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Study of Local Hard−Soft Acid−Base Principle: Effects of Basis Set, Electron Correlation, and the Electron Partitioning Method

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In this paper we perform a critical study on the applicability and reliability of the semiquantitative model based on the local hard−soft acid−base (HSAB) principle in calculating the interaction energy for the intermolecular interactions. In particular, the effects of basis sets, electron correlation, and electron partitioning methods on the calculation of interaction energy using the descriptors will be studied. The cases that we have considered for the present study are the Lewis acid−base interactions, specifically, the interaction of acids BH_3 and BF_3 with bases NH_3 and CO. The interaction energy ranges from ca. −32 to −2 kcal/mol. Since these complexes are well studied by both experimental and other conventional theoretical methods, these serve as the benchmark systems for the study of the above-mentioned effects.

I. Introduction

In recent years there have been few attempts in developing theoretical formulations to establish a relation between the total energy changes with the changes in the chemical potential, hardness parameters, and their respective derivatives.[1−3] In particular, some of the recent studies have demonstrated the possibility of calculating the interaction energy (IE) between different molecular systems using density-based descriptors within the framework of DFT.[4−7] In connection to this problem, development of quantitative models and their applicability have been critically addressed with suitable examples in our earlier studies. In particular, these studies include the description of weak to moderate intermolecular types of interactions such as several hydrogen-bonded complexes, charge-transfer complexes, adsorption of small molecules into the zeolite nonframework cations, etc.[6,7] These studies have demonstrated the validity of these models in terms of quantitative aspects, and the estimated IEs are reasonably close to the experimental and other standard theoretical values. These studies can, in principle, provide information about the nature of the molecular systems in three ways: (i) identification and nature of the reactive centers (electrophilic or nucleophilic sites) by examining the values of the global and local reactivity descriptors, (ii) estimation of the IEs between the molecular systems through the density-based reactivity descriptors in a semiquantitative way, and (iii) the role played by the chemical potential equalization and charge-transfer processes.

Over the years, the potential applicability of these descriptors has been extensively studied in identifying the reactive centers of organic molecular systems and inorganic solid oxides, etc.[4−10] The global and local reactivity descriptors (GRD and LRD) are, however, sensitive to the level of theory and basis set employed in the calculations. In addition, LRD also depend on the type of electron partitioning scheme. The electron partitioning schemes are inherently arbitrary, and their reliability in defining the charge of an atom in a molecule is not guaranteed with respect to the use of a different basis set and the level of theory.[11−13] Despite all these drawbacks, it has generally been observed that there is not much change in the reactivity order or trend when different levels of theory and basis sets are used in the calculations.[4−10] Hence, these issues have not yet posed a real problem for qualitative studies. On the other hand, these issues can cause a serious problem in quantitative estimation of the IE of the molecular complexes using these descriptors because the errors introduced in the calculations can be of a different sign and their cancellation may lead to inconsistent results. Thus, it is extremely important to study the effect of all these factors in the calculation of these descriptors and the IEs using these descriptors. At the same time, it should be noted that these problems are common even in the case of the standard method for the calculation of IE. The method of selecting the correct basis set along with a good level of theory is still considered to be a matter of experience.[14−16] In addition, there are several methods which employ the atomic charge as a basic quantity. For instance, molecular dynamics, molecular mechanics, and Monte Carlo calculations rely on these atomic charges for the interpretation of the physical properties of the solids and liquids and for chemical binding problems. Despite the arbitrariness involved in all these calculations, these models have been found to be very useful for the qualitative and semiquantitative studies.

Accordingly, in this work some of the pertinent questions are addressed. This work aims toward a systematic description of the basis set effects, different electron partitioning schemes, and the effect of electron correlation contributions in the calculation of the IE for the complexes using the reactivity descriptors. Accordingly, to study the above factors and to clarify the issues as detailed above, we consider the Lewis acid−base interactions, viz., BH_3 and BF_3 with NH_3 and CO. In particular, we calculate the IE of the four Lewis acid−base complexes, BH_3-NH_3, BH_3-CO, BF_3-NH_3, and BF_3-CO using different split valence basis sets along with polarization and diffuse functions. These calculations are performed using

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different population methods, namely, Mulliken,[17] Lowdin,[18] and molecular electrostatic potential derived charges[19] (MPA, LPA, and MESP). There are many other electron partitioning schemes available in the literature apart from the above three methods, like Bader's atoms-in-molecule (AIM) method,[20] natural population analysis (NPA),[21] Hirshfeld population analysis (HPA),[22] etc. Among all these methods, MPA, LPA, and MESP methods are often employed in this area of research, and hence, we have used in this study only these three methods for the calculation of the LRD and the IE of the complexes. In addition, we also calculate IE of the complexes using different DFT functionals and MP2 method to explore the effects of the electron correlation. We discuss the importance of using a large basis set and electron correlation correction in evaluating the bond energies of the above complexes.

II. Theoretical Background: Local HSAB Principle for the Single Interacting Site

Using energy as a functional of the number of electrons (N) and the external potential (v), the interaction energy is defined as the difference between the two interacting model systems A and B and it is given as

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

where, η_{AB} and η_{AB}* are the hardness of the complex at the equilibrium and at the isolated state respectively, and μ_A and μ_B are the chemical potential of systems A and B. For details of the derivation for the eq 1, one can refer to the work by Gazquez and Mendez[23] and by us.[6,7] Here, the interaction between system A and B is assumed to take place in two steps, ΔE_v and ΔE_μ. In the first step, the interaction takes place at constant external potential through the equalization of chemical potential, which is referred as ΔE_v.[23] In the second step, A and B evolve toward the equilibrium state through changes in the electron density of the global system produced at constant chemical potential, which is referred ΔE_μ.[24] The second step is a manifestation of the principle of maximum hardness.[25] One can relate the difference in the hardness terms present in the second term of eq 1 to the softness of system A and B with a proportionality constant (K). Thus, the second term, ΔE_μ, of eq 1 can be now rewritten in terms of the softness (S) of systems A and B as

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

An ad-hoc term λ has been introduced as the product of $2N_{AB}{}^2$ and the proportionality constant K.[6] This parameter λ cannot be computed rigorously, only through the softness of the molecular complexes. On substituting eq 2 into eq 1 one can get the global model in terms of the softness parameter of systems A and B.

$$\Delta E_{\{\text{int}\}} \approx \frac{-(\mu_A - \mu_B)^2}{2}\left(\frac{S_A S_B}{S_A + S_B}\right)_v - \frac{1}{4}\left(\frac{\lambda}{S_A + S_B}\right)_\mu \quad (3)$$

If the interaction between the systems occurs through atom x of A with atom y of B, one can express the total interaction energy from the local point of view, as[23]

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

where S_A and S_B are the global softness of system A and B, respectively, and f_{Ax} and f_{By} are the condensed Fukui function of atom x in system A and atom y in system B, respectively. We have used the local softness and Fukui functions of isolated systems, and this approximation is justified for weak to moderately weak interactions.[6,7] The parameter λ has been related to the deviation of the total softness of interacting system AB from the sum of the softnesses of individual systems A and B. It has been defined somewhat arbitrarily in the literature.[26] We have related the parameter λ as the change in the electron population at the interacting site before and after the interaction process.[6] To compute the electron population at an atomic site, standard condensed electronic population methods have been used. Electronic population will give us the number of electrons present at each atom in the molecule. Thus, the change in electronic population at the reactive sites will reflect the change in electrons or electron transfer at the reactive sites during the interaction. In cases of weak interactions, where reaction occurs primarily between a specific atomic site of the two molecules, we observed that the change in electronic population occurs only on these two reactive atoms. This was the case in our earlier study[6] of gaseous molecular interaction on a zeolite surface. In such cases, the change of electrons in the reactive site of system A is roughly the negative of the change in reactive site of the system B. However, in cases of interactions of moderate strength, as in the present study, although there is a primary reactive atom, the change in electronic population, however small, takes place in all the atoms of the interacting molecules. Hence, we propose in this paper that we include total change in the condensed electron population of all atoms reflecting the effects of the atoms surrounding the primary reactive atom. As a result, the value of λ would be equal to the total change in electrons in system A, which is trivially equal to the negative of the total change in electrons in system B. Thus, the expression for the term λ has been given as the net difference of the sum of the condensed electron population of each atom present in the system A having p-number of atoms, before and after the interaction[6]

$$\lambda_A = \sum_{i=1}^{p} Q_{Ai}{}^{\text{eq}} - \sum_{i=1}^{p} Q_{Ai}{}^{0} \quad (5a)$$

This definition of λ_A is identical to λ_B, the negative of the difference of electron density of system B, with q-number of atoms, before and after the interaction

$$\lambda_B = \sum_{j=1}^{q} Q_{Bj}{}^{\text{eq}} - \sum_{j=1}^{q} Q_{Bj}{}^{0} \quad (5b)$$

where, Q^{eq} refers to the condensed electron population of the respective atoms in the equilibrium and Q^0 refers to the condensed electron population of the respective atoms of the isolated systems. Here, one can calculate the value λ from eq 5a or eq 5b. The computation and other details of the global and local reactivity descriptors can be found elsewhere.[6-9]

III. Methodology and Computational Details

Ab initio Hartree–Fock (HF) and density functional calculations were performed to study the effect of different basis sets

TABLE 1: Global Reactivity Descriptors, Chemical Potential, and Hardness Values of All Monomers Calculated at the HF Level[a]

basis set		BH_3		BF_3		NH_3		CO	
		μ	η	μ	η	μ	η	μ	η
3-21G	**1**	−0.207	0.262	−0.199	0.364	−0.025	0.290	−0.177	0.318
3-21G(d,p)	**2**	−0.204	0.262	−0.199	0.364	−0.026	0.296	−0.177	0.318
6-31G	**3**	−0.201	0.263	−0.222	0.354	−0.048	0.270	−0.190	0.306
6-31G(d,p)	**4**	−0.198	0.264	−0.187	0.377	−0.063	0.280	−0.174	0.315
6-31++G (d,p)	**5**	−0.216	0.246	−0.260	0.311	−0.150	0.193	−0.204	0.289
6-31++G (2d,2p)	**6**	−0.216	0.246	−0.259	0.310	−0.152	0.195	−0.204	0.287
DZV(d,p)	**7**	−0.210	0.252	−0.211	0.359	−0.063	0.280	−0.186	0.305

[a] Values in atomic units.

TABLE 2: Calculated Condensed Local Softness Values Using Different Population Schemes at the HF Level[a]

basis set	BH_3			BF_3			NH_3			CO		
	MPA	LPA	MESP	MPA	LPA	MESP	MPA	LPA	MESP	MPA	LPA	MESP
1	1.234	1.523	2.668	0.944	0.920	1.615	0.744	1.058	2.054	1.117	1.112	1.571
2	1.274	1.544	2.638	0.944	0.920	1.615	0.736	1.071	1.869	1.117	1.112	1.571
3	1.024	1.427	2.464	0.923	0.908	1.477	0.997	1.290	2.453	1.129	1.084	1.584
4	1.024	1.452	2.442	0.957	0.853	1.452	0.943	1.250	1.946	1.147	1.116	1.585
5	1.656	1.800	4.628	2.664	1.481	2.602	1.652	1.973	2.949	1.089	1.027	1.723
6	1.616	1.799	4.619	2.788	1.487	2.621	1.693	1.883	2.745	0.871	1.099	1.745
7	1.644	1.755	3.456	1.236	1.069	2.896	1.003	1.293	2.003	1.160	1.139	1.139

[a] The number in the basis set column tefers to the corresponding basis set given in Table 1. The bold atoms are the reactive atoms. (values in atomic units).

and population schemes on the reactivity descriptors and subsequently on the IE of the various complexes. We have employed split-valence and double-ζ valence basis sets in this study; in particular, 3-21G, 3-21G(d,p), 6-31G, 6-31G(d,p), 6-31++(d,p), 6-31++G(2d,2p), and DZV(d,p) have been employed. Second-order Möller−Plesset (MP2) and DFT methods using different functionals, namely, Slater-VWN,[27] PBE-LYP,[28] Becke-LYP,[29] B3-LYP,[30] and BHH-LYP,[31] are applied to include the effect of electron correlation using 6-31G-(d,p) and 6-31G++(2d,2p) basis sets. The Slater-VWN functional uses the Slater exchange and Vosko, Wilk, and Nusair correlation functional. In all four functionals, the correlation part is introduced through the Lee−Yang−Parr method. The abbreviations PBE and Becke refer the exchange effect is introduced by Perdew−Burke−Ernzerhof (PBE) and Becke exchange functionals, respectively. In the case of BHH-LYP, it uses the larger proportion of the exchange effects computed by HF and Becke methods. The restricted HF method has been used for the calculation of energy of the neutral systems, and for the corresponding anionic and cationic systems, the restricted open-shell HF method has been used. The ab initio and the DFT calculations have been performed using the PC−Linux version of the GAMESS system of programs.[32] We have used the grid-based DFT in GAMESS which employs a typical grid quadrature to compute the integrals. During the SCF procedure, the grid consists of 96 radial shells with 36 and 72 angular points. We have used Mulliken, Lowdin, and the molecular electrostatic potential derived charges (MPA, LPA, and MESP, respectively) for the calculation of LRD and the parameter λ. In the case of MESP, the Spackman algorithm[19b] is used to fit the atomic charges constrained to reproduce the total molecular charge along with other default options. In conventional methods, the IE will be evaluated from the difference between the energy of complex AB and the sum of the energy of the monomers A and B, $\Delta E_{\text{int}} = E_{\text{AB}} - (E_{\text{A}} + E_{\text{B}})$.

IV. Results and Discussions

IV.1. Effect of Basis Set and Electron Population Schemes. The first aspect of the present discussion is to investigate the effect of different basis sets in calculating the GRD and LRD and subsequently for the IE of acid−base complexes at the HF level. The geometry of monomers and the complex molecular systems are optimized at the respective basis sets. Table 1 presents the chemical potential and the hardness parameters for the monomers, BH_3, BF_3, NH_3, and CO. In general, it can be seen that the chemical potential of all monomers steadily increases with increasing the number of basis functions. However, this effect is marginal. In the case of the hardness parameter, the values are slightly reduced with the number of basis functions. The local softness values for the reactive atoms, evaluated using the different population methods MPA, LPA, and MESP, are presented in Table 2. MPA and LPA values for the condensed local softness are generally seen to be less systematic than the values calculated by MESP method. The inclusion of the polarization (d,p) functions in the standard 6-31G basis set affects the local softness values marginally. On the other hand, the value of local softness increases considerably with the addition of the diffuse functions along with the polarization functions (6-31G++(d,p)), except for the case of carbon in CO. In the case of CO, the effect of polarization functions is observed to be more than that of the diffuse functions. For all the molecular systems, the values of local softness predicted by MESP are significantly greater than that of other methods for all the basis sets. On replacing fluorine for hydrogen in BH_3, there is a significant change in the values of the chemical potential, hardness, and condensed local softness of the boron atom. The predicted values of local softness of boron in BH_3 and BF_3 observed by using all three population methods using different basis sets show that the reactivity of BH_3 is greater than that of BF_3, and this is in agreement with the expected reactivity trend. The trend obtained by MPA method differs when the polarization and diffuse functions are included in the 6-31G(d,p) basis set. In the case of NH_3 and CO, it is known that the reactivity of NH_3 is greater than that of CO. More interestingly, it can be seen that the predicted reactivity order for NH_3 and CO is strongly dependent on the types of basis set used in the calculations. MPA predicts the correct reactivity trend only at the level of higher basis sets,

TABLE 3: Value of λ Calculated through Different Electron Partitioning Methods and at the Different Basis Sets for the BH_3-NH_3, BH_3-CO, BF_3-NH_3, and BF_3-CO Complexes[a]

	BH_3-NH_3			BH_3-CO			BF_3-NH_3			BF_3-CO		
basis set	MPA	LPA	MESP	MPA	LPA	MESP	MPA	LPA	MESP	MPA	LPA	MESP
1	0.257	0.445	0.395	0.047	0.415	0.441	0.204	0.439	0.320	0.029	0.114	0.121
2	0.253	0.438	0.381	0.033	0.414	0.433	0.209	0.436	0.308	0.029	0.114	0.121
3	0.200	0.409	0.365	0.145	0.381	0.422	0.217	0.467	0.321	0.032	0.071	0.100
4	0.263	0.469	0.377	0.222	0.423	0.385	0.228	0.470	0.301	0.018	0.044	0.069
5	0.290	0.328	0.357	0.191	0.292	0.383	0.201	0.495	0.281	0.029	0.059	0.064
6	0.283	0.399	0.350	0.213	0.307	0.366	0.310	0.591	0.278	0.013	0.056	0.059
7	0.355	0.415	0.404	0.293	0.330	0.409	0.379	0.459	0.302	0.023	0.071	0.065

[a] The number in the basis set column refers to the corresponding basis set given in Table 1 (values in atomic units).

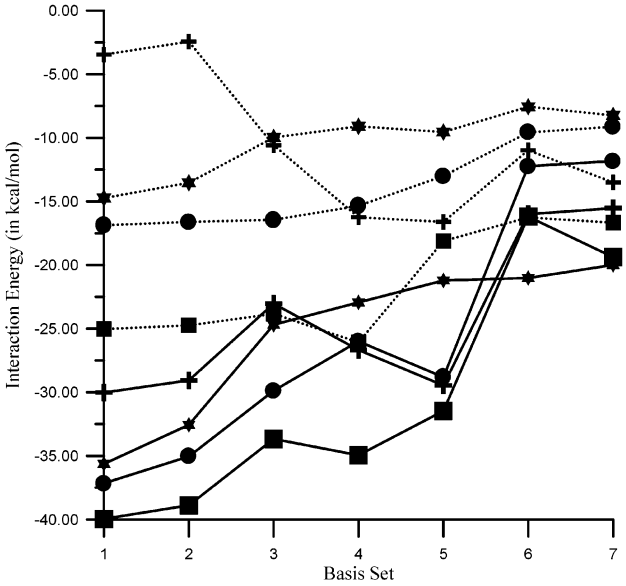


Figure 1. Interaction energy calculated by MPA (+), LPA (■), and MESP (●) using different basis sets at the HF level for the BH_3-NH_3 (—) and BH_3-CO (---) complexes. The numbers on the *x*-axis refer to the corresponding basis set given in Table 1. The symbol ★ refers to the actual interaction energy values (IE-QM).

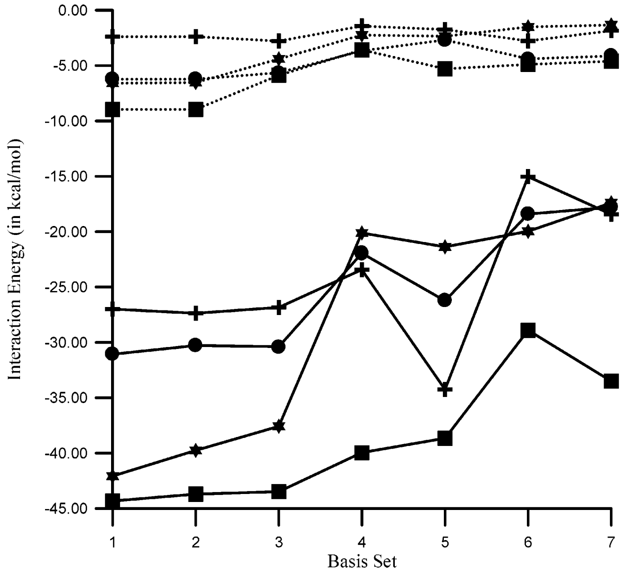


Figure 2. Interaction energy calculated by MPA (+), LPA (■), and MESP (●) using different basis sets at the HF level for the BF_3-NH_3 (—) and BF_3-CO (---) complexes. The numbers on the *x*-axis refer to the corresponding basis set given in Table 1. The symbol ★ refers to the actual interaction energy values (IE-QM).

6-31G++(d,p) and 6-31G(2d,2p), and LPA predicts the correct reactivity trend at the level of 6-31G level onward. However, reactivity order obtained by MESP does not change with the use of different basis sets.

Let us now discuss the effect of the basis sets and different population schemes on the calculation of IE of the different complexes using eq 4 at the HF level. The charge-transfer term λ calculated by MPA, LPA, and MESP methods is tabulated in Table 3. Although charges assigned in this fashion are inherently arbitrary, the approach remains useful for a comparison between similar complexes. It is, however, expected that the arbitrariness or errors introduced in the calculation of the charges through different partitioning methods may cancel each other when the difference between the absolute values of charges is considered. The calculated IEs are shown in Figures 1 and 2 in the case of BH_3-NH_3, BH_3-CO and BF_3-NH_3, BF_3-CO, respectively. Inspection of Figures 1 and 2 indicates that the trend in the calculated IEs is not too sensitive to basis sets. The IE values are more comparable to the values calculated by standard quantum chemical methods (hereafter refereed as IE-QM) at the higher level of basis sets than at the lower level. For all molecular complexes, LPA overestimates the IE more than the values calculated from MPA and MESP at the different level of basis sets. This could be due to the large value of the electron-transfer parameter, λ, calculated by LPA. In general, it is observed that the IE for most of the molecular complexes follows in increasing order of LPA > MPA > MESP. However, IE-QM values calculated at the same level of basis sets are lying between MPA and MESP, and in most of cases, it is comparable to the MPA values. However, in few cases the above order changes as LPA > MESP > MPA. For instance, the calculated IE at the 6-31G(d,p) basis set using MPA, LPA, and MESP for BH_3-NH_3 complex is −26.7, −35.0, and −26.0 kcal/mol, respectively. The calculated IE-QM at the same basis set is −22.93 kcal/mol.

In the case of BH_3-CO, the IE calculated by the 3-21G and 3-21G(d,p) basis set using MPA is also lower compared to IE-QM, and the difference is almost 10 kcal/mol. Adding more basis functions along with diffuse and polarization functions remarkably improves the IE value by more than 10 kcal/mol. An interesting feature of our results is that the discrepancies of results of different basis sets become reasonably narrow as one goes from 3-21G to 6-31++G(2d,2p). To investigate the role of polarization and diffuse functions on the IE values, we consider 6-31G, 6-31G(d,p), 6-31++G(d,p), and 6-31+G(2d,2p) basis sets using MPA, LPA, and MESP methods for the BH_3-NH_3 complex. The calculated IE values are listed according to the above basis set order: −23.0, −26.7, −16.0, −15.5 kcal/mol by MPA; −33.7, −35.0, −16.2, −19.4 kcal/mol by LPA; −29.0, −26.0, −12.2, −11.8 kcal/mol by MESP; −24.7, −22.9, −21.0, −20.0 kcal/mol by IE-QM. Comparison of the values calculated by the 6-31G and 6-31G(d,p) basis sets using MPA and LPA shows that the IE values increase by ~3 kcal/mol while MESP values show a decrease of ~3 kcal/mol. On the

TABLE 4: Global Reactivity Descriptors, Chemical Potential, and Hardness Values of All Monomers Calculated by Different DFT Functionals and MP2 Method at the 6-31G(d,p) Basis Set[a]

theoretical method		BH_3		BF_3		NH_3		CO	
		μ	η	μ	η	μ	η	μ	η
HF	1	−0.918(−0.216)	0.264(0.246)	−0.187(−0.259)	0.377(0.310)	−0.063(−0.152)	0.280(0.195)	−0.174(−0.204)	0.315(0.287)
MP2	2	−0.216(−0.237)	0.267(0.250)	−0.216(−0.290)	0.290(0.330)	−0.095(−0.182)	0.291(0.217)	−0.182(−0.216)	0.317(0.292)
SVWN	3	−0.220(−0.242)	0.251(0.232)	−0.171(−0.259)	0.355(0.284)	−0.118(−0.194)	0.284(0.217)	−0.200(−0.228)	0.314(0.292)
BLYP	4	−0.212(−0.235)	0.257(0.215)	−0.160(−0.236)	0.350(0.279)	−0.112(−0.186)	0.282(0.215)	0.193(−0.222)	0.313(0.291)
BHHLYP	5	−0.220(−0.238)	0.265(0.248)	−0.211(−0.279)	0.371(0.315)	−0.100(−0.179)	0.286(0.213)	−0.201(−0.226)	0.319(0.299)
B3LYP	6	−0.218(−0.239)	0.260(0.241)	0.194(−0.263)	0.348(0.295)	−0.109(−0.185)	0.284(0.215)	−0.199(−0.226)	0.316(0.295)
PBELYP	7	−0.212(−0.236)	0.257(0.235)	−0.160(−0.270)	0.349(0.295)	0.112(−0.188)	0.283(0.215)	−0.191(−0.223)	0.314(0.292)

[a] The values obtained by 6-31G++(2d,2p) basis set are given in parentheses (values in atomic units).

other hand, the addition of diffuse and polarization functions, i.e., use of (6-31++G(d,p) and 6-31++G(2d,2p)) basis, reduces the IE values considerably, and this trend is observed for all three population schemes. This is also in accordance with the IE-QM. The above arguments also are suitable for the other three complexes.

Considering the case of the BF_3−CO complex, the IE is ∼2−4 kcal/mol, which is considerably less than that of the other complexes (Figure 2). For weak interaction cases, in general, the use of an adequate basis set and the level of theory is the most important consideration in obtaining accurate IE values, and the basis sets usually required are much larger than those used for the strong interaction cases. The typical basis set often includes diffuse s, p, and d orbital functions in order to describe accurately the induced polarization of electrons in such weak interactions. Analysis of the results for the BF_3−CO complex, obtained by different basis sets, reveals that the effect of basis set is decreased and the predicted values are within the error limit of ∼1 kcal/mol. The IE values calculated by MPA using 3-21G, 6-31G, 6-31G(d,p), 6-31++G(d,p), and 6-31++G(2d,2p) basis sets are −2.38, −2.78, −1.42, −2.77, and −1.84 kcal/mol, respectively. It can also be observed that the IE values are less sensitive to the different electron partitioning methods than the use of different basis set (see Figure 2). Although LPA predicts high IE, the values are completely in agreement with the other scheme, MPA and MESP at the higher basis sets of calculations. It is gratifying to note that the present method could describe the weak interaction cases satisfactorily even at the HF level itself and the method is considerably less dependent on basis sets and population methods. Earlier studies based on the present methodology have also shown it to be successful for the case of weak interactions, for instance, interaction of small guest molecular interactions with the zeolite nonframework cations[6] and weak to strong hydrogen-bonding cases.[7c−d] The results are in remarkable agreement with the experimental and other theoretical results within the error limit of ∼1−2 kcal/mol.[7c,33]

The basic working equations are derived from the second-order perturbative methods. Hence, these models are more applicable to the weakly interacting complexes. For strong interaction cases, the influence of one molecule on the other system can be high, and in addition, other higher order perturbation terms can become more important.

IV.2. Effect of Electron Correlation. In this section we will study the effect of correlation using MP2 method and different exchange-correlation DFT functionals, namely, Slater-VWN, PBE-LYP, Becke-LYP, B3-LYP, and BHH-LYP. Further, the effect of different population schemes MPA, LPA, and MESP has also been studied at various theoretical levels. It is known that the order of electron correlation exhibited by the five DFT functionals follow as BHH-LYP > B3-LYP > Becke-LYP > PBE-LYP > Slater-VWN. The effect of correlation obtained by MP2 methodology is known to be better than B3-LYP and BHH-LYP. In most cases, it is observed that the HF method predicts more accurate results than the DFT Slater-VWN functional. The chemical potential and hardness values are presented in Table 4, and the local softness values are tabulated in Table 5. On comparing the values of chemical potential, the values obtained by MP2 and other DFT functionals are greater than that of HF method. Comparing the hardness values, one observes that MP2 predicts higher hardness values than the HF method and the HF values of hardness are greater than the values obtained from the DFT functionals. When one goes from Slater-VWN to BHH-LYP, the condensed local softness values of the reactive atom B in BH_3, BF_3 and the nitrogen atom in NH_3 cases decrease by small amounts. The values obtained by HF method are greater than MP2 and other DFT functionals. In the case of the carbon atom in CO, the MP2 values are slightly higher than that of HF. In most cases, MESP values are substantially more than that of MPA and LPA values. The inclusion of the polarization and diffusion functions in the standard 6-31G(d,p) basis set causes the value of condensed local softness to increase considerably, except for the case of carbon in CO.

The calculated IE values for the BH_3 and BF_3 complexes with NH_3 and CO are presented in Figures 3 and 4, respectively, using the 6-31G(d,p) and 6-31G++(2d,2p) basis sets. The λ values that are tabulated in Table 6 have been used to calculate the IE of all the systems. On analyzing Figures 3 and 4, there is a remarkable agreement between the values calculated by IE-QM and by our methodology using different DFT functionals. The changes in the IE values with respect to the different functionals are rather stable, and discrepancies are less than the effect exhibited by different basis sets. We will now discuss the effect of electron correlation on the calculation of IE using the 6-31G(d,p) basis set. The IE values for the BH_3−NH_3 complex calculated by the present methodology are −26.7 and −31.5 kcal/mol by HF and MP2 methods, respectively, and the experimental IE value is −31.1 kcal/mol. The DFT functionals predict the IE values using MPA as −30.2, −30.9, −29.6, −30.5, and −31.5 kcal/mol calculated through Slater-VWN, Becke-LYP, BHH-LYP, B3-LYP, and PBE-LYP, respectively. However, the IE calculated by LPA always overestimates in comparison with MPA and MESP values. It also indicates that the correlated level calculations are more reliable than the HF results for strong interaction cases such as BH_3−NH_3, BF_3−NH_3, and BH_3−CO. Although the HF-level calculation captures a large portion of the bonding energy of −26.7, −23.4, and −16.3 kcal/mol for BH_3−NH_3, BF_3−NH_3, and BH_3−CO, respectively, the electron correlation correction improves the calculated bonding energy to −30.5, −25.0, and −17.1 kcal/mol through the use of B3LYP DFT functional. In case of BH_3−NH_3, BF_3−NH_3, and BH_3−CO complexes, the interactions are a soft−soft type for which the standard ab initio calculations

TABLE 5: Calculated Condensed Local Softness Values Using Different DFT Functionals and MP2 Method for BH_3, BF_3, NH_3, and CO Molecules Using the 6-31G(d,p) Basis Set[a]

theor etical methods	BH_3			BF_3			NH_3			CO		
	MPA	LPA	MESP	MPA	LPA	MESP	MPA	LPA	MESP	MPA	LPA	MESP
HF	1.023(1.616)	1.452(1.799)	2.442(4.619)	0.957(2.788)	0.853(1.487)	1.452(2.621)	0.943(1.693)	1.250(1.883)	1.947(2.745)	1.147(0.871)	1.116(1.099)	1.585(1.745)
MP2	0.927(1.488)	1.401(1.753)	2.370(4.496)	0.610(2.129)	0.630(1.224)	1.122(2.505)	0.822(1.556)	1.172(1.721)	1.780(2.312)	0.900(1.095)	1.282(1.209)	1.717(1.569)
SVW N	1.289(1.434)	1.492(1.863)	2.433(4.262)	1.594(2.829)	1.021(1.525)	1.564(2.505)	0.858(1.478)	1.193(1.707)	1.769(2.312)	1.147(0.781)	1.087(1.040)	1.458(1.569)
BLYP	0.949(1.385)	1.458(1.838)	2.382(4.307)	1.577(2.921)	1.015(1.554)	1.513(2.80)	0.830(1.445)	1.180(1.713)	1.721(2.296)	1.129(0.794)	1.078(1.036)	1.441(1.549)
BHH LYP	0.987(1.442)	1.434(1.752)	2.397(4.167)	0.933(2.641)	0.838(1.413)	1.407(2.399)	0.885(1.512)	1.205(1.726)	1.835(2.441)	1.123(0.792)	1.084(1.036)	1.507(1.613)
B3LY P	0.969(1.414)	1.451(1.798)	2.388(4.145)	0.965(2.792)	0.870(1.492)	1.437(2.444)	0.856(1.473)	1.192(1.715)	1.775(2.370)	1.128(0.790)	1.081(1.020)	1.473(1.578)
PBEL YP	0.945(1.353)	0.945(1.843)	3.747(4.309)	1.574(2.714)	1.015(1.453)	1.515(2.260)	0.819(1.429)	1.174(1.716)	1.701(2.289)	1.128(0.780)	1.075(1.033)	1.434(1.543)

[a] The values obtained by 6-31G++(2d,2p) basis set are given in parentheses. The bold atoms are the reactive atoms (values in atomic units).

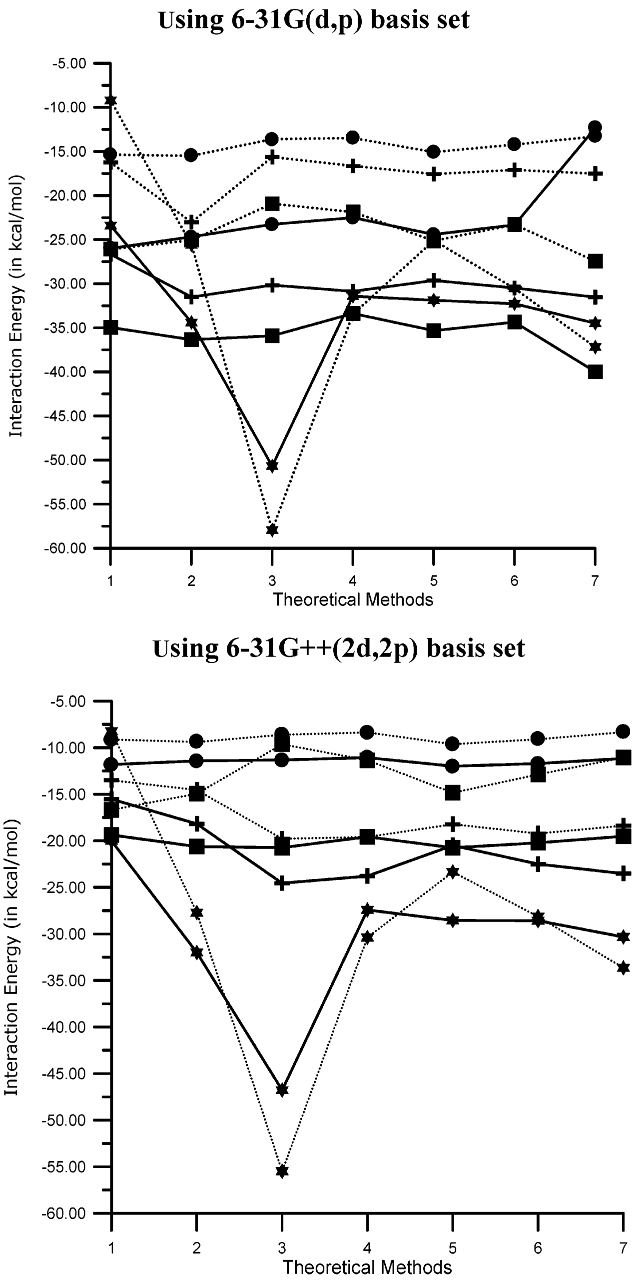
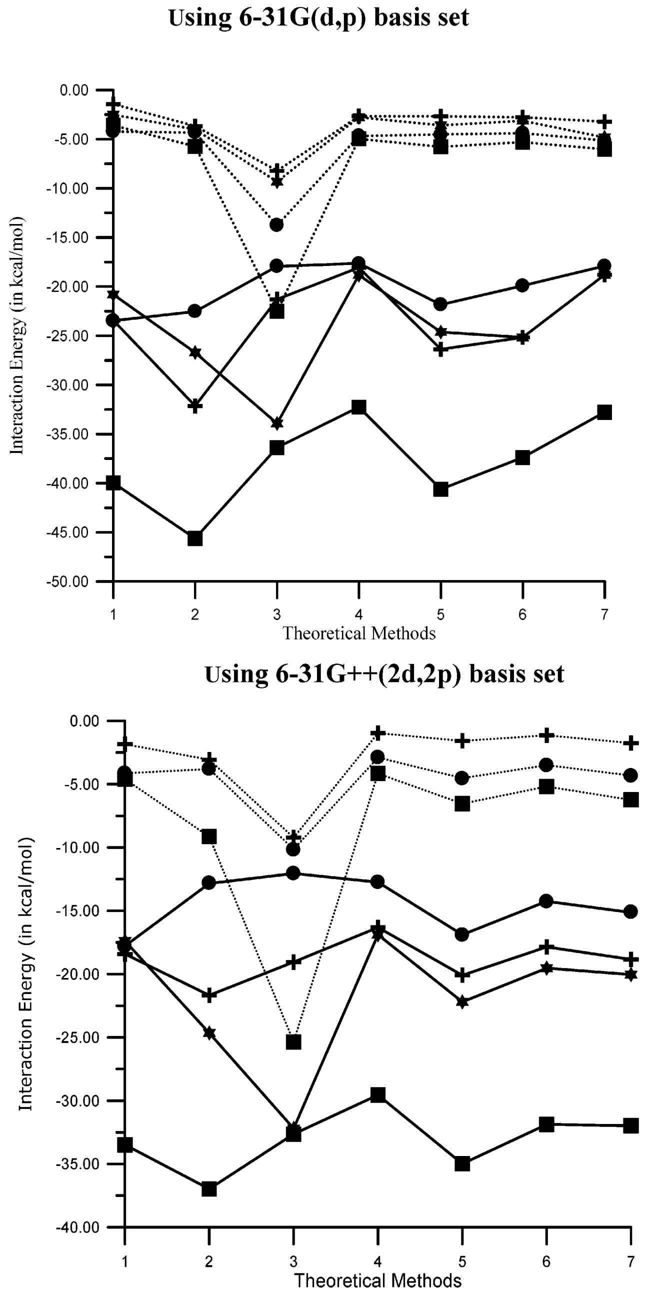


Figure 3. Interaction energy calculated by different DFT functionals and MP2 method using MPA (+), LPA (■), and MESP (●) population schemes using 6-31G(d,p) and 6-31G++(2d,2p) basis sets for the BH_3-NH_3 (—) and BH_3-CO (---) complexes. The numbers on the *x*-axis refer to the corresponding theoretical methods given in Table 4. The symbol ★ refers to the actual interaction energy values (IE-QM).

have also shown that the electron correlation corrections are essential in order to predict the correct interaction pattern.[7c,33] From Figures 3 and 4 it is imperative to note that the IE-QM calculated by Slater-VWN functional produces largely overestimated IE which are eventually corrected by other better DFT functionals. The inclusion of the HF exchange term (BHH-LYP and MP2) reduces the IE values dramatically, providing results in better agreement with the available theoretical data. The most noticeable change is produced for the case of a weak interaction (BF_3-CO system).

We also noticed that the effect of additional polarization and diffusion functions in the standard 6-31G(d,p) basis set on the calculation of IE for the above four complexes is significant, and the effect of correlation is also seen to be very substantial. For instance, the IE values for BH_3-NH_3 obtained by HF


Using 6-31G(d,p) basis set

Using 6-31G++(2d,2p) basis set

Figure 4. Interaction energy calculated by different DFT functionals and MP2 method using MPA (+), LPA (■), and MESP (●) population schemes using 6-31G(d,p) and 6-31G++(2d,2p) basis sets for the BF_3-NH_3 (—) and BF_3-CO (---) complexes. The numbers on the *x*-axis refer to the corresponding theoretical methods given in Table 4. The symbol ★ refers to the actual interaction energy values (IE-QM).

method using the 6-31G++(2d,2p) basis set and MPA method is −15.52kcal/mol, and the values obtained by MP2, SVWN, BLYP, BHHLYP, B3LYP, and PBELYP are −18.17, −24.55, −23.78, −20.49, −22.50, and −23.52 kcal/mol, respectively. In general, the same trend is observed for all three population schemes. The correlation contribution to the IE is seen to be larger in this basis set compared to the 6-31G(d,p) basis set. In section IV.1 we mentioned that the addition of diffuse and polarization functions in the standard split-valence basis set actually reduces the IE values considerably at the HF level. Similar effects are also observed even in the case of the electron-correlated level.

It was noted earlier that the reactivity order for BH_3 and BF_3 predicted by MPA, LPA, and MESP is $BH_3 > BF_3$. This order

TABLE 6: Value of λ Calculated by the Different DFT Functionals and MP2 Method Using Different Electron Population Methods for the BH_3–NH_3, BH_3–CO, BF_3-NH_3, and BF_3-CO Complexes[a]

theoretical	BH_3-NH_3				BH_3-CO			BF_3-NH_3			BF_3-CO	
methods	MPA	LPA	MESP	MPA	LPA	MESP	MPA	LPA	MESP	MPA	LPA	MESP
HF	0.263(0.283)	0.469(0.399)	0.377(0.350)	0.222(0. 213)	0.423(0.307)	0.386(0.366)	0.228(0.310)	0.470(0.591)	0.334(0.278)	0.018(0.013)	0.044(0.056)	0.080(0.059)
MP2	0.307(0.324)	0.500(0.420)	0.405(0.368)	0.264(0. 237)	0.420(0.278)	0.385(0.365)	0.264(0.353)	0.481(0.595)	0.301(0.296)	0.033(0.011)	0.066(0.109)	0.070(0.084)
SVWN	0.367(0.436)	0.054(0.443)	0.444(0.383)	0.240(0. 278)	0.341(0.178)	0.331(0.314)	0.318(0.452)	0.500(0.628)	0.351(0.298)	0.137(0.204)	0.300(0.409)	0.258(0.249)
BLYP	0.318(0.410)	0.492(0.413)	0.423(0.370)	0.218(0. 272)	0.351(0.206)	0.323(0.308)	0.265(0.386)	0.440(0.573)	0.339(0.296)	0.038(0.016)	0.062(0.064)	0.079(0.063)
BHHLYP	0.304(0.355)	0.495(0.418)	0.406(0.362)	0.235(0. 259)	0.402(0.2630)	0.369(0.350)	0.265(0.374)	0.480(0.604)	0.325(0.290)	0.035(0.011)	0.070(0.086),	0.083(0.073)
B3LYP	0.315(0.390)	0.496(0.417)	0.417(0.372)	0.227(0. 269)	0.374(0.230)	0.345(0.328)	0.268(0.385)	0.462(0.589)	0.333(0.296)	0.037(0.014)	0.066(0.075)	0.081(0.068)
PBELYP	0.324(0.399)	0.496(0.413)	0.427(0.376)	0.230(0. 249)	0.352(0.202)	0.324(0.308)	0.275(0.393)	0.446(0.579)	0.343(0.298)	0.048(0.021)	0.076(0.086)	0.088(0.074)

[a] The number in the basis set column refers to the corresponding DFT functionals given in Table 4 (values in atomic units).

is in agreement with the expected trend. Let us now compare the IE for complexes BH_3-NH_3 and BF_3-NH_3. MPA and MESP produce the correct IE order compared to the other theoretical results at all the correlated level calculations except that MPA deviates at the MP2 level. In the case of LPA, the predicted IEs are almost similar for both molecular complexes. However, at the HF level, most of the basis sets predicted that the IE for BF_3-NH_3 is greater than that of BH_3-NH_3. In the case of NH_3 and CO, the correct qualitative reactivity order is given only by the MESP method. MPA and LPA gave the correct reactivity order at the higher-level basis sets. If we compare the IEs of NH_3 and CO complexes with BH_3 and BF_3, it can be seen that the strength of $BH_{3-}NH_3$ and BF_3-NH_3 complexes is more than that of the BH_3-CO and BF_3-CO complexes. This trend does not change with the use of different basis sets, a different population scheme, and the different DFT functionals.

For the BF_3-CO complex, the agreement between the IE-QM and values obtained by the present methodology is better than the cases with stronger interactions (see Figure 4). It is also worth noting that IEs do not drastically change with the inclusion of electron correlation and with the addition of polarization and diffusion functions except in the case of the Slater-VWN functional, which is generally known to overestimate the IE for most of the complexes. This observation is also completely in agreement with our earlier claim, made in section IV.1, that the present methodology can give a more reliable description for the weak interaction cases than the stronger cases. Finally, we also point out that the problem of defining the factor λ is still an important issue.

V. Conclusions

A systematic description of the basis set effects, different population methods, and the effect of electron correlation on the calculation of IE of the complexes using global and local reactivity descriptors has been reported. The effect of electron correlation on the calculation of IE is observed to be more systematic and important than the effect of basis set. The discrepancy between the IE-QM and the IE calculated by the present methodology is found to be more in the case of the strong interaction than the weak interaction cases. Despite the arbitrariness involved in all electron partitioning schemes and the inclusion of the ad-hoc definition of the parameter λ in the present methodology, the IE calculated by this method is, in general, found to be reliable and in agreement with the experimental and other theoretical results. In general, among the different population schemes studied in this paper, we observe that LPA overestimates the IE. On the basis of our present and earlier observations, we argue that the present method can describe the weak interaction cases better than the stronger ones. These conclusions are very important in justifying the applicability and reliability of the present method in predicting the intermolecular interaction energies using the global and local reactivity descriptors. Further work should focus on the general classification of the types of interactions that are involved in a large number of complexes based on the mean values of these descriptors.

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