SOME FORMAL ASPECTS OF CHEMICAL HARDNESS AND ITS RELATION WITH ENERGIES AND MOLECULAR PROPERTIES

Thesis submitted to the
University of Poona
for the degree of
DOCTOR OF PHILOSOPHY

in

CHEMISTRY

By

RAM KINKAR ROY

Physical Chemistry Division
National Chemical Laboratory
Pune - 411008, India.

September 1995

CERTIFICATE

Certified that the work incorporated in this thesis entitled SOME FORMAL ASPECTS OF CHEMICAL HARDNESS AND ITS RELATION WITH ENERGIES AND MOLECULAR PROPERTIES was carried out by the candidate under my supervision. Such material as has been obtained from other sources has been duly acknowledged in the thesis.

Date : 22/9/95

Place : Pune

(Dr. Sourav Pal)

DEDICATED TO MY SISTER

REBA

LIST OF PUBLICATIONS DURING THE COURSE OF THE PRESENT WORK

1. **Maximum hardness : An ab initio study.**
   Sourav Pal, Nayana Vaval and Ram Kinkar Roy ;
   J. Phys. Chem. 1993, 97, 4404.

2. Stationary multideterminantal coupled-cluster response.
   Nayana Vaval, Ram Kinkar Roy and Sourav Pal ;
   Phys. Rev. A. 1994, 49, 1623.

3. Change of hardness and chemical potential in chemical binding.
   Sourav Pal, Ram Kinkar Roy and A.K.Chandra ;
   J. Phys. Chem. 1994, 98, 2314.

4. Correlation of polarizability, hardness and electronegativity : Polyatomic molecules.
   Ram Kinkar Roy, A.K. Chandra and Sourav Pal ;
   J. Phys. Chem. 1994, 98, 10447.

5. Hardness as a function of polarizability in a reaction profile.
   Ram Kinkar Roy, A.K. Chandra and Sourav Pal ;
   J. Mol. Struc. (Theochem.) 1995, 331, 261.

6. Behaviour of operational hardness : A critical study.
   Sourav Pal, A.K. Chandra and Ram Kinkar Roy ;
   J. Mol. Struc. (Theochem.) [accepted for publication].

7. Chemical potential and hardness for open shell radicals : Model for the corresponding anions.
   Ram Kinkar Roy and Sourav Pal ;
   J. Phys. Chem. (submitted).

ACKNOWLEDGEMENTS

It gives me great pleasure to express my deep sense of gratitude towards Dr. Sourav Pal, Scientist, Physical Chemistry Division, National Chemical Laboratory, Pune for his able guidance and incessant encouragement and cooperation extended to me in every respect at all phases of my doctoral work. His sincere and untiring involvement in the minutest of the details has given this thesis the present form. I am greatly indebted to him.

I am, in particular, thankful to Dr. Asit Chandra for his thought-provoking discussion with me. I also have great pleasure in extending my sincere thanks to my colleagues Nayana, Sampada, Aparna, Shailaja, Ramesh, Mahesh, Dr. Abhijit Chatterjee, Alka etc. for their cheerful and hearty cooperation.

Sincere thanks are also due to Binod, Arnab, Nikhil, Tusar, Tapas, Debashis, Abhijeet (Manna), Biswajeet and numerous other friends in N.C.L., who helped me to lead a enjoyable life during last four years.

I am deeply indebted to my parents and other family members for their constant encouragement and cooperation that have enabled me to complete this work.

I am also thankful to Prof. P. Ganguly, Head, Physical Chemistry Division, for his interest, encouragement and useful suggestions during various discussions.

Finally I thank Dr. P. Ratnasamy, Director, National Chemical Laboratory, Pune for his moral support and grant of permission to submit this work in the form of the present Thesis. I also gratefully acknowledge the Council of Scientific and Industrial Research , EMR section, Govt. of India, for financial assistance.

R. K. Roy

(R. K. ROY)

CONTENTS

CHAPTER 1 : INTRODUCTION

CHAPTER 2 : CORRELATION OF POLARIZABILITY AND HARDNESS IN POLYATOMIC MOLECULES

CHAPTER 3 : THE STABILITY OF A CHEMICAL SPECIES AND THE PRINCIPLE OF MAXIMUM HARDNESS (PMH)

CHAPTER 4 : BEHAVIOUR OF OPERATIONAL HARDNESS AND CHEMICAL POTENTIAL IN CHEMICAL BINDING

CHAPTER 5 : CHEMICAL POTENTIAL AND HARDNESS FOR OPEN SHELL RADICALS : MODEL FOR THE CORRESPONDING ANIONS

CHAPTER 6 : CONCLUSION

SYNOPSIS

The thesis comprises of some novel formal developments as well as application of the concept of chemical hardness (η) and chemical potential (μ). Though the concept of hardness is familiar in qualitative chemistry since early fifties, quantitative developments in this direction started only from early eighties. This includes analytical - followed by operational definition of hardness, which helped in rank-ordering of the chemical systems in hardness scale. Other important achievements in this direction are evaluation of hardness as transferable parameters, establishing semiqualitative relation of hardness (or softness) with polarizability and electronegativity, proposition of the principle of maximum hardness (PMH) (Parr and Chattaraj, 1991). While some of them are well established and widely accepted by chemist community, some are still in their formative stage. I have tried to address some of these features in the background of my own contribution in this thesis.

Chapter 1 gives the introductory background of the thesis. This starts from an elementary introduction of the concept of hardness and then focuses on the gradual developments of the concept from qualitative nature to the quantitative rigor, which was possible through the introduction of density functional theory based work. Motivation behind the studies, made in this thesis, has also been carefully addressed. One important empirical principle where the concept of hardness has been useful is Hard - Soft Acid and Base principle (HSAB). We discuss the recent theoretical studies of HSAB principle by Chattaraj et al

(Chattaraj et al, 1991), Chattaraj and Schleyer (Chattaraj and Schleyer, 1994), Chattaraj and Nath (Chattaraj and Nath, 1994) and Langenaeker et al (Langenaeker et al, 1992) in the context of the principle of maximum hardness (PMH). The recent efforts to correlate hardness with other chemical parameters e.g. electronegativity, polarizability, molecular valency (Chattaraj et al, 1994 ; Chandra, 1994) have also been highlighted.

Hardness (or softness, $1/2\eta$) follows from a series of other previously established qualitative concepts like polarizability, electronegativity ($\varkappa$), electron affinity, ionization potential, stability constants etc. So empirical relation of η or $1/2\eta$ with these other qualitative parameters are expected - which also have been studied from time to time. So far these studies are limited to atoms, atomic clusters and carbon clusters. In particular relation of η with polarizability, electronegativity and volume of molecules has not been tested so far. In Chapter 2, some empirical relation of η with polarizability (P) has been established. The variation of η and P with bond distances comprising of atoms having different electronegativities has also been established. From an analytical description of the polarizability its dependence on the number of electrons, atomic radius (or molecular dimension in case of molecules), HOMO - LUMO energy gap etc. has been examined. These helped in explaining our observed results i.e. why bond distance has direct relation with polarizability and inverse relation with chemical hardness in all the systems studied by us (Roy et al, 1994, 1995). Our results for polyatomic molecules also establish the identical relation between P and η as that of atoms and atomic clusters – though some sort of nonlinearity is observed in the molecular cases. The enhancement of the nonlinear effect, as observed in the relation of P and r (bond distance) as also of η and r with increasing bond distance, has been rationalized through Taylor´s series expansion. It has been speculated that the ´local bond hardness´ concept can explain the results in a more generalized fashion.

The Principle of Maximum Hardness (PMH) and the corresponding numerical demonstrations are the contents of Chapter 3. It should be mentioned that PMH was first stated in a philosophical manner by Pearson (Pearson, 1987) and later on proved rigorously by Parr and Chattaraj (Parr and Chattaraj, 1991) with the help of fluctuation - dissipation theorem of statistical mechanics. The rigorous definition of PMH states that ´at constant μ (chemical potential), v (potential due to nuclei plus any other external potential) and T (temperature) any chemical system evolves to a state of maximum hardness´. Subsequently there are efforts to verify the principle through numerical demonstrations. Datta (Datta, 1992) studied two cases e.g. the inversion (umbrella effect) of NH_3 molecule and the intermolecular proton transfer of malonaldehyde. Using MNDO level of calculation he showed that the hardness becomes minimum at the transition state – which is farthest from the equilibrium. But in his test none of μ and v remains constant because of the large variation of the geometry. Pearson and Palke (Pearson and Palke, 1992), using ab initio SCF method, have shown that for small asymmetric distortion along vibrational symmetry coordinates, hardness becomes maximum at equilibrium geometry in NH_3 and C_2H_6 molecules. But this does not hold true for symmetric stretching, in which case there is a comparable change in μ.

The constraint of constant v creates some confusion in testing the validity of PMH. As a practice it is very difficult (though not always impossible) to keep v constant. We showed (Pal et al, 1993) that indeed for asymmetric stretching, the chemical potential remains constant and thus such stretching can define a domain where the principle can be tested. The level of our calculation, presented in this thesis is the most extensive attempted so far. Our calculation of ionization potential and electron affinity are of near full CI level (multireference coupled cluster singles and doubles, i.e. MRCCSD). Using H_2O and NH_3 as typical examples we have observed that the PMH is valid in case of small asymmetric distortion around equilibrium geometry. In case of symmetric distortion there is no maxima of η at equilibrium point as none of μ and v remain constant in this case.

We have also extended our study to the case of symmetric and asymmetric distortion from a nonequilibrium (linear) geometry of H_2O (having ∠HOH = 180° and O-H bond distances same as that of stable equilibrium geometry i.e. 1.8091 au). In this case also we have seen that PMH holds true only for asymmetric distortion. Scaning some equichemical potential points around both stable equilibrium geometry and symmetric but nonstable linear geometry we have shown that hardness always becomes larger in the former case. The maximum of hardness is found for the most stable global equilibrium geometry though there are large changes in v among these points. This naturally raises the question of whether the constraint of constant v is a rigorous condition in defining the PMH. In the concluding chapter (chapter 6) we will discuss more elaborately on this issue.

In chapter 4 we have developed a novel formalism and used that to find out the changes in hardness and chemical potential with the energetics of the systems in general cases. Starting from a finite difference approximation of chemical hardness (which we call an operational definition of hardness), we show a simple general relation of operational hardness with the energies of neutral and corresponding mono - positive and negative ions (Pal et al, 1994). This can explain and rationalise the change of the hardness in a reaction surface. For example the observation of Gázquez et al (Gázquez et al, 1993), that for diatomic molecules there is no maxima in the hardness profile and the hardness values go on increasing as the bond is contracted beyond equilibrium distance, can nicely be explained by our model. It also explains the apparent anomalous results of existence of two hardness values corresponding to a single binding energy of a diatomic molecule. Our model suggests that the global hardness of a collection of noninteracting atoms of the same type is just the absolute hardness of a single atom. As a corollary to the formulae proposed, we observe that at constant chemical potential, the maximum of this hardness corresponds to maximum IP or minimum EA.

The operational definition of hardness (η) in terms of frontier orbital energies i.e. of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), poses some problem for open shell systems. In open shell cases where electrons are distributed either in degenerate or quasidegenerate orbitals, both the HOMO and LUMO will have energies either same or the difference will be unrealistically small. However, the hardness values for free radicals, are important because they can be used as model systems for the corresponding anions (Pearson, 1988). The η and μ of the anionic species are otherwise very difficult to evaluate, because of the problem of finding out the EA values. This point has been discussed in detail in Chapter 5. By using ΔSCF method η and μ of some open - shell free radicals are evaluated (Roy and Pal, 1995). The reliability of these results are critically analysed through comparison with the η and μ values calculated from experimental IPs and EAs. This also leads us to the reliability of ΔSCF procedure as these values show the proper rank ordering of the corresponding anions. The possible ways of improving the results and the problem of comparing with the exact experimental results are also pointed out.

Chapter 6 is the conclusive part of the thesis. This chapter presents an overview of the hardness concept with its merits - demerits, rigor - flexibility, analytic nature and empiricism etc.

The potential new areas, where hardness concept can be useful to extract chemical information, are also discussed. Very recenty Sebastian (Sebastian, 1994) has argued that the proof of PMH, given by Parr and Chattaraj through fluctuation - dissipation theorem of statistical mechanics, is not true in general and is valid only for particular type of ensemble distribution. In this background there is a tremendous scope for a critical re-examination of issues in this area. It is important to define more clearly the conditions of such a maximum hardness principle and rationalize the numerical results thus far available including the ones presented in this thesis. In particular, the validity of PMH in cases where there is a large change in v is still a matter of ambiguity. Pearson (Pearson, 1993) have argued that the validity of PMH depends on the rigorous condition of constant v. For example in case of isomeric transformation where v changes drastically from one form to another, PMH can not be used as a measure of stability. In such cases the nuclear repulsion term may be a dominating factor accounting for the relative stability of the isomeric forms. In this respect we have some numerical results on NOH-HNO isomers which will be presented. The results show that there is no maxima of η even at the most stable equilibrium geometry where total energy is minimum (Pal <u>et</u> <u>al</u>, 1995). Parr (Parr and Zhou, 1993) is of the opinion that at this stage the PMH is applied to cases where there are regular changes in v. However, he feels that a broader principle of maximum hardness may exist. Our study on H_2O presented in chapter 3 (Pal <u>et</u> <u>al</u>, 1993) indeed shows such a possibility. But this requires careful future study. In the conclusion we also point out to a recent paper by Chattaraj et al (Chattaraj et al, 1995), where they have laid down some conditions for validity of PMH. These will be the focus of examination and discussion in future.

CHAPTER 1

INTRODUCTION

1.1 HARDNESS AND SOFTNESS -- A USEFUL CONCEPT

The concept of chemical hardness has been of great interest in recent years. The idea of ´hard´ and ´soft´ species existed much earlier. These two terms were introduced to explain the behaviour of acid-base reactions. These terms were later used for classification of any general chemical species. After the introduction of HSAB principle by Pearson (Pearson, 1963) chemical species were classified in ´soft´, ´hard´ and ´borderline´ categories. These concepts were primarily used in qualitative understanding of chemical reaction and the behaviour of chemical species. Attempts have been made, at least in a qualitative level, to understand the trend of the ´softness´ and ´hardness´ changes with bond length, electronegativity, polarizability etc.

A strong breakthrough in the subject was achieved with the quantification of ´hardness´ or ´softness´ and since then excellent theoretical developments have taken place making these concepts more rigorous. Interest was generated primarily after a statement of the principle of maximum hardness (PMH) by Pearson (Pearson, 1987) pointing to a maximum stability criteria from maximum hardness among a class of system. A more detailed statement will be given later. The proof of Parr and Chattaraj (Parr and Chattaraj, 1991) lent credibility to the statement. Since then, however, there have been several studies on the PMH and its generality.

This thesis will deal with studies at qualitative level establishing relation of chemical hardness with properties for molecular systems for the first time. A quantitative definition of hardness (operational hardness) using the energies of the N, (N+1) and (N-1) particles has been used. In this thesis we have also undertaken a very detailed study of different aspects of PMH and the conditions thereof. We have attempted to come to conclusions, which we hope will be useful in this area. Our study will make a critical investigation on the trend of the operational hardness. The thesis also address the problem of a proper quantitative definition of hardness for open shell chemical species which have quasidegenerate states. These values are useful for rank ordering of the corresponding anionic species.

In this chapter we present a background of the work contained in this thesis by reviewing the early concepts in this area. The review traces the history of the development of hardness and softness starting from their relevance in acid-base reactions. The review finally brings us to the more recent developments and applications. This will place the work of the thesis, to be presented from chapter 2 onwards, in the correct perspective.

1.2 QUALITATIVE DEVELOPMENTS OF HARD-SOFT CONCEPT - EARLY DAYS

The earliest observation which leads to hard and soft concepts to chemical species and the recent version of it i.e. chemical (or absolute) hardness, goes back to the days of Berzelius. He first noted that some of the metals exist in nature as sulphide ores (e.g. Cd, Cu, Hg) and some as oxide ores (Ca, Mg, Fe). To give a quantitative explanation, the differrence of cohesive energies of the corresponding binary metal oxides and sulphides are used. The cohesive energy ($\Delta H^{\emptyset}$) is defined as,

$$E_{MX_{(S)}} = E_{M_{(g)}} + E_{X_{(g)}} + \Delta H^{\emptyset} \qquad 1.1$$

The cohesive energies of oxides are always greater than those of sulphides. But the difference of the cohesive energies of oxides and sulphides ($\Delta = \Delta H^{\emptyset}_{oxide} - \Delta H^{\emptyset}_{sulphide}$) varies from metal to metal. For Mg, this difference is 54 kcal/mol and for Hg it is as small as 1 kcal/mol. If we arrange the common bivalent metals in decreasing order of Δ then it will be as follows,

$$Mg^{2+} > Fe^{2+} > Ca^{2+} > Zn^{2+} > Pb^{2+} > Cu^{2+} > Cd^{2+} > Hg^{2+}$$

This order indicates that the most stable oxide is that of Mg and the most stable sulphide is that of Hg.

Although the explanation of the relative stabilities of oxides and sulphides of different metals on the basis of the difference of cohesive energies is satisfactory, this explanation is superficial because it is merely a conclusion from the observed results. No suitable explanation could be given until 1940´s due to the lack of knowledge of structure of atoms and molecules and also that of nature of chemical bonds. The first detailed explanation on the basis of electronic structure theory was given by R.S. Mulliken (Mulliken, 1952a). Mulliken, while working on molecular compounds and their spectra (i.e. origin of colour), agreed with Brackmann´s view that the molecular complex formed is due to ´complex resonance´ i.e. quantum mechanical resonance between a ´no bond´ structure and a structure arising from the formation of bond between the two partners A and B. Mulliken went one step ahead by suggesting that the bond between A and B is predominantly ionic in character with a single electron transfer from the Lewis base B to the Lewis acid A. With the help of quantum mechanical formulation, Mulliken also explained the stability of the molecular complex A.B or indirectly the strength of Lewis acid A and base B. He argued that stability of the complex A.B increases with the increasing heat of formation from A and B, which in turn depends upon the resonance energy (i.e. resonance between the no bond and ionic bond structure of A and B). From the corresponding energy profiles of the no bond and ionic bond structures, he concluded that the smaller the IP_B^{vert} (vertical ionization potential of base B) and larger the EA_A^{vert} (vertical electron affinity of acid A) the more is the resonance, which implies greater strength of Lewis acid A and base B.

Mulliken also showed that when both A and B are soft chemical species (by ´soft´ he wanted to mean less exchange repulsion between the two) the resultant compound A.B is more stable than in the case when both of them are hard species (again by ´hard´ he wanted to mean more exchange repulsion between them). So, according to him "softness in A or B, respectively, should tend to make it a better acid or base". On the basis of above definition of "softness" or "hardness" he also explained the ´exothermicity´ and ´endothermicity´ of the molecular compound A.B .

It is clear that Mulliken attributed the stability of the compound AB on the basis of softness of both the partners A and B. According to Mulliken (Mulliken, 1952a), the complex will be unstable when both the partners are 'hard'. But these definitions of 'soft' and 'hard' on the basis of exchange repulsion are not directly related to the electronic structure theory. That the softness or hardness is related to the IP_B^{vert} and EA_A^{vert}, was not pointed out by him. He discussed the stability of the compound A.B when both A and B are either 'soft' or 'hard' - without indicating the cases when one of them is soft and the other is hard. This is necessary in explaining the relative stabilities of the compounds formed by an A with different B or vice versa (e.g. MgO and MgS or MgS and HgS). He concluded that the compound A.B will be unstable if both A and B are hard. Future study reveals that this is not true. In section 1.4 we will discuss, in detail, the factors on which the stability of the compound A.B depends.

Mulliken tried to explain the 'hardness' or 'softness' depending on the thermodynamic stability i.e. based on equilibrium data. There are some related works, based on rate data, which also led to the foundation of the concept of chemical hardness. Those are by Edwards (Edwards, 1954) and independently by Schwarzenbach (Schwarzenbach, 1954) and Ahrland et al (Ahrland et al, 1958). Edwards presented a new equation for correlating the reactions of electron donors and defined a new nucleophilic scale based on electrode potential. He compared the reaction rates of various substrates with the same ligand. This comparison was made by taking the help of nucleophilic constant, characteristic of a donor and relative basicity of the donor to protons.

Schwarzenbach (Schwarzenbach, 1954) as also Ahrland et al (Ahrland et al, 1958) classified the metal ions into two classes. Their classification was based on the relative affinities of the metal ions for ligands having donor atoms from different groups and periods of the periodic table. For class (a) metal ions, the order of affinities are N >> P > As > Sb ; O >> S > Se > Te and F > Cl > Br > I ; class (b) metal ions, N << P > As > Sb ; O << S < Se $\simeq$ Te ; F < Cl < Br < I . The reason for two different behaviour is that, most metals in their common valency states show the affinities to ligands like that of H^+. This implies that the affinities of the ligands for acceptors of class (a) run roughly parallel to their basicities. However there are some exceptions, particularly when steric and other factors become prominent. The class (b) character depends on the availability of lower d-orbital electrons of metals for facilitating dative π- bonding. This is the reason that class (b) metal ions form stable complexes with olefin. Affinities of acceptor for ligand atoms along a period could not be generalized because of the lack of data at that time.

Later on, Edwards (Edwards, 1956) revised his own work and showed that the nucleophilic constant term could be replaced by a polarizability term with equal success. With this development as also other information gathered so far, Edwards and Pearson (Edwards and Pearson, 1962) assigned three important factors in determining the reactivity of nucleophilic reagents to different substrates. These are the basicity, polarizability and the alpha effects (see footnote). The basicity is caused by the high -ve potential (due to high - ve charge cloud) on the nucleophile which is the characteristic of high electronegative species. The origin of polarizability of the nucleophile is the mixing of low - lying excited states with the ground states (this is called optical polarizability). As a result of this mixing, the charge cloud of the nucleophile will be diffused, which happens when the nucleophile is less electronegative.

1.3 PEARSON'S CLASSIFICATION OF LEWIS ACIDS AND BASES IN TERMS OF HARDNESS AND SOFTNESS

It is clear that the classification of Ahrland et al (Ahrland et al, 1958) for metal ions as (a) and (b) are analogous to the substrates of Edward and Pearson (Edward and Pearson, 1962). These substrates are sensitive to the proton basicity and polarizability respectively, in the nucleophile. From this understanding as well as the information collected from other sources, Pearson classified the Lewis acids in class (a) or hard acid, class (b) or soft acid and (c) borderline between these two (Pearson, 1963).

FOOTNOTE : The effect of basicity is generally observed for substrates which resembles proton in having high +ve charge and less number of outer orbital electrons of the central atom. Polarizability plays the key role in determining reactivity to substrates having low +ve charge and many electrons in the outer orbital of the central atom. the alpha effect (α-effect) is due to the presence of unshared pairs of electrons on the atom adjacent to the nucleophilic atom and is observed in general for all substrates.

The characteristics of class (a) acids are that they are small in size and are of high +ve oxidation state. The class (b) acids are of low or zero oxidation state and of large size. Since the features of class (a) acids lead to low polarizability and those of class (b) lead to high polarizability, the former are called ´hard´ and the latter are called the ´soft´ acids. These properties of Lewis acids helped Pearson to generalize that ´hard acids prefer to associate with hard bases and soft acids prefer soft bases´ - which is the famous HSAB principle.

Pearson also correlated other properties with polarizability (Pearson, 1963), which may thus be related to the two classes of behaviour (i.e. soft and hard) of acids and bases. For example, low IP is usually linked to high polarizability and high IP to low polarizability. So IP and the related electronegativity may be considered important factors in the identification of hard and soft behaviour. Apart from this, unsaturation - which enhances the possibility of acceptor π-bonding in the acid-base complex, ease of reduction favoring strong electron transfer to the acid are also associated with polarizability.

1.4 DIFFERENT THEORIES TO EXPLAIN THE HARD--SOFT BEHAVIOUR

With the help of different theories proposed by different investigators, Pearson also tried to assign reasons of hard and soft behaviour and to highlight the chemical features associated with them. These theories are the (a) ionic - covalent theory developed by Mulliken and Grinberg ; (b) the π- bonding theory developed by Chatt and co-workers; (c) electron correlation effects developped by Pitzer and Mulliken (d) the solvation theory by Parker.

Mulliken (Mulliken, 1952a, 1952b) developed the theory of covalent bonding which is suitable for the cases of soft-acids and soft-bases as discussed earlier. In this case bonding will be stronger if EA of the acid is larger and IP of base is lower (Weiss, 1942 ; see footnote). The bonding between hard acids and hard bases is assumed to be ionic, where high +ve charge and small size of Lewis acid would favour strong ionic bonding with the bases of large -ve charge and small size (Greenberg, 1962). From the theory of covalent bonding it is known that similar electronegativities of the bonded atoms favours strong covalent bonding. That is, the coulomb integrals on both the bonded atoms should be similar, and sizes of the bonding atomic orbitals should be similar to get good overlap (Coulson, 1937). On this consideration hard acids will prefer hard bases even when resonable covalency exists. Soft bases will mismatch with hard acids for good covalency, and ionic bonding will also be week because of the small charge or large size of the base.

According to π-bonding theory of Chatt (Chatt, 1950, 1956, 1955), the class (b) acids (soft acids) should have loosely bound outer d-orbital electrons which can form π-bonds with the basic

---

FOOTNOTE : Here softness in both acids and bases implies that the repulsive part of the potential energy curve rises less steeply than for hard acids and bases. This helps in closer approach and better overlap of the wave functions used in covalent bonding.

atoms of suitable ligands. These basic atoms must have empty d-orbitals to form π-back bonding. This is the characteristics of soft Lewis bases. The class (a) acids (hard acids) would tightly bound outer electrons as also the vacant empty orbitals, not too high in energy. These empty orbitals will form π-bond with the basic atoms of the ligands. But in this case the direction of electron transfer will be from basic atoms of ligands to the empty orbitals of the hard acids. It is obvious that π-bonding theory is based mainly on the study of metallic complexes.

Pitzer (Pitzer, 1955, 1956) and Mulliken (Mulliken, 1955) pointed to the different origins for electron correlation effects. According to Pitzer the origin is London or Van der Waals, dispersion forces between atoms or groups in the same molecule. Such London forces depend on the product of polarizabilities of the interacting groups and vary inversely with sixth power of the distance between them (Slater and Kirkwood, 1931). So it is clear that for Lewis acids of class (b) (i.e. soft) these forces are most effective. Mulliken assumed that the electron correlation results from the dπ - pπ hybridization. The result is that the π_{μ} bonding orbital become stronger because of increasing overlap and π_{g} antibonding orbital gets weaker with a decreasing overlap. With the help of an approximate MO calculation Mulliken (Mulliken, 1955) also explained why Lewis acids of class (a) cannot benefit from such π - bonding whereas that of (b) do the same.

The solvation theory (Parker, 1961, 1962 ; Miller and Parker 1961) explains why the class (a) and (b) characters in the gas phase are inverted in the solution phase. This obviously depends on the particular solvents as also the acids and bases being considered. But this theory can not explain the preferential formation of stable adduct between hard-hard and soft-soft species.

There are some further developments of the concept of 'hard' and 'soft' species by C.K. Jorgensen (Jorgensen, 1964). With the help of MO calculation he explained the symbiotic tendency of various ligands as also the tendency of complex metal cations to show class (a) behaviour at intermediate oxidation state and class (b) behaviour at low and high oxidation state. Basolo et al (Basolo et al, 1964) attributed the class (a) and (b) behaviour of some metal ions in metal - ligand complexes to steric factors. Klopman (Klopman, 1968) with the help of polyelectronic perturbation theory came to the conclusion that hard-hard interactions are charge - controlled and depend mainly on the ionic interaction of the reagents, whereas the soft-soft interaction is frontier orbital controlled and takes place when the two frontier orbitals (one from the acceptor and the other from the donor) are nearly degenerate. This is in line with earlier arguments proposed by Coulson (Coulson, 1937) and Greenberg (Greenberg, 1962).

1.5 DEFINITIONS OF HARD AND SOFT ACIDS AND BASES

From the above discussion, we can now classify hard and soft acids and bases as follows,

(a) Hard acid : High +ve charge, low polarizability and small size e.g. H^+, Al^{3+} etc.

(b) Hard base : High electronegativity, difficult to oxidize and low polarizability e.g. NH_3, H_2O etc.

(C) Soft acid : Low +ve charge, high polarizability, larger size e.g. Ag^+, Hg^{++} etc.

(d) Soft base : Low electronegativity, easily oxidizable and higher polarizability e.g. H^- , NH_2^-.

1.6 LACK OF RIGOUR OF THE QUALITATIVE DEFINITIONS -- NEED FOR A MORE QUANTITATIVE DEFINITION

But the common drawback of the above definitions of hard and soft behaviour of Lewis acids and bases is that there is no scale of hardness or softness of the chemical species by which we can arrange them in increasing or decreasing order. The hard and soft behaviours are discussed only on the basis of qualitative treatment, but exact theoretical expressions were not available. Though Klopman (Klopman, 1968) tried to establish a theoretical scale of hard and soft character, that scale was valid only for reactions in solution and also required the knowledge of other parameters e.g. dielectric constant, ionic radius etc. Advancement in this direction was possible only after the introduction of density functional theory (DFT), which can now be used to explain the hardness and softness as also several local quantities.

1.7 RIGOROUS DEFINITIONS

(a) CHEMICAL POTENTIAL AND ELECTRONEGATIVITY

Iczkowski and Margrave (Iczkowski and Margrave, 1961), in an important contribution to the literature of electronegativity have defined the electronegativity $\varkappa$ of a system by the following,

$$\varkappa = -(\partial E/\partial N)_v. \qquad 1.2$$

Again Parr et al (Parr et al, 1978) have shown that in the Hohenberg - Kohn theory the Lagrange multiplier (μ), used in enforcing the normalization constraint $N = N[\rho] = \int\rho(1)d\tau_1$, in the variation of energy with respect to the electron density can be written as $(\partial E/\partial N)_v$. This ($\mu$) is known to be chemical potential. From these two expressions of $\varkappa$ and μ they made the following identification :

$$\varkappa = -\mu = -(\partial E/\partial N)_v. \qquad 1.3$$

Now according to Mulliken's definition, $\varkappa_m = (IP + EA)/2$, and hence,

$$\mu = -(IP + EA)/2 = -\varkappa_m \qquad 1.4$$

which is just a finite difference approximation to $+(\partial E/\partial N)_v$.

(b) CHEMICAL HARDNESS

While the first derivative of E vs N is called the chemical potential' (electronegativity), the second one is known as 'hardness'. Parr and Pearson (Parr and Pearson, 1983) first recognised absolute hardness as a companion parameter to absolute electronegativity. They argued that for any atom or molecule, whether neutral or charged, the first derivative of E(N) with respect to the number of electrons N (keeping nuclear charge z fixed) is the chemical potential(μ) or negative of absolute electronegativity. Similarly the corresponding second derivative is hardness i.e.,

$$2\eta = (\partial\mu/\partial N)_z = -(\partial\chi/\partial N)_z = (\partial^2 E/\partial N^2)_z \qquad 1.5$$

To offer a physical meaning of hardness, they considered the disproportionation reaction in which an electron is taken from S and given to S :

$$\dot{S} + \dot{S} \longrightarrow S^+ + \ddot{S}^- \qquad 1.6$$

The corresponding energy change is given by $\Delta E_s = IP_s - EA_s$, which is called the hardness. Small or zero hardness means that it is easy for electrons to go from S to S ; that is, S is a soft species. Since IP_S is always greater than or equal to EA_S, as shown by Nalewajski and Capitani (Nalewajski and Capitani, 1982), the minimum value of hardness is zero. Zero hardness constitutes maximum softness, which means (as it should) no energy change associated with the disproportionation reaction just shown. A bulk metal has IP = EA, $\eta = 0$ and so maximum softness.

The nonchemical meaning of the hardness is the resistance to deformation or change. Equation 1.5 shows that chemical hardness is resistance of the chemical potential to change in the number of electrons. Utilizing the newly defined concept of hardness, Parr and Pearson (Parr and Pearson, 1983) also derived the HSAB principle theoretically. In their derivation they used the hypothesis that extra stability attends bonding between a Lewis acid and a Lewis base when the ionization potentials of both of them become same in the molecule (after charge transfer).

1.8 OPERATIONAL DEFINITION OF CHEMICAL POTENTIAL AND HARDNESS

Evaluation of the hardness, chemical potential or electronegativity values from equation 2 is not practically feasible as it is not possible to derive the change of energy with respect to the fractional number of elctrons. So the operational definition of $\varkappa$, μ and η are provided by the finite difference formulae,

$$\bar{\varkappa} = (IP + EA)/2 \text{ (Mulliken)} = -\bar{\mu} \;, \qquad \bar{\eta} = (IP - EA)/2 \qquad 1.7$$

where I and A are the ionization potential and electron affinity of the species in question. These expressions originate from the parabolic approximation of the E(N) vs N curve i.e. truncating the power series expansion of E(N) as a function of N after quadratic terms (see footnote). Though this is merely an assumption, the expression of $\varkappa$ originates from here and completely matches with that of Mulliken. The numerical values obtained for $\varkappa$ and η

FOOTNOTE : Here it should be mentioned that this type of expression of energy in power series of number of electrons (actually charge) originates from the early work of Pritchard and co-workers, Margrave, Hellman et al etc. - while they were trying to derive the values of atomic electron affinity by extrapolation techniques. For details see, Margrave, J. L.: J. Chem. Phys., 22, 1937 (1954); Proc. Roy. Soc. London, Ser. A. 235, 136 (1956) and references therein.

predict the correct qualitative trends of soft and hard behaviour of chemical species in most cases.

Pearson (Pearson, 1986) incorporated the concepts of absolute electronegativity (χ) and absolute hardness (η) in the molecular orbital theory. He showed that within the validity of Koopmans´ approximaton, the IP and EA may be written in terms of frontier orbital energies,

$$-\epsilon_{HOMO} = IP \qquad \text{and} \qquad -\epsilon_{LUMO} = EA \qquad 1.8$$

Hence μ and η can be written in terms of frontier orbital energies as,

$$\mu = (\epsilon_{LUMO} + \epsilon_{HOMO})/2 \qquad \text{and} \qquad \eta = (\epsilon_{LUMO} - \epsilon_{HOMO})/2 \qquad 1.9$$

The physical significance is that the -ve of χ represents a horizontal line at the energy midpoint between HOMO and LUMO. The hardness (η) represents half of the energy gap between HOMO and LUMO.

1.9 FORMAL RELATIONSHIP BETWEEN HARDNESS AND SOFTNESS AND THE CORRESPONDING LOCAL QUANTITIES

As mentioned before, softness is the inverse of hardness and is defined by $S = 1/2\eta = (\partial N/\partial \mu)_v$. But the hardness and softness discussed so far are called global hardness and softness. Although global hardness and softness provide some information about the overall properties of the system concerned, the local hardness or softness may be more useful in the understanding of the behaviour of different sites of a system. This may throw more light on ´atom in a molecule´ properties, site selectivity in a system etc. For this, it may be necessary to define local hardness or softness. This point has been addressed by many workers recently.

(a) SOFTNESS HIERARCHY

There are different local variables both for hardness and softness which are interrelated to each other. The softness hierarchy starts from softness kernel as defined by Berkowitz and Parr (Berkowitz and Parr, 1988) as,

$$s(r, \vec{r}\,') = -\partial\rho(\vec{r})/\partial u(\vec{r}\,') \qquad 1.10$$

here $u(\vec{r}\,')$ is the difference between external and chemical potentials i.e. $u(\vec{r}) = v(\vec{r}) - \mu$.

On integrating softness kernel we get local softness (Yang and Parr, 1985), i.e.

$$\int s(r, \vec{r}\,')d\vec{r}\,' = s(\vec{r}) \qquad 1.11$$

Local softness again can be written in several alternative forms. Many of these use a Fukui function $f(\vec{r})$, as in the following.

$$s(\vec{r}) = f(\vec{r})/2\eta = f(\vec{r})S = [\partial\rho(\vec{r})/\partial N\,]_{v(\vec{r})}(\partial N/\partial\mu)_{v(\vec{r})}$$

$$= [\partial\rho(\vec{r})/\partial\mu\,]_{v(\vec{r})} \qquad 1.12$$

The function $f(\vec{r})$ is called Fukui function by Parr and Yang (Parr and Yang, 1984), because of its usefulness in explaining the frontier - orbital theory of chemical reactivity in molecules. Through a Maxwell relation it is written as,

$$f(\vec{r}) = [\ \partial\rho(\vec{r})/\partial N\ ]_{v(\vec{r})} = [\ \partial\mu/\partial v(\vec{r})\ ]_N \qquad 1.13$$

It should be mentioned that three different types of Fukui functions can be defined, accounting for reactivity towards three different types of reagents. These are,

$$f^{+}(\vec{r}) = \rho_{N+1}(\vec{r}) - \rho_{N}(\vec{r}) \simeq \rho_{LUMO}(\vec{r}) \qquad 1.14a$$

measures reactivity towards a nucleophilic reagent.

Similarly,

$$f^{-}(\vec{r}) = \rho_{N}(\vec{r}) - \rho_{N-1}(\vec{r}) \simeq \rho_{HOMO}(\vec{r}) \qquad 1.14b$$

measures reactivity towards an electrophilic reagent.

and,

$$f^{0}(\vec{r}) = [\rho_{N+1}(\vec{r}) - \rho_{N-1}(\vec{r})]/2 \simeq [\rho_{HOMO}(\vec{r}) + \rho_{LUMO}(\vec{r})]/2 \qquad 1.14c$$

which measures reactivity towards an innocuous (radical) reagent.

Fukui function is also called normalized local softness and as such local softness can be integrated to yield global softness,

$$\int s(\vec{r})d\vec{r} = S\int f(\vec{r})d\vec{r} = S \qquad 1.15$$

When a chemical system (atom, molecule or solid) can be identified as a member of grand cannonical ensemble, the global softness, local softness and softness kernel may be defined in terms of fluctuations of the number of electrons and electron densities as follows,

$$S = (\partial\langle N\rangle/\partial\mu)_{v,T} = (1/kT)[\ \langle N^2\rangle - \langle N\rangle^2\ ] \qquad 1.16$$

$$s(\vec{r}) = (1/kT)[\ \langle \rho(\vec{r})N\rangle - \langle N\rangle\langle \rho(\vec{r})\rangle\ ] \qquad 1.17$$

and

$$s(\vec{r}, \vec{r}\,') = (1/kT)[\ \langle \rho(\vec{r})\rho(\vec{r}\,')\rangle - \langle \rho(\vec{r})\rangle\langle \rho(\vec{r}\,')\rangle\ ], \qquad 1.18$$

Where k is the Boltzman constant and the brackets $\langle\ \rangle$ designate the ensemble avarages at constant T, v and μ (Yang and Parr,1985).

(b) HARDNESS HIERARCHY

The hardness hierarchy, like that of softness, starts from the hardness kernel (Ghosh and Berkowitz, 1985) - which is defined as

$$2\eta(\vec{r},\vec{r}\,') \equiv -\,\partial u(\vec{r})/\partial\rho(\vec{r}\,') = \{\partial^2 F[\rho]\} \;/\; \{\partial\rho(\vec{r})\partial\rho(\vec{r}\,')\} \qquad 1.19$$

Here $F[\rho]$ is the universal functional of the density functional theory (Hohenberg and Kohn, 1964), and comprises of the electronic kinetic energy plus the total electron-electron repulsion energy.

The hardness kernel integrates to local hardness $\eta(\vec{r})$, but not in the same sense of softness kernel integrating to local softness.

$$\eta(\vec{r}) \equiv (1/N)\int \eta(\vec{r},\vec{r}\,')\rho(\vec{r}\,')d\vec{r}\,' \qquad 1.20$$

Reciprocity relation exists between local hardness and softness as also hardness and softness kernels, similar to that of global softness and global hardness (Berkowitz and Parr, 1988)

$$2\int s(\vec{r})\eta(\vec{r})d\vec{r} = 1 \qquad 1.21$$

and

$$2\int s(\vec{r},\vec{r}\,')\eta(\vec{r}\,',\vec{r}\,'')d\vec{r}\,' = \partial(\vec{r}\,''-\vec{r}) \qquad 1.22$$

Like local softness, local hardness also integrates to the global hardness,

$$\eta = \int \eta(\vec{r})f(\vec{r})d\vec{r} \qquad 1.23$$

1.10 CHEMICAL APPLICATIONS

Apart from formal developments there are subsequent efforts to apply hardness concept in explaining and in understanding a wide variety of chemical problems. A brief discussion of some of them will be helpful to get an idea of its applicability in diverse filds of chemical physics.

From very begining the HSAB principle was proposed, there was effort to establish the principle from both theoretical and numerical front. But the studies in this area got renewed impetus after the proposition of the principle of maximum hardness (PMH) by Parr and Chattaraj (Parr and Chattaraj, 1991). The PMH, to be discussed in detail in Subsection 1.12(b) and chapter 3, briefly states that,"at constant μ, v and T any chemical species shows its maximum hardness at its equilibrium geometry." Chattaraj et al (Chattaraj, Lee and Parr, 1991) gave two proofs of the HSAB principle, both of which are based on the maximization of energy gain due to formation of bond. The first proof claimed that the validity of HSAB principle warrants the validity of PMH. The second proof is a consequence of the equal minimization of grand potential of both the partners being bonded.

Chattaraj and Nath (Chattaraj and Nath, 1994) have studied a number of protonation reactions with bases e.g., HF, HCL, H_2O, H_2S, NH_3 and PH_3. They observed that the reactions take place according to the HSAB principle and the hardness values of the resultant protonated species also confirm the validity of PMH. It is also noticed that the proton affinity values do not always reflect the HSAB principle.

Chattaraj and Schleyer (Chattaraj and Schleyer, 1994) have tested the HSAB principle by ab initio quantum mechanical calculations in both correlated and non-correlated methods. It is observed that for the interaction of hard acids like HF, with bases, HSAB principle is valid even at Hartree-Fock level of calculation, whereas correlation effect is important for soft-soft interaction. The reactions of HF acid also shows the validity of PMH. Most of the reactions of other hard acids also confirm the validity of the HSAB principle, though there are a few exceptions in their study.

There are several other recent contributions which helped in the development and understanding of the HSAB principle. Among these, the studies of Nalewajski and co-workers as well as Geerlings and co-workers are important, as they have suggested local versions of the HSAB principle. These will be discussed in different contexts later on.

Comparison of the profile of hardness with that of the molecular valency (V_M) has been done by Chattaraj et al (Chattaraj et al, 1994) and Chandra (Chandra, 1994). Chattaraj et al have shown that these profiles, obtained by distorting the geometries of C_2H_4, B_2H_6 and HCP molecules, show the maximum at equilibrium geometry supporting the PMH. Except B_2H_6, the V_m profiles of the other two molecules also exhibit maxima at equilibrium geometry showing a probable linear relation with η. Chandra has compared the η and V_M profile due to the rotation around C - C bond of C_2H_6, stretching of C - O bond of CO_2 molecule as well as umbrella inversion of NH_3 molecule. Both the profiles of η and V_M show maxima at staggered configuration of C_2H_6. The planar geometry of

NH_3 molecule corresponds to minimum η and V_M values, indicating a fairly linear relation between them. This linear relation also holds true for assymetric stretching of CO_2 molecule.

Since according to molecular orbital theory $2\eta = \varepsilon_{LUMO} - \varepsilon_{HOMO}$ (Pearson, 1986), either hardness or band gap can be used with equal confidence. However, this simple description of hardness in terms of band gap fails, wherever the description of simple MO theory fails. Zhou (Zhou, 1992) has discussed the implications of this for structural chemistry.

Hardness has also been used in providing a quantitative measure of aromaticity. Parr and co-workers have successfully correlated resonance energy per π-electron, which is a conventional valence-bond measure of aromaticity, with absolute hardness or relative hardness (Zhou and Parr, 1989 ; Zhou, Parr and Garst, 1988 ; Zhou and Parr, 1990). It has been shown that for electrophilic aromatic substitution reactions, the change in hardness from reactants to transition state on a potential energy surface, is a measure of the activation energy of a reaction.

Zhou and Navangul (Zhou and Navangul, 1990), as well as Ghosh and Parr (Ghosh and Parr, 1987), have developed the new idea of 'bond electronegativity' and 'bond hardness' and outlined a semiempirical density functional theory of molecular electronic structure and chemical bonding.

'Electronegativity difference' and 'hardness sum' have been used as co-ordinates in structure - stability diagrams (Shankar and Parr, 1985). Harbola (Harbola, 1992) has demonstrated that the most stable cluster of a given metallic element, has the largest value of hardness.

The local quantities discussed before have also potential applications in predicting chemical reactivity. The reactivity of the nucleophilic, electrophilic and radical attack can be measured properly by the corresponding Fukui functions within a density functional framework (Parr and Yang, 1984). The expression of $f(\vec{r})$ [i.e. $(\partial\mu/\partial v)$] infers a principle that generates the frontier - electron theory. This principle states "of two different sites with generally similar dispositions for reacting with a given reagent, reagent prefers the one which, on the reagent´s approach, is associated with the maximum response of the system´s chemical potential". As local softness and Fukui function are related by the equation $s(r) = f(r)S$ (where S is global softness), it is clear that the local softness contains all this information.

Local softness has been exploited by Harbola et al to study the frontier-controlled charge transfer processes. In case of acid-base reactions they have established a relation among the transferred charge, difference of local softness, μ (chemical potential after equalization) and $v_N(r)$ (coulomb potential generated due to nuclear motion). From this study they conclude that "the larger the softness difference at any place the better it is" (Harbola et al, 1991). Reactivity in chemisorption and catalysis can be discussed in terms of softness and Fukui function (Yang and Parr, 1985). For any metal at 0°K, $S = g(\varepsilon_F)$ and $f(\vec{r}) = \frac{g(\varepsilon_F, \vec{r})}{g(\varepsilon_F)}$, where $g(\varepsilon_F)$ and $g(\varepsilon_F, \vec{r})$ are density of states and local density of states of the metal at its Fermi energy ε_F. Felicov and Somorjai argued that as the local softness is related to the fluctuation in number of particles in a grand canonical ensemble, site selectivity for metals in chemisorption and catalysis, governed by the low-energy density fluctuations, can be determined by local softness (Felicov and Somorjai, 1985).

Nalewajski and co-workers (Struc. and Bonding, 1993) have introduced the concept of charge sensitivity analysis (CSA), which is based on chemical hardness with fixed external potential (Born - Oppenheimer) approximation. The charge sensitivity (CS) description is versatile as a large variety of chemically interesting response of molecular systems, due to an outflow (or inflow) of electrons from (to) a given molecule, or its fragments can be generated within the CSA method. These responses, measured by the relevant CS, are closely connected to the respective contributions to charge transfer (CT) energy, and they are directly related to the intuitive chemical treatments of the reaction mechanisms. The CSA is flexible as it is formulated in various alternative resolutions (e.g. local or L - resolution, atoms-in-molecules or AIM - resolution, groups or G - resolution etc.), as specified by a given partitioning of the molecule in a physical space. The associated sensitivities of the molecular fragments are used in monitoring the reaction progress. This aspect of the theory is vital for determining the site characteristics of reactants and thus for predicting both the site and path selectivities of chemical processes. These are demonstrated in both qualitative [e.g. Hard (Soft) Acids and Bases Principle, trans (cis) influence of ligands] and quantitative [reactivity trends in selected organic and catalytic systems] levels.

The Electronegativity Equalization Method (EEM) has been exploited by Baekelandt et al (Struc. and Bonding , 1993) to evaluate various response properties defined in the CSA of both finite and infinite systems. The EEM formalism has been developed sufficiently to take into account the entire external potential in infinite systems e.g. inorganic crystals. The method, with its extended forms, is compared with other theoretical approaches (e.g. recursive combination rules of Nalewajski, Harmonic Mean method - neglecting the external potential, Arithmetic Mean of Yang et al, Huckel Model) as well as empirical approaches dealing with the charge transfer phenomena (ESCA shifts, surface states of oxides etc.). They applied the techniques for elucidation of the general rules (named by 'Rules of Thumb') of hardness/softness - structure - reactivity relationships. Intrinsic framework properties of inorganic solids (e.g. zeolite structures, isolated SiO_4 tetrahedron, aluminosilicate frameworks etc.) as well as framework perturbations (chemical composition, adsorbed molecules etc.) can be studied with the help of this model. Such studies will be helpful to experimental chemist to understand and predict the properties of materials and their role in perturbing and activating adsorbed molecules.

Alonso, Balbas and co-workers (Struc. and Bonding ,1993) have studied how ionization potential, electron affinity and the corresponding hardness of metallic clusters vary with the cluster size. They also discussed other aspects, such as - the validity of asymtotic form of ionization potential (IP) for large clusters, shell effects and odd-even effects on the IP of metallic clusters, advantages and limitations of Spheroidal Jellium Model in evaluating the IP of metallic clusters etc. From the plot of Fukui function for clusters of different size, they have shown that the cluster surface is most suceptible for radical attack as the function value shows pronounced maximum at the surface.

Proft et al (Proft et al, 1993) calculated the intrinsic group electronegativity, hardness and softness for 30 organic groups from ab initio wave function formalism. They observed that the group hardness or softness generally follow the trends of the values of central atoms. They also used local softness and local hardness as reactivity indices in studying the influence of the isomorphous substitution of Al by B and Ga and Si by Ge on catalytic activity of zeolite systems (Langenaeker et al, 1994). The acidities of the zeolite systems were found to be dependent on several parameters which are important within the framework of HSAB principle. The concept of local hardness and local softness were used to explain the acidity differences of substituted acetic acids (Proft et al, 1994). Correlation between parameters, which are the measures of local hardness and experimental acidities, were established. They demand that the softness (polarizability) of the substituted group plays an important role on the acidity in gas phase, although same role is negligible in solution phase.

March and Parr (March and Parr, 1980) have discussed the scaling properties of the ground state energy of homonuclear diatomic molecules. Further development in this area was done by Plindov and Pogrebnya (Plindov and Pogrebnya, 1982). March has shown that for homonuclear diatomic molecules with large atomic number (Z), hardness and electronegativity can be correlated with a function of Z and scaled equilibrium distance, $R_S^{eq} = R_e Z^{1/3}$ (R_e = equilibrium bond distance). March (March, 1993) has also shown that for atomic ions, hardness and chemical potential can be related via electrostatic potential at the nucleus.

Sen and co-workers have developed the concept of Z (nuclear charge) transition state (ZTS), with fractional nuclear charge, to calculate the isoelectronic energy changes in atoms and molecules. This is comparable to the concept of Slater transition state (STS) (Slater 1974, 1972) within local density approximation (LDA), where fractional orbital occupations are employed to evaluate the density variation of energy at constant nuclear charge. The isoelectronic changes in chemical potential, as shown by March (March, 1981), have been applied to quark atoms by Sen et al (Sen et al, 1989). Sen (Sen, 1991) further extended it to calculate the isoelectronic changes in hardness $(\partial\eta/\partial z)_N$. Both $(\partial\mu/\partial z)_N$ and $(\partial\eta/\partial z)_N$ have been evaluated using STS and ZTS methods (Sen 1993) - which confirm the computational advantages of the latter method over the former one.

1.11.(a) QUALITATIVE RELATION BETWEEN DIPOLE POLARIZABILITY AND CHEMICAL HARDNESS (SOFTNESS)

The qualitative relation of hardness (softness) concept with that of polarizability, although reasonably old, studies in this area got renewed impetus after η (or S) defined precisely by electronic structure theory (e.g. in terms of HOMO and LUMO of molecular orbital theory). Any chemical species, which is difficult to be deformed by any form of perturbation (e.g. external electric field or interaction with any other chemical species) is known to be chemically hard. This can also be explained more clearly and quantitatively from the expression of polarizability (α) derived with the help of perturbation theory. While the perturbation expressions will be helpful to correlate α with η (or S) rigorously, the subsequent discussion will also point out the loopholes and inadequacies that motivate me to carry out some studies in this area.

The polarizability of a chemical species may be defined as its ability to respond to any external electric field (electric polarizability) and to acquire an electric dipole moment. It is the second derivative of energy with respect to the electric field at zero field strength i.e.,

$$\alpha_{zz} = -(\partial^2 E/\partial F_z^2)_{F_z=0} \qquad 1.24$$

[α_{zz} is the polarizability tensor along z-direction]

Here it is assumed that the applied field is in z-direction. The mean polarizability (α) is measured assuming that the system is rotating freely in a fluid and then α is written as,

$$\alpha = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3 \tag{1.25}$$

The explicit expression of α then become,

$$\alpha = (2/3)\sum_{n}{}' \{|\mu_{n0}|^2\}/\Delta_{n0} \tag{1.26}$$

where μ_{n0} is the matrix element of the dipole moment operator μ between states 0 and n and Δ_{n0} is the excitation energy from state 0 to n states. When α is divided by $4\pi\varepsilon_0$, then the new expression α' ($= \alpha/4\pi\varepsilon_0$) is called the polarizability volume - having the dimension of volume (i.e. m^3) and of the order of 10^{-24} cm^3 (similar to molecular volume). Thus, chemically α' is much more meaningful.

Applying closure approximation, the sum over the excited states may be written simply using a common denominator (which is of the same order of magnitude as the ionization potential). Hence we can write,

$$\alpha \simeq (2/3\Delta)\sum_{n}{}' \mu_{0n}.\mu_{n0} = (2/3\Delta)\{\langle 0|\mu^2|0\rangle - \langle 0|\mu|0\rangle^2\} \tag{1.27}$$

or,

$$\alpha \simeq (2/3\Delta)\delta\mu^2 \tag{1.28}$$

[where $\delta\mu^2 = \langle\mu^2\rangle - \langle\mu\rangle^2$]

where $\delta\mu$, which is the root mean square deviation of the dipole moment from the mean value, is called the fluctuation of the dipole. Even for a system for which permanent dipole moment (μ_0) is zero, $\langle\mu^2\rangle$ is not zero and so all the electronic system must have non-vanishing dipole-fluctuation. When the elctric dipole varies both in magnitude and direction, the true average of this will be zero in non-polar molecules and non-zero in polar molecules - in which case it may be considered as true fluctuation. A molecule which has a large fluctuation in the electric dipole, i.e. electrons are not under the tight control of the nuclei, is said to have high polarizability. This is also the criterion for higher softness or lower hardness. Now, intuitively we can conclude that the fluctuation of electronic charge (or other way - electronic dipole) increases with the increase in radius and number of electrons. This is obvious from the fact that the dipole moment operator $\vec{\mu} = e\vec{r}$, hence $\alpha = (2/3\Delta)e^2\langle r^2\rangle$, where $\langle r^2\rangle$ is the mean square radius of the electrons orbital and so polarizability increases as mean square radius increases. In case of a many electron atom, taking $\langle r^2\rangle = R_a^2$, where R_a is the radius of the atom, it is reasonable to assume that the polarizability be proportional to the number of electrons (N_e), i.e.

$$\alpha \simeq (2/3\Delta)e^2 N_e R_a^2 \qquad 1.29$$

Thus while comparing between the two systems, the one having larger radius and number of electrons is more polarizable (and hence softer) than the other, provided other factors remain comparable.

Application of the polarizability concept was exploited by Fajans (Fajans 1924, 1941) to explain the bonding nature of chemical species, long before the concept of hardness (or softness) appeared in chemical literature. Fajans first pointed out that high polarizability of a partner results in more covalent bonds as in AgCl compared to NaCl lattice. Pearson extended this conclusion, proving that soft acids tend to hold bases by covalent bonds, whereas ionic forces are responsible for the bond formation between hard partners. From qualitative viewpoint, softness of a chemical species implies higher polarizability or amenability to deformation, whereas hardness implies the reverse. A rigorous explanation regarding the connection between polarizability and hardness (or softness) can be given from equn. (1.28) . From this eqn. it is clear that lower the value of Δ (i.e. the excitation energy) higher the value of α. Now from orbital picture Δ can be viewed as the difference-energy between the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO). The HOMO - LUMO gap is a measure of hardness, the more is the gap - more is the value of hardness or less is the value of softness. Thus polarizability has direct relation with softness and inverse relation with hardness.

The measure of polarizability by molecular, atomic or ionic refraction data is a standard practice in chemistry for a long time. This is because of the fact that the molar refractivity (R_m) can be written in terms of the mean dynamic polarizability as,

$$R_m = (4\pi/3)L\alpha'(w) \qquad 1.30$$

[L = Avogadro's constant, $\alpha'(w)$ - polarizability volume of the dynamic polarizability]

So, as molar refractivity R_m is proportional to polarizability volume $\alpha'(w)$ - which, more or less an additive quantity, R_m is also likely to be additive. Thus refractivity of a molecule may be expressed as a sum of the refractivities of its component atoms or groups. This has been confirmed to some extent and table of atomic refractivities have been compiled. This indirectly means that refraction can be recognised as a molecular volume and so the discussion of softness/hardness may be reduced to the level of molecular or atomic dimensions.

Komorowski exploited the above idea and has shown how the atomic or ionic refractions (R_D) can be utilized to obtain the corresponding hardness indices { $\eta_1 = (4\pi\varepsilon_0 R_D{}^{1/3})^{-1}$ }. He also compared the hardness indices, evaluated through R_D, with those obtained from the covalent or Van der Waals radii, r_w { $\eta_2 = (4\pi\varepsilon_0 r_w)^{-1}$} in case of atoms and from ionic radii, r_i { $\eta_2 = (4\pi\varepsilon_0 r_i)^{-1}$ } for ionic species. From the results obtained, he concluded that for atoms, Van der Waals radii, rather than covalent radii, provide a more reliable measure of atomic hardness when compared to chemical hardness parameters (Komorowski, 1987a). Similarly the best calculations with the Parr and Pearson's absolute hardness parameter were found using the ionic radii values derived from ionic refractions.

Qualitative discussion of the correlation of hardness (η) or softness ($S = 1/\eta$) with physical properties like polarizability, electronegativity, size etc. was first discussed by Jorgensen (Jorgensen, 1967). Very recently some studies in this direction have been made by different workers. Politzer (Politzer, 1987) as well as Sen _et al_ (Sen _et al_, 1987) considered a linear relationship between polarizability (α) and softness, Vela and Gázguez (Vela and Gázquez, 1990) have expressed the ratio α/S in terms of an integral, which varies from atom to atom since it involves the electron densities of the corresponding anion and cation. Nagle (Nagle, 1990), on the other hand, has shown for atomic systems a simple linear correlation between the softness S and $(\alpha/n)^{1/3}$, where both S and α are calculated using the local density approximation (LDA) method.

More recently, Ghanty and Ghosh (Ghanty and Ghosh, 1993) have investigated the correlation of polarizability, softness and radius in case of metal and carbon clusters. They have shown that in case of Na metal a linear plot of softness vs cluster radius shows a good correlation with the correlaton coefficient 0.88. The same plot in case of carbon cluster gives a correlation coefficient 0.93. When cube root of polarizability is plotted against the softness of the metal and carbon clusters, The linear correlation coefficient becomes 0.86 and 0.93 respectively.

(b) EVALUATION OF MOLECULAR HARDNESS AND POLARIZABILITY IN TERMS OF BONDED ATOMS -- THE CONCEPT OF ATOMS IN A MOLECULE (AIM)

The discussion of the previous section can be extended to the fact that atomic softness, that should roughly parallel refractions (polarizability), may also be defined for bonded atoms. Theoretical progress in this direction is already achieved. Komorowski (Komorowski, 1987a, 1987b] suggested a new approximate theory which he termed as ´chemical approximation´ - to define the electronegativity and hardness of atoms bonded in a molecule . To take care of the chemical environment, he took the atomic energy as a function of charge q (q = Z - N) developed in the molecule. On the basis of this energy function, he defined the electronegativity and hardness of the bonded atoms as 'differential electronegativity' and 'differential hardness'. 'Differential hardness ' has dependence on the radii of the bonded atoms, which are obtained from the electrodynamical atom model. These 'radii' are evaluated by skilful analysis of the abundant refraction data. The hardness parameters evaluated in this way agree well with the known features qualitatively ascribed to the scale of hardness, e.g. (1) The classical sequence of increasing hardness is properly reproduced, $P \simeq S < N < O$, (2) Halogens are ordered in the expected sequence of increasing softness (3) The phenomenon of symbiosis may be correctly accounted for (Komorowski, 1993).

Cioslowski and Mixon (Cioslowski and Mixon, 1993) also defined hardness of an atom in a molecule, which they defined as 'bond hardness'. Their definition depends upon the values of total energies and energy derivatives calculated for molecules composed of fragments with a limited degree of charge transfer. In their method the atomic or fragment charges are calculated with the help of topological theory of atoms in molecules proposed by Bader (Bader, 1979, 1990). With the help of numerical demonstrations, they came to the conclusion that bond hardness are mostly transferable, although their dependence extend to some extent beyond that of the atoms linked directly by the bond formation.

From the discussion made so far, it is clear that monumental effort has been laid to develop the concept of hardness and softness as well as the related properties like chemical potential, electronegativity, polarizability etc. for chemical species. There are various approaches ranging from DFT, statistical mechanics, quantum topology to a wave function based formalism. Throughout the span of endeavour the focus was made on the development, understanding, as well as systematizing these qualitative concepts on firm theoretical basis. To further the applicability for real chemical systems, various techniques have been discussed to evaluate these properties for atoms, molecules, metal clusters, carbon clusters etc. Because of these enormous efforts, it has now become possible to arrange the atoms, molecules, radicals according to their hardness (softness) sequence.

This is not the complete story. Chemists are always interested in explaining the chemical properties of any species in terms of the transferable parameters characteristic of its constituents. It is this desire which is responsible for the emergence of the concept of 'Atoms in Molecules' (AIM). While AIM concept has been used successfully to define an atom in a molecule as well as the structure and shape of a molecule, it is natural that chemists will be attracted to use this concept to extract the hardness (softness), electronegativity and polarizability of atoms bonded in molecules. As we have discussed before, Cioslowski and Mixon as well as Komorowski have done some work in this area, which resulted in defining hardness of a bond in a molecule or what has been called 'bond hardness'.

1.12 ORGANIZATION OF THE THESIS

(a) CORRELATION OF HARDNESS, POLARIZABILITY AND BOND DISTANCES FOR COMPLEX POLYATOMIC SYSTEMS -- OUR CONTRIBUTION

So far, we have discussed about the hardness and softness for static systems only - i.e. systems in their equilibrium state. However, an important concern is about the dynamics of chemical systems i.e. bond breaking and bond formation in the molecule, which alternatively may be thought of as reshuffling of chemical bonds. So it must be interesting and useful to study the change of hardness, chemical potentials, polarizability etc. of chemical bonds when they are disturbed from equilibrium position. It is natural that the changes of these properties should have some dependence upon the nature of the bonded atoms (e.g. electronegativity), types of bonds (i.e. single, double, triple etc.) and also the presence of other bonds in the molecule. We have attempted to probe this area and we have established qualitative correlation between polarizability, hardness,and bond distance in polyatomic molecules (Roy et al, 1994, 1995). These relations have been obtained by ab initio wave function formalism. In chapter 2 of the thesis, we record the results of our study. Though the study presented in this thesis is preliminary and for molecules containing only single bonds, it is the first study of its kind in this area and should encourage further studies to other complex systems. We have made extensive study on the single bonded systems to reach a conclusion of this relation on this type of systems. Our study is focussed mainly on small variation of the geometry from its equilibrium position.

(b) IN SEARCH OF THE VALIDITY OF THE PRINCIPLE OF MAXIMUM HARDNESS

In the way of development of hardness concept, a major breakthrough is the 'Principle of Maximum Hardness' (see section 1.10) first stated by Pearson (Pearson, 1987) and later proved rigorously by Parr and Chattaraj (Parr and Chattaraj, 1991). Pearson stated in philosophical language that " there seems to be a rule of nature that molecules arrange themselves so as to be as hard as possible". Subsequent studies (Zhou and Parr, 1989, 1990 ; Zhou, et al, 1988) suggest that this principle may require additional constraints of constant temperature (T) and chemical potential (μ). Parr and Chattaraj (Parr and Chattaraj, 1991) proved the principle, by considering the electronic systems (be it atom, molecule or solid) as a grand cannonical ensemble and making use of the fluctuation - dissipation theorem of statistical mechanics (Chandler, 1987). Incorporating the constraints, the PMH can be stated as, 'At constant μ (chemical potential),v and T, any chemical species exhibits maximum values of hardness at its equilibrium geometry'. With the help of PMH they even successfully prove the HSAB principle (Chattaraj et al 1991).

In the above proof of PMH it was assumed that the application of statistical mechanics should be valid for the system of electrons like atoms, molecules, or metals. Datta (Datta, 1992) has shown how the PMH holds true along the reaction path (profile). Using the MNDO level of calculation he has demonstrated that hardness become minimum at the transition state for the inversion (umbrella effect) of NH_3 molecule (where no bond is broken or formed) and the intramolecular proton transfer in malonaldehyde. Datta argued that as transition point is the farthest from the equilibrium position, hardness should be minimum. However, this particular argument lacks rigor. Pearson and Palke (Pearson and Palke, 1992), using ab initio SCF method, have shown that hardness becomes maximum when NH_3 and C_2H_6 molecules are distorted in small amount from the equilibrium geometry along the vibrational symmetry coordinates. This observation became valid only in the case of assymetric distortion and not for symmetric distortion. This may be attributed to the fact that in the former case there is a reorganization of the electron densities to maintain the constraint of constant v.

Though both the tests support the validity of PMH, some sort of inadequacies are there. The first one is that the accuracy of the level of calculations used are not beyond doubt - as it is well known that though Koopmans' IP is reasonably well trusted - Koopmans' EA is not so at all because of the neglect of relaxation effects. Secondly, in the study of Datta, the constraints of constant v and μ are not maintained at all. It is true that the rigorous condition of constant v can not be obeyed strictly, as with distortion, v will be changed . The best thing one can do is to distort in a very small amount so that change in v can be minimised - what exactly Pearson and Palke (Pearson and Palke, 1992) have done. While the improvements in the methodology of calculation can be done by incorporating the relaxation and correlation effects explicitly, the limitation of constant v really limits the application of PMH to chemically interesting cases e.g. reaction dynamics. In case of polyatomic molecules there is one remedial measure i.e. to distort more than one bonds in such a way that the resultant reorganization keeps the v constant, which might happened in case of asymmetric distortion of Pearson and Palke. But in that case also μ may or may not be constant. Moreover the PMH was derived from the rigorous definition of hardness (inverse softness) - whereas the numerical support so far given are based on the operational definition (i.e. finite difference approximation) of η and μ. Hence it is also worth studying if the significance of PMH remains the same under the operational definition i.e. $\bar{\eta}$ and $\bar{\mu}$ as well as in the context of large changes in v. This is the subject of my investigation presented in chapter 3. A short resume is presented in the next paragraph.

In search of a solution of the first problem, we have studied the validity of PMH by calculating IP and EA using coupled cluster (CC) methods (Pal <u>et al</u>, 1993), which are recommended for the efficient incorporation of electron correlation and size extensivity. The CC based methods are very reliable for the estimation of difference energies like ionization potential and electron affinity (EA) as it has the inherent mechanism to take care of relaxation effect also. Taking H_2O and NH_3 as the primary test cases, we have shown in Chapter 3 that for small asymmetric distortions μ remains constant and hardness becomes maximum at equilibrium geometries. In symmetric distortion the hardness values do not show any maxima and μ does not remain constant. Additionally our study shows that the hardness values go through a local maxima around symmetric geometries with respect to asymmetric distortions. We have also compared the stable and unstable symmetric geometries of H_2O molecule to study the validity of PMH.

(c) BEHAVIOUR OF OPERATIONAL HARDNESS IN CHEMICAL BINDING

To find out how the operational hardness can be correlated with the stability of a chemical species, one needs to consider the change of it with the energies. In chapter 4, we propose a general relation of this with the energies. It has been shown that the hardness and chemical potential values of N identical noninteracting atoms are same as that of a single atom. Taking a model diatomic system we have shown that at any point of the reaction co-ordinate the change of operational hardness ($\Delta\bar{\eta}$) is explicitly related to the binding energies of the neutral species and the corresponding cations and anions. This relation can explain the change of hardness and chemical potential in a general potential surface and thus clarify many points of confusion. The studies of this thesis presented in chapter 3 show that for certain cases e.g. asymmetric distortions, where μ and v were roughly constant, the maximum hardness correlates with the minimum energy. However, when the changes are more drastic, it is difficult to keep the chemical potential and external potential constant. In such cases, PMH is not always applicable. The relation proposed in chapter 4 can explain the behaviour of the operational hardness. We also show a good correlation between $\bar{\eta}$ and vertical ionization potential, irrespective of the changes in external potential.

Thus it seems that the constancy of v may have to be followed with more rigor in case of correlation with electronic energy or total energy. This indirectly means that the points where v changes drastically from that of equilibrium values is not the domain where validity of PMH can be tested. Such observations have also been made by Pearson (Pearson, 1993). Additionally it can also be argued that the operational definitions of hardness [$\bar{\eta} = (IP - EA)/2$] and chemical potential [$\bar{\mu} = -(IP + EA)/2$] may in some cases, be severe approximations to exact hardness and chemical potential. Robles and Bartolotti (Robles and Bartolotti, 1984) as well as Gázquez and Ortiz (Gázquez and Ortiz, 1984) have shown that this operational definition gives incorrect trend of hardness parameters for typical atoms e.g. N, O, F ; P, S, Cl etc. Sen and Vinayagam (Sen and Vinayagam, 1988) have shown that this incorrect trends disappear if density functional theoretic definition $(\partial^2E/\partial N^2)/2$ is used.

In chapter 4 we have recorded the results of our study on change of $\bar{\eta}$ in different conditions. This study will throw useful hints on the trend of $\bar{\eta}$ in more general conditions.

(d) CHEMICAL POTENTIAL AND HARDNESS FOR OPEN SHELL SYSTEMS -- MODEL FOR THE CORRESPONDING ANIONS

In chapter 5, we discuss the evaluation of chemical potential and hardness for open ahell systems. In the open shell type of systems, hardness and chemical potential can not be defined in terms of frontier orbitals which are quasi-degenerate. The numbers generated by using frontier orbitals become unrealistic and can not be used for predicting observed trend. This was not addressed properly before and there are reported hardness and chemical potential values of some free radicals (Pearson, 1988a), where η and μ are calculated from experimental IP and EA in the relaxed geometries of the species. A reliable trend of η and μ values of free radicals may be used as model numbers for the corresponding anions (e.g. $^{\cdot}CH_3$ for $^{-}CH_3$, $^{\cdot}SCH_3$ for $^{-}SCH_3$ etc.), which are otherwise very difficult to evaluate both experimentally and theoretically (the EA values are unrealistic for anions). Proft et al (Proft et al, 1993) have calculated the hardness values of some common organic groups by ab initio wave function formalism in the context of evaluating the intrinsic group properties (e.g. group electronegativity, group hardness). Here they used the geometries adopted by the groups in a molecule and not the equilibrium geometry of the radicals themselves. As a result the η values obtained from such calculations may not yield a reliable trend of hardness for the corresponding anions. Keeping this in mind, we evaluate η and μ in terms of IP and EA by using ΔSCF procedure - which we have discussed in other context. In chapter 5 we have discussed how far our results (calculated by using TZP level of basis set) are reliable, at least for a qualitative trend. The possible ways of improving the theoretical results and the problems of comparing these with the experimental results have also been pointed out.

(e) CONCLUDING REMARKS AND THE POTENTIAL AREA OF FUTURE RESEARCH

Finally, in the concluding section (chapter 6) I have summarised the research presented in this thesis and discussed about the future direction. There is considerable argumentation of how far the hardness can be used as a criterion for stability and what conditions are to be followed. An important part of this thesis concerns with the above aspect. Recently Sebastian (Sebastian, 1994) has pointed out that the proof of PMH by Parr and Chattaraj (Parr and Chattaraj, 1991) does not hold good in general cases. In this background, our numerical results will throw useful hints in future. The new directions in this area are summarised briefly in this chapter.

CHAPTER 2

CORRELATION OF POLARIZABILITY AND HARDNESS IN POLYATOMIC MOLECULES

2.1 INTRODUCTION

It has been mentioned in the introductory chapter that the hard-soft concept of acids and bases was introduced first by Mulliken (1952a) and then thoroughly investigated by Pearson (1963). Pearson qualitatively related hard or soft behaviour of chemical species to the size, charge and polarizability in a systematic manner. But lack of any quantitative relation makes it difficult to arrange the chemical systems in terms of hardness. However, since then a rigorous definition of hardness has been provided by Parr and Pearson (Parr and Pearson, 1983). An operational approximation to the rigorous definition of hardness is more popular and gives definite hardness values of chemical systems. This subsequently helps in their rank ordering.

In view of the importance of hardness as an alternative measure of the stability of the system, it is worth studying the relation of hardness with other molecular properties. These are polarizability, electronegativity, molecular dimension (i.e. change of bond distances) etc. In the first chapter we have already discussed how polarizability (α), and hardness (η) and atomic or molecular dimensions are related to each other. Polarizability is related to the mean excitation energy (Δ, i.e. the HOMO-LUMO gap or indirectly 'hardness') by the expression,

$$\alpha \approx (2/3\Delta)\delta\mu^2 \qquad 2.1$$

Here $\delta\mu$ is the root mean square deviation of the dipole moment from the mean value. For polar molecules $\delta\mu$ have a non-zero value and is called the true fluctuation. When fluctuation is high the chemical species is highly polarizable or has higher softness. Now this fluctuation increases with increasing dimension as also number of electrons. These are analytically expressed as,

$$\alpha = (2/3\Delta)e^2\langle r^2\rangle \qquad 2.2$$

and

$$\alpha \approx (2/3\Delta)e^2 N_e R_a^2 \qquad 2.3$$

Here $\langle r^2\rangle$ is the mean square radius of the electrons orbital, N_e - the number of electrons, R_a is the radius of the atom assuming that $\langle r^2\rangle = R_a^2$.

Now it is natural to test the validity of the above relations in different type of chemical species. There are some related works in this direction (Jorgensen, 1967; Politzer, 1987; Sen et al, 1987; Vela and Gázquez, 1990; Chandra, 1994; Ghanty and Ghosh, 1993; Gázquez et al, 1993). Ghanty and Ghosh (Ghanty and Ghosh, 1994d, 1994e) has shown that through simple expectation values involving the frontier orbitals of DFT, good prediction of several global atomic properties (e.g. hardness, dipole and quadrupole polarizability, electronegativity and covalent radius) is possible. But most of these studies focus mainly on atoms and atomic clusters. However, molecules provide interesting cases for studying such a relation. These are interesting examples primarily because of the aspherical charge density. Due to the complex and numerous types of constructions of molecules, the expressions (2.2) and (2.3) are not easy to adapt.

In this chapter we want to present a preliminary study of the change of hardness with the distortion of the bonds in a molecule and of the corresponding changes in polarizabilities using ab initio wave function formalism. Although a quantitative analytic relation is not possible, the numerical work presented in this chapter of the thesis will be helpful in relating η with polarizability in a qualitative way for molecular systems. We studied the behaviour of the above relations as different types of bonds were distorted for a variety of systems.

The values of hardness and the corresponding chemical potential have been calculated using the operational definitions i.e.

$$\mu = -(IP + EA)/2 \quad \text{and} \quad \eta = (IP - EA)/2 \qquad 2.4$$

To check the consistency of the results the Koopmans´ approximation to equation (2.4), using frontier orbitals, has also been used i.e.

$$\mu = (\epsilon_L + \epsilon_H)/2 \quad \text{and} \quad \eta = (\epsilon_L - \epsilon_H)/2 \qquad 2.5$$

Basis sets of varying quality have been used to reach a conclusion. The chapter is organized as follows :

In section 2.2 we describe the methods and basis sets used for our calculation. In section 2.3 we present the results and discussion of our study. Essential conclusions are the content of section 2.4.

2.2 METHODOLOGY AND BASIS SET USED

Hardness (η) values have been calculated by using both the equations (2.4) and (2.5). Equation (2.4) involves the calculation of energies of the neutral species and the corresponding cations and anions for a particular nuclear configuration i.e. vertical IP's and EA's . The energy values of all these species are calculated by using separate self-consistent-field (SCF) method. This method is called ΔSCF method and we shall denote this method as a_1 for future discussion. The second approach uses equation (2.5) involving Koopmans' approximation . This method will henceforth be called a_2. The polarizability P is defined as $(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3$, where α is the polarizability tensor. It is already mentioned in the introductory chapter that this definition originated from the assumption that the molecule is freely rotating in a fluid and so the polarizability P is the mean polarizability of the three directions. The α values have been evaluated by a finite field procedure at SCF level. ACES program system (Bartlett et al, 1987) is used to perform the SCF calculations. Double-zeta basis set of Huzzinaga and Dunning are used to perform most of the calculations (Huzzinaga, 1965; Dunning, 1970). However, to study the basis set effects extensively, we choose water molecule as an example system. Special efforts are taken to study the important point i.e. how η and $P^{1/3}$ vary with bond distortions. For this purpose three different kind of basis sets are used. These basis sets are (i) Huzinaga-Dunning double-zeta (DZ), (ii) DZ plus a set of d functions on oxygen atom with exponent 1.211 and a set of p functions on hydrogen atom with exponent 0.6 (DZP), (iii) The third basis set is somewhat more extended. Here a contracted set of 5s and 4p functions from the primitive 11s and 6p on oxygen, plus a set of d functions with exponent 1.33. For hydrogen a contracted set of 3s functions from the primitive 5s on hydrogen plus a set of p function with exponent 1.00 is used. As this basis set is of near triple-zeta quality with a set of polariztion functions , we shall refer this as TZP.

2.3 RESULTS AND DISCUSSION

(*i*) CHANGE OF HARDNESS WITH BOND DISTORTION (ΔR)

The first study presented here is the change of hardness values as one of the bonds is stretched or contracted. First, we present the basis set study for water molecule using both a_1 and a_2 approaches. Table 2.1 gives some typical values of hardness at different O-H bond distances (keeping one bond at experimental equilibrium value). We see that the values of hardness obtained using a_1 approach are smaller than the ones obtained in a_2 approach in any basis. The general trend that emerges in either of the approaches and in any of the basis is that the hardness values decrease monotonically with the stretching of the bond. The results have been obtained for small distortion around equilibrium geometry. [In this context it is worth mentioning that Gázquez et al (Gázquez et al, 1993) have observed the same trend while trying to relate the hardness differences with energy differences for diatomic molecules]. We have fitted 11 sets of η and ΔR data points in different basis in each of the approaches using linear as well as different degree polynomial functions. The standard deviation (s.d.) values from these are tabulated in table 2.2 . It is again gratifying to note that the trend of the change of s.d. values from linear to different degree of polynomial fits is same in both the approaches as well as in different basis sets. The s.d. values in a higher (4th) degree polynomial fit are typically reduced by 3 orders in magnitude than that obtained from the linear fit. But the s.d. values of the linear fit itself is so small that the relation can better be considered as a linear one. The similar trend using two different approaches, although approximate, and a variety of basis sets gives us confidence to conclude that η is predominantly linear with the change in bond distance. Similar study has also been done for the change of chemical potential (μ) with the bond distance. We find that similar to η, μ also decreases with the change in O-H distance. However, this change is much more slow compared to the change in η. The trend is again similar in the different basis sets considered and in a_1 and a_2 approaches.

To strengthen the above point, we have also chosen other systems like CH_4, CH_3F and CH_3Cl in our study. Table 2.3 displays some of the typical hardness values in DZ basis using approach a_1, as C-H, C-F and C-Cl bond is stretched in the molecules CH_4 , CH_3F and CH_3Cl respectively - keeping the other C-H bond lengths fixed. Table 2.4 presents the s.d. values of η vs ΔR plots with different polynomial fits. Again, we observe that the curve is dominantly linear. This is particularly so for C-H distortion in CH_4, where the s.d. values of linear fit are reduced by only a factor of ten for higher degree polynomial fit, indicating a fairly linear relationship. But for C-F and C-Cl distortion these s.d. values are reduced by three orders of magnitude pointing to a very weak nonlinear behaviour.

The above study also helps us to understand how the hardness values change as the bond between atoms of different electronegativities or sizes is stretched in similar environment. From the results of table 2.3, it is seen that η values change more rapidly for C-Cl and C-F distortion. These results reflect that the change is in the order C-Cl > C-F > C-H . We have made another type of study where CH_3Cl molecule is taken and the changes of η with C-H and C-Cl bond distortions are studied. Similarly, we have studied the change for C-H and C-F bond stretch separately in CH_3F molecule. Hence, as an example, we have plotted in figure 2.1, the change in η with ΔR for C-H and C-F bond stretch separately for CH_3F molecule. We find in this case that the change for C-F distortion is much larger than that of C-H. While comparing, it has to be noted that in this case the environment is no longer the same. Similar plot has been presented in figure 2.2 for CH_3Cl molecule. We now see that the change in C-Cl is again larger than that of C-H and this exceeds the change of C-F over C-H in figure 2.1 . Either way (whether the environment is same or not) the change in η with ΔR somehow follows the trend C-Cl > C-F > C-H .

(ii) CHANGE OF MOLECULAR POLARIZABILITY WITH ΔR

We have also tried to establish the relation between distortion of a single bond and the molecular polarizability. Our general observation is that the cube root of polarizability, $P^{1/3}$, and not P, increases dominantly in a linear manner with the change of individual bond distance. Ghanty and Ghosh (Ghanty and Ghosh, 1993) observed a linear relation of the $P^{1/3}$ with the individual atom - atom distances in atomic clusters. It is interesting to note the validity of such a relation when a specific bond is stretched by a small amount around equilibrium in molecules. However, the linear relation of $P^{1/3}$ vs ΔR curve is present in this case, too. To make an extensive study we observed the changes of $P^{1/3}$ in the systems described before. We have presented in table 2.5 the polarizability values of H_2O molecules at typical distances of one of the O-H bonds (keeping the other O-H bond fixed) in different basis sets. Values of s.d. for different degrees of polynomial fit of $P^{1/3}$ values with ΔR for this molecule are given in table 2.6 . Again we observe that the s.d. values of the linear fits are very small indicating linear relation, although these values are reduced (typically by 3 orders in magnitude) as we fit 11 sets of points with a higher degree polynomial. This trend holds good in all three different basis sets.

In table 2.7 we have presented the s.d. values of $P^{1/3}$ vs ΔR fit using different polynomial relations for different bond distortions in CH_4, CH_3Cl and CH_3F molecules in DZ basis. In this case also while we find a linear relation between $P^{1/3}$ and ΔR, a critical study of behaviour for different type of bond distortions is again interesting. As examples, in fig. 2.3 the values of $P^{1/3}$ vs ΔR for C-H and C-F bond distortions of CH_3F molecule are plotted. As another example, the similar plot for C-H and C-Cl distortion in the case of CH_3Cl molecule is presented in fig. 2.4. From figure 2.4 it is clear that there is a much more rapid increase in $P^{1/3}$values with C-Cl distortion compared to the C-H distortion. This can be rationalised by the fact that polarizability (P) has dependence on the number of electrons as also dimension (in this case bond distortion), which is already discussed in section 2.1 . So for a specific amount of distortion, change of P will be more for C-Cl bond than that of C-H. Arguing on the same ground we can predict that $P^{1/3}$ would change more rapidly for C-F distortion compared to C-H distortion. This would have been expected also from our results of change in η for CH_3F. But we find a reverse trend to this result in fig. 2.3 . The difference in the sensitivity of the hardness and polarizability values with carbon - hydrogen and carbon - halogen stretching needs further study.

(iii) RELATION OF POLARIZABILITY WITH HARDNESS

In table 2.8 we have presented the P and η values for the molecules CH_4, CH_3F and CH_3Cl using approach $a_1$and a_2. It is clear from the table and our previous discussion that the trend of polarizability is exactly reverse to that of hardness, i.e. P increases when η decreases in either of the approaches a_1 and a_2. In case of atomic systems one expects a linear relation between $P^{1/3}$ and η . This is because $P^{1/3}$ and r (atomic radius) show a linear relation (both from dimensionality viewpoint and the spherical nature of the electronic charge) and η changes predominantly in a linear relation with r (Ghanty and Ghosh, 1993). However, molecules generally have non-spherical charge density distribution and also the volume of a molecule does not scale with the cubic power of r (in this case bond distortion). However, since both $P^{1/3}$ and η scale roughly linearly with ΔR, we naturally expect to obtain a linear relation between these two quantities studied in this presentation. In figure 2.5 we have plotted $P^{1/3}$ vs η for C-H stretch of CH_4 molecule. In figs. 2.6 and 2.7 we have presented the plots of $P^{1/3}$ vs η for C-H as well as C-F and C-Cl stretch for CH_3F and CH_3Cl respectively. We indeed find that the plots of $P^{1/3}$ vs η show a linear behaviour. So even in the case of polyatomic molecules, nonlinear behaviour is weak and $P^{1/3}$ bears a dominant linear relationship with η. From our earlier study of the change due to the stretching of bond involving different types of atoms, it may be interesting to study how the values of $P^{1/3}$ change relatively with η in such cases.

(iv) ADDITIVITY OF HARDNESS AND POLARIZABILITY

We now make a study for the case when more than one bond is stretched. The stretchings considered in the present study are small around the equilibrium geometry. The results for H_2O molecule are presented in the table 2.9. We find that the change of the values of η and $P^{1/3}$ are regular showing additivity, at least for small distortions. When a single O-H bond is distorted in the molecule H_2O, the change in $P^{1/3}$ and η is almost half of the change when both the O-H bonds are distorted symmetrically by the same amount. We have found that this additivity phenomena holds even when two dissimilar bonds are distorted. To study this, we have taken a triatomic molecule HOCl as an example. Here both the O-H and O-Cl bonds of HOCl molecule are distorted by very small amounts. The changes in η and $P^{1/3}$ are almost equal to the sum of the respective quantities obtained by distorting O-H and O-Cl bonds separately. The results are shown in table 2.10 . The additivity is a manifestation of linear behaviour for small ΔR. Taylor´s series expansion of these quantities can be made in terms of bond distortions (ΔR). When ΔR is small, the nonlinear terms in these expansion become relatively small and hence the additivity is observed. In this domain of small distortion, the chemical potential μ happens to remain nearly constant. However, when the distortions will be larger, the nonlinearity in this changes is likely to show. As expected, in the case of such large distortions, the changes of η and $P^{1/3}$ will not be additive. This is obvious from table 2.10 , when O-H bond distortions are made larger and larger, nonadditivity become more and more prominent.

2.4 CONCLUSIONS

In this chapter basically I wanted to present a study concerning the changes of hardness and polarizability with bond distortions as well as the mutual relation and dependence of hardness and polarizability on the electronegativity of the stretched atoms in polyatomic molecules. Obviously the change of molecular polarizabilities and global hardness with the change of a specific bond length is far more complex than the case of atoms or atomic clusters. From our study we conclude that if the distortion of a bond is small enough so that μ remains nearly constant, the relationship of η and $P^{1/3}$ with bond distortions is dominantly linear. Sometimes the trends of η and $P^{1/3}$ of different bonds cannot be explained on the basis of common chemical concept. As we have seen in section 2.3.(i) and 2.3.(ii), for CH_3F molecule the increase of $P^{1/3}$ with distortion of C-H bond is higher than that of C-F bond, although the reverse is expected from the change of η with ΔR. A plausible reason for this unusual behaviour may be the fact that we are trying to extract global information (η and $P^{1/3}$) from the local deformation of the molecular geometry. To gain a more clearer insight local parameters e.g local hardness (or softness) and local polarizability may be used to explain the cases of specific bond distortion. In this context, it may even be useful to define the change in polarizability along a bond or ´local bond hardness´ and see their change with ΔR. A concept of ´bond hardness´ was introduced by Cioslowski and Mixon (Cioslowski and Mixon, 1993). But these definitions depend upon the values of total energies and energy derivatives calculated for molecules in equilibrium geometry and composed of fragments with limited degree of charge transfer. But how this charge transfer varies in the case of bond distortions is a matter of detailed investigation - which may help in explaining the appearence of nonlinearity with large bond distortion. In this context it may be mentioned that Ghosh and co-worker (Ghanty and Ghosh, 1994a, 1994b ; Ghosh, 1994) have used the concept of ´bond hardness´ and ´bond electronegativity´ to explain the nature of chemical bonding in diatomic molecules. According to their formulation the reason of covalent bonding is the accumulaion of electron density at the bond center. But the origin of ionic bonding is interatomic charge transfer between the constituent atoms. To give a rigor to their derivation, they used the spin dependent electronegativity and hardness parameters for atoms calculated through spin-polarized Kohn-Sham density functional theory with self interaction correction and within the local density approximation (Ghanty and Ghosh, 1994c). Spin dependent evaluation of these parameters is analogous to the UHF calculation of energy as both these two methods can describe the bond dissociation problem more accurately. The dissociation of bonds may be considered as the limiting case of bond distortion. With the help of their formulation they generated the bond energy at an arbitrary bond distance and anharmonicity constants of some diatomic molecules with reasonable accuracy.

So the change of ´local bond hardness´ with distortion of bond would require further probe. On theoretical front, relation of ´local bond hardness´ and polarizability vis-a-vis that of ´local softness´ and polarizability requires further thought. Not only this, how far the above relations hold true for cases where multiply bonded (e.g. double, triple bonded) atoms are distorted in polyatomic molecules should also be studied. Our present study in molecular cases is new and preliminary and may provide scope for the above mentioned extensive investigation.

Table 2.1. Hardness values of the molecule H_2O when one of the O-H bonds is stretched keeping the other bond at its experimental bond length. The hardness values are calculated by both the approaches a_1 and a_2 (see the text) and also using different basis sets. All values are in atomic units.

O-H bond stretch (ΔR)	Hardness					
	DZ		DZP		TZP	
	a_1	a_2	a_1	a_2	a_1	a_2
0.00	0.306 384	0.362 417	0.307 623	0.364 054	0.331 643	0.392 303
0.02	0.305 131	0.361 487	0.306 395	0.363 163	0.330 052	0.391 056
0.04	0.303 813	0.360 520	0.305 103	0.362 239	0.328 352	0.389 745
0.06	0.302 430	0.359 516	0.303 747	0.361 280	0.326 547	0.388 374
0.08	0.300 981	0.358 474	0.302 325	0.360 285	0.324 635	0.386 939
0.10	0.299 468	0.357 393	0.300 837	0.359 254	0.322 633	0.385 443
0.12	0.297 892	0.356 274	0.299 283	0.358 186	0.320 516	0.383 886
0.14	0.296 254	0.355 117	0.297 666	0.357 081	0.318 322	0.382 269
0.16	0.294 559	0.353 922	0.295 987	0.355 938	0.316 051	0.380 597
0.18	0.292 809	0.352 689	0.294 249	0.354 757	0.313 708	0.378 870
0.20	0.291 007	0.351 421	0.292 455	0.353 538	0.311 302	0.377 092

Table 2.2. Standard deviation values obtained by fitting the hardness values of water presented in table 2.1 using polynomials of varying degrees.

Basis set	Approach	Polynomials of degreee			
		1	2	3	4
DZ	a_1	2.73 E-4	7.11 E-6	1.77 E-6	2.54 E-7
	a_2	1.68 E-4	6.57 E-7	6.28 E-7	1.31 E-7
DZP	a_1	2.82 E-4	4.33 E-6	1.91 E-6	1.99 E-7
	a_2	1.62 E-4	2.03 E-6	5.26 E-7	1.26 E-7
TZP	a_1	4.08 E-4	2.48 E-5	4.85 E-6	2.63 E-6
	a_2	2.63 E-4	5.71 E-6	1.35 E-6	1.85 E-7

Table 2.3. Hardness values of CH_4, CH_3F and CH_3Cl at different bond lengths of a particular bond keeping the other bonds fixed at their respective experimental values. The approach used is a_1. All data are in atomic units.

	CH_4	CH_3F		CH_3Cl	
ΔR	C-H	C-F	C-H	C-Cl	C-H
-0.06	0.391 398	0.340 591	0.336 044	0.278 268	0.271 852
-0.02	0.390 799	0.337 660	0.336 015	0.273 866	0.271 715
0.00	0.390 338	0.335 998	0.335 998	0.271 644	0.271 644
0.02	0.388 713	0.334 207	0.335 836	0.269 413	0.271 507
0.06	0.385 129	0.330 240	0.335 497	0.264 931	0.271 225
0.10	0.380 942	0.325 787	0.335 134	0.260 442	0.270 929
0.14	0.376 374	0.320 889	0.334 743	0.255 962	0.270 619
0.18	0.371 549	0.315 602	0.334 316	0.251 504	0.270 293
0.20	0.369 065	0.312 832	0.334 085	0.249 286	0.270 124

Table 2.4. Standard deviation values obtained by fitting (16 points) hardness values of CH_4, CH_3F and CH_3Cl with the amount of bond distortion for each of the bonds using a polynomial of different degrees.

Molecule	Bond	Polynomial of degrees 1	2	3	4
CH_4	C-H	1.43 E-3	4.33 E-4	1.43 E-4	1.24 E-4
CH_3F	C-F	8.41 E-4	3.93 E-5	6.65 E-6	2.16 E-7
	C-H	1.05 E-4	3.89 E-5	2.60 E-5	1.35 E-5
CH_3Cl	C-Cl	2.14 E-5	1.84 E-5	1.38 E-6	5.41 E-8
	C-H	6.19 E-5	2.16 E-5	1.01 E-5	7.82 E-6

Table 2.5. Variation of molecular polarizability with the distortion of a single O-H bond of the molecule water. The calculations are done using three different basis sets. All values are in atomic units.

	Polarizability		
ΔR	DZ	DZP	TZP
0.00	4.3715	5.4242	5.1276
0.02	4.4289	5.4786	5.1780
0.04	4.4875	5.5342	5.2295
0.06	4.5475	5.5910	5.2820
0.08	4.6087	5.6491	5.3358
0.10	4.6712	5.7083	5.3906
0.12	4.7350	5.7688	5.4467
0.14	4.8001	5.8305	5.5039
0.16	4.8664	5.8935	5.5623
0.18	4.9341	5.9577	5.6219
0.20	5.0030	6.0231	5.6827

Table 2.6. Standard deviation values of the fitting of $P^{1/3}$ of H_2O with the amount of bond distortions in polynomials of various degrees.

	Polynomial of degrees			
Basis	1	2	3	4
DZ	5.67 E-3	2.19 E-5	7.82 E-6	7.63 E-6
DZP	3.72 E-4	5.81 E-6	8.19 E-7	7.60 E-7
TZP	3.73 E-4	1.66 E-6	7.36 E-7	7.28 E-7

Table 2.7. Standard deviation values of polynomial fits of $P^{1/3}$ with the amount of bond distortion for various types of bonds in the molecule like CH_4, CH_3F and CH_3Cl.

Molecule	Bond Distorted	Polynomial of degree 1	2	3	4
CH_4	C-H	3.15 E-4	6.23 E-6	1.23 E-7	7.20 E-9
CH_3F	C-H	3.69 E-4	1.08 E-5	1.24 E-6	8.26 E-7
	C-F	7.60 E-4	2.75 E-5	5.52 E-7	2.32 E-8
CH_3Cl	C-H	3.59 E-4	4.67 E-6	4.51 E-7	4.35 E-7
	C-Cl	2.66 E-4	1.45 E-5	6.33 E-7	3.86 E-8

Table 2.8. Some typical hardness and polarizability values of CH_4, CH_3F and CH_3Cl molecules at different bond lengths of a particular bond keeping the other bonds fixed at their respective experimental values. All data are in atomic unit.

Molecule	Bonds					
CH_4		C-H				
	$\eta(a_1)$	$\eta(a_2)$	P			
	0.37155	0.40190	12.3050			
	0.37399	0.40427	12.2250			
	0.37870	0.40885	12.0679			
	0.38094	0.41104	11.9908			
	0.38513	0.41518	11.8397			
	0.38703	0.41710	11.7656			
	0.39034	0.42057	11.6205			
	0.39114	0.42101	11.4794			
CH_3F		C-H			C-F	
	$\eta(a_1)$	$\eta(a_2)$	P	$\eta(a_1)$	$\eta(a_2)$	P
	0.33432	0.37187	12.0354	0.31560	0.37389	11.8581
	0.33453	0.37272	11.9511	0.31830	0.37473	11.7910
	0.33494	0.37439	11.7857	0.32339	0.37622	11.6619
	0.33513	0.37520	11.7047	0.32579	0.37686	11.5999
	0.33550	0.37677	11.5461	0.33024	0.37794	11.4812
	0.33567	0.37754	11.4685	0.33229	0.37837	11.4246
	0.33600	0.37903	11.3169	0.33600	0.37903	11.3169
	0.33601	0.37897	11.1698	0.33919	0.37942	11.2169
CH_3Cl		C-H			C-Cl	
	$\eta(a_1)$	$\eta(a_2)$	P	$\eta(a_1)$	$\eta(a_2)$	P
	0.27029	0.30656	18.2593	0.25150	0.29294	18.7433
	0.27046	0.30674	18.1676	0.25373	0.29464	18.5973
	0.27078	0.30709	17.9811	0.25820	0.29803	18.3095
	0.27093	0.30726	17.9003	0.26044	0.29972	18.1677
	0.27122	0.30758	17.7285	0.26493	0.30307	17.8884
	0.27137	0.30773	17.6446	0.26717	0.30473	17.7509
	0.27164	0.30802	17.4806	0.27164	0.30802	17.4806
	0.27178	0.30800	17.3217	0.27607	0.31125	17.2165

Table 2.9. Change of hardness and cube root of polarizability ($P^{1/3}$) when a single (D_1) or both (D_2) the O-H bonds are distorted of the molecule H_2O. All values are in atomic units.

ΔR		η			$P^{1/3}$		
		DZ	DZP	TZP	DZ	DZP	TZP
0.02	D_1	0.00125	0.00123	0.00159	0.00712	0.00585	0.00563
	D_2	0.00246	0.00241	0.00309	0.01423	0.01169	0.01124
0.04	D_1	0.00257	0.00252	0.00329	0.01435	0.01180	0.01134
	D_2	0.00494	0.00484	0.00620	0.02861	0.02354	0.02264
0.06	D_1	0.00395	0.00388	0.00510	0.02166	0.01783	0.01714
	D_2	0.00744	0.00730	0.00932	0.04312	0.03552	0.03418
0.08	D_1	0.00540	0.00530	0.00701	0.02906	0.02395	0.02302
	D_2	0.00996	0.00978	0.01246	0.05777	0.04765	0.04587
0.10	D_1	0.00692	0.00679	0.00901	0.03654	0.03016	0.02899
	D_2	0.01250	0.01229	0.01561	0.07254	0.05991	0.05769

Table 2.10. Change in hardness and cube root of polarizability ($P^{1/3}$) when O-H (D_1), O-Cl (D_2) and both (D_3) the bonds of the HOCl molecule are distorted. All values are in atomic units. The basis set used is DZ.

	η			$P^{1/3}$		
ΔR	D_1	D_2	D_3	D_1	D_2	D_3
0.03	0.27243	0.27075	0.27032	2.27449	2.28281	2.29023
0.02	0.27259	0.27147	0.27117	2.27199	2.27754	2.28247
0.01	0.27275	0.27219	0.27204	2.26950	2.27228	2.27474
0.00	0.27290	0.27290	0.27290	2.26704	2.26704	2.26704
-0.01	0.27305	0.27362	0.27377	2.26460	2.26180	2.25936
-0.02	0.27320	0.27433	0.27465	2.26219	2.25658	2.25171
-0.03	0.27335	0.27504	0.27552	2.25979	2.25136	2.24408

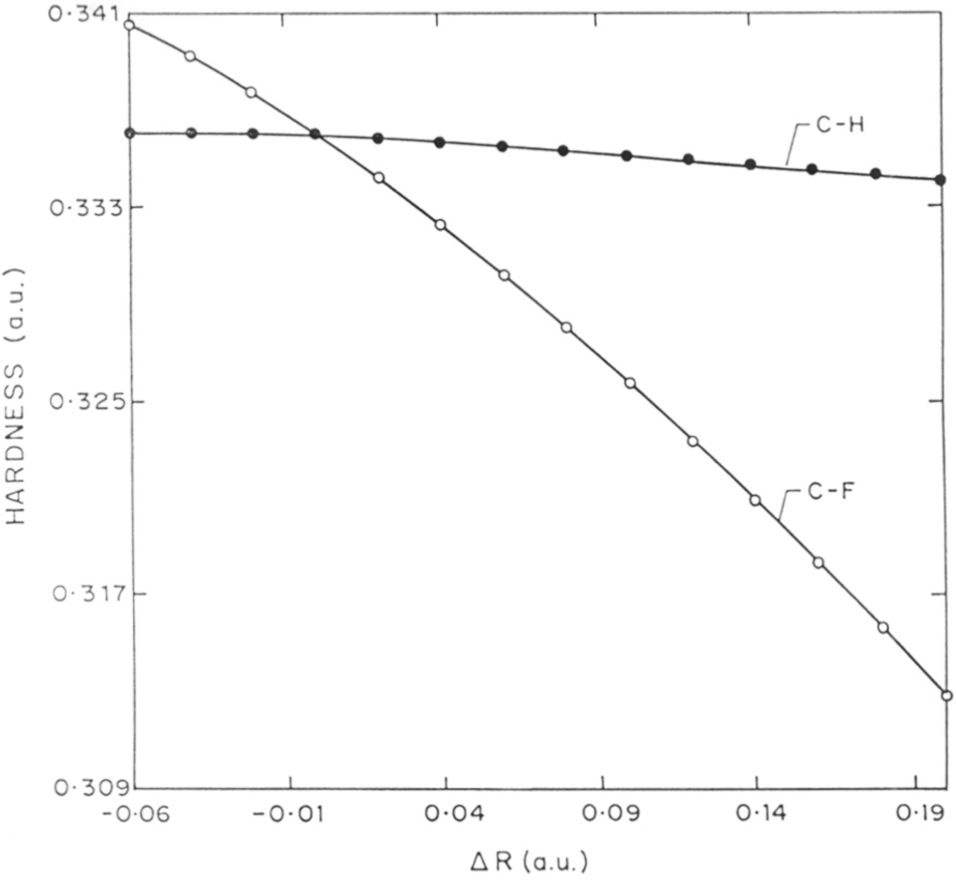

Fig. 2.1. Plot of hardness values of CH_3F with respect to the amount of single bond distortions (ΔR) of the C-H and C-F bonds keeping the other bonds fixed at their respective experimental bond lengths.

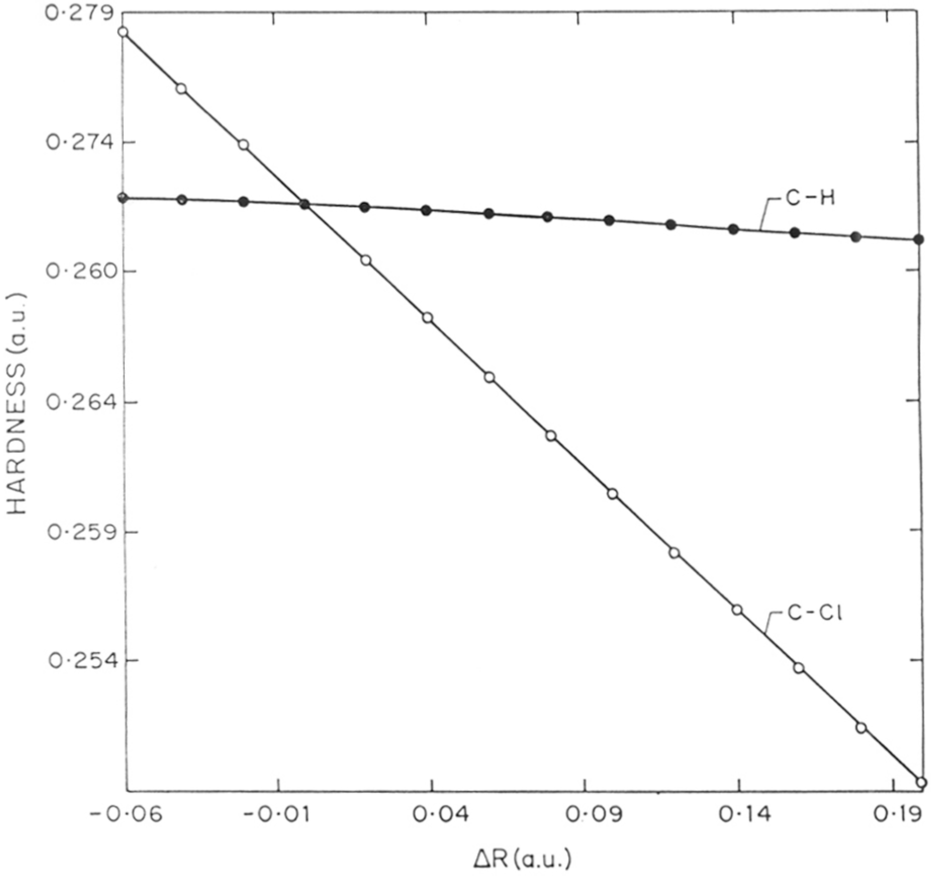

Fig. 2.2. Plot of hardness values of the molecule CH_3Cl against the amount of bond distortions of the C-H and C-Cl bonds keeping the other bonds fixed at their respective experimental values.

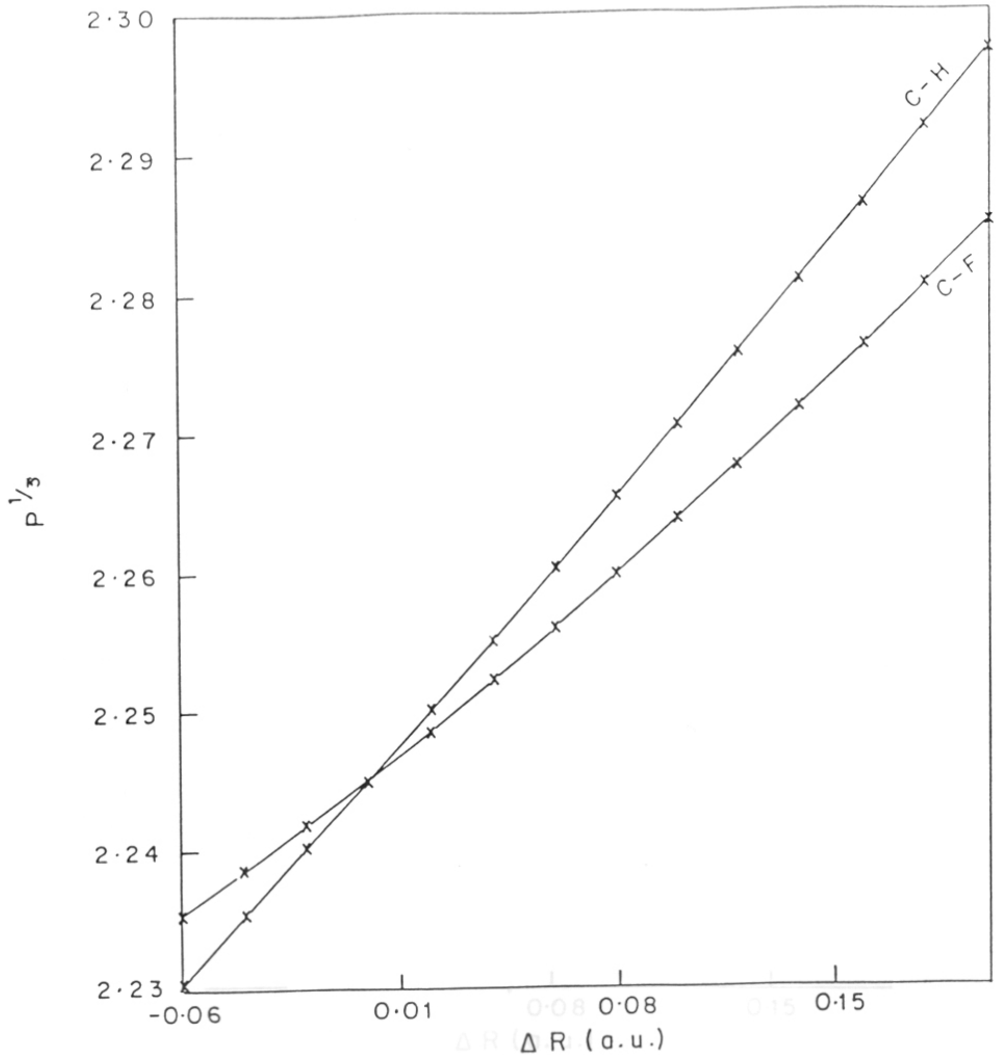

Fig. 2.3. Variation of $P^{1/3}$ (in a.u.) with the amount of single bond distortions of the C-H and C-F bonds of the CH_3F molecule.

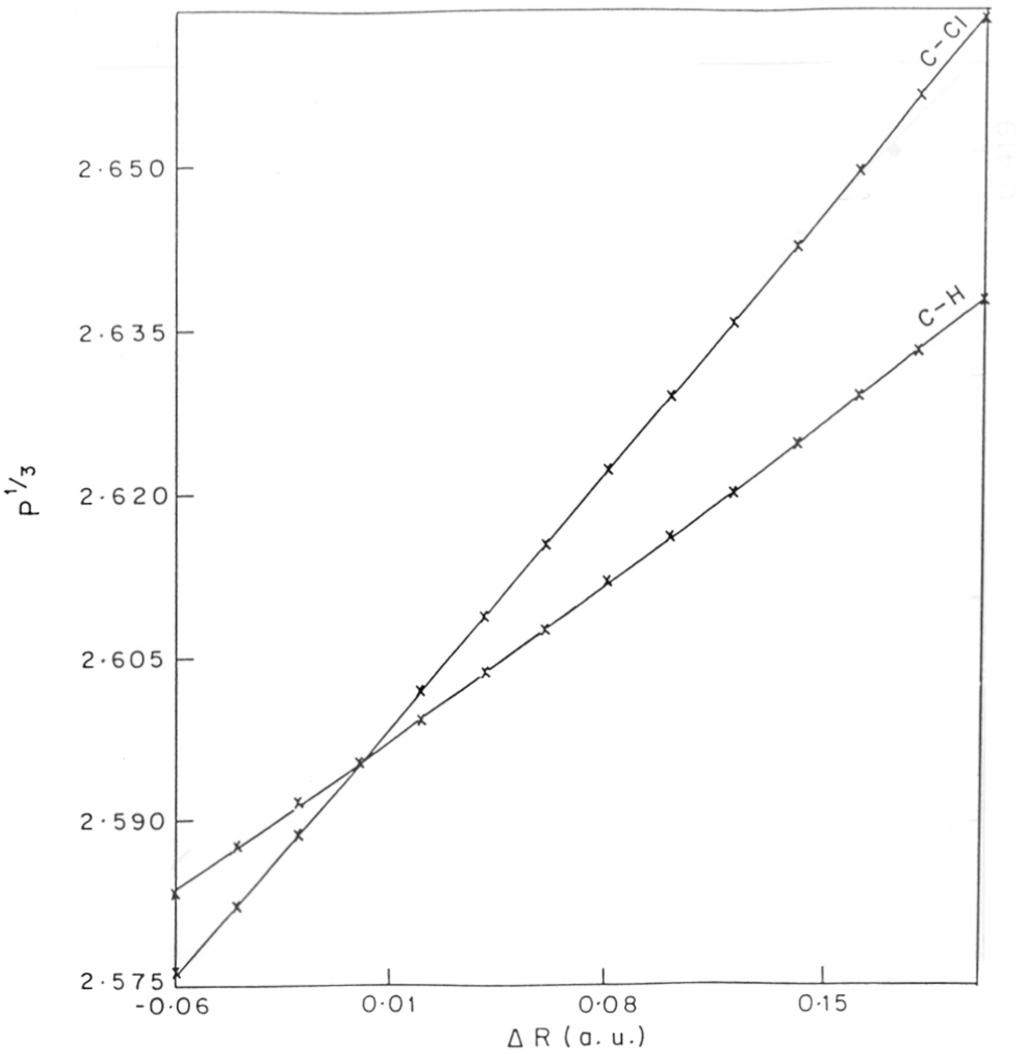

Fig. 2.4. Variation of $P^{1/3}$ (in a.u.) with the amount of single bond distortions of the C-H and C-Cl bonds of the CH_3Cl molecule.

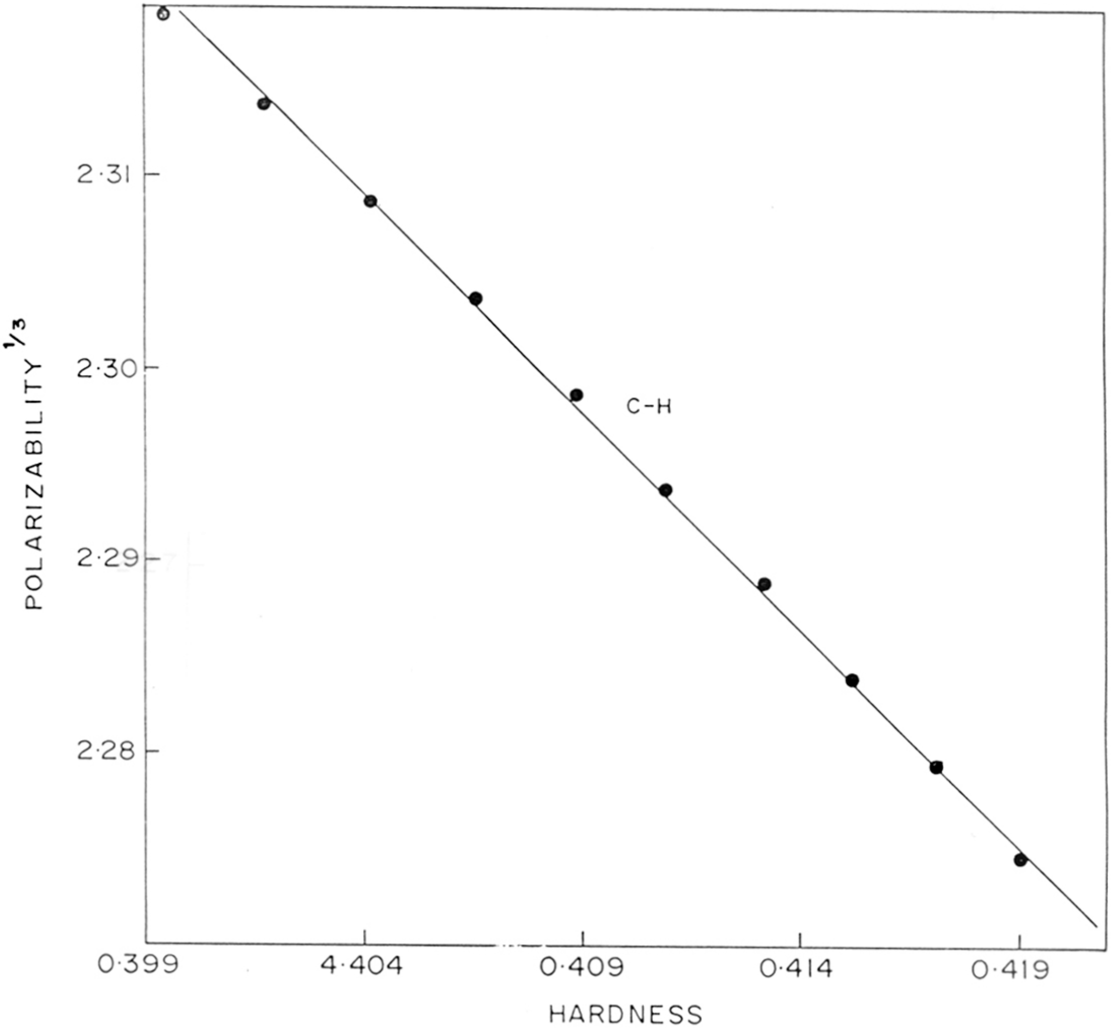

Fig. 2.5. Plot of $P^{1/3}$ (in a.u.) vs η (in a.u.) for a single C-H bond stretching of the CH_4 molecule keeping the other three C-H bonds fixed at their experimental bond lengths.

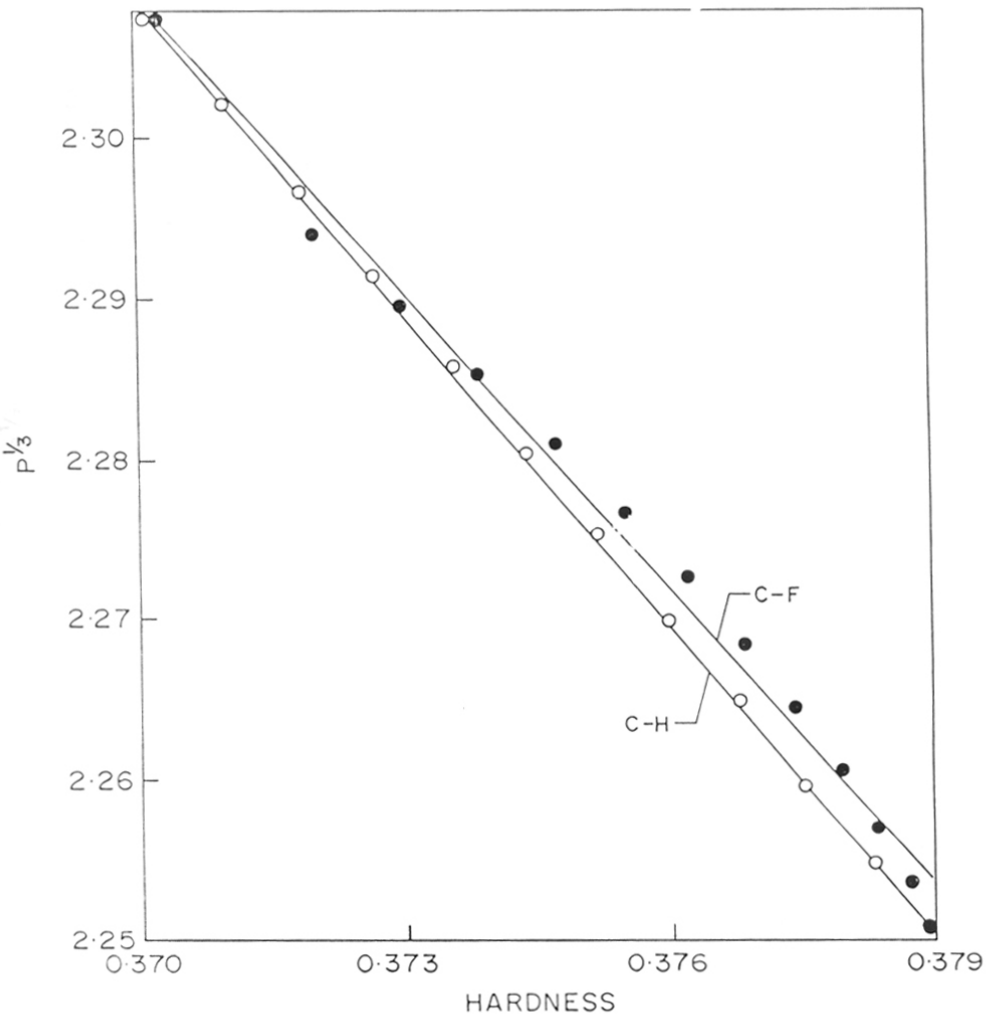

Fig. 2.6. Plot of $P^{1/3}$ (in a.u.) against η (in a.u.) for stretching of the C-H and C-F bond each at a time of the CH_3F molecule keeping the other bonds fixed at their experimental bond lengths.

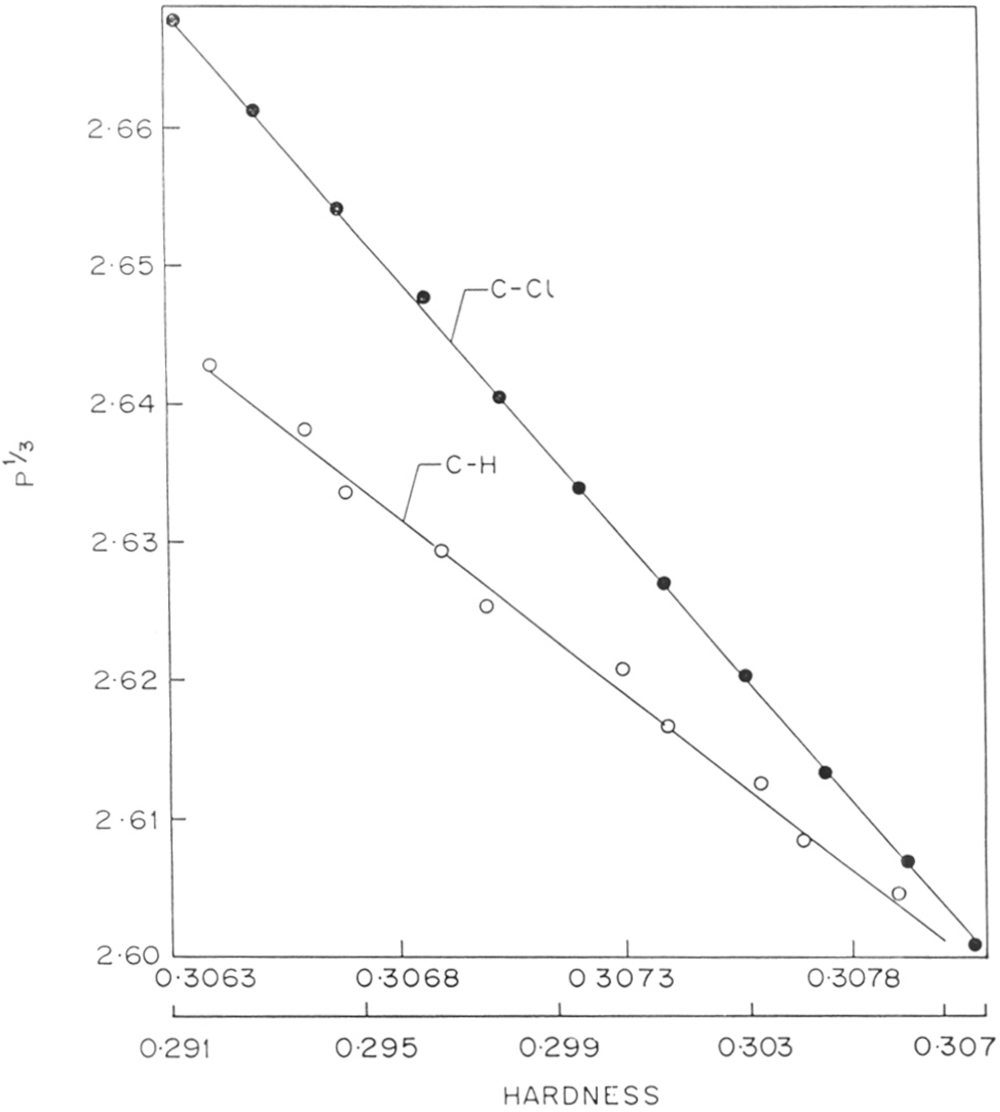

Fig. 2.7. Variation of $P^{1/3}$ with the change in η for the C-H and C-Cl bond stretching of the CH_3Cl molecule keeping the other three bonds fixed at their respective equilibrium bond lengths. Upper scale in the hardness axis is for C-H distortion and the lower one is for C-Cl distortion.

CHAPTER 3

THE STABILITY OF A CHEMICAL SPECIES AND THE PRINCIPLE OF MAXIMUM HARDNESS (PMH)

3.1 INTRODUCTION

In the preceding chapter we have discussed the relation between polarizability and chemical hardness for molecular systems. The variation of these quantities with distortion of bonds has also been studied by us. It has been observed in the cases studied that as the geometry is distorted from the equilibrium one, polarizability increases and hardness decreases. From the stability point of view we know that at equilibrium geometry any chemical species becomes most stable and possesses the minimum total energy. An association of principle of minimization of total energy with the principle of maximum global hardness was first conjectured by Pearson (Pearson, 1987). In a pedagogical paper, he mentioned philosophically that "there seems to be a rule of nature that molecules arrange themselves so as to be as hard as possible". He reached this conclusion while trying to correlate the geometry of a molecule with its HOMO - LUMO gap, i.e. hardness, and found that the most stable geometry corresponds to largest value of hardness.

Pearson also stated that hard molecules not only resist the changes in the total amount of charge but also the changes in the charge distribution within the molecule. So any chemical species (molecules, radicals or ions) resists the changes in charge distribution which takes the system from a stable equilibrium to unstable nonequilibrium geometries and the resistance is highest (maximum hardness) at the equilibrium geometry.

The first rigorous analytical proof of this qualitative statement was attempted by Parr and Chattaraj (Parr and Chattaraj, 1991). Assuming a chemical species (atom, molecule, metal etc.) as a member of a grand cannonical ensemble and applying fluctuation - dissipation theorem of statistical mechanics, they proved that a system at a given temperature will evolve to a configuration with maximum hardness, provided v and μ remain constant. This is known as the principle of maximum hardness (PMH). Though the authors expressed reservation in assuming a chemical species as a statistical system, various studies (Parr and Yang, 1989) indicate that an individual molecule can be considered as a statistical system. There has been some controversy about the general nature of this statement and proof subsequently and we will discuss this at an appropriate stage of the thesis.

3.2 SUBSEQUENT STUDIES REGARDING THE VALIDITY OF THE PRINCIPLE OF MAXIMUM HARDNESS

The statement of PMH itself generated interest in subsequent efforts to test the validity of the principle on various chemical phenomena. Among the recent ones, one may quote the efforts by Datta (Datta, 1992), who chose the dynamics of umbrella effect in NH_3 molecule and intramolecular proton transfer in malonaldehyde. He showed that hardness becomes maximum at the transition point - which is farthest from the most stable (i.e. equilibrium) geometry. Pearson and Palke (Pearson and Palke, 1992) used HF-SCF method to study the change of hardness of NH_3 and C_2H_6 molecule. They observed that asymmetric distortions along the vibrational symmetry coordinates lead to maximum η at equilibrium geometry. In this type of distortion μ can be kept reasonably constant. But for symmetric distortion, there is no maxima in the hardness profile and the value of the hardness increases with decreasing bond distances. From the symmetry properties of the corresponding integrals, they explained the maxima in hardness profiles for asymmetric distortion. They also explained the nonoccurence of such a maxima for symmetric distortion. They argued that the point group of a molecule can be ascertained from the statement of PMH - but electrostatic Hellman - Feynmann theorem will be helpful to obtain the global equilibrium geometry.

Pearson (Pearson, 1992) has also shown that for a large number of chemical reactions, hardness always increases in the direction of molecule formation. Pearson has also used this maximum hardness principle to give a very qualitative explanation of relative stability. For example, a rough calculation yields η for H_2O is 9.5 ev and that for H_2S is 6.2 ev showing that the former is more stable (Pearson, 1993). Also from simple HOMO - LUMO gaps, Pearson predicted the stability of chemical species. Harbola (Harbola, 1992) claimed that for metal clusters the stability and chemical hardness run parallel to each other. Taking lithium clusters as examples, he demonstrated that for clusters containing magic number of atoms, chemical hardness reaches a local maximum. It is also known that the second energy difference of a cluster [defined as $\Delta_2(N_A) = E(N_A + 1) + E(N_A - 1) - 2E(N_A)$, where N_A is the number of atoms of the cluster considered], which is also the binding energy of a cluster, also shows maxima at these magic numbers (i.e. N_A = 2, 8, 18, 20, 34, 40 and 58 etc.). Thus he demanded that ´the occurrence of magic numbers for metal clusters, whose stability is determined by their electronic shell structure, can be understood as a manifestation of the principle of maximum hardness´.

There is another study with metal clusters by Galván et al (Galván et al, 1993). They have shown that for Si_4 cluster the maximum hardness corresponds to the rhombic structure, which is also the most stable among other structures.

3.3 DEFICIENCIES OF THE PREVIOUS STUDIES AND THE CONTEXT OF OURS WORK

Though all the above studies show that hardness increases in the direction of stabler geometry and reaches maximum at the most stable equilibrium one, they cannot be unequivocally considered as rational test of PMH as defined by Parr and Chattaraj. For example in the study of Datta, neither μ or v would remain constant because of the wide variation of geometry. Apart from this the methodology used by him and others were also not at an accurate level and were in fact often semi-empirical in nature, as used by Datta, for example.

The reliability of the results of Pearson and Palke (Pearson and Palke, 1992) is also not beyond doubt. This is because they used the operational definition of η and μ, which is further approximated by Koopmans′ theorem. It is well known that HF-SCF method does not always yield faithful results because the effect of correlation is missing. The further drawback of Koopmans′ approximation is that in addition to the correlation, the effects of relaxation are also neglected.

In the study of Harbola, as the size of the Li cluster increases, both μ and v change, which violates the conditions of PMH. In the study of Si_4 cluster by Galván et al, the values of v and μ also change during the transformation from one structural symmetry to another. Pearson (Pearson, 1993) argued that the validity of PMH can not be tested in case of isomeric transformations, where v changes drastically. The same drastic change in v occurs in case of chemical reactions where two or more atoms or radicals react to form a molecule. So the increase in hardness, as observed by Pearson in case of molecule formation from atoms or radicals (Pearson, 1992), does not confirm the real test of PMH.

In our study, we have undertaken a systematic and detailed study, taking care of the loopholes of the previous studies. Instead of using Koopmans′ approximation we used a highly correlated level of calculation to obtain the IPs and EAs. We have used Coupled Cluster (CC) methods, which takes care of both correlation and relaxation effect, in an extensive manner. The importance of the conditions of constant μ and v has been tested by studying the hardness change for both symmetric and asymmetric distortions of H_2O and NH_3 molecule and keeping the amount of distortion very small. But what is special in our study is that we have compared the hardness values between different symmetric geometries for a symmetric molecule. Within the constant μ, we show that equilibrium symmetric geometry has the maximum hardness. Ours is also the most accurate study in the test of the PMH, keeping the conditions as far as possible.

In section 3.4 we will discuss the computational methods used with a brief overview of CC method. A critical analysis of the results including special feature of our study is given in section 3.5. Finally, in the concluding section (section 3.6) the limitations of our study is pointed out and a direction is given for accurate evaluation of difference energies in wave-function formalism. The theoretical justifications of our results from symmetry properties of point groups are also briefly discussed.

3.4 COMPUTATIONAL METHOD

Coupled cluster (CC) methods are very accurate quantum chemical methods (Cizek, 1966; Paldus and Cizek, 1973; Bartlett, 1981; Mukherjee and Pal, 1989) used as the first-choice methods in quantum chemistry. These methods are specially recommended for the efficient incorporation of electron correlation and size extensivity, which are particularly important for extended systems. Traditional CC methods have used exponential wave operator on a dominant single determinant function. However, it has now been realised (Mukherjee and Pal, 1989) that a multideterminantal model space is essential to take care of the exact or near degeneracy that arises in many cases of interest, including excited states or curve crossing for potential energy surface calculation. The problem of convergence arising out of intruder states in these cases can be solved by using a general multideterminantal model space. There are primarily two versions of such multireference CC methods - one Fock-space based and another Hilbert-space based. The difference energies like the IPs, EAs and excitation energies can be calculated very accurately in a direct manner through Fock-space based multireference CC method (Pal _et al_, 1987, 1988; Rittby _et al_, 1989, Sinha _et al_, 1986; Mukherjee, 1986; Kaldor, 1987). The failure of Koopmans´ approximation in obtaining the IP and specially EA values is well documented (Cederbaum and Domcke, 1977). These values are obtained very reliably by the use of CC methods. It is well known that though Koopmans´ IP is comparatively better, Koopmans´ EA is not trustworthy at all.

In Fock space MRCC methods the restricted Hartree - Fock (RHF) determinant of an N - electron ground state is taken as the core or vacuum and the problem of (N-1) or (N+1) electron states is reduced to a one hole/one particle problem. Thus the problem of (N-1) electrons may be considered as in the 0 particle, 1 hole Fock space sector and the (N+1) electron problems are in the 1 particle, 0 hole Fock - space sector. We use the notation of representing the number of active particle and hole sectors as supercripts. For N-1 electron states, one constructs (N-1) electron model space consisting of one-hole determinants. The model space ψ_μ^0 can be written as

$$\psi_\mu^{0(0,1)} = \sum_I C_{\mu I}\phi_I \qquad 3.1$$

Here $\{\phi_I\}$ is a set of 1-hole determinants. The exact (N-1) electron states may be written as

$$\psi_\mu^{(0,1)} = \Omega\psi_\mu^{0(0,1)} = \{ e^{T^I} \}\psi_\mu^{0(0,1)} \qquad 3.2$$

Where T^I is expressed as sum of cluster amplitudes of the 0-hole, 0-particle sector as well as new amplitudes for the 1-hole sector, and the curly bracket denotes normal ordering of the operators contained within it. Lindgren (1978) first introduced the normal ordering of the ansatz. The equations for different Fock space sectors are obtained by what is known as the subsystem embedding condition (SEC). This procedure starts from the lowest sector of the Fock space e.g. (0,0) sector in this case and then treats the higher sectors progressively keeping the lower sector amplitudes as constants. The normal ordering guarantees that in the equation for (m,n) sector, amplitudes of higher sectors do not appear. Thus SEC, along with normal ordering ensure a decoupling of the equations. The cluster amplitudes of the (0,0) sector are obtained by the projection of Schrödinger´s equation for the ground state problem to the set of N-particle excited determinants ϕ^*. The cluster amplitudes for (0,1) sector may be obtained by projection of the Fock-space Bloch´s equation of the (0,1) sector to the virtual space of determinants ϕ^*. The Bloch equation of the (0,1) sector may be written as,

$$(H\Omega - \Omega H_{eff}^{(0,1)})P^{(0,1)} = 0 \qquad 3.3$$

Similarly the Bloch equation of (1,0) sector may be written as,

$$(H\Omega - \Omega H_{eff}^{(1,0)})P^{(1,0)} = 0 \qquad 3.4$$

We have used an approximation where the cluster amplitudes for the (0,1) and (1,0) sector contain only singly and doubly excited parameters and the ground state cluster amplitudes are truncated to only a two-body approximation. This model has been shown to provide accurate values of ionization and electron attachment energies for medium-sized systems (Pal et al, 1987, 1988; Rittby et al, 1989; Sinha et al, 1986; Mukherjee, 1986).

Initially we carry out a CC calculation with only doubly excited parameters for the ground state. Then a transformed hamiltonian $\bar{H}$ as $\bar{H} = e^{-T(0,0)} H e^{T(0,0)}$ is constructed and only one and two body parts of this $\bar{H}$ are kept for further use (ignoring higher body components of $\bar{H}$). This is an additional approximation used. However, it is expected that the three and higher body parts, which are of higher orders in perturbation, will not change the results significantly. Using the one and two body parts of $\bar{H}$ in CCD approximation, the equation (3.3) is projected to one and two body virtual space of the (0,1) sector. Similarly, the equation (3.4) is projected to virtual configurations belonging to the (1,0) sector. The resulting equations as well as the ground state CC for (0,0) sector amplitudes are systems of nonlinear equations furnishing the corresponding cluster amplitudes. The effective hamiltonian for the (0,1) and (1,0) problem is subsequently obtained by the P-space projection of equation (3.3) and (3.4) respectively. The eigenvalues of the effective hamiltonian furnish the energies of the (N-1)/(N+1) electron systems. This is characteristic of the effective hamiltonian based theories. Analysing the transformed hamiltonian $\bar{H}$ diagrammatically, we see that $\bar{H}$ has a component which consists of only closed diagrams and another which consists of different open diagrams. The closed part is the vacuum expectation value of $\bar{H}$ and corresponds to the ground state energy obtained by the solution of (0,0) sector. If these closed diagrams pertaining to the ground state energy are dropped from $\bar{H}$, the eigenvalues of $H_{eff}^{(0,1)}$ and $H_{eff}^{(1,0)}$ represent the ionization and electron affinity of the N-particle system respectively. The nature of the effective hamiltonian theory provides us with multiple number of state energies at a time. However, in our case we are interested in obtaining only the lowest IP as well as the lowest EA.

3.5 RESULTS AND DISCUSSION

We have chosen two example systems, H_2O and NH_3 molecules and used the above mentioned method to obtain the IP and EA and subsequently to test the validity of PMH. Let us first consider the case of H_2O. Starting from the equilibrium geometry the O-H bonds are stretched both symmetrically and asymmetrically. To search the global maxima of the hardness profile we carried out the same study by distorting the O-H bonds for nonstable (linear) geometry. Computations were carried out by using the ACES program system (Bartlett et al, 1987) using a double ζ basis set plus a set of polarization functions on the oxygen and hydrogen atoms. The d-exponent on oxygen is 0.90 and the p-exponent on hydrogen is 1.0 . The basis set, although not extensive, may be considered to be good enough to test this principle. Table 3.1 (a) contains the results for the symmetric distortion of H_2O, which include ionization potentials and electron affinities in Koopmans´ approximation as well as the correlated MRCCSD approximation. The corresponding hardness and chemical potential values are given in table 3.1 (b). From table 3.1 (a) it is clear that the correlated IPs are substantially lower than that of Koopmans´ IPs, whereas the correlated EAs are greater than Koopmans´ EA. When we go from stretching to contraction region through equilibrium, we see that IP values increase in both the methods without any maxima in equilibrium. This is true even for increase or decrease of bond angle. This means that only IP values can not be taken as a measure of stability.

However, when we analyse the data of table 3.1 (b) we see that the totally symmetric stretch gives a result in which there is no maximum or minimum in μ or η near the equilibrium geometry. This applies to the symmetric distortion in bond angles and bond lengths both. The same trend have also been observed by Pearson and Palke (Palke, 1992) in their study also. But this cannot be considered as a domain where PMH can be tested as μ itself is not constant.

From table 3.1 (b) it is also clear that the correlated values of μ are significantly higher than that of Koopmans´ approximation, whereas correlated η values are smaller than Koopmans´ η values. This can be easily explained from the IP and EA values obtained by these two methods as given in table 3.1 (a). The hardness values tend to decrease with the increasing bond distance and bond angle. The reverse trend in η values is observed as the bonds are contracted and <H-O-H angle is reduced. The trend remains same in both Koopmans´ and MRCCSD approximation.

Table 3.2 reports the μ and η values in both Koopmans´ and MRCCSD approximation for asymmetric stretch of H_2O. In this case the principle of maximum hardness can be tested as was also done by Pearson and Palke (Pearson and Palke, 1992). This is because from symmetry arguments we can infer that at any level of calculation the values of IP, EA, η and μ for positive deviation will be the same as those for the negative deviation from the equilibrium. So, for small asymmetric distortions μ remains fairly constant - which is a condition for the validity of PMH. Here we see that even at the correlated level of calculation, the hardness is maximum at equilibrium geometry. That this trend does not change from the Koopmans´ calculation even after the inclusion of extensive correlation and relaxation effects is indeed gratifying. From table 3.2 it is also obvious that the effect of correlation and relaxation tend to diminish the values of hardness and increase the values of chemical potential. This aspect can be attributed to the relative effects of relaxation and correlation of (N-1) and (N+1) electron systems vis-a-vis the correlation effect of the ground state N-electron system. As at large distances μ changes quite significantly, the principle can not be tested. Only among those regions where μ and the external potential (v) are fairly constant, η is maximum at the symmetric equilibrium point.

So far we have studied the change of η and μ for symmetric as well as asymmetric distortion from stable equilibrium geometries. But a more useful and convincing test can be provided by the distortion of H_2O around nonstable geometries as this will allow us to compare symmetric stable geometry with symmetric nonstable cases. The results of the symmetric and asymmetric distortions from linear unstable geometry are given in table 3.3 and 3.4 respectively. One can see that for symmetric distortions the trend of the results in table 3.3 is qualitatively similar to that of the table 3.1 (b). Here also the values of η_{MRCC} are less than those of η_k and μ_{MRCC} are greater than those of μ_K. The η values tend to increase as bonds are contracted and decreases as bonds are stretched. But as μ is not constant, this case cannot be considered to test the PMH. However, when we try to analyse the results for asymmetric distortion (table 3.4), we see that the hardness value again reaches a maximum at the symmetric point (with the O-H bond distances same as equilibrium geometry). The η_{MRCC} values are again less than η_K values. However, if we compare this symmetric point of the linear H_2O (with O-H bond distances as 1.8091 au) and the equilibrium point of the H_2O [as in table 3.1

(b) and 3.2], we observe that μ is nearly constant (varying only in the fourth digit after decimal point), while η_K for equilibrium point is higher by an amount of 0.03 ev. The η and μ values are computed for some other symmetric configurations with the H-O-H angle varying slightly from 180°. At all these points either of η_K or η_{MRCC} values are less than those of the corresponding equilibrium symmetric configuration. Not only that, if we compare the results of table 3.1 (b) and 3.3 we see that the η values of the corresponding distortions are higher for table 3.1 (b). So, while η values have local maxima at symmetric points for all asymmetric distortions, the global maximum in η is reached only at the equilibrium symmetric geometry (provided μ is constant). Thus we see that in the example case at different geometries, as long as μ is constant, the most stable point (i.e. the equilibrium point) is provided by the one having globally maximum η. This is a convincing test of the principle of maximum hardness. The principle is quite far reaching in its utility, being limited by the constraints of constant μ and v.

In table 3.5 , we have presented the results for asymmetric distortion of a more complex example i.e. ammonia. Similar to the observation of Pearson and Palke (Pearson and Palke, 1992) and in the case of H_2O, a symmetric distortion will not lead to constant chemical potential. The results presented in table 3.5 are only for asymmetric distortion, where μ is roughly constant and η is maximum at the equilibrium point. In this case, the trends are again similar to those in the table 3.2 (for H_2O).

3.6 CONCLUSION

Although the philosophical statement of Pearson suggests that molecules become hardest at global equilibrium geometry, it is difficult to test this under the rigorous condition of PMH, as given by Parr and Chattaraj. This is because of the condition of constant external potential (v). So PMH can not be used to locate the global equilibrium geometry in a rigorous sense (which can be done by electrostatic Hellmann-Feynmann theorem), but can be used to find out the point group of any chemical species - as mentioned by Pearson and Palke. This is because of the fact that the point group of any chemical species depends upon the exact equilibrium geometry (bond distances, bond angles etc.) and the symmetry is broken by very small distortion.

In a recent paper Makov (Makov, 1995) has stated that ´all the invariants (e.g. energy, chemical potentials, hardness) will be extremal with respect to asymmetric variations about a symmetric nuclear configuration´. This was derived by employing group theoretical symmetry arguments as well as density functional theory. The above statement holds to be true whether the asymmetric distortions are carried out around symmetric equilibrium or nonequilibrium geometries. This proof of Makov also explains the results presented in this chapter i.e. the nonoccurence of extrema of η and μ values in table 3.3 as well as the extrema of these values in table 3.4. However, Makov´s proof can not point out if this extrema is maxima or minima. The concept of PMH attempts to do this.

The definitions of η and μ used for the above study are the operational definitions, whereas the PMH is defined for rigorous definitions. So it may be interesting if in the wavefunction formulation, one can find a rigorous way of obtaining the derivatives of the E vs N plot more directly and thus provide a more direct test of this principle.

The chemical species chosen so far as example systems are those having only single bonds (e.g. H_2O, NH_3 and C_2H_6) and so it would be useful to carry out some tests with molecules containing multiple bonds. Although the EAs of H_2O and NH_3 do not exist in a rigorous sense, the present approach, which computes η and μ through operational definition, but at a near full CI level of accuracy, nevertheless provides the most credible validation of the PMH as yet.

Table 3.1 (a) : Symmetric Distortion of Water [a]

O-H bond	IP_K	EA_K	IP_{MRCC}	EA_{MRCC}
+0.2[c]	0.495 825	-0.194 048	0.421 200	-0.172 008
+0.1	0.498 750	-0.209 091	0.428 818	-0.187 800
+0.02	0.501 670	-0.220 344	0.435 202	-0.199 808
Equil[b]	0.502 486	-0.223 031	0.437 078	-0.202 696
-0.02[c]	0.503 332	-0.225 655	0.438 770	-0 205 554
-0.1	0.507 076	-0.235 556	0.445 626	-0.216 283
-0.2	0.512 570	-0.246 430	0.454 690	-0.228 209
H-O-H angle				
+5°	0.500 717	-0.223 587	0.435 337	-0.202 997
+1°	0.502 127	-0.223 191	0.436 727	-0.202 840
Equil[b]	0.502 486	-0.223 031	0.437 078	-0.202 696
-1°	0.502 809	-0.222 854	0.437 274	-0.202 562
-5°	0.504 130	-0.221 914	0.438 638	-0.201 822

[a] All values are in atomic units (au) except bond angles, which are in degrees. [b] Equilibrium condition when the O-H bond distance is 1.8091 a.u. and the H-O-H bond angle is 104.5° . [c] (+) for stretching and (-) for contraction of the O-H bond.

Table 3.1 (b) : Symmetric Distortion of Water[a]

O-H bond	η_K	μ_K	η_{MRCC}	μ_{MRCC}
+0.2[c]	0.344 937	-0.150 889	0.296 604	-0.124 596
+0.1	0.353 920	-0.144 830	0.308 309	-0.120 509
+0.02	0.361 007	-0.140 663	0.317 505	-0.117 697
Equil[b]	0.362 758	-0.139 727	0.319 887	-0.117 191
-0.02[c]	0.364 493	-0.138 839	0.322 162	-0.116 608
-0.1	0.371 316	-0.135 760	0.330 955	-0.114 672
-0.2	0.379 500	-0.133 070	0.341 449	-0.113 240
H-O-H angle				
+5°	0.362 152	-0.138 565	0.319 167	-0.116 170
+1°	0.362 659	-0.139 468	0.319 784	-0.116 943
Equil[b]	0.362 758	-0.139 727	0.319 887	-0.117 191
-1°	0.362 832	-0.139 977	0.319 918	-0.117 356
-5°	0.363 022	-0.141 108	0.320 230	-0.118 408

[a] All values are in atomic units (a.u.) except bond angles, which are in degrees. [b] Equilibrium condition when the O-H bond distance is 1.8091 a.u. and the H-O-H bond angle is 104.5° . [c] (+) for stretching and (-) for contraction of the O-H bond.

Table 3.2 : **Asymmetric Distortion of Water**[a]

O-H bond	η_K	μ_K	η_{MRCC}	μ_{MRCC}
0.2	0.357 197	-0.146 466	0.313 773	-0.123 304
0.04	0.362 513	-0.140 019	0.319 508	-0.117 359
0.02	0.362 695	-0.139 801	0.319 762	-0.117 206
Equil[b]	0.362 758	-0.139 727	0.319 887	-0.117 191

[a] All values are in atomic units (a.u.). [b] Equilibrium condition in which O-H bond distance is taken to be 1.8091 a.u. and H-O-H bond angle is 104.5° .

Table 3.3 : Symmetric Distortion of Water Molecule at Linear Geometry[a]

O-H bond	η_{K}	μ_{K}	η_{MRCC}	μ_{MRCC}
+0.2[c]	0.301 827	-0.155 032	0.256 114	-0.132 811
+0.1	0.319 853	-0.146 271	0.275 756	-0.125 231
+0.02	0.334 332	-0.139 567	0.291 582	-0.119 316
0.00[b]	0.337 928	-0.137 960	0.295 524	-0.117 826
-0.02	0.341 506	-0.136 386	0.299 461	-0.116 433
-0.1	0.355 557	-0.130 508	0.315 887	-0.110 090
-0.2	0.372 204	-0.124 383	0.333 264	-0.105 433
H-O-H angle				
-5°	0.338 222	-0.137 926	0.295 769	-0.117 807
-3°	0.337 980	-0.137 952	0.295 603	-0.117 902
-1°	0.337 945	-0.137 956	0.295 533	-0.117 869

[a] All values are in atomic units (a.u.) except bond angles, which are in degrees. [b] Reference linear geometry when the O-H bond distance is 1.8091 a.u. and the H-O-H bond angle is 180°.
[c] (+) for stretching and (-) for contraction of the O-H bond.

Table 3.4 : Asymmetric Distortion of Water Molecules at Linear Geometry[a]

O-H bond	η_K	μ_K	η_{MRCC}	μ_{MRCC}
0.2	0.329 739	-0.145 571	0.287 301	-0.125 010
0.08	0.336 513	-0.139 282	0.294 095	-0.119 125
0.04	0.337 570	-0.138 295	0.295 160	-0.118 191
0.00[b]	0.337 928	-0.137 960	0.295 524	-0.117 826

[a] All values are in atomic unit (a.u.). [b] Reference linear geometry when the O-H bond distance is taken to be 1.8091 a.u. and the H-O-H bond angle is 180° .

Table 3.5 : Asymmetric Distortion of Ammonia Molecule[a]

N-H bond	η_K	μ_K	η_{MRCC}	μ_{MRCC}
0.1	0.328 376	-0.089 581	0.289 582	-0.083 944
0.04	0.329 223	-0.088 717	0.290 303	-0.083 232
0.01	0.329 437	-0.088 532	0.290 523	-0.083 029
Equil[b]	0.329 478	-0.088 508	0.290 693	-0.082 868
H-N-H angle				
8°	0.327 609	-0.086 021	0.288 748	-0.080 639
5°	0.328 379	-0.086 896	0.289 503	-0.081 455
3°	0.328 844	-0.087 520	0.289 955	-0.082 045

[a] All values are in atomic units except bond angles, which are in degrees. [b] Equilibrium geometry in which the N-H bond distance = 1.91 a.u. and the H-N-H bond angle is 106.7° .

CHAPTER 4

BEHAVIOUR OF OPERATIONAL HARDNESS AND CHEMICAL POTENTIAL IN CHEMICAL BINDING

4.1 INTRODUCTION

The numerical demonstrations by different workers (including one by us), in support of the validity of PMH, raise an important question regarding the limit upto which the condition of constant v or μ can be relaxed for the statement of PMH to remain valid. Of course, if the nuclei positions are sufficiently changed, PMH can not be applied. In this context, it may be additionally relevent to ask about the use of operational definition of hardness. Robles and Bartolotti (Robles and Bartolotti, 1984) as also Gázquez and Ortiz (Gázquez and Ortiz, 1984) have shown that in some cases the operational definition provides incorrect trend of hardness parameters for typical atoms, e.g. N, O, F ; P, S, Cl etc. This incorrect trend disappears if density functional theoretic definition, $[\partial^2E/\partial N^2]/2$ is used (Sen and Vinayagam, 1988). Moreover, the rigorous definition of PMH and the subsequent numerical demonstrations (using operational definition) claim that for any chemical species global hardness will attain its maximum value at the most stable equilibrium geometry, i.e. where total energy is minimum. But Gázquez et al (Gázquez et al, 1993) have shown that in case of H_2, Li_2 and N_2 molecules at constant chemical potential the hardness is maximum where electronic energy is minimum and that the hardness is minimum where the electronic energy is maximum. Not only that, they observed that there is no maxima in hardness profile and the hardness values increase when A-A bond (A = H, O, Li and N) is contracted beyond equilibrium.

This behaviour can be attributed to the artifact of the operational definition or to the fact that in the stretching /contraction of a bond in diatomic molecules, chemical potential is not constant. In this context, it may be worth mentioning our results in the last chapter that for symmetric polyatomic molecules, asymmetric distortions can keep chemical potential constant providing a region where the maximum hardness principle works. There are more recent works on the change of these quantities with respect to the nature of distortions. In this chapter, though, we will primarily be interested in the behaviour of operational hardness under general conditions as well as the conditions of constant chemical potential. However, the question of different types of distortion is also an important one and in the concluding chapter we will present the recent works in this direction, particularly in the background of our results in chapter 3. In this chapter we record a study of the trend of the operational definition at different atomic positions on analytical, numerical as well as pedagogical level.

In the next section [4.2] a quantitative model has been demonstrated in which the operational hardness and chemical potential are written in terms of the energetics of the neutral system and the corresponding cation and anion. Some model calculations are presented in section 4.3 which support this model. Section 4.4 contains the essential conclusions.

4.2 QUANTITATIVE MODEL

For simplicity of derivation, let us consider a diatomic molecule AB where A is more electropositive compared to B. The model that we will use for calculation of hardness is the one proposed by Parr and Pearson (Parr and Pearson, 1983). This uses three point fit by considering the N, (N-1) and (N+1) particle energies, E_N, E_{N-1} and E_{N+1} respectively. We will call the corresponding expressions as operational hardness ($\bar{\eta}$) and operational chemical potential ($\bar{\mu}$). Hence,

$$\bar{\eta} = (IP - EA)/2 \; ; \quad \bar{\mu} = -(IP + EA)/2 \qquad 4.1$$

where IP and EA refer to the first ionization potential and electron affinity respectively. The same expression can also be written as,

$$\bar{\eta} = (E_{N+1} + E_{N-1} - 2E_N)/2 \; ; \quad \bar{\mu} = (E_{N+1} - E_{N-1})/2 \qquad 4.2$$

where the energies refer to the ground states at N electron geometry. Writing equation (4.2) for a diatomic molecule AB the expression of $\bar{\eta}$ and $\bar{\mu}$ become,

$$\bar{\eta} = (\, E_{AB^+} + E_{AB^-} - 2E_{AB} \,)/2 \; ; \quad \bar{\mu} = (\, E_{AB^-} - E_{AB^+} \,)/2 \qquad 4.3$$

Now let us consider the separated atom limit of AB. As there is no interaction between the two species A and B, the ground state of AB^+ is expected to separate into A^+ and B. Similarly, AB^- will separate into A and B^-, and AB separates into neutral atoms. It is assumed, for simplicity, that AB is not sufficiently ionic to separate into A^+ and B^-. In such a case, $\bar{\eta}$ at the separated limit (SL) may be written as,

$$\bar{\eta}_{SL} = [\, E_{A^+} + E_{B} + E_{A} + E_{B^-} - 2E_{A} - 2E_{B} \,]/2$$

$$= [(\, E_{A^+} - E_{A} \,) - (\, E_{B} - E_{B^-} \,)]/2$$

$$= [\, IP(A) - EA(B) \,]/2 \qquad 4.4$$

So the result is the difference of the ionization potential of the more electropositive atom and the electron affinity of the electronegative atom. Similarly $\bar{\mu}_{SL}$ can be written as,

$$\bar{\mu}_{SL} = [\, E_{A} + E_{B^-} - E_{A^+} - E_{B} \,]/2$$

$$= [-(\, E_{A^+} - E_{A} \,) - (\, E_{B} - E_{B^-} \,)]/2$$

$$= -\,[\, IP(A) + EA(B) \,]/2 \qquad 4.5$$

It may be remembered that similar formulae were also obtained by Perdew et al (Perdew et al, 1982) through the use of density functional theory. They derived the equation (4.5) at the separated atom limit by considering an averaged statistical ensemble at the $T \longrightarrow 0$ limit. In this context, reference should be mentioned of an earlier work on electronegativity by Mulliken (Mulliken, 1934). Mulliken assumed electronegativity to be an average of ionization potential and electron affinity thus defining $\varkappa$ as,

$$\varkappa_{A} = [IP(A) + EA(A)]/2 \qquad 4.6$$

It is already mentioned in the first chapter that Parr et at (Parr et al, 1978) have shown that electronegativity is negative of chemical potential. The only difference is that Mulliken´s definition, in those early days, was mainly concerned for atoms. For homonuclear diatomic molecule A_2, we get the value of hardness at the separated limit as,

$$\bar{\eta}^{A_2}_{SL} = [\ IP(A) - EA(A)\ ]/2 = \bar{\eta}(A) \qquad 4.7$$

The significance of equation (4.7) is that the atomic hardness is same as the diatomic molecular hardness in the separated limit. If we extend the above argument for homonuclear polyatomic molecule A_N , we get at the separated limit,

$$\bar{\eta}^{A_2}_{SL} = (\ E_{A_N^+} + E_{A_N^-} - 2E_{A_N}\ )/2 \qquad 4.8$$

Simplifying the expression (4.8) we get only atomic hardness. The physical meaning is that the global hardness of a collection of non-interacting atoms of the same type is just the absolute hardness of the atom. The same conclusion can be drawn for chemical potential also. In a molecular orbital (MO) picture the global hardness is half of the gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). In the separated limit, HOMO and LUMO go over to the atomic orbitals of different atoms. This simple picture can also be used to rationalise the result of equation (4.7) or its generalization. In fact, the result of equation (4.4) may also be understood in this simple MO representation. This MO picture can easily be extended to interpret the non-interacting limit values of chemical potential.

Now let us consider the case of binding of the diatomic molecule AB . As the two atoms approach each other from separated atom limit to the binding region, the energy of the molecule decreases until binding energy reaches a maximum at the equilibrium point. Using equation (4.3) at any point of interaction, the global hardness of the molecule ($\bar{\eta}_{IL}$) may be written as,

$$\bar{\eta}_{IL} = (E_{A^+} + E_{B} - \Delta E_1 + E_{A} + E_{B^-} - \Delta E_2 - 2E_{A} - 2E_{B} + 2\Delta E_3)/2 \tag{4.9}$$

Where ΔE_1 and ΔE_2 are the vertical binding energies of AB^+ and AB^- respectively, where as ΔE_3 is the binding energy of AB. Therefore the change in molecular hardness $(\Delta\bar{\eta})$ from the separated atom limit is given by,

$$\Delta\bar{\eta} = \bar{\eta}_{IL} - \bar{\eta}_{SL} = (2\Delta E_3 - \Delta E_1 - \Delta E_2)/2 \tag{4.10}$$

Thus equation (4.10) can explain the general surface of $\bar{\eta}$ as atomic positions are changed. It is our normal expectation that $\Delta\bar{\eta}$ should increase as the binding energy of diatomic molecule increases. But our model suggests that it is not so simple. The change is also dependent on the vertical binding energies of the cation and anion respectively. In practice, however, in many cases of interest where AB is formed, AB^+ and AB^- are comparatively less stable than AB ; hence $\Delta\bar{\eta}$ will be positive as the bond is formed. But this cannot be generalized in all cases. However, this is not in conflict with the inequality $\partial E/\partial\eta < 0$ for constant μ as pointed out by Parr in a private communication. The above inequality suggests that as the energy of a system decreases (in this specific case of bond formation this coincides with the increase of binding energy), the hardness would only increase. But a closer look reveals that these two are not contradictory. The inequality is true only for constant $\bar{\mu}$. If we investigate the change of $\bar{\mu}$ for a diatomic molecule formation, we find that it is not quite constant. We have studied the change of $\bar{\mu}$ with the change in R (bond length) for some molecules like H_2, HF, CO etc. The results obtained for the molecules H_2 and HF are presented in table 4.1 . One can easily find out that $\bar{\mu}$ changes significantly, particularly in the case of heteronuclear diatomics.

In diatomic molecules since $\bar{\mu}$ is not constant, the binding energy of the molecule itself is not an index of the change in hardness. Equation (4.10) is a more correct index (at least in the model which we have used). As shown by Gázquez et al (Gázquez et al, 1993), for diatomic molecules, η increases monotonically as the bond length (R) decreases. However, when R decreases from its equilibrium value (R_0), ΔE_3 will not increase, and thus by considering only the stability of the system one cannot explain why $\bar{\eta}$ increases as R decreases further from R_0. The ΔE_1 and ΔE_2 terms play a vital role here. The cationic and anionic systems are destabilized more rapidly than the neutral system. Hence, although ΔE_3 decreases as R decreases ($< R_0$), ΔE_1 and ΔE_2 more than compensate $2\Delta E_3$, and as a result η increases.

Now let us investigate the change in chemical potential as the chemical binding takes place. From equation (4.3), the chemical potential at the interacting limit can be written as ,

$$\begin{aligned}\bar{\mu}_{IL} &= [\, E_A + E_{B^-} - \Delta E_2 - E_{A^+} - E_B + \Delta E_1 \,]/2 \\ &= -[\, (E_{A^+} - E_A) + (E_B - E_{B^-}) \,]/2 + (\Delta E_1 - \Delta E_2)/2 \\ &= -[\, IP(A) + EA(B) \,]/2 + (\Delta E_1 - \Delta E_2)/2 \qquad 4.11\end{aligned}$$

So the change in chemical potential is,

$$\Delta\bar{\mu} = \bar{\mu}_{IL} - \bar{\mu}_{SL} = (\Delta E_1 - \Delta E_2)/2 \qquad 4.12$$

Thus, the change in electronic chemical potential (in the operational definition) solely depends upon the vertical binding energies (at the geometries of the neutral N-electron systems) of cationic and anionic species of the diatomic molecule under consideration. The relative magnitude of ΔE_1 and ΔE_2 will determine the change in $\bar{\mu}$ with R. Constancy of $\bar{\mu}$ thus means that at least for diatomic molecules, both the cationic and anionic species are either equally stable or unstable.

We can now investigate in this context the principle of maximum hardness, if $\bar{\mu}$ is kept constant during binding. Hence from equation (4.12), when $\Delta\bar{\mu} = 0$ we get,

$$\Delta E_1 = \Delta E_2 \qquad 4.13$$

This means that both the cationic and anionic species are equally stable or unstable. Now putting the equation (4.13) into equation (4.10) one gets,

$$\Delta\bar{\eta} = (\ \Delta E_3 - \Delta E_1\ ) = (\ E_A + E_B - E_{AB} + E_{AB^+} - E_{A^+} - E_B\ )$$

$$[\ \text{As, } E_{AB} = E_A + E_B - \Delta E_3$$

$$E_{AB^+} = E_{A^+} + E_B - \Delta E_1\ ]$$

$$= (\ E_{AB^+} - E_{AB}\ ) - (\ E_{A^+} - E_A\ )$$

$$= IP(AB) - IP(A) \qquad 4.14$$

So, using operational definition we incidentally come to the conclusion that at maximum $\bar{\eta}$, the first vertical ionization potential of the molecule will also be maximum (as the first IP of A is constant). It should be mentioned that a similar expression was derived by Gázquez *et al* (Gázquez *et al*, 1993) in the context of DFT. Similarly one can very easily show that, at constant $\bar{\mu}$, maximum $\bar{\eta}$ means minimum first vertical EA. A system harder to ionize or with lesser tendency to gain an extra electron will obviously be more stable.

In our definition, the binding energy is negative of the change in total energy (electronic energy plus nuclear - nuclear repulsion energy). But in the equation (4.14) we see that, at constant $\bar{\mu}$, the change in hardness is not necessarily proportional to the negative of the change in total energy of the molecule. Gázquez et al claimed that $\Delta\eta$ is proportional to the negative of the change in electronic energy at constant μ. From our expression (4.10) we observe that if the nuclear-nuclear repulsion part of ΔE_3 cancels with the ΔE_1 term (vertical binding energy of the corresponding cation) then observation of Gázquez et al (Gázquez et al, 1993) as also that of Parr and Gázquez (Parr and Gázquez, 1993) would be compatible with equation (4.14) . We want to emphasize that this comes as a corollary to our general results of the change of $\Delta\bar{\eta}$ with R (for any $\bar{\mu}$). It is not quite clear as to whether such cancellation can take place in the general formula (4.10), without any precondition of the constancy of $\bar{\mu}$. But this must also involve anionic binding energy ΔE_2 . In the concluding chapter (chapter 6) we will make further comments regarding this.

4.3 DEMONSTRATIVE CALCULATION

In this subsection two demonstrative calculations on H_2 and HF will be presented, which will test the model just described

(Pal et al, 1994). The binding energies are calculated at the ab initio SCF level. For both the molecules the basis set used is that of Huzzinaga - Dunning double zeta (Huzzinaga, 1965 ; Dunning, 1970) augmented with one set of polarization functions (for hydrogen the p- exponent is 0.6, and for fluorine the d- exponent is 1.58). The changes in hardness and chemical potential values are evaluated from equations (4.10) and (4.12) . Table 4.1 presents the binding energies and the change in hardness and chemical potential of the molecules H_2 and HF. It is obvious from the table that for both H_2 and HF molecules, hardness changes monotonically with the change of bond distance (R). This is also obvious from the figures 4.1 and 4.2 . The chemical potential of H_2 remains almost constant with the change in R (fig. 4.1), whereas that of HF decreases monotonically as R decreases (fig. 4.2). The hardness increases with contraction of bond and decreases with the bond stretching. An analysis of the ΔE values will be helpful to explain the above trend of change of hardness. When the bond is stretched from its equilibrium value (R_0), the stability of the system decreases (ΔE_3 is less positive). From table 4.1 it is clear that H_2^+ is progresively more bound (i.e. ΔE_1 is more positive) within the stretching region considered here. The corresponding anionic species are always unbound, but the magnitude of ΔE_2 decreases with increase in R from R_0 . In the case of HF, ΔE_1 passes through a maximum (at the equilibrium bond length of HF^+, i.e. 1.90 a.u.). However, if R is increased further, although ΔE_1 decreases, ΔE_2 and ΔE_3 together overwhelm the effect of ΔE_1 such that $\bar{\eta}$ always decreases as R increases from R_0. When R decreases from R_0, the system becomes more unstable (i.e., the energy increases), but $\bar{\eta}$ still increases due to the predominating role of ΔE_1, and ΔE_2 over ΔE_3 in this region. Hence, in this situation $\bar{\eta}$ does not play the role of an index of stability of the system. Of course, this does not violate the PMH, since $\bar{\mu}$ is not constant.

An apparently anomalous and puzzling result is obtained when we plot $\Delta\bar{\eta}$ against $-\Delta E_3$ (fig. 4.3). Here we see that for the same value of ΔE_3, two different values of $\bar{\eta}$ are possible. If one considers the potential energy of a diatomic molecule, then it is very easy to find out two different values of R for which ΔE_3 values are the same (i.e., the system is equally stable at both configurations). Inspite of the equal stability for two different configurations, the hardness values are different. This apparent anomaly can be explained from the present model. From equation (4.10) it is obvious that though the value of ΔE_3 is same, the contribution of ΔE_1 and ΔE_2 may be different at those two different regions, and this leads to different values of $\bar{\eta}$. This indirectly explains why PMH does not show the expected trend of $\bar{\eta}$ for a diatomic molecule, although the principle of maximum stability exists.

It is to be kept in mind that the exact relations of hardness and chemical potential with binding enegies will differ from the ones presented here to the extent that this model of calculation of $\bar{\eta}$ and $\bar{\mu}$, (through the equation 4.1) is inaccurate. Inspite of this, many of these results, obtained through the operational definitions, can be generalized by our simple model to polyatomic molecules where a single bond is broken or formed. Moreover, in polyatomic molecules, as there are more than one bond, we can changes the bond distances in a way (e.g. asymmetric distortions of a symmetric molecule, like H_2O, as considered in chapter 3) so as to keep μ constant. In this context we can use operational definition of $\bar{\eta}$ and $\bar{\mu}$ to check the validity of our model (particularly equation 4.14). In the concluding chapter (chapter 6) we will discuss this in the light of a critical re-evaluation of PMH.

4.4 CONCLUSION

In this chapter, starting from an analytical derivation we have shown through numerical demonstration and pedagogical discussion, the behaviour of the finite difference approximation to the hardness (i.e. operational hardness) in chemical binding. From the change of $\bar{\eta}$ with the energies, we can explain the general hardness surface, the typical hardness profile of diatomic molecules as observed by Gázquez et al (Gázquez et al, 1993), the existence of two hardness values for any particular binding energy of a diatomic molecule etc. Specifically we see that for constant $\bar{\mu}$, the maximum of $\bar{\eta}$ leads to maximum vertical ionization potential (although the external potential is not constant). We also demonstrate that $\bar{\eta}$ may not follow the same trend as expected from the rigorous definition.

Table 4.1. Change of binding energies, hardness and chemical potential with the change in bond length (R) for H_2 and HF molecules. All data are in atomic units (a.u.) .

R	ΔE_1	ΔE_2	ΔE_3	$\Delta\eta$	$\Delta\mu$
H_2					
1.30	0.051 36	-0.038 10	0.133 51	0.126 88	0.044 73
1.35	0.060 80	-0.029 73	0.135 05	0.119 52	0.045 26
1.40	0.068 81	-0.022 50	0.135 42	0.112 27	0.045 66
1.45	0.075 58	-0.016 26	0.134 79	0.105 13	0.045 92
1.50	0.081 27	-0.010 83	0.133 32	0.098 10	0.046 05
1.55	0.086 03	-0.006 10	0.131 12	0.091 16	0.046 07
1.60	0.089 97	-0.001 95	0.128 32	0.084 31	0.045 96
HF					
1.60	0.108 36	-0.102 83	0.144 94	0.142 18	0.105 60
1.65	0.115 87	-0.091 28	0.148 19	0.135 89	0.103 57
1.70	0.121 15	-0.081 45	0.149 21	0.129 36	0.101 30
1.75	0.124 57	-0.072 98	0.148 41	0.122 62	0.098 78
1.80	0.126 47	-0.065 60	0.146 10	0.115 67	0.096 04
1.90	0.126 74	-0.053 29	0.138 03	0.101 30	0.090 01
2.00	0.123 64	-0.043 30	0.126 67	0.086 50	0.083 47

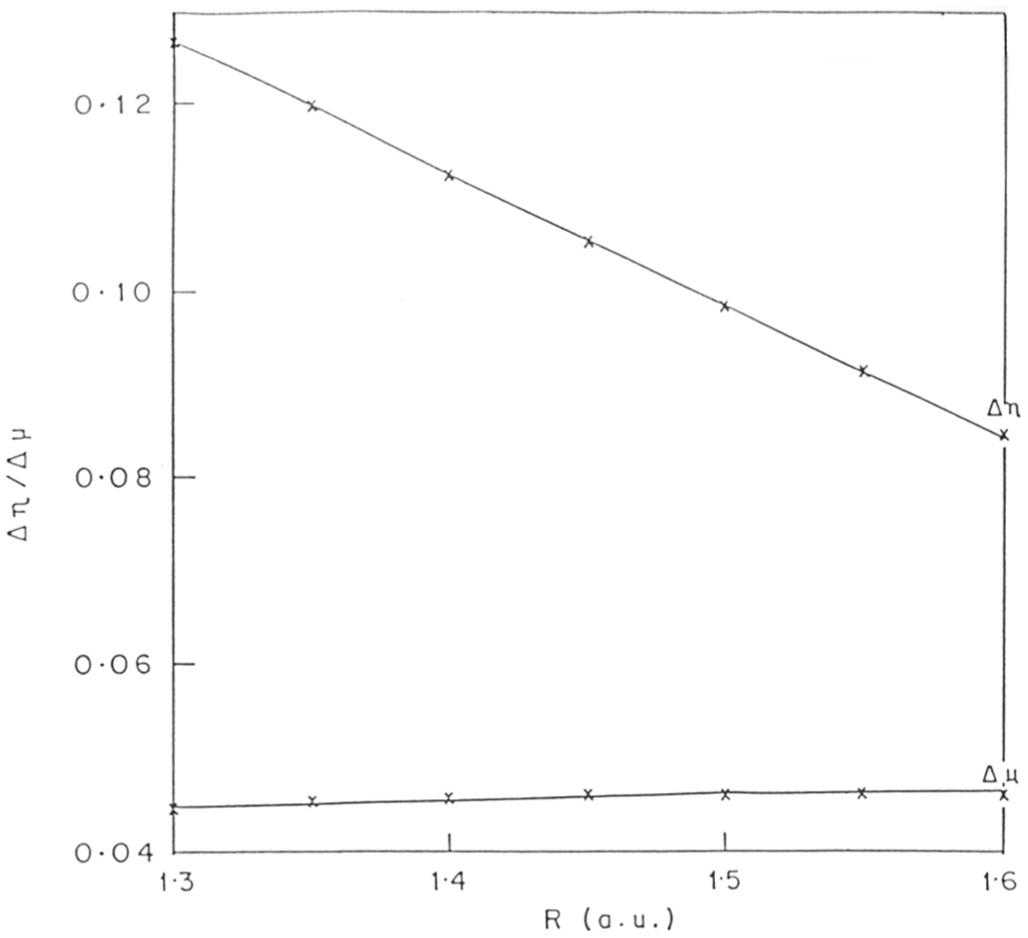

Fig. 4.1. The change in chemical hardness ($\Delta\eta$) and potential ($\Delta\mu$) with the change in bond length (R) for the molecule H_2.

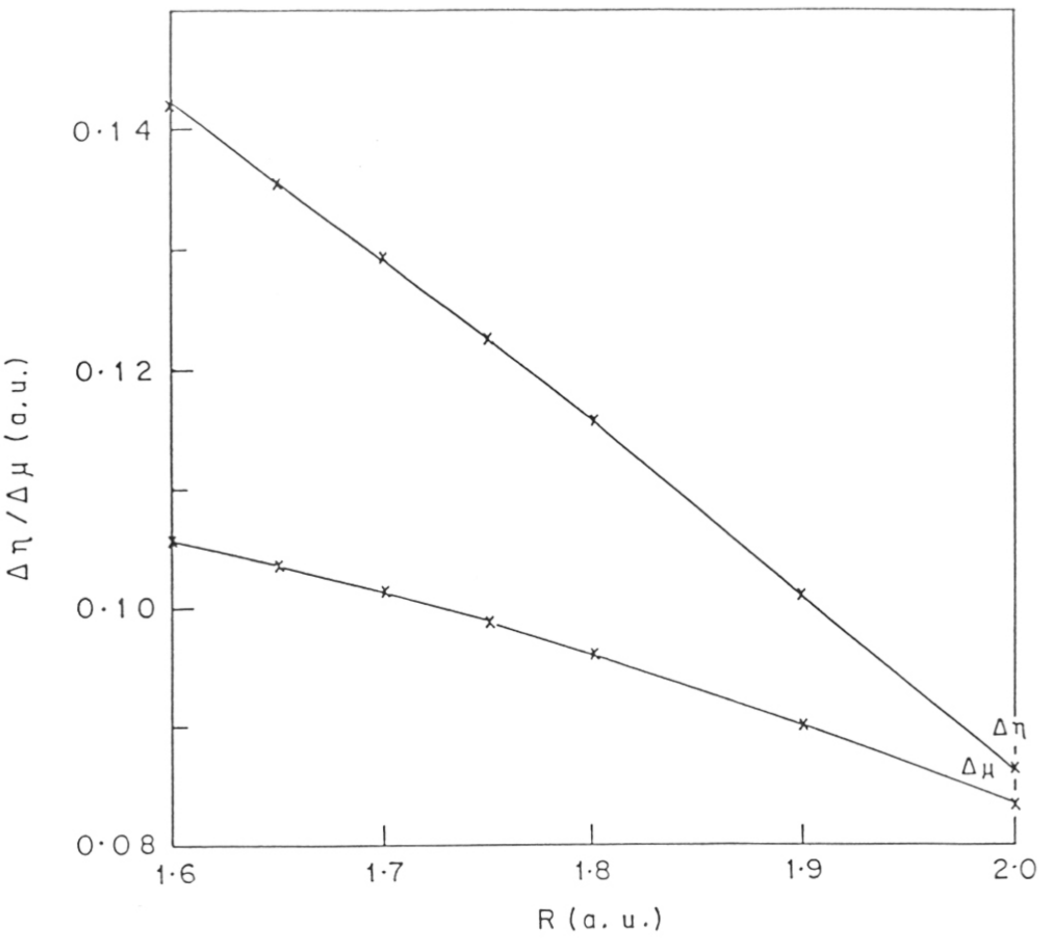

Fig. 4.2. The plot of change in chemical hardness and potential with the change in bond length (R) for the molecule HF.

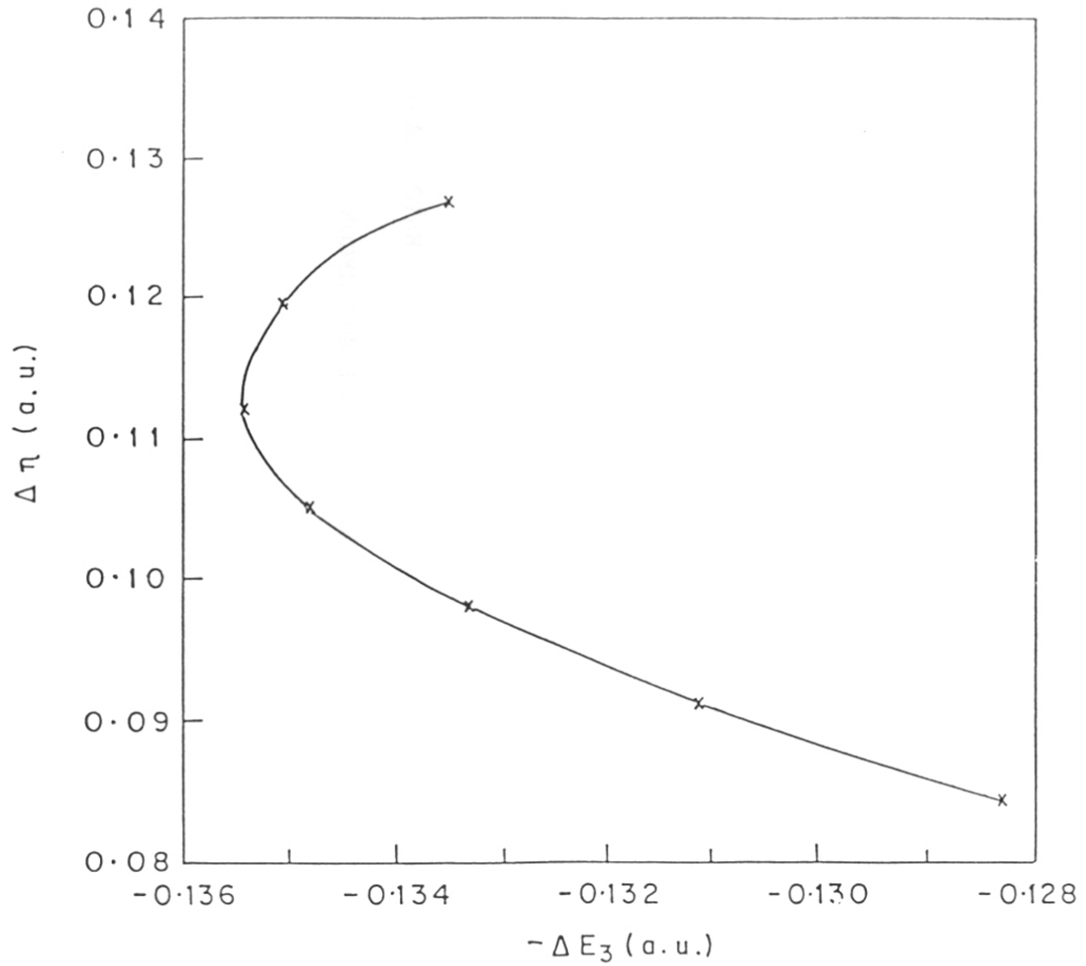

Fig. 4.3. The plot of change in hardness ($\Delta\eta$) with the change in binding energy (ΔE_3) of the molecule H_2.

CHAPTER 5

CHEMICAL POTENTIAL AND HARDNESS FOR OPEN SHELL RADICALS : MODEL FOR THE CORRESPONDING ANIONS

5.1 INTRODUCTION

As discussed in the previous chapters, we know that the quantitative definition of hardness (Parr and Pearson, 1983) and chemical potential (Parr et al, 1978) are given by,

$$\eta = (\delta^2 E/\delta N^2)_{V,T} \quad \text{and} \quad \mu = (\delta E/\delta N)_{V,T} \tag{5.1}$$

As these definitions in terms of the derivatives of energy with respect to number of electrons are not very useful, a finite difference approximation of these using E_N, E_{N+1} and E_{N-1} has been taken as valid and working definition of hardness and chemical potential (Parr and Pearson, 1983),

$$\eta = (IP - EA)/2 \quad \text{and} \quad \mu = -(IP + EA)/2 \tag{5.2}$$

Applying Koopmans´approximation to equation (5.2) , the expressions of η and μ can be re-written in terms of frontier orbitals as (Pearson 1985),

$$\eta = (\varepsilon_L - \varepsilon_H)/2 \ , \quad \text{and} \quad \mu = (\varepsilon_L + \varepsilon_H)/2 \tag{5.3}$$

Both the expressions (5.2) and (5.3) have been used to calculate η and μ of a variety of chemical species in different context. As discussed in Chapter 3, the principle of maximum hardness (PMH) was supported through numerical demonstrations by different workers (Pearson and Palke, 1992 ; Datta, 1992) including one by us (Pal et al, 1993), using the above definitions of η and μ. Using H_2O and NH_3 as typical examples, we have shown that asymmetric stretch can keep the chemical potential constant for polyatomic molecule and thus provide a region in which the PMH can be tested. It is clear from our study that either of the expressions (5.2) and (5.3) yields the same trend of hardness -

differing only by numerical values. Again in Chapter 2 we have seen that using similar expressions a linear relation between hardness and cube root of polarizability was obtained when a particular bond is stretched in polyatomic molecules (Pal et al, 1994). In this case also expressions (5.2) and (5.3) yield the same trend - leading to the apparent belief that either of the two equations can be used to obtain a reliable trend of η values.

One important point which is to be borne in mind is that in all the above theoretical studies the chemical species concerned are closed shell systems, thus having the distinct HOMO and LUMO energy levels. So, even if we apply Koopmans´ approximation, we will get a nonzero hardness value when η is expressed in terms of the frontier orbitals. But problem arises when we apply the same expression of η to the open shell chemical species. Let us consider the open shell cases where electrons are distributed over a set of strictly degenerate orbitals. In such cases both HOMO and LUMO will be degenerate having the same energy, leading to the zero value of η from equation (5.3). Even in the case of near - degeneracy, the value may not be zero, but would be unrealistically small. Thus open shell systems are the typical examples where Koopmans´ approximation to (IP - EA)/2 definition of hardness becomes very severe. This severity has not been addressed properly by previous workers. At the minimum level the ionization potentials and electron affinities have to be obtained by ΔSCF procedure. There are reported results of some open shell atoms or radicals (Pearson, 1988a, 1985), where η has been calculated by using equation (5.2) and the corresponding IP and EA values from the experimental results.

It has been recently realized that the values of chemical hardness of open shell systems (particularly free-radicals) are important as these are used for rank ordering of the corresponding anions. But it is well known that the evaluation of the hardness of anions poses a special problem since we do not know the electron affinity (EA) of the anions. Even if we get some EA values, these numbers would have little physical or chemical significance. The important chemical information for anions would be the size of the HOMO-LUMO gap, in the absence of added interelectronic repulsion. It is needless to mention that this would enable us to rank anions in the order of increasing chemical polarizability or decreasing hardness (Pearson, 1988a). But practically it is very difficult to extract this information either from Vis-UV spectra or optical polarizabilities.

To overcome this difficulty Pearson (Pearson, 1988a) suggested that the IP and EA values of the radicals can be used approximately to evaluate the η values for the corresponding anions. It is obvious that hardness of any particular neutral species would be higher than the corresponding anions. This is due to the fact that hardness has a reciprocal relation to polarizability, which is larger for anions (because of larger volume). But this enhancement of hardness value in going from neutral species to the corresponding anion is true for all the chemical systems, thus it may be worth expecting that the values for the neutral systems will provide correct trend of hardness for the anions. The η values of some free radicals calculated from experimental IP and EA also confirm this.

But so far there are no theoretically calculated η values of the isolated free radicals in their relaxed geometries, which can be used to test the above argument. It should be mentioned in this context that Proft et al (Proft et al, 1993) have evaluated the hardness values of some common organic groups by ab initio wave function formalism in the context of evaluating intrinsic group properties (e.g. group hardness, group electronegativity). Hence they considered a geometry which these groups adopt in a molecule and not their isolated equilibrium relaxed geometries. The η values obtained for such geometry can not be used with confidence for rank ordering of the corresponding anions as these are susceptible to change from molecule to molecule.

We want to present in this chapter the calculated η and μ values of some common free radicals (i.e. open shell systems) and also correlate these with the ones obtained from experimental IPs and EAs (Roy and Pal, 1995). The values of IP and EA and consequently of η and μ are obtained at the experimental relaxed geometries of the radicals. The methodology used is a ΔSCF procedure i.e. the IP and EA values are evaluated by carrying out separate SCF calculations for radicals and the ions at the geometry of the neutral systems. While the errors of ΔSCF procedure in obtaining the IPs and EAs are well known, our work will examine the reliability and stability of this method in obtaining the difference of IPs and EAs for free radicals.

In section 2 we represent methodology and basis sets used for the calculation. The reliability of the results obtained by performing the calculation on some common free-radicals are critically examined and compared with the experimental values in section 3. The factors, which have to be taken care for the improvement of the results, have been discussed in the concluding section (section 4).

5.2 METHODOLOGY AND BASIS SET

In our calculation we have considered the open shell species as restricted open shell systems with spin 1/2, whereas the corresponding cations (except in two cases of F and Cl) and anions are closed shell systems with spin value 0. So for neutral species ROHF and for ionic species RHF level of calculations have been performed. For F^+ and Cl^+ a ROHF wavefunction corresponding to the spin value 1 has been used. F^- and Cl^- are of course closed shell systems for which a RHF method is adequate. The calculations have been performed by using TURBOMOLE package (see footnote a). The basis set used is of TZP quality. For H the contraction used is (5S)/[3S] and for first row atoms 10S6P primitive Gaussians are contracted to 6S3P. For the second row atoms the contraction used (12S9P)/[7S5P]. These basis sets are as contained in the TURBOMOLE program system. The exponents of the polarization functions used are given in footnote [see footnote b(i)]. To test the basis set effects calculations have been performed with another TZ2P basis set, in which contractions are similar to TZP but has two sets polarization functions which are quoted in footnote b(ii).

It is usually known that the diffuse functions have much more important role to play, particularly for the anionic systems. So we have performed a separate set of calculations on some systems in a basis consisting of extended DZP (EDZP) and then added diffuse functions separately [EDZP + diffuse (sp)]. The contraction used for H in this new basis is (5S)/[3S] and for the first row atoms (C, N and O) 11S6P primitive Gaussians are contracted to 5S3P. For Si and S the contractions used are (13S9P)/[6S5P] and (13S10P)/[6S5P] respectively. The exponents for the polarization functions as well as diffuse functions are given in footnote [see footnote c(i) and c(ii)]. The effects of these diffuse functions will be discussed in results and discussion section (section 3).

FOOTNOTE a : TURBOMOLE, an ab initio quantum chemistry program system developed by Ahlrichs, R. and co-workers, see Häser, M. and Ahlrichs, R. J. Comp. Chem. <u>10</u> , 104, 1989 .

FOOTNOTE b : The exponents (α) of the polarization functions are - (i) For TZP : H (α_p) = 0.8 ; α_d of C, N, O and F are 0.8, 1.0, 1.2 and 1.4 respectively. For second row atoms Si, P, S and Cl α_d values are 0.35, 0.45, 0.55 and 0.65 respectively.

(ii) For TZ+2P : H : α_{1p} = 1.39, α_{2p} = 0.46 ; The α_{1d} and α_{2d} values of the other atoms are tabulated below,

Atoms	α_{1d}	α_{2d}	Atoms	α_{1d}	α_{2d}
C	1.58	0.44	Si	2.00	0.50
N	1.73	0.58	S	2.00	0.55
O	2.08	0.69	Cl	2.00	0.58
F	2.42	0.81			

5.3 RESULTS AND DISCUSSION

The results of the calculation using TZP basis are given in table 5.1 and 5.2 . Table 5.1 contains the values of the calculated vertical IP and EA as also the experimental IP and EA taken from Pearson (Pearson, 1988). In table 5.2, the values of η and μ from our calculated IP and EA values as well as the experimental ones are reported. We have checked that in the more extensive TZ2P basis, IP and EA values and consequently η and μ values do not change significantly from the TZP values (typical difference is 10^{-7} to 10^{-8} a.u. only for open shell atoms and about 10^{-3} to 10^{-4} a.u. for other radicals). The results obtained from the calculations using EDZP and EDZP + diffuse (sp) basis are presented in table 5.3 . It is clear from the table that there is no significant change in the values of η and μ due to this additional diffuse functions. Particularly the trend of the values, which is the most important purpose of this study, remains the same. So our TZP basis set can be taken to be fairly extensive

---

FOOTNOTE C : The exponents (α) of the polarization functions are -
(i) For EDZP : H (α_p) = 1.00 ; α_d values of C, N, and O are 0.72, 0.98 and 1.28 respectively. For the second row atoms Si and S, the α_d values are 0.388 and 0.542 respectively.

(ii) Exponents (α) of the diffuse s function of H is 0.036. The shared exponents of the diffuse (sp) functions of other elements are ,

Atom	α_s	α_p	Atom	α_s	α_p
C	0.0438	0.0438	Si	0.0331	0.0331
N	0.0639	0.0639	S	0.0405	0.0405
O	0.0845	0.0845			

and we will restrict our discussion to the results obtained from TZP basis only.

As seen from table 5.2, the calculated values of η are larger than the experimental values in all cases. The same trend follows in the case of chemical potential also - except for CH_3S, for which the calculated μ is lower. For NO_2 and CF_3, the experimental values are not known exactly, but bounds to these are known. Our calculation in a given basis takes care of the relaxation effects only. The effects of correlation are known to increase the IP values. Hence in a given basis our calculated IP values will be less than the full configuration interaction (CI) IP values in that basis. Similarly the correlation effects will increase the EA values where the system has a positive EA. The systems considered in our examples have positive EA. So our computed values will be less than the full CI values. However, for the difference of IP and EA (i.e. η) one can not specify whether the computed values will be larger or smaller than the full CI results. Our results throw light on how ΔSCF method performs to extract the difference of IPs and EAs for free radicals. No trend is known for this difference earlier. In the absence of full CI numbers, they are compared with those obtained from experimental IPs and EAs. Since our basis is extensive, this may be a reasonable comparison. We find that the hardness values are obtained with a reasonable degree of reliability.

About the chemical potential values, one can argue that the correlation will depress those obtained via the ΔSCF procedure in our example cases. In the results reported in table 5.2 , our calculated μ values are higher in comparison with the full CI μ values in most examples. In comparison, the η values should be better represented by ΔSCF procedure than the μ values. However, the agreement of the values of chemical potential with the experimental ones is as good as that of hardness values. This only shows that the experimental results are quite different from the possible full CI numbers. This may be attributed to the fact the experimental numbers are derived from adiabatic IP´s and EA´s and the geometry of the ions are quite different from the geometry of the neutral radical.

We see that our results offer proper ordering of the anions according to their hardness sequence. Chemical evidence as well as the experimental η values confirm the following hardness sequence of the common anions,

$$F^- > Cl^- > Br^- > I^- \quad ; \quad OH^- > SH^- > SeH^- \quad ; \quad CH_3^- > SiH_3^-$$

$$\text{and} \quad F^- > OH^- > NH_2^- > CH_3^-$$

From table 5.2 we see that the ordering of η values obtained by ΔSCF method, matched with the above ordering. This gives us confidence that at least for qualitative trend ΔSCF results can be considered sufficiently reliable.

Looking at our result it seems that H^- ion should be a hard species whereas actually it is very soft. But this uneasy situation exists even if we also look at the experimental η value of H^- ion (Proft et al, 1993).

5.4 CONCLUSION

Our calculations of chemical hardness and potential for open shell systems to use them as a model for rank ordering of the corresponding anions are the first of its kind. The ΔSCF level of calculation reported here gives reasonably good values of chemical hardness and potential at least for a qualitative trend. However, by performing a correlated level of calculation the quantitative improvement of the results are expected. In this context it should be mentioned that, Proft et al (Proft et al, 1993) have shown that there is lowering of the intrinsic group hardness values when calculated in the CISD level. The CISD values thus show better correlation with the experimental results.

It is difficult to compare the trend of the values of hardness and chemical potenial obtained by ΔSCF procedure with those from Koopmans′ like approximation for open shell systems. The definition of the eigenvalues of an open shell Fock operator is ambiguous and these will differ depending on ROHF or UHF procedure adopted. Thus while for closed shell systems, such comparison has been done, the same can not be done unambiguously for the open shell cases.

Another problem may arise in using UHF calculation for open shell species like F, Cl etc. Here five electrons are to be evenly distributed in three degenerate orbitals (p_x , p_y and p_z). But UHF level of calculation breaks this three-fold degeneracy, thus losing the spherical symmetry. The same thing happens to the case of F^+ and Cl^+, where now four electrons are equally distributed among three degenerate p-orbitals.

It may be interesting to check how far hardness and chemical potential values, using calculated adiabatic IP and EA, match with the experimental results quoted in this paper. However, the definition of hardness and chemical potential use vertical IP and EA. It is gratifying to note that for qualitative rank ordering, these hardness values appear to be trustworthy.

Table 5.1. Calculated and experimental values of Ionization Potential (IP) and Electron Affinity (EA) of some common open shell species (mostly radicals). The calculated values are at TZP basis sets. All values are in atomic units.

Radicals	Expt.IP	Calcd.IP	Expt.EA	Calcd. EA
F	0.640168	0.629584	0.124947	0.037000
OH	0.483985	0.550701	0.067251	-0.020893
NH_2	0.418939	0.427858	0.027194	-0.051044
CH_3	0.360876	0.325640	0.002940	-0.070912
Cl	0.478105	0.466261	0.133032	0.084957
SH	0.382557	0.423025	0.084523	0.032645
SiH_3	0.299137	0.309130	0.051816	-0.017281
H	0.499419	0.499810	0.027194	-0.033312
OOH	0.423716	0.318831	0.043731	-0.092410
NO2	>0.371165	0.443832	0.084523	0.030729
CH_3S	0.296197	0.377007	0.069823	0.014729
CF_3	0.339929	0.440190	>0.040424	-0.029654

Table 5.2. Calculated and experimental values of chemical hardness (η) and chemical potential (μ) of the common open shell species mentioned in the previous table. The η and μ are calculated on the basis of IP and EA values given in the previous table.

Radicals	Expt. (η)	Calcd. (η)	Expt. (μ)	Calcd. (μ)
F	0.257611	0.296292	-0.382557	-0.333292
OH	0.208367	0.285797	-0.275618	-0.264904
NH_2	0.195872	0.239451	-0.223067	-0.188407
CH_3	0.178968	0.198276	-0.182275	-0.127364
Cl	0.172720	0.190652	-0.305384	-0.275609
SH	0.150671	0.195190	-0.235194	-0.227835
SiH_3	0.123844	0.163206	-0.175660	-0.145924
H	0.235929	0.266561	-0.263491	-0.233249
OOH	0.189993	0.205621	-0.233724	-0.113211
NO_2	>0.143321	0.206552	<-0.227844	-0.237280
CH_3S	0.113922	0.181139	-0.183745	-0.195868
CF_3	<0.149936	0.234922	<-0.190360	-0.205268

Table 5.3. The values of chemical hardness (η) and chemical potential (μ) calculated at EDZP and EDZP + diffuse (sp) basis sets. All values are in atomic units.

Radicals	η_{EDZP}	$\eta_{EDZP+diff(sp)}$	μ_{EDZP}	$\mu_{EDZP+diff(sp)}$
H	0.26611	0.25634	-0.23370	-0.24348
OH	0.27672	0.27090	-0.41670	-0.42300
NH_2	0.24501	0.23938	-0.27557	-0.28166
CH_3	0.19715	0.19172	-0.12961	-0.13504
SH	0.19321	0.18917	-0.23000	-0.23447
SiH_3	0.16107	0.15823	-0.14802	-0.15110
OOH	0.14572	0.14000	-0.11407	-0.12157
NO_2	0.20624	0.20157	-0.23747	-0.24259
CH_3S	0.17961	0.17630	-0.19770	-0.20140

CHAPTER 6

CONCLUSION

6.1 SUMMARY AND CRITICAL ANALYSIS OF THE RESEARCH WORK CONTRIBUTED IN THIS THESIS

In this thesis I have presented some new formal developments as well as applications of chemical hardness (η). We have studied the qualitative relation of η with polarizability (P), electronegativity ($\varkappa$) and volume in case of complex polyatomic molecules. We have established the nature of variation of η and P as the distances between bonds comprising of atoms having different electronegativities are changed by a small amount around the equilibrium. Our results establish that the relation between $P^{1/3}$ and η is essentially linear as in the case of atoms and atomic clusters. However, a weak nonlinear behaviour exists in certain cases. We have attempted to delineate such cases. Enhancement of nonlinear effect at large bond distortions can also be rationalised. We point out that the concepts like ´local bond hardness´ or ´polarizability along a bond´ may be more consistently related.

The principle of maximum hardness (PMH) has been studied by ab initio wave function formalism. Through near full CI level of calculation (multireference coupled cluster singles and doubles i.e. MRCCSD) we have shown that for asymmetric distortion chemical potential remains nearly constant and thus provides a domain where PMH can be tested. We have extended our study to the cases of both symmetric and asymmetric distortions from a nonequilibrium (linear) geometry of H_2O molecule and have found that PMH holds true only for asymmetric distortion, in this case also (our numerical results show that the hardness reaches a local maximum at any symmetric configuration of the molecule for all asymmetric distortions around it). This part of the results has been rationalised by a recently given group theoretical proof of Makov (Makov, 1995). Significantly, our results show that for constant μ, the hardness is globally maximum for equilibrium geometry.

Another important contribution of this thesis is to investigate the behaviour of the operational hardness ($\bar{\eta}$) and chemical potential ($\bar{\mu}$) in the process of chemical binding. Starting from the finite difference approximation, we have shown the existence of a simple general relation of $\bar{\eta}$ and $\bar{\mu}$ with the energies of the neutral species and the corresponding cations and anions. This new expression can explain the hardness surface in a reaction profile. The non-existence of maxima in the hardness profile of diatomic molecules is justified by our expression. It also explains the apparent anomalous existence of two different hardness values corresponding to a single binding energy in a diatomic molecule. A bye product of our general result is that the global hardness of a collection of non-interacting atoms of the same type is just the absolute hardness of a single atom. Our formalism suggests that at the points where $\bar{\mu}$ remains constant, maximum of $\bar{\eta}$ corresponds to maximum IP or minimum EA.

The problems in evaluating hardness of degenerate and quasi-degenerate open-shell systems (atoms, radicals etc.) as well as their importance in qualitative rank-ordering of the corresponding anions have been discussed in details. The reliability of our results is critically judged by comparing with the η and μ values obtained from experimental IPs and EAs. Our calculated η values provide proper rank-ordering of the corresponding anions.

Throughout the last few chapters, I have tried to give a picture how hardness concept originated and was developed by several workers. Though it is very difficult to give a complete account of all of them, we can get a feeling of the general trend of this development. At the begining hardness was mere naive and qualitative, depending on the size, charge, polarizability etc. of a chemical species and was proposed to explain the behaviour of Lewis acids and bases. On the basis of this qualitative concept, another empirical principle of soft and hard acids and bases (HSAB) was proposed. The HSAB principle was proposed after the observation of numerous chemical reactions which also helped to interpret lot of other chemical problems. Even the Lewis acids and bases were classified into hard, soft and borderline categories on the basis of this HSAB principle, although exceptions are there. The story of the hardness concept was a success as long as it was considered as a qualitative one. But a mixture of success and failure became apparent in an effort to define hardness (or softness) as a quantitative one. As soon as Parr and Pearson (Parr and Pearson, 1983) gave rigorous definition of chemical hardness [η = (IP - EA)/2], there was an effort from different corners to arrange the chemical species (e.g. atoms, molecules, radicals etc.) according to their hardness sequence. These numbers are sometimes helpful in explaining chemical reactions, but sometimes they fail to reflect on the actual chemical significance. This happens particularly when we compare the hard or soft behaviour of different chemical species on the basis of their hardness values. There are examples in which the hardness values of the systems do not reflect their behavioural sequence expected from their experimental observation or chemical intuition (Pearson, 1988a). The reason may be the lack of rigor of the methodology by which these numbers are generated or insufficient information about the environment in which the reaction is taking place or may be the fact that the hardness parameter alone is not sufficient to give a complete description of a chemical process.

Pearson (Pearson, 1988b), while trying to explain the preferential formation of Lewis acid - base complex (AB), on the basis of hard-hard and soft-soft interaction, agreed with Kutzelnigg´s view (Kutzelnigg, 1984) that the stability depends on "many other bond - determining factors such as the electronegativities of A and B, their charges and sizes, the matching of orbital overlaps and steric repulsions. It is impossible to keep all of these factors constant, but at least one should only compare acids, or bases, of same charge. Also, a series of acids, or a series of bases, should only be compared when their mean bond strengths to the reference acids, or bases, are about the same".

When we come to the point of stability of a chemical species, still now it seems that absolute value of the total energy is a more reliable quantity than the global hardness (or softness) value. As pointed out by Pearson and Palke (Pearson and Palke, 1992), the determination of the most stable equilibrium geometry uses electrostatic Hellman - Feynmann theorem. Chemical hardness (η), under the conditions of constant μ and v, will be helpful in evaluating the point group of a chemical species. But hardness (or softness) values have advantage over energy values in predicting preferential formation of bonds on a particular site of a reactant. By calculating the local hardness or local softness of different sites of a chemical species, we can predict the favourable reaction sites depending on the attacking reagent. Parr (Parr and Yang, 1989) is of the opinion that the ´hard-likes-hard and soft-likes-soft´ rule may also apply when all quantities are evaluated in a local version. The HSAB principle in its local version is more reliable than the global one.

In a recent article, Geerlings and co-workers (Langenaeker et al, 1995) have defined some working equations of the local hardness as also a new quantity, the hardness density. Hardness density fits as a better counterpart of local softness. With the help of molecular electrostatic potential (MEP), local softness, and the newly defined local hardness quantities he explained the intra- and intermolecular reactivities of the electrophilic aromatic substitutions on mono-substituted benzene. Extensive exploitation of these newly defined quantities for predicting reaction mechanisms is necessary.

Another problem of using the hardness concept is to define the hardness for open shell and excited state chemical species. As discussed in chapter 5, definition of hardness of degenerate or quasidegenerate open shell systems poses some problems. These open shell systems can be used as model systems for the corresponding anions. Pearson (Pearson, 1988a) has given theoretical support in favour of this assumption which was also supported by our numerical demonstration (Roy and Pal, 1995). But to be sure, more rigorous calculations on a variety of radicals are to be performed.

The problem of defining hardness for excited states is not simple. For atoms depending on the level of excitation, the electronic configouration varies. As a result the IP and EA values also differ which are the key parameters to evaluate chemical hardness (η). Klopman (Klopman, 1964) has shown that the continuous energy curve is valid only for those valence electrons having a particular value of n (principal quantum number) and l (azimuthal quantum number). If there is a change in n and l for some of the valence shell electrons, this continuity is lost. There will be substantial changes in IP and EA and consequently in the values of $\varkappa$ and η, when n and l change for the next electron. These effects will be very large if we add an electron to or remove an electron from the valence shell.

In this context, it may be interesting to investigate into a definition and evaluation of hardness for excited states of molecular and atomic systems. A thorough investigation is required on the reliability of the conventional methods e.g., ΔSCF procedure or Koopmans' approximation to evaluate the hardness and chemical potential of the excited states.

6.2. PROBABLE NEWER AREAS OF APPLICATION

(i) ACTIVATION HARDNESS

In spite of the fact that there is difficulty in defining and evaluating chemical hardness for excited states, open shell and anionic species, it has been used as a reliable reactivity index for a variety of chemical reactions. One such area where η has potential future application is to predict the orientation of aromatic substitution. Zhou and Parr (Zhou and Parr, 1990) have defined a new reactivity index called, 'activation hardness' to predict the orientation effect of electrophilic aromatic substitution. Considering Wheland's intermediate (Wheland, 1942) as the transition state, they showed that the activation energy is the negative of twice the change in hardness in going from reactant to transition state i.e.,

$$\Delta E^{\#} = -2(\eta_{N-2} - \eta_{N}) = 2(\eta_{N} - \eta_{N-2}) = 2\Delta\eta^{\#} \qquad 6.1$$

Here $\Delta\eta^{\#}$ is defined as the 'activation hardness'. The η_{N-2} and η_{N} are the hardness values of the Wheland's transition state and the reactant respectively. From equation 6.1 it is clear that minimum change in $\Delta E^{\#}$ is equivalent to minimum change of $\Delta\eta^{\#}$. Hence reaction will be preferred in the direction for which $\Delta\eta^{\#}$ is minimum. Applying HMO approximation to $\Delta\eta^{\#}$ they showed that the sites for which $\Delta\eta^{\#}$ is minimum or Hammett´s σ^{+} constant is maximum, is the most preferable site for electrophilic aromatic substitution. They also proposed an extremum principle that other things being equal, the softer reactant favours the reaction and the harder the transition state is the better.

In this context, it should be mentioned that in a recent article Cárdenas-Jirón et al (Cárdenas-Jirón et al, 1995) have defined ´activation hardness´ for systems showing rotational isomerisation and having ´double-well´ and ´double-barrier´ shaped potential functions. Activation hardness in this case has dependence on the activation energy of the transition state as also the energy difference between the two reference conformations. From the expression of activation hardness they also defined the conditions under which PMH holds.

Ray and Rastogi (Ray and Rastogi, 1993) used the ´activation hardness´ parameter, as defined by Zhou and by Parr, to examine the modes of sigmatropic shift. They have shown that hardness value for (1, 4n + 1) thermal sigmatropic shift is higher for suprafacial transition state thus favouring suprafacial mode of shift. But for photochemical process antarafacial shift leads to a harder transition state, thus favouring this mode of shift. The reverse is true for (1, 4n + 3) sigmatropic shift. So by using activation hardness parameters, they got similar results as predicted by Woodward - Hoffmann (Woodward and Hoffmann, 1989).

But in using the ´activation hardness´ as an index of orientation of electrophilic aromatic substitution only electronic effect is considered. To predict the relative amount of different isomers steric effects are also to be considered, as pointed out by Zhou and Parr. To calculate $\Delta\eta^{\#}$, Zhou and Parr have used HMO approximation, whereas Ray and Rastogi followed the approximations of Coulson and Longuet-Higgins (Coulson and Longuet-Higgins, 1947). So to achieve more reliable results rigorous ab initio methods may be used. Cases of nucleophilic aromatic substitutions can be tested by using ´activation hardness´ concept to predict the preferable attacking site. The key factor for this study is to define the exact transition state as it will suggest the corresponding extremum principle.

(ii) CORRELATION OF HAMMETT PARAMETERS WITH ACTIVATION HARDNESS

As is obvious from the works of Zhou and Parr (Zhou and Parr, 1990), electrophilic aromatic substitution is preferred in most cases only for those sites for which the activation hardness is minimum or Hammett´s σ^{+} constant, better known as ´relative basicity´ for benzenoid hydrocarbons (Streitwieser, 1961), is maximum. It means that both these parameters ultimately lead to the same physical interpretation of chemical reactivity. The relative basicity of any position of a benzenoid hydrocarbon depends upon the stability of the resultant carbonium ion through extended resonance. More the resonance stability, more preferable is the site for electrophilic aromatic substitution, which indirectly means more relative basicity. Now from the expression of activation hardness, $\Delta\eta^{\#} = (\eta_R - \eta_T)$, we see that $\Delta\eta^{\#}$ will be lower when η_T or hardness of the transition state (here the resultant carbonium ion) is large as η_R is constant. Now from the relation of hardness with stability it is expected that the most stable transition state should have maximum hardness. Thus minimum $\Delta\eta^{\#}$ indirectly means maximum relative basicity and they are complementary to each other in predicting preferable reactive sites for electrophilic aromatic substitution. The correlation of $\Delta\eta^{\#}$ with the preferable reaction sites for substituted benzenes, heterocycles etc. can be made on the basis of inductive and resonance effect of the substituent, as these factors determine the stability of the resultant transition state.

It may be interesting to compare the $\Delta\eta^{\#}$ with Hammett's σ constants for predicting the reaction rates of substituted benzene derivatives. Sensitivity of $\Delta\eta^{\#}$ can be tested for cases such as substituted aliphatic compounds and ortho substituted benzene derivatives, where Hammett's σ constants cannot provide satisfactory information.

(iii) CHANGE OF HARDNESS WITH ELECTRIC AND MAGNETIC FIELD

Our finding of the change of hardness with the change in binding energies of the corresponding cationic, anionic and neutral species (chapter 2) belongs to more general feature of the change of hardness with energy change with respect to external parameters. This is the case studied in this thesis. However, one can study the changes with respect to other parameters like electric field, magnetic field etc.

6.3 ON THE PROBLEM OF THE PRINCIPLE OF MAXIMUM HARDNESS

Both from chemical intuition and logical arguments, it is expected that chemical hardness (η) should be maximum at the most stable (i.e. equilibrium) geometry. This is also supported by the frontier-orbital theoy, i.e. more the gap between HOMO and LUMO of a chemical species, more chemically nonreactive it is. So at the stable equilibrium geometry, the HOMO - LUMO gap i.e. the chemical hardness should be maximum. A general proof was first put forward by Parr and Chattaraj (Parr and Chattaraj, 1991). Subsequent numerical studies, including the work presented in this thesis have supported the statement. Some numerical results showed that the principle may work even when the conditions of constant μ and v are not rigorously obeyed. For example, the tests carried out by Pearson and Palke (Pearson and Palke, 1992) and the one contributed in this thesis [chapter 3, around equilibrium geometry of H_2O molecule] maintained the conditions of constant μ and v. But the studies of Datta (Datta, 1992) could not maintain these conditions, although η was shown to be maximum at equilibrium stable geometry.

The above study automatically raises the question whether the constraint of constant μ and v are necessary in defining the PMH. Pearson (Pearson, 1993) claimed that these two conditions must have to be maintained in order to make the PMH valid. He stated that, "in the case of isomers where a difference in the bonding between atoms occurs, the PMH does not predict that the most stable isomer has the largest HOMO - LUMO gap. Such isomers will necessarily have quite different value of v, though μ can be fairly constant". Instead he suggested considering the nuclear - nuclear repulsion terms to predict the relative stability of such isomers. In table 6.1 we have presented the results for NOH <->HNO isomeric changes by varying bond distances and bond angles (see footnote A), so that μ remains almost constant (upto 4th decimal points). The results show that the most stable geometry with minimum total energy ($-E_T$) does not correspond to the maximum hardness value (Pal <u>et al</u>, 1995). Instead maximum hardness corresponds to maximum IP, which we proved analytically in chapter 4.

However, Parr and Zhou (Parr and Zhou, 1993) are of the opinion that the relaxation of the constraints of constant μ and v may not necessarily violate the PMH. In favour of his argument, he stated that, "The maximum hardness principle was originally drawn from empirical comparisons between different compounds. We ordinarily apply the principle only to closely related systems through which the external potential change is regular. Change in the potential is subsequently offset by change in chemical

---

FOOTNOTE A :- The O-N and O-H bond lengths (a.u.) and <N-O-H bond angles (deg.) are given sequentially for various configurations of NOH molecule - (a) 2.4535, 1.8178, 114.55; (b) 2.4431, 1.0, 160; (c) 2.3504, 0.8, 140; (d) 2.42056, 0.8, 180; (e) 2.1646, 0.8, 80; (f) 2.1608, 0.7, 90; (g) 2.1325, 0.6, 90.

potential. On the basis of empirical evidences -------------, we believe that a more general maximum hardness principle probably exists, justifying comparison of hardnesses between different external potentials." In this context it is to be mentioned that our study (Pal <u>et al</u>, 1993) with H_2O molecule at nonequilibrium geometry supports the view of Parr and Zhou. In table 6.2 we have presented the results of another study made on CO_2, where the geometries are varied without maintaining the condition of constant v or preserving the symmetry of the molecule (see footnote B for distortions of bond distances and bond angles). Here in spite of the changes in nuclear positions, (μ is kept almost constant), the maximum hardness corresponds to the minimum total energy of the most stable equilibrium geometry (Pal <u>et al</u>, 1995). In this case also it is observed that maximum IP corresponds to maximum η, confirming the proof of chapter 4.

Kar and Scheiner (Kar and Scheiner, 1995) have also shown that PMH holds for 1,2 - hydrogen shift reaction in some HAB molecules and HAB^+ ions though there is a drastic change in v. It seems to be worth reconsidering the studies by Datta (Datta, 1992), Harbola (Harbola, 1992), Pearson (Pearson, 1992, 1993) and Galvan <u>et al</u> (Galvan <u>et al</u>, 1993) on the basis of this newer understanding.

Recently Sebastian (Sebastian, 1994) has shown that the proof

---

FOOTNOTE B :- The C=O bond distances (a.u.) and <O-C-O bond angles (deg.) are given below sequentially for various configurations : (a) 2.15, 2.15, 180; (b) 2.15, 1.94, 170; (c) 2.16, 1.758, 160; (d) 2.16, 1.62, 150; (e) 2.15, 1.514, 140; (f) 2.15, 1.4405, 130; (g) 2.16, 1.404, 120.

of PMH, given by Parr and Chattaraj (Parr and Chattaraj, 1991) is in error in general. Using the Gyftopoulos and Hatsopoulos three state model (Gyftopoulos and Hatsopoulos, 1965) he has shown that for Na atom the plots of $\bar{S}/\langle S\rangle$ against $\beta(\bar{\mu} - \mu)$ for different values of temperature, do not show any minimum when $\bar{\mu} = \mu$ [see footnote C]. Applying a four level non-degenerate model to O atom (corresponding to the species, O^{+}, O, O^{-} and O^{2-}) he showed that the point for which $\beta(\bar{\mu} - \mu) = 0$ is not the point when $\bar{S}/\langle S\rangle$ is minimum. Both of the above two observations go against the validity of PMH. To search for the reason of this failure, Sebastian has shown analytically that the proof given by Parr and Chattaraj is not true in general and may be valid only for particular non-equilibrium ensemble distributions.

The above examples and counter examples of the PMH have led Parr and his co-workers to carry out a more critical study of the PMH to reach a more transparent conclusion. Very recently Chattaraj et al (Chattaraj, Liu and Parr, 1995) have proposed a number of versions of the PMH, depending on the conditions maintained in different type of chemical changes. Their derivations are also based on the Gyftopoulos and Hatsopoulos three-level model. These are,

[A] (i) For the change of one equilibrium state to another, each

---

FOOTNOTE C :- Here $\beta = 1/kT$, where k is the Boltzman's constant. $\langle S\rangle$ and μ are the softness and chemical potential for the equilibrium ensemble distribution. $\bar{S}$ and $\bar{\mu}$ are the corresponding quantities for a non-equilibrium ensemble distribution obtained by slight variation of chemical potential μ of the electrons and external potential v(r), from the equilibrium ones.

having the same average number of electrons, the ensemble-average softness increases or decreases as the ensemble-average electronic energy increases or decreases relative to E_0 (here E_0 is the energy of the neutral species at equilibrium geometry). the value of μ_0 (chemical potential for neutral species at equilibrium geometry) is not required to be constant.

(ii) Decrease in E_0 itself, for fixed $(E_+ + E_-)/2$, goes with increase of the pure state hardness η_0. Here E_+ and E_- are the energies of the monopositive and mononegative ions at the equilibrium geometry of the neutral species.

[B] The maximum hardness principle is always valid if the nonequilibrium state is generated by changing μ alone. Here μ is the chemical potential of the nonequilibrium state.

[C] The maximum hardness principle is always valid if the nonequilibrium state is generated by changing μ and also changing v(r) by a constant such that there is a constant shift in all energy levels. Here v(r) is the potential due to nuclei plus any other external potential.

[D] If the nonequilibrium state is generated by changing v(r) and μ, keeping the average number of particles fixed, the maximum hardness principle is valid if the average electronic energy in the equilibrium state is less than in the nonequilibrium state.

In a very recent article, Makov (Makov, 1995) proposed that "a general variational principle for the chemical potential or the hardness will exist only if the electrostatic force arising from respective charge distributions, $x(r)$, is zero at the equilibrium positions of the nuclei. There is at present no evidence (or claim) for such behaviour" (see footnote D). However, from group theoretical symmetry arguments he proved that the extremum principle exists for certain classes of variation of the geometry. Thus, all the invariants (e.g., energy, chemical potential and hardness) will pass through extremum with respect to asymmetric variations about a symmetric nuclear configuration. From this argument he has rationalised the observations presented in the chapter 3 of the thesis, where we considered the symmetric and asymmetric variations of the nuclei about linear configuration of water molecule. Also the results of Datta (Datta, 1992) could be explained by the same argument. But obviously Makov´s arguments can be applied only to those cases where asymmetric distortions are performed around symmetric geometries. From this as well as the studies of this thesis, one can say with a degree of positiveness that hardness will go through a maximum with respect respect to all asymmetric distortions about the symmetric configurations.

FOOTNOTE D :- For chemical potential, $x(r) = [n_{N+1}(r) - n_{N-1}(r)]/2$ and for chemical hardness $x(r) = [n_{N+1}(r) + n_{N-1}(r) - 2n_{N}(r)]/2$. Here, $n_N(r)$, $n_{N+1}(r)$ and $n_{N-1}(r)$ are the ground state densities of N (neutral), N+1 (anion) and N-1 (cation) electrons in the same potential [i.e. $v(r)$].

The future studies related PMH should focus on the critical re-evaluation of the propositions made by Parr and co-workers on the basis of already existing and recently found results.

Table 6.1. The electronic and total energy, ionization potential, hardness and chemical potential of the NOH molecule at various configurations. Geometrical parameters of the molecule are given in the footnote of the text. All values are in atomic unit.

Config.	E_{el}	E_T	IP	$\bar{\eta}$	$\bar{\mu}$
1 (eqm.)	-158.87032	-129.70565	0.4056	0.2425	0.16310
2	-162.01378	-129.03328	0.3967	0.2336	0.16309
3	-164.37332	-128.21948	0.4040	0.2409	0.16310
4	-163.50465	-128.19598	0.3955	0.2324	0.16310
5	-167.21503	-128.12363	0.4207	0.2576	0.16309
6	-167.84776	-127.42100	0.4215	0.2584	0.16310
7	-169.04399	-126.29056	0.4225	0.2594	0.16310

Table 6.2. The electronic energy, total energy, ionization potential, hardness and chemical potential of the CO_2 molecule at different configurations. The geometrical parameters are given in footnote of the text. All values are in atomic units.

Config.	E_{el}	E_T	IP	$\bar{\eta}$	$\bar{\mu}$
1 (eqm.)	-247.21329	-187.67841	0.5437	0.3814	0.16233
2	-250.40971	-187.63437	0.5388	0.3765	0.16232
3	-253.59862	-187.48854	0.5219	0.3596	0.16238
4	-256.62300	-187.25543	0.5022	0.3399	0.16235
5	-259.53773	-186.95681	0.4813	0.3190	0.16230
6	-261.88378	-186.65190	0.4578	0.2955	0.16234
7	-263.42097	-186.42906	0.4326	0.2703	0.16232

REFERENCES

Ahrland et al (1958) : Ahrland S. , Chatt J., and Davies N. ; Quart. Revs. (London) 12, 265 (1958).

Alonso and Balbas (1993) : Alonso J. A. and Balbas L. C. ; In *Chemical Hardness* (Structure and Bonding, vol. 80, Sen K.D., ed.). Heidelberg : Springer-Verlag, pp. 229 (1993) and the references therein.

Bader (1979) : Bader R. F. W.; J. Am. Chem. Soc. 101, 1389 (1979).

Bader (1990) : Bader R. F. W. ; *Atoms in Molecules : A Quantum Theory*. Oxford : Clarendon Press (1990).

Baekelandt et al (1993) : Baekelandt B. G., Mortier W. J. and Schoonheydt R. A. ; In *Chemical Hardness* (Structure and Bonding, vol. 80, Sen K. D., ed.). Heidelberg : Springer-Verlag, pp. 187 (1993) and the references therein.

Bartlett (1981) : Bartlett R. J. ; Ann. Rev. Phys. Chem. 32, 359 (1981).

Bartlett et al (1987) : Bartlett R. J., Purvis G. D. III , Fitzgerald G. B., Harrison R. J., Ritby M., Sosa C., Lee Y. S., Trucks G. W., Cole S. J., Salter E. A., Pal S., Watts J. D., Laidig W. D., Magers D. H., Stanton J. F. and Bernhold D.; ACES (Advanced Concepts in Electronic Structure program system) ; Quantum Theory Project, University of Florida (1987).

Basolo et al (1964) : Basolo F., Baddley W. H. and Burmeister J. L.; Inorg. Chem. 3 , 1202 (1964).

Berkowitz and Parr (1988) : Berkowitz M. and Parr R. G.; J. Chem. Phys. 88, 2554 (1988).

Cardenas-Jiron et al (1995) : Cardenas-Jiron G. I., Lahsen J. and Toro-Labbe A.; J. Phys. Chem. 99, 5325 (1995).

Cederbaum and Domcke (1977) : Cederbaum L. S., Domcke W.; Adv. Chem. Phys. 36, 205 (1977).

Chandler (1987) : Chandler D.; In *Introduction to Modern Statistical Mechanics* . Oxford : New York (1987).

Chandra (1994) : Chandra A. K. ; THEOCHEM. 312, 297 (1994).

Chatt and Wilkins (1950) : Chatt J. and Wilkins R. G.; Nature 165, 859 (1950).

Chatt and Venanzi (1956) : Chatt J. and Venanzi L. M.; Nature 177, 852 (1956).

Chatt et al (1955) : Chatt J., Duncanson L.A. and Venanzi L. M. ; J. Chem. Soc. 4456 (1955).

Chattaraj et al (1991) : Chattaraj P. K., Lee H. and Parr R. G. ; J. Am. Chem. Soc. 113, 1855 (1991).

Chattaraj et al (1995) : Chattaraj P. K., Liu G. H. and Parr R. G.; Chem. Phys. Lett. 237 , 171 (1995).

Chattaraj and Nath (1994) : Chattaraj P. K. and Nath S.; Ind. J. Chem. SectA, Inorg., Bio-inorg., Phys., Theor., Anal. Chem. 33A, 842 (1994).

Chattaraj et al (1994) : Chattaraj P. K., Nath S. and Sannigrahi A. B.; J. Phys. Chem. 98 , 9143 (1994).

Chattaraj and Schleyer (1994) : Chattaraj P. K. and Schleyer P. v. R.; J. Am. Chem. Soc. 116, 1067 (1994).

Cioslowski and Mixon (1993) : Cioslowski J. and Mixon S. T. ; J. Am. Chem. Soc. 115 , 1084 (1993).

Cizek (1966) : Cizek J. ; J. Chem. Phys. 45, 4256 (1966).

Coulson (1937) : Coulson C. A. ; Proc. of Phil. Soc. 33, 111 (1937).

Coulson and Longuet-Higgins (1947) : Coulson C. A. and Longuet-Higgins H.C. ; Proc. Roy. Soc. A191, 39 (1947).

Datta (1992) : Datta D. ; J. Phys. Chem. 96, 2409 (1992).

Dunning (1970) : Dunning T. H.; J. Chem. Phys. 53, 2823 (1970).

Edwards (1954) : Edwards J. O.; J. Am. Chem. Soc. 76, 1540 (1954).

Edwards (1956) : Edwards J.O.; J. Am. Chem. Soc. 78, 1819 (1956).

Edwards and Pearson (1962) : Edwards J. O. and Pearson R. G. ; J. Am. Chem. Soc. 84, 16 (1962).

Fajans (1941) : Fajans K. ; J. Chem. Phys. 9, 28 (1941).

Fajans and Joos (1924) : Fajans K. and Joos G.; A. Physik 23, 1 (1924).

Felicov and Somorjai (1985) : Felicov L. M. and Somorjai G. A. ; Proc. Natl. Acad. Sci. USA 82, 2207 (1985).

Galvan et al (1993) : Galvan M., Dal Pino A. and Joannopoulos J. D. ; Phys. Rev. Lett. 70, 21 (1993).

Gázquez et al (1993) : Gázquez J. L., Martinez A. and Méndez F. ; J. Phys. Chem. 97, 4059 (1993).

Gázquez and Ortiz (1984) : Gázquez J. L. and Ortiz E. ; J. Chem. Phys. 81, 2741 (1984).

Ghanty and Ghosh (1993) : Ghanty T. K. and Ghosh S. K. ; J. Phys. Chem. 97, 4951 (1993).

Ghanty and Ghosh (1994a) : Ghanty T. K. and Ghosh S. K. ; THEOCHEM. 309, 143 (1994).

Ghanty and Ghosh (1994b) : Ghanty T. K. and Ghosh S. K. ; J. Phys. Chem. 98, 1840 (1994).

Ghanty and Ghosh (1994c) : Ghanty T. K. and Ghosh S. K. ; J. Am. Chem. Soc. 116, 3943 (1994).

Ghanty and Ghosh (1994d) : Ghanty T. K. and Ghosh S. K. ; J. Am. Chem. Soc. 116, 8801 (1994).

Ghanty and Ghosh (1994e) : Ghanty T. K. and Ghosh S. K. ; J. Phys. Chem. 98, 9197 (1994).

Ghosh (1994) : Ghosh S. K. ; Int. J. Quantum Chem. 49, 239 (1994).

Ghosh and Berkowitz (1985) : Ghosh S. K. and Berkowitz M. J. Chem. Phys. 83, 2976 (1985).

Ghosh and Parr (1987) : Ghosh S. K. and Parr R. G. ; Theor. Chim. Acta. 72, 379 (1987).

Greenberg (1962) : Greenberg A. A. ; *An Introduction to The Chemistry of Complex Compounds* : Translated by J. R. Leach. London : Pergamon Press (1962), Chapter 7.

Gyftopoulos and Hatsopoulos (1965) : Gyftopoulos E. P. and Hatsopoulos G. N. ; Proc. Natl. Acad. Sci. US 60, 786 (1965).

Harbola (1992) : Harbola M. K. ; Proc. Natl. Acad. Sci. USA. 89, 1036 (1992).

Harbola et al (1991) : Harbola M. K., Chattaraj P. K. and Parr R. G. ; Israel J. Chem. 31, 395 (1991).

Hohenberg and Kohn (1964) : Hohenberg P. and Kohn W. ; Phys. Rev. B136, 864 (1964).

Huzzinaga (1965) : Huzzinaga S. ; J. Chem. Phys. 42, 1293 (1965).

Iczkowski and Margrave (1961) : Iczkowski R. P. and Margrave J. L.; J. Am. Chem. Soc. 83, 3547 (1961).

Jorgensen (1964) : Jorgensen C. K. ; Inorg. Chem. 3, 1201 (1964).

Jorgensen (1967) : Jorgensen C. K. ; In Structure and Bonding, vol. 3 . Berlin : Springer-Verlag New York Inc., pp. 106 (1967).

Kaldor (1987) : Kaldor U. ; J. Comp. Chem. 8, 448 (1987).

Kar and Scheiner (1995) : Kar T. and Scheiner S. ; J. Phys. Chem. 99, 8121 (1995).

Klopman (1964) : Klopman G. ; J. Am. Chem. Soc. 86, 1463 (1964).

Klopman (1968) : Klopman G. ; J. Am. Chem. Soc. 90, 223 (1968).

Komorowski (1987a) : Komorowski L. ; Chem. Phys. Lett. 134, 536 (1987).

Komorowski (1987b) : Komorowski L. ; Chem. Phys. 114, 55 (1987).

Komorowski (1993) : Komorowski L. ; In *Chemical Hardness* (Structure and Bonding, vol. 80, Sen K. D., ed.). Heidelberg : Springer-Verlag, pp. 60 (1993).

Kutzelnigg (1984) : Kutzelnigg W. ; Angew. Chem. Int. Ed. 23, 272 (1984).

Langenaeker et al (1994) : Langenaeker W., Coussement N., De Proft F. and Geerlings P. ; J. Phys. Chem. 98, 3010 (1994).

Langenaeker et al (1995) : Langenaeker W., De Proft F. and Geerlings P. ; J. Phys. Chem. 99, 6424 (1995).

Lindgren (1978) : Lindgren I. ; Int. J. Quantum Chem. Symp. 12, 33 (1978).

Makov (1995) : Makov G. ; J. Phys. Chem. 99, 9337 (1995).

March (1981) : March N. H.; Phys. Lett. A 82, 73 (1981).

March (1993) : March N. H. ; In *Chemical Hardness* (Structure and Bonding, vol. 80, Sen K. D., ed.). Heidelberg : Springer-Verlag, pp. 70 (1993).

March and Parr (1980) : March N. H. and Parr R. G.; Proc. Natl. Acad. Sci. USA 77, 6285 (1980).

Miller and Parker (1961) : Miller J. and Parker A. J. ; J. Am. Chem. Soc. 83, 117 (1961).

Mukherjee (1986) : Mukherjee D. ; Int. J. Quantum Chem. Symp. 20, 409 (1986).

Mukherjee and Pal (1989) : Mukherjee D. and Pal S. ; Adv. Quantum Chem. 20, 291 (1989).

Mulliken (1934) : Mulliken R. S. ; J. Chem. Phys. 2, 782 (1934).

Mulliken (1952a) : Mulliken R. S. ; J. Am. Chem. Soc. 74, 811 (1952).

Mulliken (1952b) : Mulliken R. S. ; J. Phys. Chem. 56, 801 (1952).

Mulliken (1955) : Mulliken R. S. ; J. Am. Chem. Soc. 77, 884 (1955).

Nagle (1990) : Nagle J. K. ; J. Am. Chem. Soc. 112, 4741 (1990).

Nalewajski and Capitani (1982) : Nalewajski R. F. and Capitani J. F. ; J. Chem. Phys. 77, 2514 (1982).

Nalewajski (1993) : Nalewajski R. F.; In *Chemical Hardness* (Structure and Bonding, vol. 80, Sen K. D., ed.). Heidelberg : Springer-verlag, pp. 115 (1993) and the references therein.

Pal et al (1995) : Pal S., Chandra A. K. and Roy R. K. ; Accepted for publication in THEOCHEM special issue.

Pal et al (1987) : Pal S., Rittby M., Bartlett R. J., Sinha D. and Mukherjee D. ; Chem. Phys. Lett. 137, 273 (1987).

Pal et al (1988) : Pal S., Rittby M., Bartlett R. J., Sinha D. and Mukherjee D. ; J. Chem. Phys. 90, 3214 (1988).

Pal et al (1994) : Pal S., Roy R. K. and Chandra A. K. ; J. Phys. Chem. 98, 2314 (1994).

Pal et al (1993) : Pal S., Vaval N. and Roy R. K. ; J. Phys. Chem. 97, 4404 (1993).

Paldus and Cizek (1973) : Paldus J. and Cizek J. ; In *Energy, Structure and Reactivity*, Smith D. W. and Mc Rae W. B., ed. New York : Wiley, pp. 389 (1973).

Parker (1961) : Parker A. J. ; J. Chem. Soc. 1328 (1961).

Parker (1962) : Parker A. J. ; Quart. Rev. (London, 14, 163 (1962).

Parr and Chattaraj (1991) : Parr R. G. and Chattaraj P. K. ; J. Am. Chem. Soc. 113, 1854 (1991).

Parr et al (1978) : Parr R. G., Donnelly R. A., Levy M. and Palke W. E. ; J. Chem. Phys. 68, 3801 (1978).

Parr and Gázquez (1993) : Parr R. G. and Gázquez J. L. ; J. Phys. Chem. 97, 3939 (1993).

Parr and Pearson (1983) : Parr R. G. and Pearson R. G. ; J. Am. Chem. Soc. 105, 7512 (1983).

Parr and Yang (1984) : Parr R. G. and Yang W. ; J. Am. Chem. Soc. 106, 4049 (1984).

Parr and Yang (1989) : Parr R. G. and Yang W. ; *Density Functional*

Theory of Atoms and Molecules. New York : Oxford University Press (1989).

Parr and Zhou (1993) : Parr R. G. and Zhou Z. ; Acc. Chem. Res. 26, 256 (1993).

Pearson (1963) : Pearson R. G. ; J. Am. Chem. Soc. 84, 16 (1963).

Pearson (1985) : Pearson R. G. ; J. Am. Chem. Soc. 107, 6801 (1985).

Pearson (1986) : Pearson R. G. ; Proc. Natl. Acad. Sci. USA 83, 8440 (1986).

Pearson (1987) : Pearson R. G. ; J. Chem. Edu. 64, 561 (1987).

Pearson (1988a) : Pearson R. G. ; Inorg. Chem. 27, 734 (1988).

Pearson (1988b) : Pearson R. G. ; J. Am. Chem. Soc. 110, 7684 (1988).

Pearson (1992) : Pearson R. G. ; Inorg. Chim. Acta. 198-200, 781 (1992).

Pearson (1993) : Pearson R. G. ; Acc. Chem. Res. 26, 250 (1993).

Pearson and Palke (1992) : Pearson R. G. and Palke W. ; J. Phys. Chem. 96, 3283 (1992).

Perdew et al (1982) : Perdew J. P., Parr R. G., Levy M. and Balduz J. L. ; Phys. Rev. Lett. 49, 1691 (1982).

Pitzer (1955) : Pitzer K. S. ; J. Chem. Phys. 23, 1735 (1955).

Pitzer and Catalano (1956) : Pitzer K. S. and Catalano E. ; J. Am. Chem. Soc. 78, 4844 (1956).

Plindov and Pogrebnya (1982) : Plindov G. I. and Pogrebnya S. K. ; Phys. Lett. A91, 219 (1982).

Politzer (1987) : Politzer P. ; J. Chem. Phys. 86, 1072 (1987).

Proft et al (1994) : De Proft F., Choho K., Amira S. and

Geerlings P. ; J. Phys. Chem. 98, 5227 (1994).

Proft et al (1993) : De Proft F., Langenaeker W., Geerlings P. ; J. Phys. Chem. 97, 1826 (1993).

Ray and Rastogi (1993) : Ray N. K., and Rastogi R. C. ; Indian J. Chem. Sect.A, 32A , 927 (1993).

Rittby et al (1989) : Rittby M., Pal S. and Bartlett R. J. ; J. Chem. Phys. 90, 3214 (1989).

Robles and Bartolotti (1984) : Robles J. and Bartolotti L. J. ; J. Am. Chem. Soc. 106, 3723 (1984).

Roy et al (1994) : Roy R. K., Chandra A. K. and Pal S.; J. Phys. Chem. 98, 10447 (1994).

Roy et al (1995) : Roy R. K., Chandra A. K. and Pal S. ; THEOCHEM 331, 261 (1995).

Roy and Pal (1995) : Roy R. K. and Pal S. ; Communicated for publication.

Schwarzenbach (1954) : Schwarzenbach G.; Experentia Suppl.5 , 163 (1954).

Sebastian (1994) : Sebastian K. L. ; Chem. Phys. Lett. 231, 40 (1994).

Sen (1991) : Sen K. D. ; Chem. Phys. Lett. 184, 318 (1991).

Sen (1993) : Sen K. D. ; In *Chemical Hardness* (Structure and Bonding, vol. 80, Sen K. D., ed.). Heidelberg Springer-Verlag, pp. 87 (1993).

Sen et al (1987) : Sen K. D., Böhm M. C. and Schmidt P. C. ; In *Electronegativity* (Structure and Bonding, Vol. 66 , Sen K. D. and Jorgensen C. K., ed.). Heidelberg : Springer-verlag, pp. 99 (1987).

Sen et al (1989) : Sen K. D., Seminario J. M. and Politzer P. ; Phys. Rev. A 40, 2260 (1989).

Sen and Vinayagam (1988) : Sen K. D. and Vinayagam S. C. ; Chem. Phys. Lett. 144, 178 (1988).

Shankar and Parr (1985) : Shankar S. and Parr R. G. ; Proc. Natl. Acad. Sci. USA 82 , 264 (1985).

Sinha et al (1986) : Sinha D., Mukhopadhyay S. K., Prasad M. D. and Mukherjee D. ; Chem. Phys. Lett. 125, 213 (1986).

Slater (1972) : Slater J. C. ; Adv. Quantum Chem. 6, 1 (1972).

Slater (1974) : Slater J. C. ; *The self-consistent-theory for molecules and solids.* New York : McGraw-Hill (1974).

Slater and Kirkwood (1931) : Slater J. C. and Kirkwood J. G. ; Phys. Rev. 37, 682 (1931).

Streitwieser (1961) : Streitwieser A. Jr. ; *Molecular Orbital Theory For Organic Chemists.* New York : Wiley, pp. 326 (1961).

Vela and Gázquez (1990) : Vela A. and Gázquez R. ; J. Am. Chem. Soc. 112, 1490 (1990).

Weiss (1942) : Weiss J. ; J. Chem. Soc. 245 (1942).

Wheland (1942) : Wheland G. W. ; J. Am. Chem. Soc. 64, 900 (1942).

Woodward and Hoffmann (1989) : Woodward R. B. and Hoffmann R. ; *The Conservation of Orbital Symmetry.* New York : Academic Press (1989).

Yang and Parr (1985) : Yang W. and Parr R. G. ; Proc. Natl. Acad. Sci. USA 82, 6723 (1985).

Zhou (1992) : Zhou Z. ; Int. Rev. Phys. Chem. 11, 243 (1992).

Zhou and Navangul (1990) : Zhou Z. and Navangul H. V. ; J. Phys. Org. Chem. 3, 784 (1990).

Zhou and Parr (1989) : Zhou Z. and Parr R. G. ; J. Am. Chem. Soc. 111, 7371 (1989).

Zhou and Parr (1990) : Zhou Z. and Parr R. G.; J. Am. Chem. Soc. ; 112, 5720 (1990).

Zhou et al (1988) : Zhou Z., Parr R. G. and Garst J. F. ; Tetrahedron Lett. 29, 4843 (1988).