CFF for electrophilic/nucleophilic attack with respect to zero fields against electric field applied perpendicular to the principal axis for reactive atoms in HCHO (—△—) and O_3 (—□—) molecules. Dashed line represents the values of electrophilicity while solid line represents the values of nucleophilicity when the field is applied in perpendicular directions to the principal axis.

3.3 Effect of Electric Field on DNA bases and base pairs

3.3.1 Methodology and Computational Details

In this section, we study the influence of electric field on reactivity descriptors on changing the symmetry. For this, we choose the DNA bases, namely Adenine (Ade), Guanine (Gua), Cytosine (Cyt) and Thymine (Thy) and their base pairs, namely Ade-Thy and Gua-Cyt. All were optimized at DFT level using 6-31++G (d, p) basis set with B3LYP hybrid functional at zero field. These equilibrium geometries were further confirmed by frequency calculations. The electric field was applied towards the atoms forming H-bonds i.e., in a direction parallel to the H-bonds (we designate it as $E_{\|}$), to calculate the energy of the neutral, cationic and anionic systems for field value increasing up to 0.006 au, with an increment of 0.001 au at each step. The reason for choosing such small field values is due to the problem of convergence to the correct ground state for the charged species. Hence, the global and local parameters were calculated at each field value using the equations (2.5), (2.6) and (2.13), respectively. The local parameters such as CFF were calculated using the Lowdin based method of population analysis.[5] Additionally, the electric field was applied in the two perpendicular directions, i.e., perpendicular to the H-bonds and in the plane of the molecule ($E_{\perp}$) and the other direction is perpendicular to the molecular plane. Similarly, all the global and local parameters for the bases were calculated at each field value. For calculating the interaction energy of the base pairs, we employ equation (2.21) along with equation (2.19-2.20). All the calculations were performed by GAMESS software.[6] The quantum chemical method of calculating the interaction energy is the difference between the energy of the complex AB and sum of the energy of the monomer A and B, $\Delta E = E_{AB} - (E_A + E_B)$.

3.3.2. Results and Discussion

3.3.2.1. Behavior of Global and Local Reactivity Descriptors

We, here, try to analyze the response of reactive atoms (forming the H-bonds) under external electric field for Ade, Thy, Gua and Cyt molecules. We explain the results in a compact form of figures, Figures 3.7-3.12. The optimized geometries of the bases and the base pairs are presented in Figure 3.5 and 3.6, respectively. The reactivity of the atoms forming H-bond is only discussed i.e., the O and H atoms in Thy; N and H atoms in Ade; O, N and H in Cyt; O and H atom in Gua (Figure 3.5).

Let us first discuss the response of the descriptors when the field is applied parallel and towards the atoms forming the H-bonds i.e., in $E_{\|}$ direction. In all the above DNA bases, CP and CH decreases with the increase in field strength along this direction (Figure 3.7 (a)-3.10 (a)).

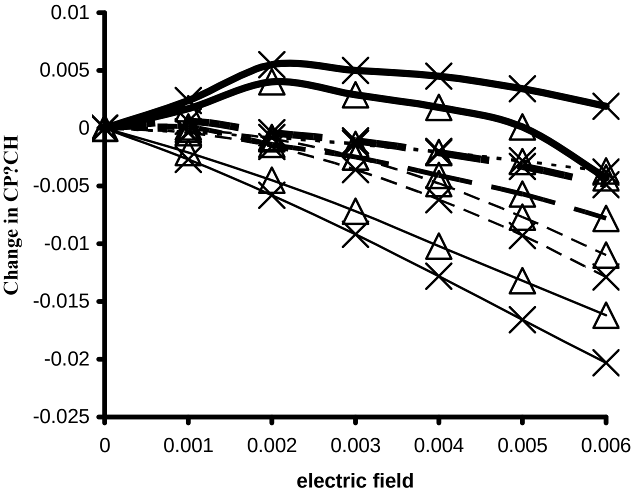

***Figure 3.7 (a):** Variation of Change in CP and Hardness (CH) (in au) with respect to zero field for Thymine against electric field (in au). **Δ** represents CH and × represents CP.

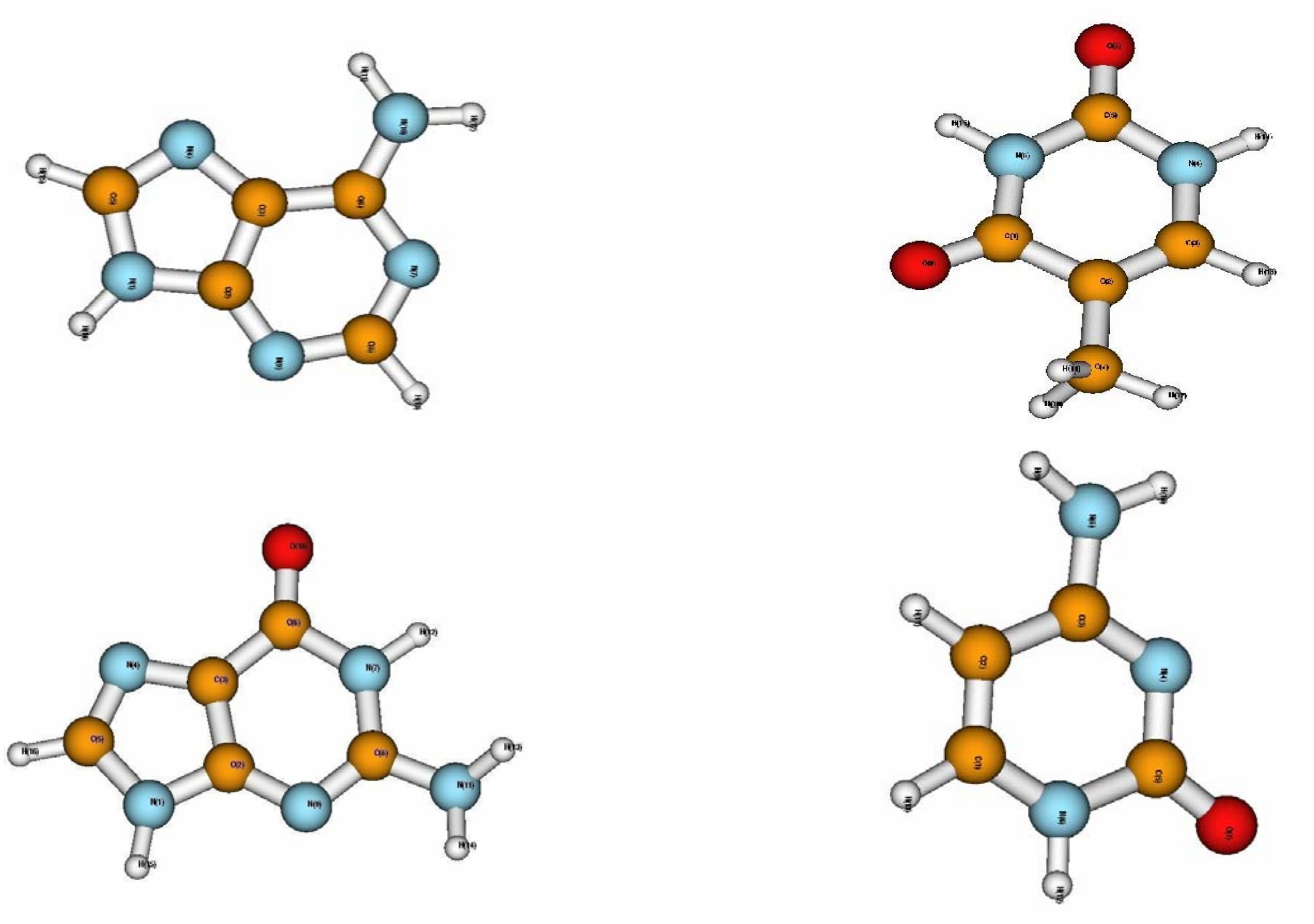

Figure 3.5: Optimized geometry of (a) Adenine (b) Thymine (c) Guanine and (d) Cytosine using 6-31++G (d,p) basis set with B3LYP hybrid functional.

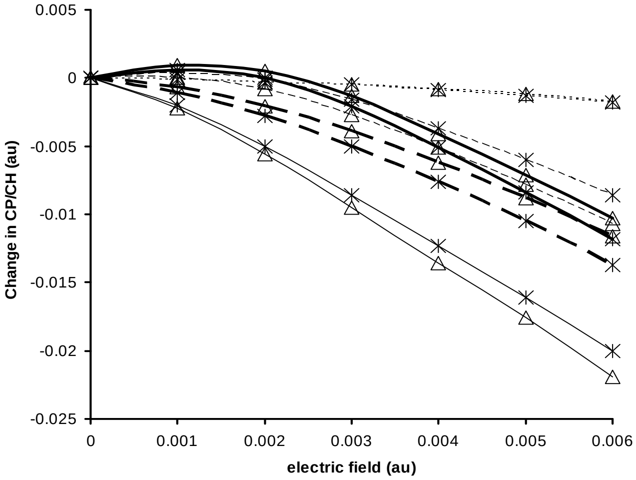

***Figure 3.8 (a):** Variation of Change in CP and CH (in au) with respect to zero field for Adenine against Electric field (in au). **Δ** represents CH and × represents CP.

*Solid line means that the field is parallel and towards the atoms forming H-bonds (E‖ direction). Half dashed line means that the field is in perpendicular directions to the hydrogen bonds but in the plane of the molecule (E⊥). Fully dashed lines are for the field in the perpendicular direction to the plane of the molecule. Dark lines represent the values of the parameter for the fields in opposite direction.

The CFF for electrophilic attack (nucleophilicity) for the more electronegative atom increases while the electrophilicity of the H atoms decreases with the increase in the field values. For instance, the nucleophilicity of O atom in Gua and Thy (Figure 3.7 (b), 3.10 (b)); N atom in Ade (Figure 3.8 (b)**)**; both O and N atoms in Cyt (Figure 3.9 (b)**)**, all forming H-bonds, increase with increasing field values. On the other hand, the electrophilicity of H atoms, forming H-bonds, in all the above bases decreases as the field value is increased (Figure 3.7 (b)-3.10 (b)).

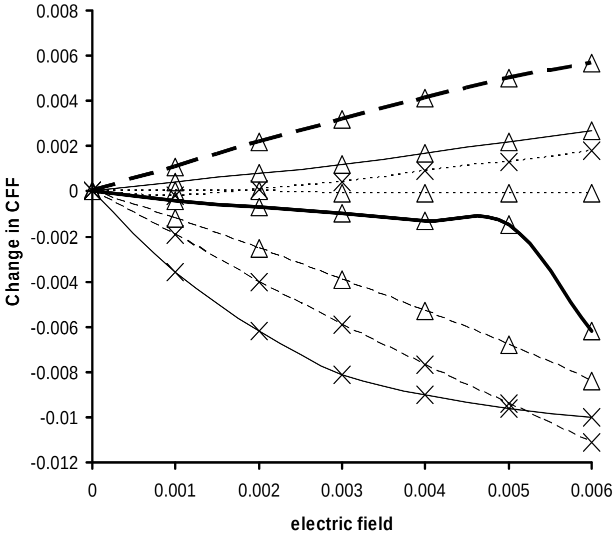

***Figure 3.7 (b):** Variation of Change in CFF with respect to zero fields for Thymine against electric field (in au). **Δ** represents CFF for electrophilic attack for O atom while × represents CFF for nucleophilic attack for H atom.

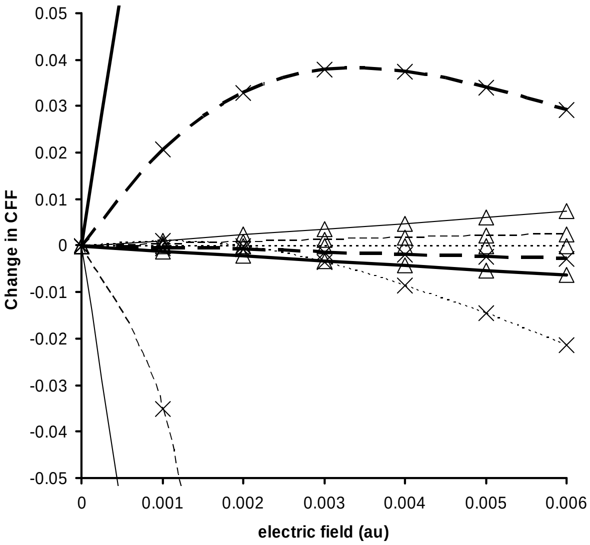

***Figure 3.8 (b):** Variation of Change in CFF with respect to zero fields for Adenine against Electric field (in au). **Δ** represents CFF for electrophilic attack for N atom while × represents CFF for nucleophilic attack for H atom.

Now, as the field is applied in opposite direction, the GRD increases up to some value of field and then starts decreasing with the increasing field values in all bases (Figure 3.7 (a)-3.9 (a)), except in case of Gua where CP and CH decreases with increasing field (Figure 3.10 (a)). At this point it should be mentioned that this is in contrast with the analyses performed earlier where as the field direction was reversed, the behavior of the descriptors reversed.[1] However, the behavior of the LRD gets reversed as the field direction is reversed (Figure 3.7 (b)-3.10 (b)). This anomaly may be attributed to the cooperative effect of all the atoms present in these molecules. Moreover, the complexity of the molecule has to be also taken into account.

When the field is applied perpendicular to the H-bonds and in the plane of the molecule ($E_\perp$) i.e., the field is directed towards the H atom in all the bases. For Thy and Gua, the CP and CH decrease (Figure 3.7 (a), 3.10 (a)). But, for the other two, Cyt and Ade, they first increase and then start decreasing (Figure 3.8(a), 3.9(a)). On the other hand, the nucleophilicity of the O and N atom(s) in Gua, Thy and Cyt, participating in the H-bond formation, decreases with the increasing field. Moreover, the electrophilicity of the reactive H atom (forming H-bonds) in these bases increases. Conversely, when the field is directed towards the reactive hydrogen atom in Ade its electrophilicity decreases while the nucleophilicity of reactive N atom increases. This may be due to the non planarity of the amide H-atoms.

Similarly, when the field direction is reversed, the behavior of GRD and LRD does not reverse. Incidentally, the CP and CH decrease with the increase in field values, except in Thy where they increase and then begin to decrease (Figure 3.8 (a)-3.10 (a)). Although, in case of Thy, the behavior of LRD reverses as the field direction is reversed, but the behavior of the reactive atoms in the other bases is different. As can be seen from Figure 3.8 (b)-3.10 (b), the nucleophilicity of O atom in Cyt and Gua reverses along with the N atom in Ade while that of the N atom in Cyt remains constant and then starts decreasing at higher fields. Furthermore, the electrophilicity of the reactive amide H atom in Gua and Cyt decreases, but the electrophilicity of the other reactive H atom in Gua and the amide H atom in Ade increases and then decreases. This difference may also be attributed to the non planarity of the amide H atoms.

Now, we would confer out qualitative results when the field was applied perpendicular to the plane of the molecule. It is interesting to note that the CP and CH decrease with the increasing field for all the bases (Figure 3.7 (a)-3.10 (a)). On the other hand, the nucleophilicity of the more electronegative reactive atom(s) remains almost constant. For example, the nucleophilicity of O and/or N atom(s) in Ade, Thy, Gua and Cyt remains almost constant with the increase in the field values (Figure 3.7 (b)-3.10 (b)). However, the electrophilicity of the amide H atom in Cyt and Gua decreases with increasing field while that of Ade first increases slightly and then decreases (Figure 3.8 (b)-3.10 (b)). However, the electrophlicity of the other H atom in Gua and Thy increases with increasing field values (Figure 3.7(b), 3.10(b)).

3.3.2.2 Response of field on Stabilization of base pairs

We would try to understand the effect of electric field on the stabilization energy of the base pairs by the local HSAB based model. The equilibrium structures of the base pairs Gua-Cyt and Ade-Thy are shown in the Figure 3.6 (a) and (b), respectively. The interaction energy of these pairs is shown in the Figures 3.11-3.12

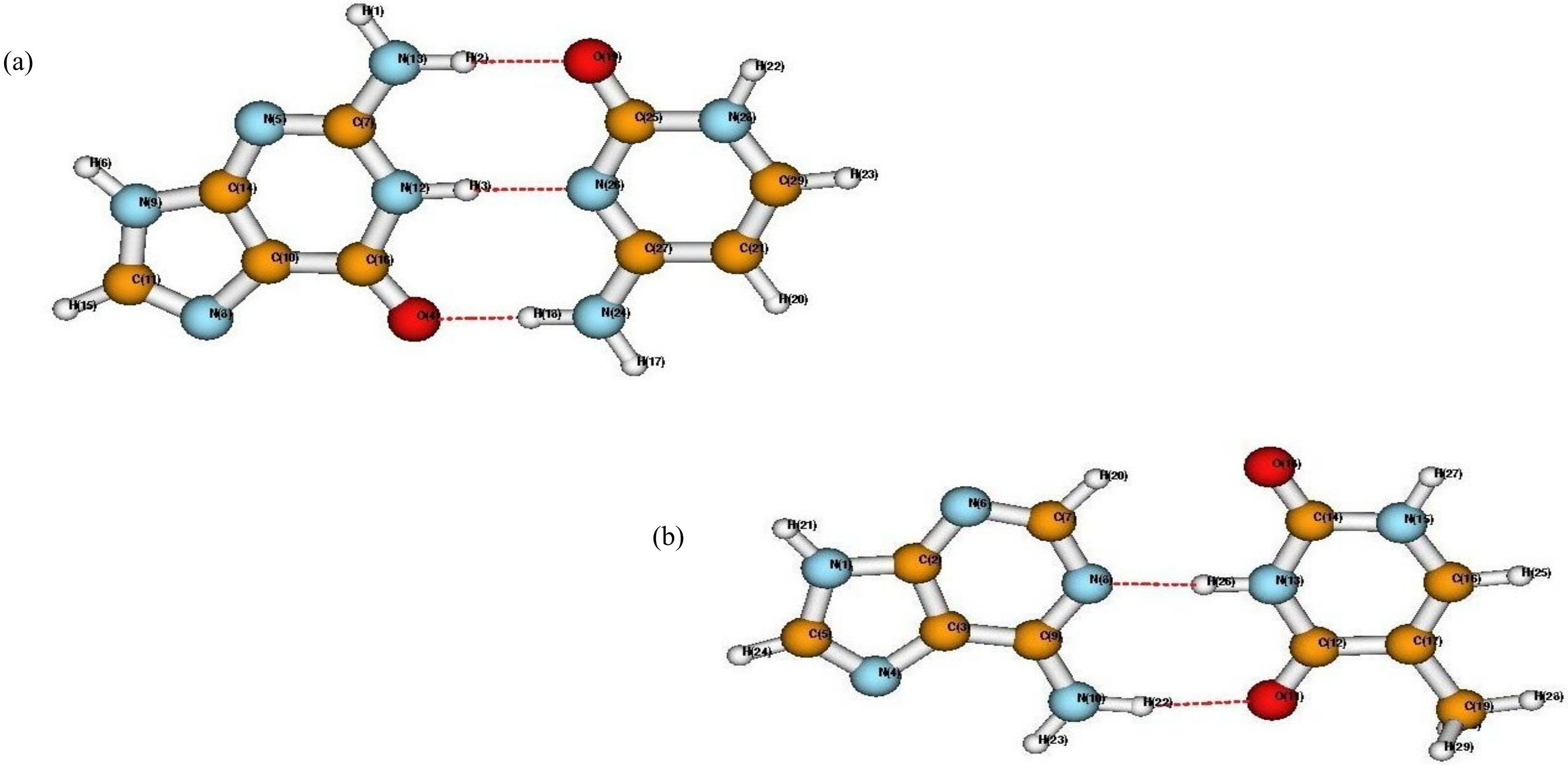

Figure 3.6: Optimized geometries of the base pair (a) Guanine- Cytosine and (b) Adenine- Thymine using 6-31++G (d, p) basis set with B3LYP hybrid functional.

When the field is applied along the H-bond towards the Ade molecule in Ade-Thy or Cyt molecule in Gua-Cyt base pair, the complex gets stabilized with the increasing field value. However, in the case of Gua-Cyt base pair, the variation is almost linear in this field range (Figure 3.11-3.12). Moreover, they seem to be in well accordance with the variation in QC methods.

It should, however, be noticed that the variation in QC methods are almost linear in all cases. The nonlinearity in the model interaction energies may be closely observed and attributed to the variation of the FF of the reactive atoms in the molecules. On the other hand, when the field is applied towards the Thy or Gua molecule, the base pair gets destabilized with the increasing field. This is an important conclusion which has to play a significant part when the base pairs are under some external perturbation. This is to say that, the stability of the base pairs can be designed (stabilize or destabilize) with the field direction.

On the other hand, when the field is in perpendicular direction i.e. in the plane of the base pairs and when it is towards the amide H atom, the interaction energy (local HSAB) of the Gua-Cyt and Ade-Thy base pair decreases (Figure 3.11-3.12). However, the Gua-Cyt base pair gets stabilized irrespective of the field direction and the stability increases when the field direction is towards the amide H atom (Figure 3.11). It should, however, be noted that the QC interaction energy of the complexes in this field direction is reverse. This may be due to the FF values of the reactive atoms which play a key role in deciding the stability of a complex.

When the field is in a perpendicular direction to the plane of the molecule, the interaction energy of the base pair Gua-Cyt increases slightly and then gets stabilized with the increasing field strength. However, there is a linear decrease in the QC interaction energy of the base pair (Figure 3.11). Contrary to this, the Ade-

Thy base pair gets destabilized with the increasing field values. Moreover, this is in complete disagreement with the QC interaction energy (Figure 3.12). Now, closely analyzing the anomaly reveals that the local HSAB interaction energy is dependent on both charge transfer term and FF of the reactive atoms and these factors decide the interaction energy hence, such variations.

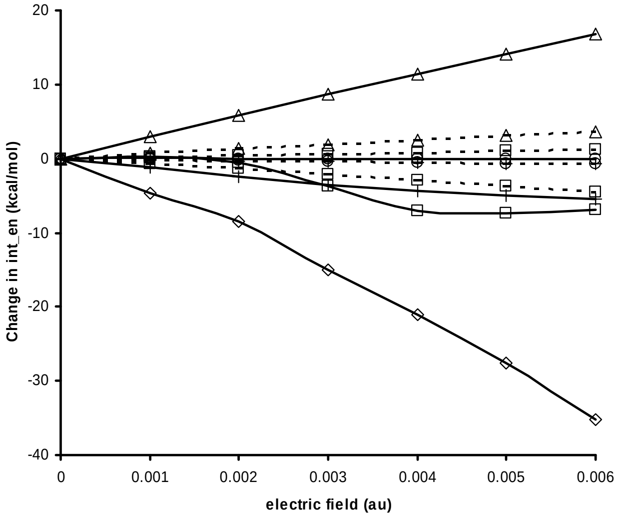

Figure 3.11: Variation of Change in Interaction energy (IE) both Quantum Chemical (QC) and local HSAB (in kcal/mol) for Gua-Cyt base pair with respect to zero field against electric field (in au). Local HSAB and QC IE is denoted by □ when the field is applied parallel to the H-bonds and directed towards Cyt while denoted by Δ when the field is directed towards Gua; perpendicular to the H-bonds (in the plane of the molecule) is denoted by ◊ when the field is directed towards the amide H-atom while denoted by + when the field is in opposite direction; perpendicular to the molecular plane is denoted by O; Dashed line represents QC IE while solid line represents local HSAB IE.

3.4. Conclusions

We have investigated the effect of electric field on reactivity of some nonlinear molecules i.e., C_{2V} symmetry molecules and DNA bases. Under such external parameter, their stability and reactivity were systematically studied using the density based reactivity descriptors. In order to understand the behavior of these descriptors in the presence of electric field for nonlinear polyatomic molecules, we have studied the effect of application of external field towards the principal axis as well as in the perpendicular directions. In the case of application of electric field perpendicular to the principal axis, there is change in both GRD and LRD unlike linear molecules. Our results once again support that the variation of the hardness parameter is actually dependent on the net cooperative effect exhibited by the collection of all the atoms present in the molecule. We observe from the strength of interactions that our study is applicable to effect of weak interactions on the descriptors. Moreover, we try to present some perturbative analysis to our findings and numerically show the breakdown of linearity of reactivity descriptors. However, the electric field applied in case of DNA bases is in a direction parallel to the H-bonds formed by the base pairs. The perpendicular directions were also considered for the study. It was observed that the variations of the reactivity descriptors with the field are not always linear for the case of DNA bases. In addition, the stability of the base pairs in the presence of the electric field has been analyzed using the local HSAB model-based interaction energy. Moreover, the values of the local HSAB interaction energy enlightens about the stability of the base pairs in the presence of the field which have been compared with the actual quantum chemical calculations. In addition, the variation of interaction energy of the base pairs with the electric field guides us to propose an artificial receptor molecule. Although, the analysis is not very rigorous, further study in this regard is needful.

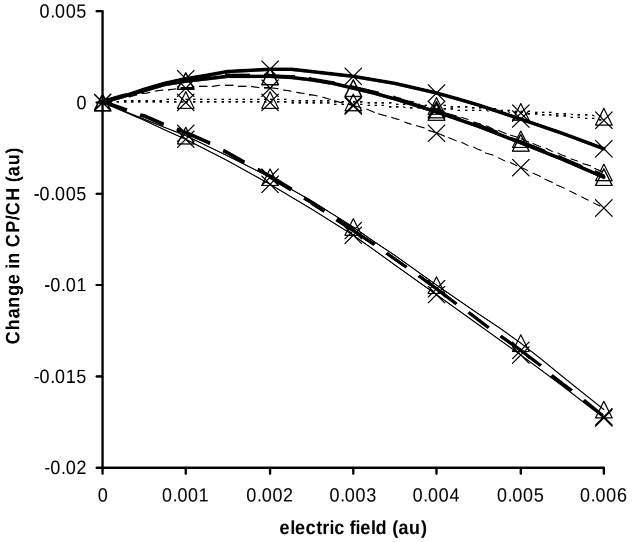

***Figure 3.9(a):** Variation of Change in CP and CH (in au) with respect to zero field for Cyt against Electric field (in au). Δ represents CH and × represents CP.

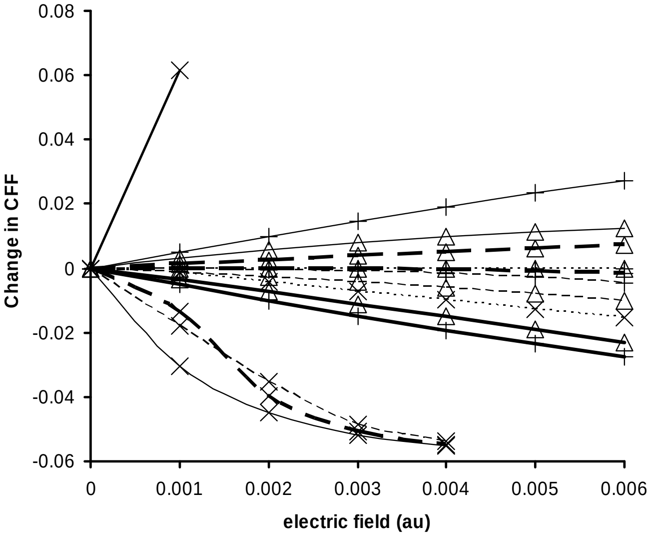

***Figure 3.9(b):** Variation of Change in CFF with respect to zero field for Cyt against Electric field. Δ represents CFF for electrophilic attack for O atom and × represents CFF for nucleophilic attack for H atom and + represents change in CFF for electrophilic attack for N atom.

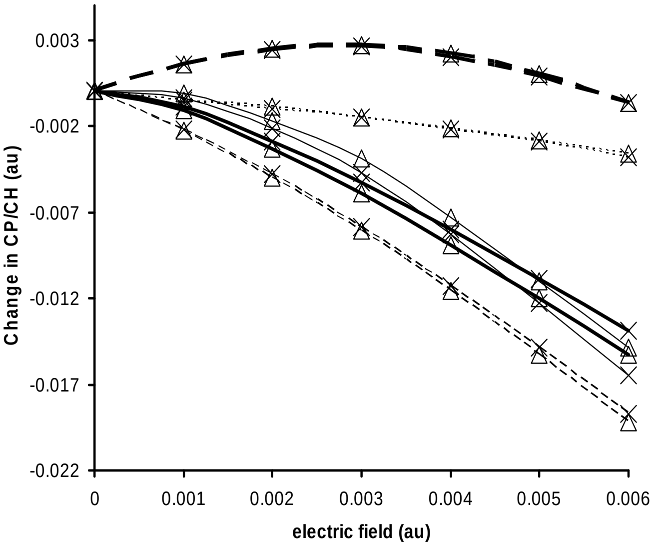

***Figure 3.10(a):** Variation of Change in CP and CH with respect to zero field for Gua against Electric field. Δ represents CH and × represents CP.

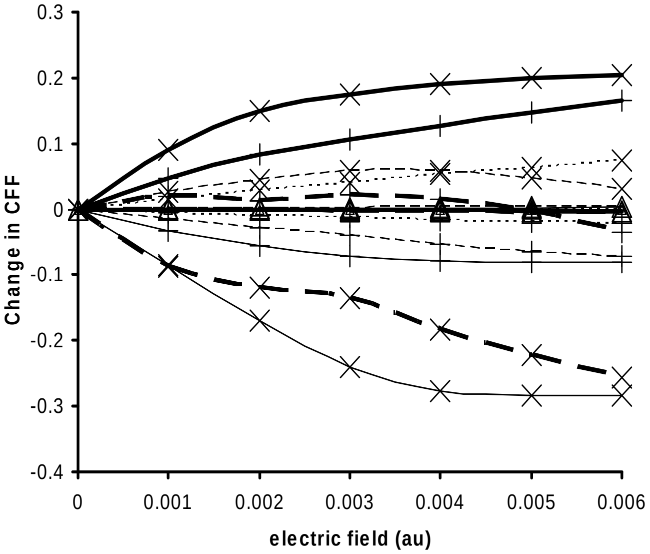

***Figure 3.10(b):** Variation of Change in CFF with respect to zero field for Gua against Electric field. Δ represents CFF for electrophilic attack for O atom, × represents CFF for nucleophilic attack for amide H atom and + represents CFF for nucleophilic attack for the other H atom.

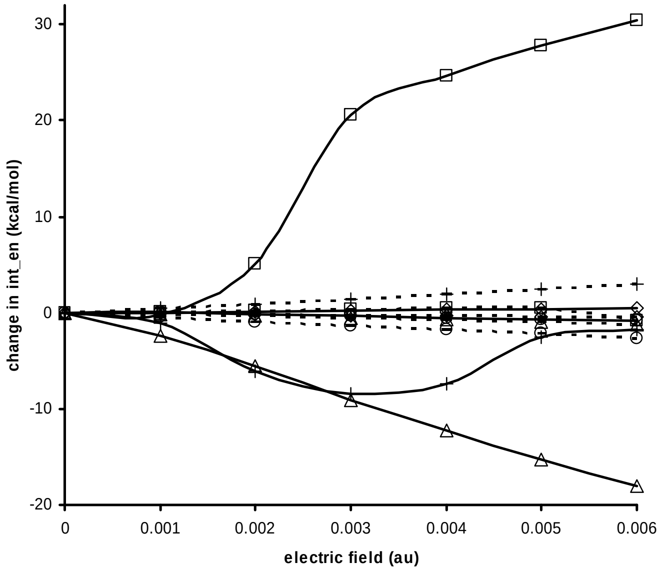

Figure 3.12: Variation of Interaction energy (IE) both Quantum Chemical (QC) and local HSAB (in kcal/mol) for Ade-Thy base pair against Electric field (in au). Local HSAB and QC IE is denoted by □ when the field is applied parallel to the H-bonds and directed towards Thy while denoted by Δ when the field is directed towards Ade; perpendicular to the H-bonds (in the plane of the molecule) is denoted by + when the field is directed towards the amide H-atom while denoted by O when the field is in opposite direction; perpendicular to the molecular plane is denoted by ◊; Dashed line represents QC IE while solid line represents local HSAB IE.

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Chapter 4

Effect of Solvents having Different Dielectric Constant on Chemical Reactivity

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4.1 Introduction

In the previous chapters, our focus was to analyze the effect of external electric field on the reactivity descriptors. However, solvent environment can be another external perturbation parameter. A vast majority of chemical reactions are performed in solutions. Generally, the electron distribution of a molecule in gas phase is altered by the presence of solvent surroundings. Therefore, it is essential to understand the chemistry of molecules in solutions. It is known that the reactivity of chemical species depends on the solvent molecules.[1] However, solvents are broadly classified as protic and aprotic, based on their ability to donate hydrogen. Several theoretical models have been developed to mimic the actual solvent environments. For a detailed discussion, one may refer to the review article by Tomasi and Persico.[2] Recently, a self-consistent reaction field calculation was carried out to assess the significance of water as a solvent.[3] In general, it was observed that the reactivity of the molecules increases from their gas phase values to the solvent medium.[3]

The solution phase chemistry is of great interest and conceptual density functional theory (DFT) has provided enough support to explain the observations.[4-7] In a recent study by De Luca et. al., using the polarizable continuum model, it was shown that the three working formulas used to calculate the hardness of neutral and charged species in solvent gives different values.[4] However, using the explicit models for solvent with the sequential Monte Carlo/quantum mechanics methodology, Jaramillo et. al. have studied the effect of solvent on the HOMO, LUMO energies along with the global reactivity indices for neutral and anionic species.[5] Conceptual DFT is one of the most explored areas in recent times.[8] The various concepts involved in conceptual DFT along with their applications have been recently reviewed by Geerlings et. al.[9] Most of these studies are performed in the gas phase.[10-11] However, effects of external perturbations or medium on the gas phase reactivity has been the subject of recent study. In the previous chapters, detailed study on the effect of the external electric field on the reactivity descriptors for some linear molecules as well as planar nonlinear molecules with C_{2V} symmetry were presented.[12-14] Moreover, the importance of the solvent effect on the reactivity of molecular systems has been realized and several studies were performed considering mostly water as a solvent medium.[15-19]

In the present chapter, the effect of solvation, with different solvents, on the reactivity and stability of acetaldehyde (CH_3CHO) and propionaldehyde (CH_3CH_2CHO) are analyzed using the density based global reactivity descriptors such as chemical potential,[20] hardness[21-22] etc., and the local reactivity descriptors. The calculations have been performed using DFT. The local descriptor, Fukui functions[23] (FF) is employed to understand the sites that are prone to nucleophilic or electrophilic attack. However, the solvents studied in this chapter are classified as protic and aprotic solvents. Protic solvents include water, methanol and ethanol while the aprotic solvents studied are n-hexane, diethyl ether and pyridine. They have different dielectric constant and solvents having different dielectric constant would mimic different field strengths. The main objective is to understand the variation in the reactivity and stability using two examples in solvent medium with varying dielectric constants.

The chapter is organized as follows: The computational details of the present chapter are summarized in Section 4.2. The results and discussions of the behavior of the reactive atoms in the different solvent media are presented in Section 4.3 of this chapter. The conclusions are presented in Section 4.4.

4.2 Computational Details

The molecules CH_3CHO and CH_3CH_2CHO were completely optimized using the double numeric quality (i.e., there are approximately two atomic orbitals for each one occupied in the free atom) with polarization functions (DNP)[24] basis set along with generalized gradient approximation (GGA) functional BLYP in gas phase using DMOL^3 program.[25] The optimized geometries were confirmed by frequency calculations. Further, these two molecules were re-optimized at BLYP/DNP level using six different types of solvents having different dielectric constants (shown in parenthesis), such as n-hexane (1.89), diethyl ether (4.335), pyridine (12.3), ethanol (24.3), methanol (32.63) and water (78.54), and their minima were confirmed at the same level of calculations. The global descriptors, such as the chemical potential and the hardness, are calculated using the equations (2.5) and (2.6). The local parameters like the condensed Fukui function were calculated using Hirshfeld population scheme[26] (Stockholder partitioning scheme) as implemented in the DMOL^3 package using equations (2.13). In addition, the same procedure was carried out using different GGA functional, PW91 and PBE, to illustrate the consistency of the results presented. The COSMO[26] (COnductor-like Screening Model is a continuum solvation model in which the solute molecule forms a cavity within the dielectric continuum of permittivity that represents the solvent) solvation model as employed in DMOL^3 is utilized to compute the global as well as the local parameters in the different solvent surroundings.

4.3. Results and Discussions

We first present a correlation study of a series of nucleophiles in different solvents with known reactivities to validate our own results. It was shown in an experimental study, how different nucleophiles in acetonitrile solvent were arranged in an increasing order according to their nucleophilicity[28]. In the present context, we have tried to make a correlation with the above study. For this, we consider the following nucleophiles thiourea, N-methylthiourea, thioacetamide and N-acetylthiourea in acetonitrile solvent (aprotic solvent). The results are presented in Table 4.1. It can be observed that the order of nucleophilicity, calculated using the Hirshfeld population scheme, is as follows: thiourea > N-methylthiourea > acetamide > N-acetylthiourea (Table 4.1). This is what is exactly observed and hence, we can conclude our present study has a strong correlation and validates the experimental findings. Moreover, in order to validate the change in nucleophilicity with different solvents, we tried to correlate with a recent experimental work carried to study the kinetics of the reaction between methyl 2, 4-dichloro-3, 5-dinitrobenzoate and piperidine in different solvents[29]. The nucleophilicity of the N atom of piperidine in four different solvents, such as methanol, ethanol, acetonitrile and benzene (aprotic solvent) was calculated using the Hirshfeld population scheme and the results are presented in Table 4.2. The nucleophilicity of the N atom increases in the following order: benzene < methanol = ethanol < acetonitrile (Table 4.2). However, the experimental study showed that the rate of the reaction increases as methanol < ethanol < benzene < acetonitrile[29]. This difference may be due to the fact that the above reaction has been carried out at 25-45 °C while our study was performed at zero temperature.

Nucleophile	f_S^-
Thiourea	0.673
N-methylthiourea	0.667
Thioacetamide	0.653
N-acetylthiourea	0.594

Table 4.1: Values of CFF for electrophilic attack (nucleophilicity) of S atom in a series of nucleophiles in acetonitrile solvent using Hirshfeld population analysis

Solvents (Dielectric constant)	f_N^-
Methanol (ε=32.63)	0.340
Ethanol (ε=24.3)	0.340
Acetonitrile (ε=37.5)	0.341
Benzene (ε=2.284)	0.324

Table 4.2: Values of CFF for electrophilic attack (nucleophilicity) of N atom of Piperidine in different solvents using Hirshfeld population analysis

Now, we would present the influence of aprotic and protic solvents having different dielectric constant on the reactivity of model systems, CH_3CHO and CH_3CH_2CHO molecules, using the density functional theory. The values of chemical potential and hardness of the CH_3CHO and CH_3CH_2CHO molecules are presented in Tables 4.3 and 4.4 for different functionals. However, the CFF values of the reactive atoms, basically the carbonyl C and O atoms, of CH_3CHO and CH_3CH_2CHO molecules are presented in Tables 4.5 and 4.6, respectively, employing different functionals.

It can be noticed that the global reactivity descriptors, the chemical potential and hardness, of both the carbonyl compounds decreases in going from gas phase to the solvent medium. These also increase with the dielectric constant of the solvent medium from n-hexane to water (Table 4.3-4.4). It should be mentioned that the variation of the global descriptors is significant for the aprotic solvents n-hexane, diethyl ether and pyridine with the dielectric constant from 1.89 for n-hexane, 4.335 for diethyl ether to 12.3 for pyridine. This is seen for both acetaldehyde and propionaldehyde molecules and for the case of all three functionals used.

Functional	GRD	Medium	Solvent (Dielectric constant)					
			Aprotic			Protic		
		Gas	n-hexane	Diethyl ether	Pyridine	Ethanol	Methanol	Water
BLYP	μ	-0.1413	-0.1420	-0.1431	-0.1440	-0.1442	-0.1443	-0.1444
	η	0.2213	0.1821	0.1486	0.1281	0.1220	0.1204	0.1176
PW91	μ	-0.1466	-0.1474	-0.1485	-0.1492	-0.1495	-0.1497	-0.1497
	η	0.2211	0.1820	0.1484	0.1279	0.1218	0.1202	0.1175
PBE	μ	-0.1445	-0.1453	-0.1464	-0.1474	-0.1477	-0.1477	-0.1478
	η	0.2208	0.1816	0.1480	0.1275	0.1214	0.1198	0.1170

Table 4.3: Values of chemical potential (in au) and hardness (in au) of acetaldehyde in gas phase and in solvent medium having different dielectric constant using different functionals.

On the contrary, for the protic solvents with dielectric constant variation from 24.3 to 78.54, the variation in the global parameter is quite insignificant (Table 4.3-4.4). Specifically, the variation in chemical potential on increasing the dielectric constant for different protic solvents is negligible using all three functionals. However, the hardness values change somewhat more in comparison, though these are not as much compared to the corresponding changes in the presence of the aprotic solvents (Table 4.3-4.4). It can be observed that the trends are consistent with different functionals such as BLYP, PW91 and PBE (Table 4.3-4.4) for both acetaldehyde and propionaldehyde molecules. The changes in hardness are, however, much larger than those of chemical potential for either protic or aprotic solvent medium.

Functional	GRD	Medium	Solvent (Dielectric constant)					
			Aprotic			Protic		
		Gas	n-hexane	Diethyl ether	Pyridine	Ethanol	Methanol	Water
BLYP	μ	-0.1399	-0.1403	-0.1413	-0.1430	-0.1434	-0.1436	-0.1438
	η	0.2106	0.1744	0.1430	0.1235	0.1177	0.1162	0.1135
PW91	μ	-0.1448	-0.1459	-0.1475	-0.1489	-0.1494	-0.1495	-0.1497
	η	0.2106	0.1741	0.1425	0.1229	0.1172	0.1156	0.1129
PBE	μ	-0.1427	-0.1438	-0.1456	-0.1469	-0.1473	-0.1475	-0.1476
	η	0.2103	0.1738	0.1421	0.1225	0.1168	0.1153	0.1126

Table 4.4: Values of chemical potential and hardness (all in au) of propionaldehyde in gas phase and in solvent medium having different dielectric constant using different functionals

The change in electron density while adding or removing an electron, as the condensed Fukui function (CFF) around an atom, reflects the reactivity pattern of that atom. The reactivity of the molecules in gas phase can be altered by introducing the solvent medium. In such case, the electron density would be redistributed in the presence of the solvents and the reactivity would be revealed through CFF. Instead of studying reactivity descriptors of all atoms of both the molecules, we have studied the most reactive atoms. For example, the electrophilic CFF is highest for carbonyl C and the nucleophilic CFF is the highest for carbonyl O atom in both cases. These values (fc^+ and fo^-) are presented in Table 4.5-4.6.

Functional	CFF	Medium	Solvent (Dielectric constant)					
			Aprotic			Protic		
		Gas	n-hexane	Diethyl ether	Pyridine	Ethanol	Methanol	Water
BLYP	fc^+	0.307	0.314	0.320	0.324	0.325	0.326	0.326
	fo^-	0.402	0.412	0.422	0.429	0.432	0.432	0.433
PW91	fc^+	0.306	0.313	0.319	0.323	0.324	0.324	0.325
	fo^-	0.401	0.411	0.420	0.427	0.430	0.430	0.431
PBE	fc^+	0.306	0.313	0.319	0.323	0.324	0.324	0.325
	fo^-	0.401	0.411	0.421	0.428	0.431	0.431	0.432

Table 4.5: Values of CFF of reactive atoms of acetaldehyde in gas phase and in solvent medium having different dielectric constant using different functionals.

The CFF for nucleophilic attack for C atom (i.e., the electrophilicity of C atom) for both CH_3CHO and CH_3CH_2CHO molecules increases as we move on from gas phase to solvent medium with increasing the dielectric constant of the solvent medium (Table 4.5-4.6). Likewise, in going from gas phase to solvent medium and increasing the dielectric constant of the solvent medium, the CFF for electrophilic attack for O atom (i.e., the nucleophilicity of O atom) for both CH_3CHO and CH_3CH_2CHO molecules also increases (Table 4.5-4.6). Again, it is to be pointed out that the change in the reactivity, either the electrophilicity of C atom or the nucleophilicity of O atom, is significant for the aprotic solvents (Table 4.5-4.6). The change in protic solvent with high dielectric constant, ranging from 24.3 for ethanol to 78.54 for water, do not affect either the electrophilicity of C atom or the nucleophilicity of O atom in both the molecules (Table 4.5-4.6).

Functional	CFF	Medium	Solvent (Dielectric constant)					
			Aprotic			Protic		
		Gas	n-hexane	Diethyl ether	Pyridine	Ethanol	Methanol	Water
BLYP	fc^+	0.297	0.303	0.307	0.314	0.315	0.315	0.316
	fo^-	0.385	0.397	0.406	0.415	0.417	0.418	0.419
PW91	fc^+	0.295	0.303	0.309	0.313	0.315	0.315	0.316
	fo^-	0.384	0.394	0.405	0.412	0.415	0.415	0.416
PBE	fc^+	0.296	0.303	0.309	0.314	0.315	0.315	0.316
	fo^-	0.384	0.394	0.405	0.412	0.414	0.415	0.416

Table 4.6: Values of CFF of reactive atoms of propionaldehyde in gas phase and in solvent medium having different dielectric constant using different functionals.

On closer inspection, one can observe that the dielectric constant has more impact on the nucleophilicity of O atom, in both the molecules, rather than the electrophilicity of C atom i.e., the variation of the nucleophilicity of O atom is more compared to the electrophilicity of C atom with the increase in the dielectric constant of the aprotic solvents (Table 4.5-4.6). However, in case of protic solvents neither the nucleophilicity of O atom nor the electrophilicity of C atom varies significantly. It is to be also mentioned that the most reactive site in the molecules does not alter while using different solvents having different dielectric constant. Again, the trends are consistent with the use of different functionals BLYP, PW91 and PBE (Table 4.5-4.6). Although the studies have been presented for the most reactive atoms, the conclusions hold true for all other atoms.

4.4. Conclusions

The present chapter is focused on the study of the influence of aprotic and protic solvents having different dielectric constant on the reactivity of model systems, CH_3CHO and CH_3CH_2CHO molecules, using the density functional theory. It is observed that for aprotic solvents, the chemical potential and hardness decreases significantly with relatively minor changes in the dielectric constants. For protic solvents, the variation in chemical potential and hardness are less compared to the ones for aprotic solvents. However, in either case, it is observed that the hardness values change much more than the chemical potential values. On the other hand, the nucleophilicity as well as the electrophilicity of the reactive atoms increases while going from gas phase to aprotic solvents and for protic solvents their variations are again insignificant. Moreover, it is also observed that the conclusion does not alter with the different functionals employed. Although the present analysis is not very rigorous, a further detailed study should be made in this direction.

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Chapter 5

Intercluster Reactivity of Metalloaromatic and Antiaromatic Compounds

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5.1 Introduction

In the preceding chapters, our discussion was mainly on the response of the global and local reactivity descriptors in the presence of external perturbations, like the external electric field and solvents. However, in the next two chapters, we would present some applications of these reactivity descriptors to understand the reactivity of the mixed metal clusters and study the [2+2] cycloaddition reactions.

Recently, all-atom metal clusters were shown to have aromaticity and anti-aromaticity [1-13], thus opening a new area of metallo-aromatic and anti-aromatic compounds. Li *et al.*[1] for the first time synthesized the metallo-aromatic compounds *viz.* Al_4Li^-, Al_4Na^-, Al_4Li_2 etc. These compounds, on the basic criteria such as planarity, cyclic conjugation, Huckel's (4n+2) π electron rule were shown to have aromaticity. Motivated by this work, Shetty *et al.* [9] predicted the possibility of anti-aromaticity in Al_4Li_4 metal cluster using *ab initio* calculations. At same time, in an interesting work, combining both experimental and theoretical studies, Kuznetsov *et al.*[10] confirmed the existence of anti-aromaticity in $Al_4Li_3^-$ and Al_4Li_4 clusters. As an extension of this work, more metallo-antiaromatic compounds were discussed.[13] Very recently, magnetic properties of these compounds were investigated.[14-16] Surprisingly, the magnetic properties in these compounds were shown to have somewhat different trend than the organic aromatic and anti-aromatic compounds.[14-16] The metallo-aromatic compounds were shown to have a diamagnetic ring current arising from the σ-electron delocalization rather than the conventional π-electron delocalization.[14] Therefore these metal clusters are said to have σ aromaticity rather than the π aromaticity. On the other hand, metallo-anti-aromatic compounds were shown to have a diamagnetic current in the plane due to the σ electrons and a paramagnetic current out of the plane due to π electrons.[15, 16] This shows that, only on the basis of electron counting rule, it is difficult to decide the existence of metallo-aromatic and anti-aromatic compounds and the issue remains unresolved.[16, 17]

The investigations of these kinds of mixed metal clusters have been important in understanding the electronic, stoichiometric and surface properties during the alloy formation. The Al-Li alloys form very strong material and are used for aerospace applications.[18] More interestingly, in the last decade, Al-Li alloys have been widely used as electron injecting materials in organic light emitting diodes (OLED).[19-21] It has been shown that the efficiency of the OLED's depends on the number density of electrons and holes in the organic emission layer. This has been achieved by using high work-function material such as indium tin oxide (ITO) for hole injection and Li as low work-function material for electron injection.[20] Haskal *et al.* showed that the use of Li causes the organic layer to degrade due to its diffusion in the organic layer.[19] To avoid this, Al-Li alloys were used as electron injecting devices for OLED. They further showed that there is charge transfer from Li to Al at the interface causing contraction of the Li-Al interface.[19] This kind of bonding arrangement allows the Li-Al atoms to cluster at the interface.[19, 21] More importantly, the high efficiency of the Al-Li alloy as a cathode was on the account of enhanced charge transfer from the Li to Al and the clustering of Al-Li atoms at the interface. In the last few years more attention has been given to the study of the interaction of the organic layer with the metal cathodes and anodes. Tris(8-

hydroxyquinolinato) aluminum (Alq_3) has been the prototypical electroluminescent molecule for the organic layer in the applications of OLED.[21] Curioni and Andreoni[21] have studied the interaction of the Alq_3 molecule with the metal cathode surfaces such as Li, Al and Ca using *ab initio* simulations. Their investigation reveals that the Alq_3 accepts electron from the metal and thus acts as an electrophile, where the oxygen atoms were shown to be the electrophilic centers.[21] Hence, it is clear that the metal which donates electron would act as a nucleophile. Tang *et al,* with the help of photoelectron spectroscopy showed that the metal electronegativity is linearly dependent on the charge injection barrier.[22]

From the work of Haskal *et al.*[19] it can be inferred that the crucial part for the high efficiency of the Al-Li cathode is the cluster formation of the Al-Li atoms and the charge transfer from the Li to Al atoms at the Al-Li interface. It is also important to note that the Al atoms at the interface should have a low work-function (high nucleophilicity) to allow the easy injection of electrons in the organic layer. Hence, a deeper understanding of the formation of the Al-alkali clusters at the interface and the nucleophilicity of the Al in these clusters at the microscopic level is needed. Motivated with this, in the present chapter, we use the approach of local reactivity descriptors,[23] to investigate the inter-cluster reactivity of some Al-alkali clusters which have been shown to be metallo-aromatic and anti-aromatic compounds. Furthermore, we study the trend of the nucleophilicity of the Al_4 unit in these compounds to clarify the role of Al in the Al-alkali clusters for the applications of OLED's.

Local reactivity descriptors, such as local softness and Fukui Function (FF), based on density functional theory (DFT), have been used to determine the site reactivity in a system.[23] Intra-molecular reactivity has been studied extensively using these descriptors.[24] However, while these are reasonably reliable descriptors for intra molecular reactivity, there is considerable ambiguity in using these descriptors for understanding the inter-molecular reactivity.[24(b)] De Proft *et al*[25] have used the concept of group hardness, softness and electronegativity to study a series of organic compounds. Recently, Krishnamurty and Pal[26] used the concept of group softness for studying the inter-molecular reactivity in carbonyl compounds and organic acids. The group softness is defined as the summation of the local softness of a group of atoms around the most reactive site in a molecule.[26] These studies have shown that the molecule with the maximum group soften ss is the most reactive molecule within a series.[25, 26] Hence, the reactivity descriptors are the indicators of the strength of the electrophilicity (electron acceptance) and nucleophilicity (electron donation) of a single site or group of sites in a molecular system.

In this chapter, the concept of group FF for comparing the reactivity of the Al-alkali clusters, belonging to the class of metallo-aromatic and anti-aromatic compounds, has been introduced. The group FF is somewhat similar to the group softness defined earlier. However, group FF is defined as the group softness divided by the total softness. In the present study, both group softness and group FF have been used for intermolecular reactivity. These concepts are applied to explain as to why it is favorable for the formation of clusters at the Al-alkali interface in the cathode for applications in molecular electronics.

The present chapter has been organized as follows; in section 5.2 we discuss the theoretical background to calculate the group softness and group FF, followed by the computational detail in Section 5.3. In section 5.4 we present the results and discussion on the structure and reactivity of the Al based alkali clusters.

5. 2. Theoretical Background

The detailed description of the global and local reactivity descriptors has been outlined in the previous chapters. However, in the present context, a brief summary of group softness and group Fukui function would be helpful in dealing with these types of systems.

In many cases, the interaction takes place not just with a single atom, but a group of atoms. In such cases group softness and group FF can be defined as a sum of the local softness or FF of the group of atoms participating in the interaction. The group softness, s_g is defined over the set of the atoms n_g is written as

$$s_g = \sum_{k=1}^{n_g} s_k \qquad (5.1)$$

This concept is very useful when reaction does not take place through a single atom, but through neighbouring atoms in a cooperative manner, in other words, in cases where a group of atoms participate in bonding together. We can also define a concept of group FF, f_g, which is nothing but the sum of the FF of the atoms of the group. It is obvious that the f_g is nothing but $\frac{s_g}{S}$, where S is the total softness of the system. For intra-molecular reactivity, however, f_g and s_g will contain the same information. On the other hand, in comparing reactivity across different molecules, i.e. in comparing inter-molecular, f_g and s_g will not necessarily give the same trend, since global softness of the systems vary.

Along the lines of electrophilic and nucleophilic condensed FF, we can define the electrophilic and nucleophilic condensed group softness and group FF, $s_g^{+/-}$ and $f_g^{+/-}$ etc. For the systems of metal clusters that are being studied, Al_4 unit of atoms behave as a superatom in acceptance of electrons and hence the concept of group softness or group FF will be extremely useful.

5.3 Computational Details

Geometry optimization of the metallo-aromatic and anti-aromatic clusters *viz.* Al_4Li^-, Al_4Na^-, Al_4Li_4 and Al_4Na_4 were performed at the ab initio Moller-Plesset MP2 level with all electron using 6-31+G* basis set. The initial geometries of these clusters were obtained from the earlier experimental and theoretical work. The structural parameters of these clusters are in good agreement with the earlier work, which is discussed in the next section. Further, the geometries of these clusters have been checked by frequency analysis. Chemical potential, global hardness and global softness are calculated using the equations (2.4), (2.5) and (2.6). The local reactivity parameters such as condensed local softness (CLS) and condensed Fukui function (CFF) are obtained from equation (2.14) and (2.13), respectively, using Lowdin population analysis (LPA)[27]. The group softness and the group FF values are calculated using the above definitions. All the calculations in the present chapter have been performed by using GAMESS software.[28]

5.4. Results and Discussion

We begin this section with a brief discussion of the structural properties of the metallo-aromatic and anti-aromatic compounds *viz.* Al_4Li^-, Al_4Na^-, Al_4Li_4 and Al_4Na_4. Later, we discuss the use of group FF to analyze the reactivity in these systems.

5.4.1. Structure

The ground state geometries of Al_4Na^-, Al_4Li_4 and Al_4Na_4 are shown in Figure. 5.1. The ground state geometry of Al_4Li^- has also a pyramidal structure similar to Al_4Na^- as shown in the Figure 5.1 (a). For more detailed study on the stability of these clusters, studies by Shetty *et al*[13 (a)] and Kuznetsov *et al*[10] may be referred. The ground state of Al_4Li^- and Al_4Na^- metallo-aromatic clusters shows that the Al_4 unit has a square structure with the Al-Al bond lengths being 2.61 and 2.62 Å, respectively. However, the Al_4 units of the metallo-anti-aromatic Al_4Li_4 and Al_4Na_4 clusters have rectangular geometries (Figure 5.1 (b) and (c)). The bond lengths of these clusters obtained from MP2 calculations in the present chapter are in good agreement with the earlier results.[1, 13]

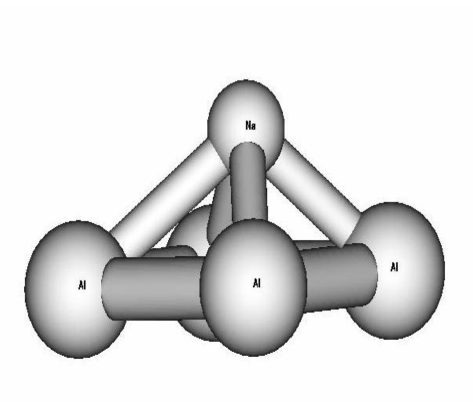

Figure 5.1 Optimized equilibrium geometries of (a) Al_4Na^- at MP2 level with 6-31+G*

It is worth mentioning that in all the above mentioned metallo-aromatic and anti-aromatic compounds the Al atoms group to form one Al_4 unit in the whole cluster. This arrangement allows the Al_4 unit to form a superatom.[29] Shetty *et al* have discussed the role of Al_4 superatom in the Al_4Na_4 and $Al_4Na_3^-$ metallo-antiaromatic compounds.[13] It should be noted that if there is no formation of Al_4 superatom in the metallo-aromatic and anti-aromatic compounds, such as Al_4Li_2, Al_4Li_4, Al_4Na_4 etc., the charge transfer from the Li and Na atoms to the Al_4 unit would be difficult. Hence, the existence of aromaticity and anti-aromaticity in these compounds is not possible. It is worth mentioning that the charge transfer from Li to Al at the Li-Al interface as discussed by Haskal *et al*,[19] would be due to the formation of Al_n superatom. Detail theoretical study of charge transfer and optical properties in the metallo-anti-aromatic compounds have been discussed by Datta *et al*.[30]

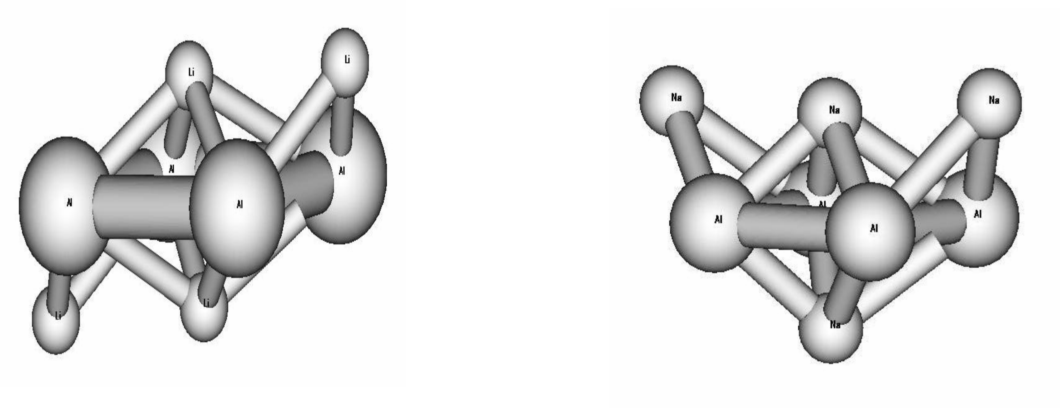

Figure 5.1 Optimized equilibrium geometries of (b) Al_4Li_4 and (c) Al_4Na_4 at the MP2 level with 6-31+G*

5.4.2. Reactivity

We now focus our discussion on the inter-cluster reactivity of the metallo-aromatic and anti-aromatic compounds. We investigate the trend of the nucleophilicity of the Al_4 unit in all the four clusters *viz.* Al_4Li^-, Al_4Na^-, Al_4Li_4 and Al_4Na_4 using the group softness and FF. Let us discuss first the metallo-aromatic compounds: Al_4Li^-, Al_4Na^-.

The chemical potential, global hardness and global softness values of Al_4Li^-, Al_4Na^-, Al_4Li_4 and Al_4Na_4 clusters are given in Table 5.1. It can be seen that the Al_4Na^- cluster has the highest global softness and hence would be the most reactive cluster. However, from the experimental point of view we are only interested in the reactivity of the Al atoms rather than the alkali atoms. The local reactivity parameters such as the condensed local softness for the electrophilic (s^-) and the nucleophilic (s^+) attack, condensed FF for the electrophilic (f^-) and the nucleophilic (f^+) attack , group softness (s_g^-) and the group FF (f_g^-) for the electrophilic attack of the Al_4 unit in the Al_4Li^-, Al_4Na^-, Al_4Li_4, Al_4Na_4 clusters are given in Table 5.2. Since, we are only interested in the strength of the nucleophilicity (for the electrophilic attack or the strength of electron donation) of the Al_4 unit, we only discuss s_g^- and f_g^- for the electrophilic attack on the Al_4 unit i.e. the nucleophilicity of the Al_4 unit.

Cluster	Chemical Potential	Hardness	Softness
Al_4Na^-	-0.0055	0.0695	7.194
Al_4Li^-	-0.0055	0.0775	6.452
Al_4Na_4	-0.0565	0.0970	5.128
Al_4Li_4	-0.0845	0.1128	4.405

Table 5.1: Chemical potential, global hardness and global softness of Al_4Li^-, Al_4Na^-, Al_4Li_4 and Al_4Na_4 (values are in atomic units)

It is seen from the Table 5.2 that the condensed local softness and the condensed FF values for the electrophilic (s^-, f^-) and the nucleophilic attack (s^+, f^+) of all the 4 Al atoms of the Al_4Li^- and Al_4Na^- clusters are identical. This is due to the electron delocalization in the Al_4 unit in both the systems. Hence, all the four Al atoms in these systems have the same reactivity.

We can clearly see from Table 5.2 that the Al_4 unit of the Al_4Li^- has lower value of s_g^- than the Al_4Na^-. Surprisingly, the trend of the group FF for these systems shows a different behavior (Table 5.2). This shows that the trend in the group softness and the group FF are not necessarily identical. However, from the definition of the group FF, we believe that the group FF is a more reliable indicator for the electrophilic or the nucleophilic attack than the group softness. Hence, only on the basis of the group FF we can say that in the metallo-aromatic compounds the Al_4 unit of the Al_4Li^- cluster can act as a better electron donating system than the Al_4Na^- cluster.

Al_4 unit	s^+	s^-	s_g^+	s_g^-	f^+	f^-	f_g^+	f_g^-
Al_4Li^- [a]	0.129	1.336	0.516	5.344	0.020	0.207	0.080	0.828
Al_4Na^- [a]	0.201	1.388	0.804	5.552	0.028	0.193	0.112	0.772
Al_4Li_4 [b]	0.366 0.344	0.542	1.420	2.168	0.083 0.078	0.123	0.322	0.492
Al_4Na_4 [b]	0.415 0.133	0.487	1.096	1.948	0.081 0.026	0.095	0.214	0.380

Table 5.2: Condensed local softness, Condensed Fukui function for nucleophilic and electrophilic attack and the respective group softness and group Fukui functions for Al_4Li^-, Al_4Na^-, Al_4Li_4 and Al_4Na_4 clusters.

[a] Values of condensed local softness and FF for nucleophilic and electrophilic attack for the four Al atoms in the Al_4 unit of the metal clusters Al_4Li^-, Al_4Na^- are same.

[b] Values of condensed local softness and FF for nucleophilic attack for two Al atoms are different than the other two Al atoms in the Al_4 unit of the metal clusters Al_4Li_4 and Al_4Na_4 .

The local reactivity parameters of the Al_4Li_4 and Al_4Na_4 clusters are given in Table 5.2. Interestingly, the condensed local softness and FF of the metallo-anti-aromatic compounds show a different trend than the metallo-aromatic compounds. From Table 5.2, we see that the values of the condensed local softness and the FF for the electrophilic attack of all the four Al atoms of the Al_4Li_4 and Al_4Na_4 clusters are same. Surprisingly, the values of the condensed local softness and condensed FF for the nucleophilic attack of two of the Al atoms are different than the other two Al atoms (Table 5.2). This shows that the ability to donate the electrons of all the four Al atoms in both the clusters is same. However, the ability to accept the electrons of two Al atoms is different than the other two. The reason for this may be the electron localization along the shorter Al-Al bonds.

Unlike the metallo-aromatic compounds the group softness and FF results of the Al_4 unit of the metallo-anti-aromatic compounds shows a similar trend. The Al_4 unit of the Al_4Li_4 cluster has higher group softness and FF than the Al_4Na_4 cluster. If we compare the strength of nucleophilicity of the Al_4 unit only on the basis of group FF of all the four clusters *viz.* Al_4Li^-, Al_4Na^-, Al_4Li_4 and Al_4Na_4, the trend is as follows.

$$Al_4Li^- > Al_4Na^- > Al_4Li_4 > Al_4Na_4$$

The above discussion demonstrates that the nucleophilicity of the Al atoms in the Al-Li systems is more compared to that of Al-Na systems. However, the stoichiometry of the Al and Li also plays a crucial role in deciding the nucleophilicity of the Al cluster. From the present calculations we can interpret that the strength of the nucleophilicity of the Al decides the work function of the Al-Li cathode. Hence, we can say that, higher the nucleophilicity of the Al atoms, lower is the work function of the Al atoms in the Al-Li cathode.

Curioni *et al.* proved in their study that the oxygen atoms of the Alq_3 molecule are the electron withdrawing groups (electrophiles).[21] Hence, from the present study one can consider that the metallo-aromatic and anti-aromatic systems to be molecular cathodes for injecting electrons where the Al can act as electron injecting sites in a single electroluminescent molecule, such as, Alq_3.

5.5 Conclusions

On the background of the experimental studies of the Al-Li cathodes to understand the enhanced efficiency of the electron injection due to the charge transfer from Li to Al and the clustering of the Al-Li atoms at the interface. In the present chapter, we demonstrate the strength of the nucleophilicity of the Al atoms of various Al based alkali clusters. For the first time, we have compared the inter-cluster reactivity of metallo-aromatic and anti-aromatic compounds using the local reactivity descriptors. The results suggest that the Al_4 unit in all the four clusters *viz.* Al_4Li^-, Al_4Na^-, Al_4Li_4 and Al_4Na_4 acts as a nucleophile (electron donating groups). The group reactivity of the Al_4 unit based on the local reactivity descriptors suggest that the highest nucleophilicity of the Al_4 unit is in the Al_4Li^- cluster. Hence, we can say that the metallo-aromatic (Al-Li) kind of cluster formation, such as Al_4Li^-, at the interface of Al-Li alloys would be responsible for an efficient electron injection in the organic layer of OLED. Moreover, these kinds of clusters can be thought to be probable candidates for molecular cathodes. However, more experimental and theoretical work is needed to understand this issue.

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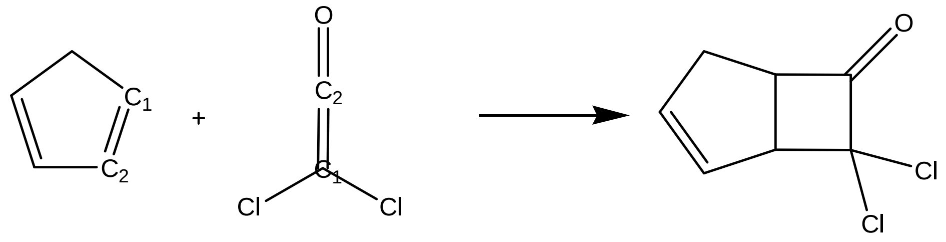
Chapter 6

A local HSAB approach to [2+2] Cycloaddition Reaction

6.1 Introduction

Chemists, especially experimental chemists are very much interested to predict the feasibility of a reaction and hence theoretical calculations go hand in hand with the experiment. Among so many typical organic reactions, one of the most important reactions is the reaction between cyclopentadiene (I) and dichloroketene (II) to form cyclobutanones (III).[1-2] The reaction is an easy one when the ketene has an electron withdrawing group (such as Cl) and when the olefin is electron rich. One such example is shown below:



(I) (II) (III)

It can be easily seen that the reaction is a [2+2] cycloaddition reaction. These reactions are important because the final product is a medicinally important compound. However, we must look more closely at this reaction, for at first sight it seems to be disobedient to the Woodward-Hoffmann rules.[2] Nonetheless, there is evidence of concertedness and it is thought to find an allowed pathway in which a [π2s+ π2a] process occurs.[2]

The density based reactivity descriptors classified as either global or local reactivity descriptors, such as chemical potential, chemical hardness, Fukui function, local softness etc., are more commonly and widely used in understanding the chemistry of a variety of molecules.[3] The review article by Geerlings et. al. helps in understanding the concepts involved along with their various applications.[4] The local hard-soft acid-base (HSAB) semi-quantitative model, along with its extensions, for calculating stabilization energy, has been exploited several times to prove its potential with the conventional quantum chemical methods.[5-7] However, these models are based on the principle of local HSAB which states that sites having similar local softness can interact.[8-9]

Very recently, the regioselectivity of [2+2] photocycloaddition reaction of acrolein and olefin has been studied systematically.[10] In an another recent study, a second-order change in electron density to changes in the number of electrons i.e., the dual descriptors has been employed in understanding the Woodward-Hoffmann (WH) rules for pericyclic reactions.[11] At the same time, the WH rules were revisited using the initial hardness response theory.[12]

On the other hand, in the present chapter, we would like to focus on studying the [2+2] cycloaddition reaction of alkenes with ketenes. Specifically, the cycloaddition reaction between cyclopentadiene and dichloroketene is considered. At the first sight, it seems that the above reaction is disobedient to the Woodward-Hoffmann rules.[2] However, there is evidence of a [π2s+ π2a] process occuring.[2] However, from the perspective of the local HSAB principle we would like to study the above cycloaddition reaction between cyclopentadiene and dichloroketene.

The present chapter is as follows: Section 6.2 will discuss the computational details and the methodology involved in the present study. Results and discussions are presented in Section 6.3. Finaly, in Section 6.4, the conclusions for the present chapter will be presented.

6.2 Computational Details

In order to compute the values of local softness, first the reactants, cyclopentadiene and dichloroketene, were completely optimized at 6-31++G (d, p) basis set using B3LYP hybrid functional. In order to confirm their minima, their frequencies were calculated. Next, the energies of the neutral, cationic and anionic systems were computed to calculate the values of chemical potential, chemical hardness and softness from equation (2.4), (2.5) and (2.6), respectively. The local parameters were calculated from equations (2.13) and (2.14) using Mulliken[13] as well as Lowdin[14] population technique. All the above calculations were performed using GAMESS software.[16] The validation of the present study is tested using another basis set, 6-311++G(d, p) along with different functionals, BLYP and BHHLYP.

6.3 Results and Discussion

The values of condensed local softness (CLS) calculated using both Lowdin population analysis (LPA) as well as Mulliken population analysis (MPA) are presented in Table 6.1 and Table 6.2 for cyclopentadiene and dichloroketene, respectively using different basis sets and different exchange-correlation functionals.

Let us first analyze the results for the combination of basis set, say 6-31++ G (d, p), with functional, say B3LYP. For the reaction between cyclopentadiene and dichloroketene, it can be noticed that the bond is formed between the C1 atom of the former with the C2 atom of the later. Now from the values of CLS, calculated from Lowdin based method of population analysis (LPA), it can be observed that the local parameter matches for both the reactants. For instance, the $s_{C_1}^{-}$ value of cyclopentadiene (Table 6.1) is similar to the $s_{C_2}^{+}$ value of dichloroketene (Table 6.2).

Basis	CFF	Functional					
		BLYP		BHHLYP		B3LYP	
		MPA	LPA	MPA	LPA	MPA	LPA
6-31++G(d, p)	$s_{C_1}^{-}$	1.122	1.310	1.354	1.419	1.216	1.402
	$s_{C_2}^{+}$	-4.925	0.219	-4.824	0.177	-0.126	0.192
6-311++G(d, p)	$s_{C_1}^{-}$	1.066	1.392	1.255	1.414	1.150	1.394
	$s_{C_2}^{+}$	-5.885	0.212	-5.715	0.171	-5.928	0.185

Table 6.1: Values of CLS for reactive atoms in cyclopentadiene using different functionals and population analysis

Since they have similar CLS values, we can suggest from the local HSAB view point that they will direct towards the specified product (III). This is, in addition, a proof for the reaction to be a concerted and to find an allowed pathway in which a [π2s+ π2a] process occurs rather than to be disobedient to the Woodward-Hoffmann rules.

Basis	CFF	Functional					
		BLYP		BHHLYP		B3LYP	
		MPA	LPA	MPA	LPA	MPA	LPA
6-31++G(d, p)	$s_{C_1}^{-}$	0.288	1.033	0.433	1.132	0.340	1.064
	$s_{C_2}^{+}$	-0.281	1.360	0.084	1.469	-0.132	1.417
6-311++G(d, p)	$s_{C_1}^{-}$	0.261	1.023	0.066	1.118	0.333	1.055
	$s_{C_2}^{+}$	0.241	1.421	0.541	1.515	0.377	1.470

Table 6.2: Values of CLS for reactive atoms in dichloroketene using different functionals and population analysis

On further inspection for rest of the functionals, BLYP and BHHLYP, it can be observed that all the $s_{C_1}^{-}$ value of cyclopentadiene (Table 6.1) is similar to the $s_{C_2}^{+}$ value of dichloroketene (Table 6.2). Moreover, the consequences of our study does not change much on improving the basis set from 6-31++ G (d, p) to 6-311++ G (d, p) (Table 6.1-6.2). Therefore, we can conclude that the local hard-soft acid-base principle may be a used as a guide line for predicting the feasibility of these types of reactions. However, one has to take a wide range of chemical reactions and a detailed study has to be made for the confirmation of the above facts.

6.4 Conclusions

We have studied the reaction between cyclopentadiene and dichloroketene, which is in first instance, is disobedient to WH rules but later on proved to be otherwise. Our study involves the local reactivity descriptors, mainly the condensed local softness and the local HSAB principle. The regioselectivity of the above reaction can be predicted by the local HSAB principle. We have proposed that the local HSAB principle may be used to predict the final product hence, a supportive factor for the WH rules.

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List of Publications

1. Intercluster Reactivity of Metalloaromatic and Antiaromatic Compounds and Their Application in Molecular Electronics: A Theoretical Investigation

Sharan Shetty, **Rahul Kar**, Dilip G. Kanhere and Sourav Pal

J. Phys. Chem. A (**2006**) 110, 252-256

2. The Influence of Electric Field on Global and Local Reactivity Descriptors: Reactivity and Stability of weakly bonded complexes

Rahul Kar, K. R. S. Chandrakumar and Sourav Pal

J. Phys. Chem. A (**2007**) 111, 375-383

3. Electric field response of molecular reactivity descriptors: a case study

Rahul Kar and Sourav Pal

Theor. Chem. Acc. (**2008**) 120, 375-383

4. External Field Effects and Chemical Reactivity

Rahul Kar and Sourav Pal

Chemical Reactivity Theroy: A Density Functional View, CRC Press, Ed. P. K. Chattaraj, (**2008**) 363-377

5. Effect of Solvent having different dielectric constant on reactivity: A Conceptual DFT approach

Rahul Kar and Sourav Pal

Int. J. Quant. Chem. (**2009**) (in press)

6. Theoretical Investigation of Reactivity and Stability of DNA bases and their base pairs in presence of Electric Field

Rahul Kar, K. R. S. Chandrakumar and Sourav Pal (manuscript under preparation)

7. [2+2] Cycloaddition Reactions: Application of Local HSAB principle

Rahul Kar and Sourav Pal (manuscript under preparation)