## CHAPTER 1

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CHAPTER 1

Introduction

1.1 Electron Donor Acceptor, EDA, Complexes

The electron donor acceptor, EDA or charge transfer complexes are formed as a result of chemical interaction between an acid and base. Lewis [1] classified acid and base as chemical system receiving a pair of electrons and a chemical system donating a pair of electron respectively. The chemical process of formation of a bond between an acid (A) and a base (L) leading to the formation of an adduct AL was first classified by Lewis [1] as electron pair donor–acceptor. In terms of Lewis [1] definitions, the bases are electron donors having unshared pair(s) of electrons and the acceptors are acids having stable but empty orbitals. The complexes are formed by the donation of unshared pair of electrons of the Lewis bases in to the formally empty orbitals of the Lewis acids and thus a new bond is formed between the acid and base. According to Kosower [2], a charge transfer complex is a combination of a donor and acceptor called a charge-transfer transition. A donor (L) may be defined as any molecule capable of giving electron and hence the donor ability may be conveniently measured by its ionization potential. An acceptor (A) is any molecule capable of acquiring an electron, but acceptor ability is not so easy to measure, since it is relatively difficult to obtain the relevant electron affinity. Pauling [3] classified the chemical bond as electrostatic, covalent or metallic. Under the subsection of covalent bonding, he introduced [3] the new type of bonding – coordinate bond. He considered this bond as “a sort of bond consisting of one single covalent bond and one ionic bond of unit strength”–named as semipolar bond. He shows that “the only difference between a covalent bond and dative
bond is where the electrons come from." When $\text{H}_3\text{N-BH}_3$ is formed from $\text{H}_3\text{B}$ and $\text{NH}_3$, the two electrons forming $\text{B-N}$ bond comes from $\text{N}$, but $\text{H}_3\text{C-CH}_3$ may be formed from $\text{CH}_3^+$ and $\text{CH}_3^-$—then it would seem that a distinction between covalent and dative bond is artificial. Haaland [4] defined this dative bond in view of the fact that the dissociation of a Lewis type donor-acceptor complex gives two closed shell fragments of which, one is an electron lone-pair donor (L) and the other is an electron pair acceptor (A). The chemists [5] knew a large number of such type complexes with a wide variation in stability and physical and chemical characteristics from the first decade of twentieth century. The nature and strength of bonding between the acids and bases ranges from weak van der Waals attraction at one end and strong covalent binding at the extreme end through a continuous variation in stability. The elucidation of the structure and binding in the donor-acceptor complexes are mainly due to the pioneering work of:—

1. G. N. Lewis
2. J. Weiss
3. R. B. Woodward
4. W. C. Price
5. F. Fairbrother
6. H. A. Benesi
7. J. H. Hildebrand
8. R. S. Mulliken
9. S. Ahrland
10. J. Chatt
11. N. R. Davies
12. A. A. Grinberg
While all other approaches were at the qualitative level, Mulliken and Fukui developed quantitative model.

The donor–acceptor interaction always leads to an adduct or combined system which are now labeled as supermolecule. The situation may be pictorially described as follows:

\[
\begin{align*}
A & \quad \text{(Acceptor subsystem)} & + & \quad L & \quad \text{(Donor Subsystem)} \\
\downarrow & \quad \text{(A} & \quad \text{L)} & \quad \text{(Adduct Supermolecule)}
\end{align*}
\]

**Figure 1.1 Formation of super molecule by the interaction of two donor–acceptor subsystems**

The new ‘dative’ bond, formed between Lewis acid and Lewis base, has tremendous importance in the matter of rationalization of the kinetics of the acid base reaction and thermodynamic stability of the complexes. Thus the view that a molecular complex is the result of the combination of an electron donor or Lewis base, \( L \), with an electron acceptor or Lewis acid, \( A \), is widely held [6]

Weiss [7] made a significant contribution to the theory of molecular complexes. According to him molecular complexes have an essentially ionic structure \( L^+A^- \). He
also pointed out that a low ionization potential for the Lewis base (L) and a high electron affinity for the Lewis acid (A) would favor the stability of the complex.

\[ A + L \leftrightarrow (AL)_h \rightarrow [A^+][L^-] \]

Woodward [8] showed that collision between donor (L) and acceptor (A) results in electron transfer followed by formation of a dipolar aggregate, held together by ionic forces. This was probably occurred further by inter-particular overlapping of the orbitals of the non-bonded electrons in each half. He put forward his theory of \textit{intermolecular semi-polar bond} in the formation of molecular complex.

\[ A + L \leftrightarrow [A^+][L^-] \rightarrow [A^+][L^-] \]

Benesi and Hildebrand [9], using the spectroscopic methods, have shown definitely that benzene and mesitylene form 1:1 complexes of good stability with iodine. Again they have shown that iodine-mesitylene complex is a much stronger one than the iodine-benzene complex. The fact, the iodine-mesitylene complex is more stable than the iodine-benzene complex, was decided by noting the position of the absorption maxima (\(\lambda_{\text{max}}\)) of the complexes. By noting the \(\lambda_{\text{max}}\) of iodine and some aromatic hydrocarbon complexes, it is found that \(\lambda_{\text{max}}\) increases in the series Benzotrifluoride < Benzene < Toluene < O-Xylene < p-Xylene < Mesitylene. This increasing absorption maximum indicates that the HOMO–LUMO energy gap decreases monotonically. It is obvious that the site substituents in the benzene nucleus act as electron withdrawing (F) and electron releasing (CH\(_3\) group, etc) via interaction with the \(\pi\)-cloud of the benzene nucleus. Benesi and Hildebrand have concluded correctly that the entire series of changes from Benzotrifluoride to mesitylene are correlated with increasing ability of the different substituted benzenes to act as electron donors. The idea that the site groups of the benzene ring interacts with \(\pi\)-cloud to generate the hypsochromic
and bathochromic effect is verified and substantiated for the work of Price [10] who determined the ionization potential of the above compounds, e.g., 9.24 eV for benzene, 8.92 eV for toluene, probably about 8.3 eV for the xylenes and 8.1 eV for mesitylene. Fairbrother [11], also, verified the formation of charge transfer complexes between iodine and aromatic hydrocarbon.

Mulliken [12] presented a simple quantum mechanical theory for the interaction of electron acceptors and donors (Lewis acids and bases respectively) to form 1:1 or n:1 molecular complexes ranging from complexes formed by loose attachment to stable compounds. The theory invokes significant dative structures \( (A^- - L^+) \), where \( A \) is an acceptor atom, molecule or ion and \( L \) is a donor atom, molecule or ion. Strength of any Lewis acid–base interaction is governed largely by the characteristics of the dative structure \( (A^- - L^+) \), especially favorable are low ionization energy \( (I) \) of \( L \) and close approach between the centers of gravity on charges on \( L^+ \) and \( A^- \).

The wave function of the ground state of any molecular compound \( AL \) as

\[
\Psi = a\Psi_0 + b\Psi_1
\]

where \( \Psi_0 \) is no bond wave function and \( \Psi_1 [\Psi_1 = \Psi(A^- - L^+)] \) is a dative wave function corresponding to transfer of an electron from \( L \) to \( A \) accompanied by the establishment of a covalent bond between the odd electrons in \( A^- \) and \( L^+ \).

Charge transfer transition takes place between HOMO of the donor and LUMO of the acceptor. High electron affinity \( (E) \) for \( A \) is also helpful. Close approach between \( L^+ \) and \( A^- \) lowers the energy of \( L^+A^- \) both through increased coulomb interaction and through strong covalent binding. It was suggested by Mulliken that the class of such complexes could be identified by their electronic absorption spectra. It was found that the characteristics of spectra of such compounds were of high intensity because of
charge transfer and the spectra of such complexes were labeled as "charge transfer spectra". The forces of attraction developed through physical process of charge transfer leading to the formation of complex are weak and comparable to London's dispersion forces. The nature of the attraction is therefore of the van der Waals type. Benesi and Hildebrand predicted charge transfer mechanism of formation of benzene-iodine and related complexes by their characteristic absorption peak. Its position and intensity were in good agreement with the theory. The mechanism of formation of charge transfer complexes was not confined to homogeneous media but was found significantly important in heterogeneous systems.

1.2 Pearson’s HSAB Principle: Systematization of accumulated facts regarding Lewis acid and base

Pearson [13] attempted a systematic classification of the Lewis acids and Lewis bases on the basis of preference of one acid for some particular type of bases and the generalization is known as HSAB principle or Hard–Soft Acid–Base principle. The generalization was a significant input in conceptual chemistry and used for rationalization of acid base reactions.

The HSAB principle divides the acids and bases into two categories—hard and soft. Softs are those that are easily polarizable and hards are those that are non-polarizable. Klopman [14] introduced the idea of frontier orbitals in HSAB theory. These are the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). The HSAB relationship is discussed as: hard species have a large HOMO-LUMO gap whereas soft species have a small HOMO-LUMO gap. The presence of low lying unoccupied MOs capable of mixing with the ground state accounts for the polarizability of soft atoms or molecules.
The useful generalization of HSAB principle is "hard acids prefer to associate with hard bases, and soft acids prefer soft bases". The polarizability of atoms, ions and molecules can be guessed easily from ionization potentials and electron affinity of the chemical spices. A low ionization potential is usually associated with the large polarizability and a high ionization potential with the low polarizability. In the quest for theoretical justification of HSAB principle, which is found to work nicely for rationalization of reactions between large number of acids and large number of bases, a number of theoretical models were suggested. Of which, the following approaches are considered with due importance in order to rationalize the observed hard–hard and soft–soft interactions. The suggested models are as follows:–

1. The ionic–covalent theory of Grinberg
2. The π–bonding theory of Chatt
3. Electron correlation theory of Pitzer
4. Solvation theory of Parker

A short resume of the models is furnished below.

1.2.1 Grinberg's Polarization theory

Coulson,[15] from the view point that both bonded atoms be of similar electronegativity to have strong covalent bonding, drew conclusion that hard acids will prefer hard bases even when considerable covalency exists. Due to good covalency, soft bases will mismatch with hard acids, and ionic bonding will also be weak because of the small charge or large size of the base. It has already been stated that Mulliken [12] has developed a theory of covalent bonding in relation to the donor–acceptor charge transfer complexes suitable for discussing the interaction between the soft bases and soft acids (vide supra). It is apparent that Mulliken's
treatment is silent about hard-hard interaction. The theoretical reason for hard-hard preference was put forward by Grinberg [16] in terms of the polarization theory. "The hard acids are assumed to bind bases with primarily ionic forces and the soft acids prefer bases by covalent interaction."

1.2.2 The $\pi$-bonding theory:

The donor-acceptor complexes formed by strong interaction involve important contribution from $\pi$-bonding in addition to the $\sigma$-bonding. Experimental proof like Photo-electron spectra of H$_3$B-CO system provides evidence in support of hyperconjugative back-donation [17]. It is suggested that, in all probability, the chemical interaction between metals and the $\pi$-acidic ligands leading to the formation of $\pi$-complexes, takes place through a simultaneous donation and back-donation of charge [18-19]. In terms of hard-soft acid base classification such metals are classified as soft acids and such ligand are classified as soft bases. We may mention that BH$_3$ is a soft Lewis acid and represents transition metals in their low oxidation state.

The majority of the cases of soft-soft interaction are found to occur between transition metals in their low oxidation state and $\pi$-acidic ligands. Chatt [20-23] tried to theoretically correlate the reason behind the preference of soft acid for soft bases by suggesting a simultaneous $\sigma$-donation and $\pi$-back-donation of donor-acceptor charge transfer interaction between the reacting acids and bases. The donation takes place from the filled $\sigma$-symmetric molecular orbital of the ligand to the empty d orbital of the metal whereas back-donation takes place from the filled $d_{xy}$ orbital of the metal into the empty $\pi^*$ (having matching symmetry with the $d_{xy}$ orbital of the metal) orbital of the ligand. Large number of ligands like carbon monoxide (CO), isonitriles (NC−),
Nitrosonium cation, olefinic, acetylenic compounds, etc. are found to enter into \textbf{chemical interactions} with transition metals and boranes through the same mechanism of bonding and back-bonding. We have already mentioned that such $\pi$-back donation is not only confined in the metallic cases but also extended in the non-metallic cases, e.g., non-metallic boron coordination compounds, which is our special interest in this particular study. A review of multiple bonding and back-donation in complexes of transition and non-transition elements has been given by Petit [24]. However, Chatt's suggestion was qualitative one. No quantitative data was available in support of the model of charge transfer interaction between soft acids (metals) and soft bases ($\pi$-acidic ligands).

\textbf{1.2.3 Electron correlation theory}

Electron correlation phenomena are represented by London forces and orbital hybridization. Pitzer [25-26] has suggested that London or van der Waals, dispersion forces between atoms or groups in the same molecule may lead to an appreciable stabilization of the molecule. Such London forces depend on the product of the polarizabilities of the interacting groups and vary inversely with the sixth power of the distance between them [27]. London correlation occurs due to electrostatic repulsion of electrons for each other. London force always exists in a complex formed between a polarizable acid and a polarizable base and thus stabilizes the soft-soft combination. Mulliken [28] proposed $\pi$-orbital hybridization, which shows stabilization due to $\pi$-antibonding orbital. Mulliken pointed out that this effect is more important than more usual $\pi$-bonding because the antibonding orbital is more antibonding than the bonding orbital is bonding if overlap is included. The proposed $\pi$-orbital hybridization occurs largely because of non-bonded repulsion effects arising due to Pauli exclusion
principle. The orbital overlap interactions correlation is more important for interaction between bonded atoms whereas the London force is more important for remote interaction. Thus for the interaction of a soft acid and a soft base, orbital hybridization should usually be more important than stabilization due to van der Waals forces.

1.2.4 Solvation effect destroys the hard character and enhances the soft character

Parker [29-30] has stressed the effect of solvents on reducing the basicity of small anions and hence causing large anions to appear abnormally strong. The implication that such solvation is the common explanation for strong binding, or high rates of reaction, of polarizable bases seems to be incorrect. As was pointed out above, differences in solvation energies between neutral molecules such as ROH and RSH are very much smaller than the differences for the corresponding anions. Actually solvation effect alone would not cause a division into two distinct classes of acids as are found. Though solvation effect has great importance, particularly for ions, this theory has no explanation why some acids prefer hard bases and why some acids prefer soft bases. The explanation for this must come from interactions existing in the acid-base complex. Such interactions include ionic-covalent σ-bonding, π-bonding, and electron-correlation-effects – all of which seem to play a role in determining hard and soft character.

1.3 Quantitative DFT definition

The history of chemistry shows evidently that the definition and concept of chemical hardness has evolved with time from qualitative perception to rigorous quantum mechanical definition by Parr and Pearson [31]. Parr did the definitive work introducing the quantitative idea of hardness and formalized hardness as a quantitative thumb rule of chemical reactivity. Density Functional Theory, DFT has wonderfully
solved the problem of HSAB theory by developing a rigorous definition of hardness. The formalism will be discussed later (CHAPTER 4) in details.

1.4 The theoretical method of locating the origin and mechanism of charge transfer during donor–acceptor interaction

Kenichi Fukui, [32-33] the proponent of the frontier orbital theory, developed a theoretical method of analysis of electronic structure of the adduct (supermolecule) formed by the chemical interaction of donor and acceptor sub-systems, in which the origin of charge transfer and the mechanism of binding through the physical process of charge transfer becomes self evident and straightforward. The whole interaction between two sub–systems leading to the formation of super molecule become distinctly revealed in a chemically graspable form. The model suggest that the two interacting sub–systems approach each other and prior to the chemical interaction the sub–systems become reorganized and favorably oriented with respect to each other so that chemical interaction may initiate by the interaction of the frontier orbitals of the donor and the acceptor. The method computes charge donated and accepted with regard to each of the molecular orbital (MO) of the interacting systems. The results demonstrate that most affected orbitals in the chemical interaction via the physical process of charge transfer are the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the interacting fragments. In a molecule the highest occupied molecular orbital is called HOMO and lowest unoccupied molecular orbital is called LUMO. They are altogether termed as frontier orbitals [34]. However, it must be mentioned that the condition precedent of charge transfer interaction between the frontier orbitals of the donor and the acceptor is that the interacting MO's must be of
matching symmetry, i.e., such orbitals of the separated sub-systems must span the similar irreducible representations.

The charge transfer process depends on two opposing processes—(I) donation from the formal donor into the formal acceptor and (II) back-donation from the formal acceptor into the formal donor. The back-donation is very much necessary for the stability of such donor–acceptor complexes.

Electrons are distributed in various molecular orbitals of the molecules. So when the sub-systems or the fragmental parts chemically interact, the actual interaction occurs through the process of charge transfer and coulomb interaction between the molecular orbitals of the interacting systems. The orbital energies and the symmetry species have tremendous influence in the physical and chemical process of donor–acceptor interaction. However, the main type of interaction may be classified as follows:

1. Between the occupied MO's of the acceptor with the occupied MO's of the donor
2. Between the unoccupied MO's of the acceptor with the occupied MO's of the donor
3. Between the occupied MO's of the acceptor with the unoccupied MO's of the donor and
4. Between the unoccupied MO's of the acceptor with the unoccupied MO's of the donor.

Of which, it is found that 2 and 3 are very much important in explaining the formation of the bond. Thus although, the entire spectrum of MO's of both the donors and the acceptors are found to participate in the process of charge transfer and bond formation, the frontier orbitals play an important role in such chemical interaction most distinctly. The only restriction is the symmetry restriction to the effect that the orbital
pairs involved in the process of charge transfer must have a matching symmetry, i.e., interacting orbitals must span the same irreducible representations of the point groups to which the interacting molecules belong. Otherwise, the process of charge transfer can not initiate because the overlap integral between such molecular orbitals vanishes identically. However, there is a general prediction regarding the stability of the complexes on the basis of the amount of net charge transfer due to a bimolecular interaction. It is the general prediction that the large value of net transfer of charge leads to the formation of stronger dative bond and complexes, and small amount of net charge transfer leads to the formation of weaker bond and complexes.

The net transfer of charge between two interacting species is expected to depend upon the following parameters:–

(I) the distance of inter molecular separation

(II) their mutual orientation

(III) states of oxidation

(IV) the difference of energy of the orbitals involving in charge transfer, i.e., the difference in energy between the HOMO of the donor and the LUMO of the acceptor (for donation process) and that between the HOMO of the acceptor and the LUMO of the donor (for back-donation process).

(V) the magnitude of difference of chemical potential between the donor and the acceptor before their chemical interaction in the reorganized geometry.

The above four factors, I–IV, are straightforward and self-evident in the light of the discussion already made. For the fifth factor—dependence of charge transfer on chemical potential of the sub-systems will be evident in the following discussion.
Although a number of SCF calculations [35-39] seem to support both donation and hyper conjugative back–donation [40] on the basis of atom and bond populations, the method developed by Fukui et al [32-33] gives transparent, straight–forward and quantitative data concerning these matters. Ghosh [41] has applied the method in studying the charge transfer mechanism in a number of systems.

Realizing the importance of this method of analysis of electronic structure in a chemically graspable form Ghosh [41] cast the theoretical formalism in a simpler matrix form and in quest for standardizing a simpler molecular orbital method computing the charge rearrangement of Fukui in a reliable manner so that the method could be applied to larger systems, found that the CNDO/2D formalism is quite reliable for the said purpose.

1.5 The present day thinking of formation of adduct molecules by addition of a Lewis acid and a Lewis base.

With passage of time the thinking in chemistry has been receiving the tone of sophistication. Although the chemists are involved in the same process of making and breaking of bonds and majority of chemical thinking is centered around the lone pair and bond pair, acid and base, the sophistication of the physico–chemical methods and theoretical formalisms is anybody’s guess. The same chemical phenomenon— the reaction between a Lewis acid and a Lewis base forming the adduct molecule has been remodeled as a formation of a supermolecule (adduct) or supersystem by the interaction of two sub–systems.

1.6 Frontier electron theory of chemical reactivity

Acid–base interaction may be divided in two types [14] – charge controlled reaction and frontier controlled reaction. The later is discussed below. Lewis acid like BF$_3$, BH$_3$
occurs in a planar (D$_{3h}$) form at the ground state but reorganizes to pyramidal (C$_{3v}$) shape in response to chemical attack of Lewis bases. This transformation of molecular shape is associated with the changes in all the intrinsic fundamental properties of molecules [42]. The theoretical models in quest of discovering surprising quantities fundamentally controlling the equilibrium shapes of molecules are:— (I) the rules of Walsh [43] based upon the Jahn–Teller effect and the energetic behavior of HOMO on distortion, (ii) the HOMO postulate of Deb [44] within the frame–work of electrostatic Hellmann–Feynman theorem, and (iii) the symmetry rules of Pearson [45]. These theoretical models seems to have explored that the factors like energetic behavior, alteration of electron populations in, and change in symmetry type of the HOMO, and the change in symmetry type and the energetic behavior of the LUMO, on distortion of geometry largely determine the equilibrium shapes of molecules. Fukui, [34,46] the proponent of frontier orbital theory, first noticed the prominent role of the frontier orbitals in governing chemical reactions to the extent that the HOMO and LUMO solely determine the reaction path. Recent investigations have revealed that the height of the energy gap between the HOMO and LUMO is an important stability index of molecules [47-50] The theoreticians engaged in calculating the electronic structures and energies with the paradigm of MO theory, seems to converge to the opinion that the most stable structure has the largest HOMO–LUMO energy gap. A large gap implies high stability and small gap implies low stability. The high stability in turn indicates low chemical reactivity and small gap predicts that the system should be highly chemically sensitive, responsive, structurally unstable and fluxional. Ghosh and Jana [51] have justified the order of chemical reactivity of a series of structurally related compounds in terms of the computed values of global hardness and energy gap between
the highest occupied molecular orbitals, HOMO, and the lowest unoccupied molecular orbitals, LUMO. Ghosh and Jana [42] have studied the change in reactivity of BH$_3$ and BF$_3$ molecule (both are Lewis acids) with reorganization of geometry from planar ($D_{3h}$) to pyramidal ($C_{3v}$) in terms of molecular orbital theory and DFT. They have concluded that the reactivity is not a steric, but a dynamic concept.

1.7 Density Descriptor Approach to the hard–soft acid–base interaction and charge transfer

We have already discussed the method of Fukui et al [32-33] regarding the origin and mechanism of charge transfer and binding of EDA complexes. Now let us study the hard–soft acid–base behaviour of the chemical systems – acceptors and the donors in the light of density functional theory. The qualitative hard–soft acid base concept of Pearson has been quantified by Parr and Pearson [31,52,53] by the application of the Density Functional Theory, DFT, of Hohenberg and Kohn [54]. DFT has emerged as a very powerful theory of electronic structure of atoms and molecules because of its simplicity and computation friendly nature. Parr, Pearson [31] have invoked the DFT to define hardness as a measure of resistance to change of the electron cloud of a chemical system and global hardness ($\eta$) acts as a good stability scale to find the stability among the molecules. Parr and coworkers, while working with DFT, discovered a new theoretical concept like electronic chemical potential ($\mu$)[52]. The theory provides numerical values of hardness parameter, and its inverse concept, the softness parameter ($S$), to molecules to estimate their intrinsic hardness or softness, and also to determine the relative order of hardness and chemical reactivity of a series of molecules.
The density functional theory gains momentum after the introduction of the principle of maximum hardness, PMH [55], which states that the chemical systems evolve towards the state of minimum softness or maximum hardness. It is established that when a system evolves toward a state of greater hardness, its stability increases, and when it evolves toward a state of lower hardness, its stability decreases. Thus, the thermodynamic stability of a molecular configuration and its global hardness are directly related and proportional to each other. The implication of PMH is that the global hardness of a molecule decreases along the reaction path and is minimum at the transition state. The PMH has been found to be valid in case of structural changes in molecules caused by deformation of structure [56]. It is a general observation that the interacting chemical systems necessarily reorganize their geometry prior to chemical reaction and the changes hardness quantities as a function of structural reorganization. The change in hardness during reorganization generates hardness profile, which is certainly very useful tool to analyze the interaction between different chemical species [57]. It transpires from the above discussions that the hardness quantities of a molecule are not constant and absolute rather these are variable parameters and are continuous functions of conformations obtained by a continuous evolution of the geometry of molecules. The donors as well as acceptors evolve towards the unstable non-equilibrium conformations through a physical process of reorganization of their equilibrium shapes as a condition precedent to occur the chemical event of charge transfer and bond formation. Such a transition in molecular geometry is associated with concomitant decrease in HOMO–LUMO energy gap and global hardness entailing an increase in chemical reactivity of molecules. The increase in chemical activity of electron pair donors, the Lewis bases, must be associated with the increase in their
ability to donate electron density and such a condition of increased ability of Lewis bases to donate charge density is computed in terms of increase in the chemical potential of the density functional theory. It is predicted in terms of density functional theory that the chemical potential (a measurement of escaping tendency of electron from a species) of the acceptor be smaller than that of the donor be larger and as soon as the charge transfer begins, the chemical potential of the donor starts decreasing and that of the acceptor starts increasing and the process of charge transfer continues till the chemical potentials of the donor, acceptor and the adduct become equal [53,58] i.e. charge transfer takes place between two species following chemical potential equalization principle.

1.8 Local Density Functional Approach

Parallel to the above developments with global quantities, the local quantities—the concepts of a local softness and hardness have emerged where the principle of hardness and softness has been invoked in a local sense in order to explain, in terms of density functional definition of fukui function \( f \), the response of a chemical system to different kinds of reagents.

It is well−known that the different parts of a molecule have different reactivities [53]. While chemical potential is constant everywhere within a molecule, the hardness is not constant rather it is a function of position [59]. Although the definition of local hardness is ambiguous, the local softness has been defined clearly [60]. The fukui function, \( f \), [34] is a local quantity and has different values at different points in a chemical species. Parr and Yang [61,62] have demonstrated that most of the frontier orbital theory of chemical reactivity can be rationalized from DFT of electronic
structure and it has been shown that the reactive sites in a molecule are determined by fukui function $f$.

In the case where electron transfer is important, chemical reaction occurs at the site where $f$ has its largest value. Thus the frontier electron theory of chemical reactivity transcribes into a postulate that $f(r)$ determines site selectivity in chemical reaction. In this study of donor–acceptor complexes of BF$_3$ the molecule is not only acting as a Lewis acid for receiving electrons in the LUMO but also a simultaneous back–donation from HOMO is equally important and the summation of the opposing two processes is the actual chemical activity of the molecule [32,33,41,63]. Now associating concept of hardness and fukui function with the theory of chemical reactivity in molecules the concept of local softness $\sigma(r)$ of an orbital is obtained.

According to Parr and Yang [61-62] the softest atom is the most reactive atom to the electrophilic and nucleophilic attack. This general statement was verified by several groups [64-67] of scientists. Later, Gázquez and Mendez, [68] from the atom in a molecule viewpoint, showed that the energy of stabilization between two reacting systems A and L is greater if the fukui functions of the reacting atoms in molecules A and L are greater, and also interaction between A and L does not necessarily occur through the softest atoms of A and L, but through those atoms whose fukui functions are approximately equal.

In deriving the equality of fukui functions, the global HSAB principle was assumed i.e. global softness of A ($S_A$) was assumed to be equal to that of L ($S_L$). Under these conditions the local softness of atom k in A is also equal to that of atom l in L.

In another test of local HSAB principle with a number of reacting systems of different global softness, it is found that the local HSAB principle is satisfied and the
equality of Fukui functions of the atoms participating in the reaction is not the same as equality of local softness [69]. The local parameters will be discussed later (vide infra, CHAPTER 4) in details.

1.9 The quantum chemical methods investigating theoretically the donor–acceptor interactions and stability of the complexes

In the quest for exploring the characteristics of the donor–acceptor interactions and the nature of the complexes formed by them, a number of theoretical models were suggested and extensive works have been reported. Fukui et al [32-33] carried out an ab initio molecular orbital calculation of the addition compound of boron hydride and ammonia and carbon monoxide. The origin of charge transfer and bond formation between the two interacting species has been computed in a straightforward way whereas the ordinary SCF method calculates the net balance sheet of charge in which the origin and the mechanism of charge transfer is not very straightforward. The mechanism of the formation of the donor–acceptor complexes through a process of charge transfer is transparent in this method and it deserves a special mention in connection with a theoretical study of the chemical event of the formation of the donor–acceptor complexes. Morokuma and Umeyama [35] performed the molecular orbital studies of electron donor–acceptor (EDA) complexes where interaction energies of the strong EDA complexes were analyzed in terms of electrostatic, exchange, polarization and charge transfer components as functions of intermolecular separation and orientation. Decompositions of intermolecular forces and charge distributions were also performed. The four parameters conjointly tell the whole story of the donor–acceptor complexes but the charge transfer and electrostatic effect are the dominating. Redmon et al. [71] calculated the accurate heat of formation of a number of complexes by
exploiting the many body perturbation theory (MBPT) which carefully takes into account the electronic correlation effects. But it is mentioned by Redmon et al. that, although the method calculates the accurate heat of formation, the procedure is extremely difficult. Zirz et al. [72] showed that theoretical computation of the binding energy is a difficult case. The reaction energy, $\Delta E$ is investigated for donor–acceptor type interaction reaction by means of large scale ab initio calculations. The $\Delta E$ values obtained in the usual way or by the counter poise method reveal serious basis saturation problems if an accuracy of 1 Kcal mol$^{-1}$ are desired for $\Delta E$.

Bonaccorsi et al.[73] analyzed the interaction energy in molecular interactions by the use of a MO polarized basis. The interaction energy decomposition scheme proposed by Morokuma which gives more emphasis to polarized MOs is presented and tested. A more systematic utilization of polarized MOs, i.e., of orbitals of the interacting molecules computed with the SCF formalism in the coulombic field of the other molecular components of the system, is adopted and the connection of this decomposition of the supermolecule interaction energy with perturbation approaches utilizing such polarized MOs is discussed. Bonaccorsi et al.[74] made the counter poise corrections to the components of bimolecular energy interactions. Where counter poise corrections for the basis set superposition error to the components of the bimolecular interaction energy are defined for three methods of decomposition. Cammi et al.[75] by the counter poise corrections evaluated the bimolecular interaction energy components. Counter poise corrections to the coupling terms of the bimolecular interaction energy decomposition are introduced and examined on a set of electron donor–acceptor dimers. Cioslowski [76] proposed a new population analysis, based on atomic polar tensors, which provides values of atomic charges in molecules. The atomic charge is
related to trace of the corresponding atomic polar tensor (tensor of the derivatives of
dipole moment with respect to atomic Cartesian coordinates). The resulting electron
populations are independent of any direct reference to the basis set used, and they can
be calculated for both Hartree–Fock and correlated wave functions. The charges are
computed for several molecules and compared with the results of Mulliken [12,70]
population analysis.

Allen et al.[77] devised a new quantum mechanical operator whose expectation
value is the difference in average one–electron energy for canonical Hartree–Fock
wave functions between the valence shells of atom A and bonded atom L in a molecule
or solid. Elaborate CI wave functions or simple semi–empirical schemes may be
fruitful. This operator obtains the polarity for bond AL and quantifies the concept of
"ionic character" introduced by Pauling [3] about 70 years ago and long desired by
organic and inorganic chemists. Røeggen [78] studied the electron donor–acceptor
(EDA) complexes by applying an extended geminal model. The changes in the one
electron density during the formation of the complexes are analyzed in terms of charge
centroids and charge ellipsoids of the of the (localized) geminal densities. The
intermolecular potential is decomposed into a sum of distortion energies for the
subsystems and the interaction energy between the distorted subsystems. The latter
term is decomposed into a coulombic, exchange and correlation part where the
coulombic component is further partitioned into an electrostatic and induction
component. Again, the strongly bonded EDA complexes are compared with the H–
bonded systems and the weakly bonded EDA complexes. For all the complexes the
coulombic part is found to be the dominating attractive term. The apportioning of the
coulombic term shows that the induction component is larger in magnitude than the electrostatic one for all the systems.

Holme et al [79] tested the density functional theory for dative bonding systems. Density functional calculations are carried out on donor–acceptor type complex and compared with experimental and *ab-initio* theoretical data. Calculations that use non-local exchange–correlation potentials are capable of providing excellent geometries, dative bond energies and dipole moments, as well as adequate estimates of vibrational frequencies and barriers to internal rotations. The local density approximation can provide reasonable structure information, but significantly overestimates the dative bond energy, without perturbative non–local corrections. Glendening and Streitwieser [80] presented a procedure for partitioning the Hartree–Fock self–consistent–field (SCF) interaction energy into electrostatic, charge transfer and deformation components with application to weak hydrogen bonding, strong ionic and moderate donor–acceptor interactions. The natural bond orbital (NBO) approach of Weinhold and coworkers is employed to construct intermediate supermolecule and fragment wave functions that satisfy the Pauli exclusion principle, thereby avoiding the principal deficiency of the popular Kitaura–Morokuma energy decomposition scheme. The function counter poise method of Boys and Bernardi enters the procedure naturally, providing an estimate of basis set superposition error (BSSE). They showed that the energy components exhibit little basis set dependence when BSSE is small. Electrostatic interaction is found to dominate the long–range region of the potential energy surface and charge transfer is strongly stabilizing for fragments within van der Waals contact.

There have been several attempts to elucidate the nature of the donor–acceptor interactions by physical partitioning of the SCF interaction energies into physically
intuitive components. In this approach the interaction energy is usually obtained from the "supermolecule" calculations. For two interacting chemical species A and L it is given as follows:

$$\Delta E = E(A - L) - E(A) - E(L)$$

where $E(A-L)$ is supermolecule, $E(A)$ and $E(L)$ are isolated subsystems. Such a partitioning attempt of interaction energy dates back the work of:-

(I) Coulson [81]

(II) Kitaura and Morokuma [82]

(III) Morokuma and Umeyama [35]

(IV) Glendening and Streitwieser [80]

(V) Korchowiec and Uchimaru [83]

The interaction energy was decomposed into various components—1. electrostatic 2. Polarization 3. Dispersion 4. Exchange and 5. charge transfer. However, such supermolecule approach necessitates the accurate calculation of $E_{\text{INT}}$ or binding energy or heat of formation of supersystem. But such supermolecule approach gives a little information about the origin of physical nature of the interaction between the subsystems leading to the formation of supersystem. Redmon and Pervis [71] pointed out that the accurate computation of binding energy of supermolecule is only possible through many body perturbation calculations, which is a very sophisticated and difficult method.

In the present venture we are not after computing anything very accurately. We are after conceptual aspects of donor-acceptor interactions. Our main interest is to study the variation of the chemical reactivity of the subsystems—donors and acceptors, with the reorganization of geometries which occur inevitably prior to the event of chemical
reaction computed in terms of density functional descriptors, and also to study the mechanism of charge transfer and bond formation by the reorganized or activated subsystems.

"Theoretical models we rely on are the method of configuration interaction developed by Fukui and the density functional descriptors like chemical potential, global hardness, local softness and fukui functions."

References:

81. C. A, Coulson, Research (London), 1957, 10, 149.