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A Systematic Study on the Reactivity of Lewis Acid−Base Complexes through the Local Hard−Soft Acid−Base Principle

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The present paper addresses the stability of Lewis acid−base complexes using the recently developed local hard−soft acid−base (HSAB) principle. The principal role of electronegativity equalization and the charge redistribution process in stabilizing the complexes is demonstrated. The soft−soft and hard−hard types of interactions are well distinguished by the electron transfer parameter. The effect of correlation on the reactivity descriptors and subsequently on the soft−soft as well as hard−hard interactions has been studied. The validity of the present model in calculating the interaction energy of these complexes with varying degrees of strength is demonstrated.

I. Introduction

The rationalization and understanding of the relationship between the molecular structure and reactivity have been considered as among the most important subjects in the area of theoretical chemistry.[1,2] Many of the important chemical concepts and mechanisms have been derived and several descriptors, such as chemical potential and hardness, called global reactivity descriptors (GRD) within the framework of density functional theory (DFT),[3,4] are proposed. These descriptors have a potential role in relating the charge transfer and the stability of the systems. Later, Parr and co-workers have proposed the well-known local reactivity descriptors (LRD), such as Fukui function and local softness and these relate the changes in electron density to the number of electrons and the chemical potential, respectively.[3,5] LRD have direct relation with the Fukui's frontier molecular orbital and the success of the descriptors has been verified in identifying the electrophilic and nucleophilic reactive centers in a molecule.[6−10] Later, using these descriptors, the Pearson's hard−soft acid−base (HSAB)[11] principle was theoretically validated and proved by many groups.[7,12−15] This principle explains qualitatively the reactivity of molecules in terms of the hardness and softness parameters. It says that there is an extra stabilization when the soft acid combines with soft base and hard acid combines with hard base and this has been verified in most of the chemical reactions. However, the quantification of this qualitative principle has been a theoretical challenge. This particular issue has been emphasized by many groups in the context of explaining the relative bond strengths of acid−base complexes.[16−18]

In recent years, DFT based reactivity descriptors have been extensively used in explaining the aromaticity,[19] the intra- and intermolecular reactivity,[20] regioselectivity,[21] electrophilicity, nucleophilicity of organic reactions,[22] and prediction of the reactive sites in various molecular systems.[8,9] It has also been possible to understand the behavior of different kinds of reactions using the principle of maximum hardness and minimum polarizability.[23,24] Chattaraj and co-workers have extended the applicability of these descriptors in analyzing the reactivity of the molecular excited states.[25] Using Sanderson's principle of electronegativity equalization, Toro-Labbè et al. have attempted to evaluate the bond energies of the hydrogen-bonded complexes.[26] In a recent study, Ponti has described the regioselectivity criteria for cycloaddition reactions where the pair of interacting atoms does not have matching softness.[21] The criteria are deduced from the atomic grand potential variation instead of the grand canonical potential and it is called as a separate minimization of the grand potential. In his study, it is assumed that the charge-transfer process is the more dominating term than the charge-reshuffling process. He has also shown that there are no unique criteria to set up the local version HSAB principle.

At the same time, Pal and co-workers have shown the failure of conventional electrophilic and nucleophilic Fukui function and local softness in predicting the intramolecular reactivity trends in several organic carbonyl compounds and subsequently proposed new relative reactivity descriptors to explain the reactivity trend.[10] Nguyen and co-workers also noticed the failure of Fukui function indices in rationalizing the regioselectivity of protonation in the fluoro- and chloro-substituted phenols.[27] More recently, Roy et al. have analyzed the difficulty of obtaining the rank ordering of reactivity in a molecule when the Fukui functions become negative and they have prescribed Hirshfeld population scheme to obtain the non-negative Fukui functions.[28] Fuentealba et al. have also discussed the possible existence of negative values of the Fukui functions by computing the Kohn−Sham frontier orbital density.[29] In a recent study, we have also made a critical analysis on these local reactivity descriptors in predicting the site reactivity order in the various molecular systems.[30,31]

The use of these descriptors for chemical binding, especially to evaluate the stability of the molecular complexes, is an important issue. There have been very few attempts in the literature and the developed methods involve many empirical parameters.[30−36] The method formulated by Ghanty and Ghosh is based on Pauling's electronegativity model and it involves covalent radii and other empirical parameters that can be related to electron density.[33] In another method, they obtained the interaction energy expression through the concept of generalized electronegativity equalization procedure.[33] The calculated bond

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energies for simple heteronuclear diatomic molecules are in agreement with the experimental results. Pal et al. have discussed the energetics of the systems with the changes in the hardness and chemical potential parameters.[34] Gazquez has calculated bond energies for several diatomic molecular systems using GRD.[35a] He has also shown that activation energy of a chemical reaction depends mainly on the difference between the hardness of the initial state of a reaction and hardness of the transition state.[35b] All these models have been formulated to calculate the bond energy only for some simple diatomic molecules in terms of the chemical potential and hardness parameters. For the complex polyatomic molecular systems, the models are not directly applicable and it requires many parameters which are empirical in nature.

In a recent study, we have also made an attempt to calculate the intermolecular interaction energies for weakly interacting complexes.[30−32] The method is basically derived from the local HSAB principle developed by Gazquez and Mendez.[14] This is based on second-order density perturbation theory and the chemical bonding is viewed as resulting from the charge transfer (chemical potential equalization) and the reorganization or redistribution of electron density in the presence of various atomic nuclei in the molecules.[14,30] The model involves a parameter λ,[30] related the ratio of softness of the complex and the sum of the softnesses of the reacting systems. Without taking recourse to the calculation of the complex, several ad hoc definitions have been proposed by different groups depending on the systems.[30,35,36] However, we have defined this parameter as charge-transfer term and the same expression is used irrespective of the molecular systems.[30−32] The model merits detailed discussion and analysis. The applicability of this model has been shown in our earlier study on the interaction of various small molecules (N_2, CO_2, and CO) at the different cationic sites (Li, Na, and K) of zeolite systems.[30] The obtained interaction energy was in agreement with the experimental results. Recently, this model has also been used to study the reactivity of several cationic sites in dioctahedral clays by Chatterjee and co-workers with some degree of success.[9e] The systems studied are only weakly interacting systems and mostly, they are restricted to ionic electrostatic interactions. The local HSAB principle describes the soft−soft interactions (frontier molecular orbital controlled reactions) better than the hard−hard interactions (charge controlled interactions). To establish and validate the present semiquantitative approach for the purpose of studying chemical binding in a broad way, a detailed study of interactions, including the hard−hard ones, is in order. The objective of the present paper is to undertake such a study. Specifically, we would like to address the following issues: (i) the validity of the present model in calculating the interaction energy of the molecular complexes with varying degrees of strength, especially, weak-to-moderate type of interactions; (ii) the effect of electron correlation on GRD and LRD and subsequently on the interaction energy calculations and on the parameter λ; (iii) how important are chemical potential equalization process and maximum hardness principle during the molecular interactions; (iv) what parameters act as driving forces for the interaction between them so as to have a maximum stabilization.

We hope that study of such a nature will help us explain how these individual molecular descriptors determine or distinguish the nature of various types of interactions that are normally observed in the formation of complexes. To solve the above issues, we have considered the typical Lewis acid−base complexes (LABC) of BH_3−NH_3 and its flouro and methyl derivatives. Different kinds of acid−base complexes have been synthesized and used as reagents and as catalysts to accelerate organic, organometallic, and biochemical reactions.[37] These types of complexes are ideally suited for the present study and these complexes are well studied in the literature by experimental and by theoretical methods.[37−40] Moreover, the softness/hardness (S/η) values of these complexes can easily be tuned by substituting a group of atoms or by single atom in acids and bases. LABC comprises molecules that can be formed by electrostatic, covalent, or van der Waals interactions and hence the present study will encompass bond strength from weak-to-medium nature. We will confirm our results with the well-documented experimental and theoretical studies.

The paper is organized as follows: In section II, we give a brief theoretical background of the reactivity descriptors and the quantitative model. In Section III, the methodology and computational details are given. In section IV, we present the results of our study and discuss the implications as well as limitations of the results.

II. Theoretical Background

II.1 Global Quantities. In DFT, the ground-state energy of an atom or a molecule in terms of its electron density $\rho(r)$ is written as [3,41]

$$E[\rho] = F[\rho] + \int dr\, v(r)\rho(r) \tag{1}$$

where $v(r)$ is the external potential that includes the nuclear potential also, and $F[\rho]$ is the universal Hohenberg−Kohn functional composed of the electronic kinetic energy and the electron−electron repulsion energy. The first and second partial derivatives of $E[\rho]$ with respect to the number of electron N under the constant external potential $v(r)$ are defined as the chemical potential μ and the global hardness η of the system, respectively.[3]

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

$$\eta = \left(\frac{\partial^2 E}{\partial N^2}\right)_{v(r)} \tag{3}$$

The inverse of the hardness is expressed as

$$S = 1/2\eta \tag{4}$$

The global descriptor of hardness has been an indicator of overall stability of the system. It has been customary to use a finite difference approximation for μ and η. Using the energies of N, $(N + 1)$, and $(N - 1)$ electron systems, we get the operational definition of μ and η as[3]

$$\mu \approx -(IP + EA)/2 \tag{5}$$

$$\eta \approx (IP - EA)/2 \tag{6}$$

where IP and EA are the first vertical ionization energy and electron affinity of the chemical species, respectively.

II.2 Local Quantities. The site-selectivity of a chemical system cannot, however, be studied using the global descriptors of reactivity. For this, appropriate local descriptors need to be defined. An appropriate definition of local softness $s(r)$ is given by[5]

$$s(r) = \left(\frac{\partial \rho(r)}{\partial \mu}\right)_{v(r)} \tag{7}$$

such that

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

Combining eq 7 and the definition of global softness, we can write

$$s(\mathrm{r}) = \left(\frac{\partial\rho(\mathrm{r})}{\partial N}\right)_{\upsilon(r)}\left(\frac{\partial N}{\partial\mu}\right)_{\upsilon(r)} = \left(\frac{\delta\mu}{\delta\upsilon(\mathrm{r})}\right)_{N} S \qquad (8)$$

$$= f(\mathrm{r})\, S \qquad (9)$$

where $f(\mathrm{r})$ is defined as the Fukui function,[5] and it describes the sensitivity of the chemical potential of a system to local external potentials. Using left and right derivatives with respect to the number of electrons, electrophilic and nucleophilic FF and local softness can be defined. To describe site selectivity or reactivity of an atom in a molecule, it is necessary to condense the values of $f(\mathrm{r})$ and $s(\mathrm{r})$ around each atomic site into a single value that characterizes the atom in a molecule. This can be achieved by electronic population analysis. Thus, for an atom k in a molecule, depending upon the type of electron transfer, we have three different types of condensed Fukui function of the atom k,[5,6]

$$f_{\mathrm{k}+} = [q_{\mathrm{k}}\,(N+1) - q_{\mathrm{k}}\,(N)] \text{ for nucleophilic attack} \qquad (10a)$$

$$f_{\mathrm{k}-} = [q_{\mathrm{k}}(N) - q_{\mathrm{k}}\,(N - 1)] \text{ for electrophilic attack} \qquad (10b)$$

$$f_{\mathrm{k}0} = [q_{\mathrm{k}}(N+1) - q_{\mathrm{k}}(N - 1)] \text{ for radical attack} \qquad (10c)$$

where q_{k} is the gross electronic population of atom k in the molecule. The corresponding condensed local softnesses $s_{\mathrm{k}+}$, $s_{\mathrm{k}-}$, and $s_{\mathrm{k}0}$ can be defined. Parr and Yang proposed that a larger value of Fukui function indicates more reactivity. Hence, the greater the value of the condensed Fukui indices, the more reactive is the particular atomic center in the molecule.[6] Subsequently, Mendez and Gazquez proposed a local version of HSAB principle, which generally states that the interaction between any two chemical species will occur through the centers with nearly equal condensed Fukui indices.[14,36] This can determine the behavior of different reactive sites with respect to the hard and soft reagents.

II.3 The Expression for the Interaction Energy. Using energy as a functional of number of electrons (N) and the external potential (υ), the interaction energy is defined as the difference between the two interacting model systems A and B, and it is given as[14,30,36]

$$\Delta E_{\mathrm{int}} = \Delta E_{\mathrm{v}} + \Delta E_{\mu} \qquad (11)$$

$$\Delta E_{\nu} \approx \frac{-1}{2}\left(\frac{(\mu_{\mathrm{A}} - \mu_{\mathrm{B}})^2}{(\eta_{\mathrm{A}} + \eta_{\mathrm{B}})}\right)_{\upsilon} \qquad (12)$$

$$\Delta E_{\mu} = -\frac{1}{2} N^2\,(\eta_{\mathrm{AB}} - \eta^*{}_{\mathrm{AB}})_{\mu} \qquad (13)$$

where η_{AB} and $\eta^*{}_{\mathrm{AB}}$ are the hardness of the complex at the equilibrium and at the noninteracting limit of AB, respectively. For the details of the mathematical part of derivation for eqs 11−13, one can refer to the work of Gazquez and Mendez[14,36] and by us.[30] Here, the interaction between system A and B is assumed to take place in two steps. In the first step, the interaction takes place at constant external potential through the equalization of chemical potential (ΔE_{v}). In the second step, A and B evolve toward the equilibrium state through changes in the electron density of the global system at constant chemical potential (ΔE_{μ}). The second step is actually a manifestation of principle of maximum hardness. One can relate the difference in the hardness terms present in the above eq 13 to the softness of system A and B with a proportionality constant (K). Thus, eq 13 can be now rewritten in terms of the softness of the systems A and B as

$$\Delta E_{\mu} = -\frac{1}{2} N_{\mathrm{AB}}{}^2 K\left(\frac{1}{(S_{\mathrm{A}} + S_{\mathrm{B}})}\right) = -\lambda\,[1/(\,S_{\mathrm{A}} + S_{\mathrm{B}}\,)]/4 \qquad (14)$$

Herein, we introduce an ad-hoc term λ as the product of $2N^2$ and the proportionality constant K. The term λ introduces in a way the change of total softness of AB, as the complex is formed. There is no way to obtain this term rigorously without the actual calculation of softness of AB vis-à-vis the ones of the interacting systems. In the literature, there are several different definitions of this ad-hoc parameter.[14,30,35] Geerlings and co-workers have used the value of λ as 0.5 and 1.0 for certain organic reactions.[35c,d] In our earlier study, we have defined the parameter λ as the changes in the electron densities of the systems before and after the interaction process that will give the effective number of valence electrons that has participated in the interaction process.[30,31] Thus, an expression for the term λ can be written as the difference of electron densities of the system A before and after the interaction

$$\lambda_{\mathrm{A}} = \sum_{i=1}^{M} \rho^{\mathrm{eq}}{}_{\mathrm{A}i} - \sum_{i=1}^{M} \rho^{0}{}_{\mathrm{A}i} \qquad (15)$$

Alternately, the term λ can be defined as the difference of electron densities for the system B

$$\lambda_{\mathrm{B}} = \sum_{j=1}^{N} \rho^{\mathrm{eq}}{}_{\mathrm{Bj}} - \sum_{j=1}^{N} \rho^{0}{}_{\mathrm{B}j} \qquad (16)$$

where the first terms in eq 15 and eq 16 refer to the sum of the electron densities of each atom in A and B in the molecule AB, respectively, and the second terms of these equations refer to electron densities of isolated systems A and B. For most practical cases, λ is almost the same as the difference of electron density on the reacting atom of A or B. The densities of each atom are obtained by population analysis and there are several choices in this. We have used in our earlier calculation as well as in the present work Mulliken population analysis. This model has also been recently used by Chatterjee and co-workers with some degree of success.[9e]

If the interaction between the systems occur through the kth atom of A with the lth atoms B, one can express the total IE from the local point of view as

$$\Delta E^{\mathrm{AB}}{}_{\mathrm{int}} = (\mu_{\mathrm{A}} - \mu_{\mathrm{B}})^2\left(\frac{s_{\mathrm{Ak}} s_{\mathrm{Bl}}}{s_{\mathrm{Ak}} + s_{\mathrm{Bl}}}\right)_{\upsilon} - \frac{\lambda}{4}\left(\frac{1}{s_{\mathrm{Ak}} + s_{\mathrm{Bl}}}\right)_{\mu} \qquad (17)$$

where μ_{A} and μ_{B} are the chemical potential of the A−B, respectively. The s_{Ak} and s_{Bl} refer to the condensed local softness of the atom k in the system A and l of the system B, respectively.

III. Methodology and Computational Details

Ab initio Hartree−Fock (HF) and Möeller−Plesset second-order (MP2) quantum chemical calculations have been used to evaluate the global and local reactivity descriptors. All the monomers and molecular complexes were optimized without

TABLE 1: The Chemical Potential (μ), Global (S), and Local Softness (s(r)) Values of the Acid and Bases[a]

system	μ		S		local softness	
	HF	MP2	HF	MP2	HF	MP2
BH_3	−0.198	−0.216	1.897	1.845	1.023	0.913
BH_2F	−0.180	−0.185	1.785	1.783	1.041	0.836
BHF_2	−0.190	−0.196	1.512	1.495	0.989	0.706
BF_3	−0.187	−0.215	1.327	1.245	0.957	0.592
BCl_3	−0.194	−0.201	2.165	1.837	0.569	0.232
NH_3	−0.063	−0.095	1.789	1.700	0.943	0.813
NH_2F	−0.089	−0.116	1.704	1.641	0.805	0.797
NHF_2	−0.115	−0.132	1.619	1.549	0.672	0.755
NF_3	−0.122	−0.162	1.423	1.459	0.518	0.716
$N(CH_3)_3$	−0.023	−0.061	2.067	1.886	0.700	0.414
CO	−0.174	−0.181	1.587	1.548	1.147	1.356

[a] Values are given in atomic units. For the acids, the reactive atom is boron (S_k^+) and for the bases, NH_3, and for CO is N and C (S_k^-), respectively. HF and MP2 refer to HF/631G(d,p)//HF/631G(d,p) and MP2/6-31G(d,p)//MP2/6-31G(d,p).

any symmetry constraints, using HF and MP2 level of the theory through the standard split valence basis set, 6-31G(d,p). The restricted HF method has been used for the energy calculations of neutral and for the corresponding anionic and cationic systems, the restricted open shell HF method has been performed. The condensed Fukui function and local softness for each reactive atom were calculated via eq 10 using Mulliken population analysis. The ab initio molecular orbital calculations were carried out using the GAMESS[42] system of programs on an IRIX-6.2 silicon graphics workstation. The parameter λ was calculated using eq 15 through the Mulliken population scheme.[43]

IV. Results and Discussions

The optimized geometry and the structural parameters of the LABC are compared with the reported literature values. In Table 1, the chemical potential and global and local softness values of acids and bases are given. It can be seen that there is a substantial decrease in the values of the global and local softness of acids and bases by the successive fluorine substitutions. The chemical potential of the Lewis acids is less than that of Lewis bases and it indicates that the electrons will flow from the bases to acids. The values obtained by HF and MP2 follow the same trend. However, the HF predicts the value of global and local softness values higher than MP2 and in chemical potential, MP2 value is greater than HF. From the value of the softness parameters, one can order the softness of the given Lewis acids and bases. Accordingly, with reference to BH_3, the soft acid will be BH_3 and the hard acid will be BF_3. Similarly, NH_3 will be the soft base and NF_3 will be the hard base, with reference to NH_3. CO can be considered as a harder base than NH_3. On the basis of these values, one can qualitatively predict the reactivity and stability of the Lewis acids and bases using the HSAB principle. We will now explain to what extent these global and local properties will determine or control the stabilization (or the interaction energy) of the complexes.

Table 2 presents the computed interaction energy of all possible combinations of Lewis acids and bases along with the available experimental and other theoretical interaction energy values. The agreement between the calculated energy using our model and the experimentally observed and theoretically calculated results (MP2 and HF) is quite satisfactory.[16,17,37−40] The interaction energy of the complexes computed through expression 17 by HF method is consistently improved by adding the correlation effects. In most of the complexes, the HF value is considerably less than the value obtained by MP2 method. For instance, the experimentally observed interaction energy for BH_3-NH_3 complex is −34.4 kcal/mol, and this value is more comparable to the value obtained by MP2 method (−31.82 kcal/mol) than that of HF method (−26.67 kcal/mol). Thus, it shows the effectiveness and validity of the usage of our model. The correlation effect is observed to be important in describing both the soft−soft and hard−hard interactions. In particular, for the most weakly interacting complexes (BH_2F-NF_3, BHF_2-NF_3, BF_3-NF_3, $CO-BF_3$, and $CO-BCl_3$), there is a strong correlation effect in predicting the stabilization order and the interaction energy. Although the lack of appropriate experimental interaction energy values of some complexes prevents the direct verification of our theoretical prediction, our results are in complete agreement with other available theoretical calculations. The interaction energy of BH_3-NH_3 (soft acid−soft base) is higher than other complexes and it changes from −31.8 to −17.5 kcal/mol, for BH_3 with NH_3 to NF_3. Similarly, the stability order for other sets of complexes, BH_2F, BHF_2, and BF_3 with NH_3 to

TABLE 2: The Calculated Interaction Energy (in kcal/mol) of the Complexes at the Level of HF and MP2[a]

acid−base complexes	λ		ΔE_v		$\Delta E\mu$		ΔE_{tot}		ΔE^{TE}
	HF	MP2	HF	MP2	HF	MP2	HF	MP2	
BH_3-NH_3	0.263	0.307	−5.67	−3.94	−20.99	−27.88	−26.67	−31.82	−34.4[b](23.4[c])
$-NH_2F$	0.237	0.273	−3.38	−2.63	−20.24	−25.03	−23.62	−27.66	−30.9[b]
$-NHF_2$	0.193	0.229	−1.78	−1.79	−17.84	−21.53	−19.62	−23.32	−23.9[b]
$-NF_3$	0.121	0.175	−1.26	−0.72	−12.29	−16.80	−13.55	−17.52	−13.3[b]
BH_2F-NH_3	0.239	0.280	−4.29	−2.10	−18.90	−26.66	−23.20	−28.76	−24.8[b]
$-NH_2F$	0.205	0.247	−2.37	−1.20	−17.46	−23.73	−19.83	−24.93	−18.6[b]
$-NHF_2$	0.142	0.201	−1.10	−0.68	−12.97	−19.81	−14.07	−20.49	
$-NF_3$	0.003	0.015	−0.74	−0.13	−0.29	−1.47	−1.03	−1.60	
BHF_2-NH_3	0.228	0.267	−4.91	−2.42	−18.49	−27.60	−23.40	−30.02	−21.5[b]
$-NH_2F$	0.180	0.227	−2.84	−1.48	−15.72	−23.69	−18.56	−25.17	
$-NHF_2$	0.008	0.158	−1.42	−0.92	−0.79	−16.93	−2.21	−17.85	
$-NF_3$	0.004	0.007	−0.99	−0.25	−0.39	−0.80	−1.38	−1.05	
BF_3-NH_3	0.228	0.264	−4.61	−3.11	−18.81	−29.49	−23.42	−32.61	−26.7[b] (20.8[c])
$-NH_2F$	0.178	0.218	−2.63	−2.08	−15.79	−24.59	−18.42	−26.67	
$-NHF_2$	0.005	0.143	−1.30	−1.42	−0.47	−16.64	−1.75	−18.06	
$-NF_3$	0.003	0.004	−0.89	−0.57	−0.25	−0.50	−1.17	−1.07	−3.6[b]
BH_3-TMA	0.257	0.307	−7.99	−4.24	−23.34	−36.31	−31.33	−40.54	−41.3[c] (25.5[c])
BF_3-TMA	0.199	0.226	−6.80	−3.60	−18.84	−35.28	−25.63	−38.88	−36.1[c] (25.0[c])
$CO-BH_3$	0.222	0.264	−0.20	−0.42	−16.04	−18.25	−16.24	−18.67	−25.6[c] (9.2[c])
$CO-BF_3$	0.018	0.033	−0.05	−0.31	−1.37	−2.62	−1.42	−2.93	−4.0[c] (2.5[c])
$CO-BCl_3$	0.006	0.014	−0.09	−0.05	−0.58	−1.36	−0.66	−1.41	−2.0[c] (0.7[c])

ΔE^{TE} is the available interaction energy of the complexes in the literature, obtained by MP2/6-31G(d,p) and the values written in the parentheses correspond to the HF/6-31G(d,p). The value of the parameter λ is given in atomic units. [b] Reference 17b. [c] Reference 17a.

NF_3, can also be found. The lowest interaction energy (less stable complexes) is observed for the case of maximum fluorine substitution. For instance, BF_3−NF_3 complex is less stabilized than BH_3−NF_3 complex by an amount of ~16 kcal/mol and BH_3−NH_3 is more stabilized than BH_3−NF_3 by 14 kcal/mol. In these series of complexes involving the interaction of BH_3 to BF_3 with NH_3 to NF_3 (decreasing order of softness and the parameter λ), one can see the direct influence of the S/η parameters on the interaction energy or the stability of the complexes.

It is also interesting to compare the stability of carbon monoxide (CO) with BH_3 and BF_3 with that of NH_3. Owing to the strong basic nature of NH_3, the Lewis acids BH_3 and BF_3 are more stabilized with NH_3 rather than with CO by an amount of 12 kcal/mol for BH_3 and the interaction energy for BF_3 with CO is significantly lower than that of NH_3. The calculated interaction energy of the CO−BX_3 (X = H, F, and Cl) shows that the substitution of H by F and Cl in the Lewis acids has a predominant effect on the determination of bond strength and it can even alter the nature of bonding. This result is consistent with the literature predictions. Although we have followed a different method to predict the interaction energy, it is gratifying to note that the essential complex bonding effects are still recaptured in our model without any loss of the general reactivity of the molecular systems. To illustrate the effect of methyl group substitution in the base, NH_3 and its binding ability with other Lewis acids (BH_3 and BF_3), we have considered TMA−BH_3 and TMA−BF_3 complexes, where TMA is tri-methylamine. The substitution of methyl group in NH_3 increases the softness of TMA and hence, it is expected that the stability should be greater than that of the unsubstituted NH_3. Evidently, one can see from Table 2 that the interaction energies for TMA−BH_3 and TMA−BF_3 complexes (−40.5 and −38.9 kcal/mol, respectively) are higher than that of any other complexes that has been studied in the present study. The difference between the interaction energy of NH_3 and TMA complexes with BH_3 and BF_3 is ~8.5 and 6.2 kcal/mol, respectively.

There has been a lot of interest in studying the puzzling features of the formation of these complexes and in particular, considerable efforts have been made to correlate the charge transfer and the stability of the complexes.[17,37−40,44,45] In a recent study, Schaefer et al.[38] have made a detailed study on these complexes and have shown that there is no correlation between the stability with the degree of charge transfer. They have also concluded that the electrostatic interaction plays a significant role in the formation of these LABC and this study is in agreement with the earlier work made by Reetz et al.[17a] The Morokuma analysis of the NH_3−BH_3 complex suggests that the stabilization is mainly due to the electrostatic interaction and for the CO−BH_3 is due to the significant nonelectrostatic forces.[44] On the other hand, Glendening and Streitwieser predicted that the main contribution of bonding of the above complexes is due to the charge-transfer interactions.[45] Using our model, we are in a position to provide some insights into the driving force for the formation of the complexes and the underlying factors that govern the strength of these complexes. A closer inspection of the contribution of the energy terms to the total interaction energy, tabulated in Table 2, reveals that for the soft−soft complexes, the most important component arises from the ΔE_μ term and another term, ΔE_v, contributes marginally to the total interaction energy. This trend remains the same at MP2 level, though the individual values are affected by correlation effects. The term ΔE_v signifies the chemical potential equalization principle, the process of flow of electrons from the Lewis base to acid at constant external potential and it will continue until the system attains an equilibrium state. The second term actually is related to the charge redistribution process within the complex at constant chemical potential. In view of this argument, we can arrive at a conclusion that these complexes are actually more stabilized by the charge redistribution process (maximum hardness) than the energy contribution due to the chemical potential equalization. The process of charge distribution among the atoms in the molecules at the equilibrium geometry actually increases the hardness of the complex and consequently, the molecules become more stable. For the weakly bound complexes, which are of hard−hard type, both the terms ΔE_v and ΔE_μ contribute significantly in the stability of the complexes. Here, one can observe that the trend of relative importance of these two terms is changed because of correlation effects. At the Hartree−Fock level, though the relative importance of ΔE_v is the same as in soft−soft interactions, the ΔE_μ term still contributes to a larger extent. On the other hand, at the MP2 level, this trend is not necessarily observed. ΔE_v term is relatively as important or even more important compared to ΔE_μ at this level for such complexes.

One common factor can be noticed in Table 2; the factor λ plays an important role in predicting the stability of the LABC. The contribution of the second term ΔE_v largely depends on the parameter λ and this term is actually related to the effective number of valence electrons (or frontier orbital electrons) that has been transferred from system A to B (see Section II.3). The value of λ for soft−soft interaction cases is significantly greater than that for hard−hard interaction cases. The quantification of the parameter λ in terms of the frontier orbitals and its relation with interaction energy confirms that the soft−soft interaction is controlled by the orbital electrons and this argument is exactly similar to Klopman's chemical reactivity theory.[2,46] Klopman has shown that the soft−soft interaction is highly dependent on the energy difference between the frontier orbitals of the interacting systems.[2] From the definition of λ, one can infer that the BH_3, NH_3, and the corresponding TMA complexes (soft−soft interaction) are more stabilized by the term λ. By substituting more fluorine atoms in the acids and bases, the hardness increases considerably and hence, the reactivity is directly affected by lowering the parameter λ. It can be considered as one of the reasons why the hard−hard interaction is weaker than the soft−soft interaction. In a similar way, one can also observe that there is a linear correlation between the factor λ and ΔE_μ term for the complexes of BH_3 to BF_3 with NH_3 to NF_3 and for the complexes CO with BX_3 (X = H, F, and Cl). It implies that the interaction energy of the complexes is varied in proportion with the degree of charge transfer. This linear correlation is valid only within a set of complexes. For a general case, there is no correlation between the value of λ with the interaction energy of the complexes, for instance, the value of λ is the same for BH_3−TMA and BH_3−NH_3, 0.307 in atomic unit, but the computed interaction energy through MP2 differs significantly by ~9 kcal/mol. The above conclusions drawn from our calculations are significantly consistent with the experimental and other theoretical results.

Before we conclude this section, we would like to also mention the limitations of our present approach. In particular, the effectiveness and accuracy of the present method lies on the computation of the local descriptors and these are highly dependent on the basis set and level of theory that is used in the calculation. However, these issues are quite common in any kind of model and the accuracy will ultimately depend on the price that we pay for the computation. Despite the arbitrary nature of the population analysis and the basis set that has been applied in the computation of each term present in our approach, we could still get the reliable values of λ (i.e., difference in electron densities) and subsequently, the interaction energy values that are in agreement with the experimental or available theoretical results. In certain cases, for example, BHF_2-NHF_2 and BF_3-NHF_2, the λ values differ considerably from HF to MP2 methods. In general, these values can be further improved by making judicious choice of basis set and population methods. We have also carried out a study of basis set effects on the global and local reactivity descriptors by introducing the polarization and diffusion functions. Subsequently, it has also been tested for the evaluation of interaction energy for all the complexes that we have considered in this present study. We have checked that the calculated interaction energy using the present model is consistent with the value of interaction energy calculated by the conventional quantum chemical methods in different basis sets. The details of this study can be referred elsewhere.[47] Recently, Roy et al. has shown that Hirshfeld population scheme would be a better choice for the computation of condensed Fukui function values, and this method seems to be less sensitive to the basis set.[28] The problem of defining the factor λ is still an issue. Further, we would like to also make a remark that emerges from our study on the applicability of the descriptors and the perturbation methods for the interaction study. The perturbation method (with truncated lower order perturbation series) can give the information about the behavior of the molecular interactions only at the initial stages and it is restricted to the weak interaction cases that occur at relatively large distances.[1,2,18] It becomes difficult to apply the perturbation method when the interaction is much influenced by the short range and other complex multiple type of interactions. In this present study, we have considered a wide variety of complexes ranging from the covalent, van der Waals, and other weak electrostatically held molecules and the interaction energy ranges from -40.5 to -1.5 kcal/mol. Although the energy expression is derived by second-order perturbation theory, we could demonstrate that it is even applicable for the more complex interaction cases, such as charge transfer or donor−acceptor complexes, having moderate-to-weak interaction cases. The present approach may be valid for the systems where the influence of each molecule on another system is relatively small.

Conclusion

In this paper, we have presented the effect of softness or hardness parameters on the chemical reactions. These factors can be considered as among the deterministic factors to control the strong or weak kind of interactions along with other factors μ and λ. The soft−soft and hard−hard types of interactions are related to the parameter λ or the participation of effective number of valence electrons during the interaction between the molecular systems. The role of the chemical potential equalization and the maximum hardness principle in the formation of acid−base complex is explained. It is also observed that there is a consistent improvement in the interaction energy values of the acid−base complexes by the inclusion of the correlation effects. These effects are observed to be important in describing the very weak interaction cases. A further study should be made in this direction to investigate more complex type of interactions by considering the higher order terms in the perturbation series.

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References and Notes

(1) (a) Fukui, K. Theory of orientation and stereo selection; Springer-Verlag: New York, 1975. (b) Fukui, K. *Acc. Chem. Res.* **1971**, *4*, 57. (c) Fukui, K. *Science*, **1982**, *218*, 747.

(2) Klopman, G. *J. Am. Chem. Soc.* **1968**, *90*, 223.

(3) Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules;* Oxford University Press: New York, 1989.

(4) (a) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533. (b) Parr, R. G.; Pearson, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 7512. (c) Parr, R. G.; Donnelly, R. A.; Levy, M.; Palke, W. E. *J. Chem. Phys.* **1978**, *68*, 3801. (d) Pearson, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 6801. (e) *Chemical Hardness Structure and Bonding*; Sen, K. D., Ed.; Springer-Verlag: Berlin, 1993; Vol. 80.

(5) (a) Parr, R. G.; Yang, W. *J. Am. Chem. Soc.* **1984**, *106*, 4049. (b) Yang, Y.; Parr, R. G. *Proc. Natl. Acad. Sci. U.S.A.* **1985**, *821*, 6723. (c) Berkowitz, M.; Ghosh, S. K.; Parr, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 6811. (d) Berkowitz, M.; Parr, R. G.; *J. Chem. Phys.* **1988**, *88*, 2554. (e) Ayers, P. W.; Levy, M. *Theor. Chem. Acc.* **2000**, *103*, 353. (f) Ayers, P. W.; Parr, R. G. *J. Am. Chem. Soc.,* **2000**, *122*, 2010.

(6) Yang, W.; Mortier, W. J. *J. Am. Chem. Soc.* **1986**, *108*, 5708.

(7) Li, Y.; Evans, J. N. S. *J. Am. Chem. Soc.* **1995**, *117*, 7756.

(8) Berkowitz, M. *J. Am. Chem. Soc.* **1987**, *109*, 4823.

(9) (a) De Proft, F.; Amira, S.; Choho, K.; Geerlings, P. *J. Phys. Chem.* **1994**, *98*, 5227. (b) Langenaeker, W.; De Decker, M.; Geerlings, P.; Raeymaekers, P. *J. Mol. Struct.* (THEOCHEM) **1994**, *207*, 115. (c) Langenaeker, W.; Coussement, N.; De Proft, F.; Geerlings, P. *J. Phys. Chem.* **1994**, *98*, 3010. (d) Damoun, S.; Van de Woude, Mendez, F.; Geerlings, P. *J. Phys. Chem. A* **1997**, *101*, 886. (e) Chatterjee, A.; Ebina, T.; Iwasaki, T. *J. Phys. Chem. A* **2001**, *105*, 10694. (f) Chatterjee, A.; Iwasaki, T. *J. Phys. Chem. A* **2001**, *105*, 6187. (g) Chatterjee, A.; Ebina, T.; Iwasaki, T. *J. Phys. Chem. A* **1999**, *103*, 2489.

(10) Roy, R. K.; Krishnamurthy, S.; Geerlings, P.; Pal, S. *J. Phys. Chem. A* **1998**, *102*, 3746.

(11) (a) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533. (b) Pearson, R. G. *J. Chem. Educ.* **1987**, *64*, 561. (c) Pearson, R. G. *Science* **1966**, *151*, 172 (d) Pearson, R. G. *Inorg. Chem. Acta* **1995**, *240*, 93.

(12) (a) Chattaraj, P. K.; Lee, H.; Parr, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 1855. (b) Chattaraj, P. K.; Schleyer, P. V. R. *J. Am. Chem. Soc.* **1994**, *116*, 1067. (c) Chattaraj, P. K.; Gomez, B.; Chamorro, E.; Santos, J.; Fuentealba, P. *J. Phys. Chem. A* **2001**, *105*, 8815.

(13) Nalewjski, R. F. *J. Am. Chem. Soc.* **1984**, *106*, 944.

(14) (a) Mendez, F.; Gazquez, J. L. *J. Am. Chem. Soc.* **1994**, *116*, 9298. (b) Gazquez, J. L.; Mendez, F. *J. Phys. Chem.* **1994**, *98*, 4591.

(15) Chattaraj, P. K. *J. Phys. Chem. A* **2001**, *105*, 8815.

(16) (a) Drago, R. S. *Struct. Bonding* **1973**, *15*, 73. (b) Drago, R. S.; Kabler, R. A. *Inorg. Chem.* **1972**, *11*, 3144. (c) Drago, R. S. *Inorg. Chem.* **1973**, *12*, 21. (d) Shoeib, T.; Gorelsky, S. I.; Lever, A. B. P.; Siu, K. W. M.; Hopkinson, A. C. *Inorg. Chim. Acta* **2001**, *315*, 236.

(17) (a) Jonas, V.; Frenking, G.; Reetz, M. T. *J. Am. Chem. Soc.* **1994**, *116*, 8741. (b) Skancke, A.; Skancke, P. N. *J. Phys. Chem.* **1996**, *100*, 15079. (c) Anane, H.; Boutalib, A.; Nebot-Gil I.; Tomas, F. *J. Phys. Chem. A* **1998**, *102*, 7070. (d) Anane, H.; Boutalib, A.; Nebot-Gil I.; Tomas, F. *Chem. Phys. Lett.,* **1998**, *287*, 575.

(18) (a) Cohen, M. H. Theory of Chemical Reactivity. *Topics in Current Chemistry;* Nalewajski, R. F., Ed.; Springer-Verlag: Berlin, 1996; Vol. 183, p 143. (b) Cohen, M. H.; Ganduglia-Pirovano, M. V.; Kudrnosky, J. *J. Chem. Phys.* **1995**, *103*, 3543. (c) Cohen, M. H.; Ganduglia-Pirovano, M. V.; Kudrnosky, J. *J. Chem. Phys.* **1994**, *101*, 8988.

(19) De Proft, F.; Geerlings, P. *Chem. Rev.*, **2001**, *101*, 1451.

(20) (a) Geerlings, P.; De Proft, F.; Langenaeker, W. *Adv. Quantum Chem.* **1999**, *33*, 303. (b) Chandra, A. K.; Nguyen, M. T. *J. Phys. Chem. A* **1998**, *102*, 6181. (c) Chandra, A. K.; Nguyen, M. T. *J. Chem. Soc., Perkin. Trans. 2* **1997**, 1415. (d) Chandra, A. K.; Geerlings, P.; Nguyen, M. T. *J. Org. Chem.* **1997**, *62*, 6417.

(21) (a) Herrera, R.; Nagarajan, A.; Morales, M. A.; Mendez, F.; Jimenez-Vazquez, H. A.; Zepeda, L. G.; Tamariz, J. *J. Org. Chem.* **2001**, *66*, 1252. (b) Ponti, A. *J. Phys. Chem. A* **2000**, *104*, 8843.

(22) Parr, R. G.; Szentpaly, L. V.; Liu, S. *J. Am. Chem. Soc.* **1999**, *121*, 1922.

(23) (a) Parr, R. G.; Chattaraj, P. K. *J. Am. Chem. Soc.* **1991**, *113*, 1854. (b) Pearson, R. G.; Palke, W. E. *J. Phys. Chem.* **1992**, *96*, 3283. (c) Datta, D. *J. Phys. Chem.* **1992**, 96, 2409. (d) Pal, S.; Vaval, N.; Roy, R. K. *J. Phys. Chem.* **1993**, *97*, 4404.

(24) (a) Chattaraj, P. K.; Sengupta, S. *J. Phys. Chem.* **1996**, *100*, 16126. (b) Ghanty, T. K.; Ghosh, S. K. *J. Phys. Chem.* **1993**, *97*, 4951 (c) Chattaraj, P. K.; Fuentealba, P. Gomez, B.; Contreras, R. *J. Am. Chem. Soc.* **2000**, *122*, 348.

(25) (a) Chattaraj, P. K.; Poddar, A. *J. Phys. Chem. A* **1999**, *103*, 1274. (b) Chattaraj, P. K.; Poddar, A. *J. Phys. Chem. A* **1998**, *102*, 9944. (c) Chattaraj, P. K.; Poddar, A. *J. Phys. Chem. A* **1999**, *103*, 8691.

(26) (a) Sanderson, R. T. *Science*, **1955**, *121*, 207. (b) Gutierrez-Oliva, S.; Jaque, P.; Toro-Labbe, A. *J. Phys. Chem. A* **2000**, *104*, 8955.

(27) Tishchenko, O.; Pham-Tran, N. N.; Kryachko, E. S.; Nguyen, M. T. *J. Phys. Chem. A* **2001**, *105*, 8709.

(28) Roy, R. K.; Hirao, K.; Pal. S. *J. Chem. Phys.* **1999**, *110*, 8236. (b) Roy, R. K.; Hirao, K.; Pal. S. *J. Chem. Phys.* **2000**, *113*, 1372. (c) Roy, R. K.; Pal. S.; Hirao, K. *J. Chem. Phys.* **2001**, *115*, 2901.

(29) Fuentealba, R.; Perez, P.; Contreras, R. *J. Chem. Phys.* **2000**, *113*, 2540.

(30) Pal, S.; Chandrakumar, K. R. S. *J. Am. Chem. Soc.* **2000**, *122*, 4145; Note that the factor λ was defined as the product of N^2 and the proportionality constant K in this paper.

(31) Chandrakumar, K. R. S.; Pal, S. *Colloids Surf., A* **2002**, *205*, 127. (b) Chandrakumar, K. R. S.; Pal, S. *Int. J. Mol. Sci.* **2002**, *3*, 324.

(32) Chandrakumar, K. R. S.; Pal, S. *J. Phys. Chem. B* **2001**, 105, 4541. (b) Chandrakumar, K. R. S.; Pal, S. *J. Phys. Chem. A* **2002**, *106*, 5737.

(33) (a) Ghanty, T. K.; Ghosh, S. K. *J. Phys. Chem.* **1994**, *98*, 1840. (b) Ghanty, T. K.; Ghosh, S. K. *J. Phys. Chem.* **1996**, *100*, 17429. (c) Ghanty, T. K.; Ghosh, S. K. *J. Inorg. Chem.* **1992**, *32*, 1951. (d) Ghanty, T. K.; Ghosh, S. K. *Chem. Commun.* **1992**, 1502.

(34) Roy, R. K.; Chandra, A. K.; Pal, S. *J. Phys. Chem.* **1994**, *98*, 2314.

(35) (a) Gazquez, J. L. *J. Phys. Chem. A* **1997**, *101*, 9464. (b) Gazquez, J. L. *J. Phys. Chem. A* **1997**, *101*, 8967. (c) Mendez, F.; Tamaiz, J.; Geerlings, P. *J. Phys. Chem. A* **1998**, *102*, 6292. (d) Damoun, S.; Van de Woulde, G.; Choho, K.; Geerlings, P. *J. Phys. Chem. A* **1999**, *103*, 7861. (e) Mendez, F.; Garcia-Garibay, M. A. *J. Org. Chem.* **1999**, *64*, 7061.

(36) Gazquez, J. L.; Martinez, A.; Mendez, F. *J. Phys. Chem.* **1993**, *97*, 4059.

(37) (a) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levine, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, (Suppl 1). (b) Haaland, A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 992. (c) Gal, J. G.; Maria, P. C. *Prog. Phys. Org. Chem.* **1990**, *17*, 159. (d) Ren, J.; Workman, D. B.; Squires, R. R. *J. Am. Chem. Soc.* **1998**, *120*, 10511.

(38) Timoshkin, A. Y.; Suvorov, A. V.; Bettinger, H. F.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1999**, *121*, 5687.

(39) Leopold, K. R.; Canagarathna, M.; Phillips, J. A. *Acc. Chem. Res.* **1997**, *30*, 57.

(40) Mo. Y.; Gao, J.; Peyerimhoff, S. D. *J. Chem. Phys.* **2000**, *112*, 5530.

(41) Hohenberg, P.; Kohn, W. *Phys. Rev. B* **1964**, *136*, 864.

(42) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunga, N.; Nguyen, K. A.; Su, S. J.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. (Department of Chemistry, North Dakota State University and Ames Laboratory, Iowa State University). GAMESS, General Atomic and Molecular Electronic Structure System. *J. Comput. Chem.* **1993**, *14*, 1347.

(43) Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1833.

(44) (a) Morokuma, K. *Acc. Chem. Res.* **1977**, *10*, 294. (b) Umeyama, H.; Morokuma, K. *J. Am. Chem. Soc.* **1976**, *98*, 7208.

(45) Glendening, E. D.; Streitwieser, A. *J. Chem. Phys.* **1994**, *100*, 2900.

(46) Chattaraj, P. K. *J. Phys. Chem. A* **2001**, *105*, 511.

(47) Chandrakumar, K. R. S. Theoretical studies on some aspects of the chemical reactivity using density based descriptors. Ph.D. Thesis, Poona University, 2002.