Scrutiny of the HSAB Principle in Some Representative Acid−Base Reactions

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Received: May 9, 2001; In Final Form: June 25, 2001

A thorough quantitative analysis of the HSAB principle is performed. Complex formation reactions of a typical soft acid, Ag^+, and typical hard acid, HF, with the bases XH_3 (X = N, P, As) are studied using the DFT/B3LYP method with the 6-311G** basis set. For the molecules containing Ag^+ and As, corresponding pseudopotentials are used. Results of the calculations pertaining to the interactions of the hard acid, HF, are robust in comparison to those of Ag^+. Correlation and nuclear relaxation effects are important in the case of the interactions of Ag^+. Basis set superposition error changes the trend, and the results vary drastically with the quality of the basis set. Pseudopotentials do not introduce any error, and the zero-point energy represents at most 5% of the binding energy. The presence of the solvent, modeled as in Onsager's dipole method and in PCM, does not significantly change the trend. In the exchange reactions, both HSAB and maximum hardness principles are shown to be valid.

1. Introduction

One of the important electronic structure principles in chemistry is the hard−soft acid−base (HSAB) principle proposed by Ralph Pearson,[1−4] which states that "all other things (like strength) being equal, hard acids prefer to coordinate with hard bases and soft acids prefer to coordinate with soft bases for both their thermodynamic and kinetic properties". Several formal proofs of this principle have been provided,[5−8] taking care of variations in the number of electrons[5−8] as well as in the external potentials.[8] A state of the art ab initio study[9] has also been performed for understanding the HSAB principle in the context of the gas-phase reactions of a typical hard acid (HF) and a typical soft acid (Ag^+) with several bases. It has been observed[9] that the Hartree−Fock level calculation is adequate in explaining the interactions involving the hard acid. However, the effect of correlation is important for the reactions of a soft acid like Ag^+ because of its highly polarizable core. Even at the MP4SDTQ level, Ag^+ has been shown[9] to prefer to bind to NH_3 rather than to PH_3, which violates the HSAB principle.[10] The hard−soft behavior has been believed[3,10,11] to change drastically in the presence of a solvent. Moreover, the hard−hard interactions are ionic in nature and hence charge-controlled, while the soft−soft interactions are covalent in nature and hence frontier-controlled.[12] Therefore, it is expected that the factors which are important in the two cases ought to be different. To have a more transparent picture vís a vís all the points discussed above, in the present paper, we try to provide a critical survey of the reactions of Ag^+ as well as HF with bases H_3X (X = N, P, As) studied within a density functional framework.[13] We analyze the problem in terms of amounts of correlation, pseudopotentials, solvents, and basis set dependences including the basis set superposition errors.

For an N-electron system with energy E and external potential $v(\vec{r})$ the hardness (η) is defined within density functional theory (DFT) as[5]

$$\eta = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_{v(\rho/r)} \tag{1}$$

A finite difference approximation to eq 1 gives[5]

$$\eta = \left(\frac{I - A}{2}\right) \tag{2}$$

where I and A are the ionization potential and the electron affinity, respectively.

Koopmans' theorem can be applied to approximate it further as[14]

$$\eta = \left(\frac{E_{\mathrm{LUMO}} - E_{\mathrm{HOMO}}}{2}\right) \tag{3}$$

where E_{LUMO} and E_{HOMO} are the energy values associated with the lowest unoccupied and highest occupied molecular orbitals, respectively. Note, however, that the Kohn−Sham orbitals are different from canonical orbitals, albeit the difference is not very large.[13]

Another important related hardness principle is the "maximum hardness principle"[4,15] (MHP), which states that "there seems to be a rule of nature that molecules arrange themselves so as to be as hard as possible". Since the validity of the HSAB principle is related to that of the MHP,[8,9,16] we would also like to explore the implications of the latter in the present context. For this purpose, we calculate the hardnesses (as HOMO−LUMO gaps; eq 3) along with the binding energies of different complexes of HF and Ag^+ with H_3X (X = N, P, As). Theoretical background of the present work is given in section 2. Section 3 presents the necessary computational details, and the results

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10.1021/jp011767w CCC: $20.00
Published on Web 08/09/2001

TABLE 1: Pseudopotentials and Basis Set Used for Ag and As Atoms

atom	basis set			pseudopotential		
Ag	Ag 0			Ag 0		
	s	3 1.00		ag-ecp-mwb 4 28		
		9.0884420	−1.5844552			
		7.5407310	2.1466804		1	
		2.7940050	0.4165536	2	1.00000000	0.00000000
	s	1 1.00				
		1.4801580	1.0000000		2	
	s	1 1.00		2	13.13000000	255.13936452
		0.6538510	1.0000000	2	6.51000000	36.86612154
	s	1 1.00				
		0.1244880	1.0000000		2	
	s	1 1.00		2	11.74000000	182.18186871
		0.0492640	1.0000000	2	6.20000000	30.35775148
	s	1 1.00				
		0.0160000	1.0000000		2	
	p	2 1.00		2	10.21000000	73.71926087
		4.4512400	−6.3305736	2	4.38000000	−6.3305736
		3.6752630	−6.3305736			
	P	2 1.00			2	
		1.2912880	−6.3305736	2	14.22000000	−6.3305736
		0.6525780	−6.3305736	2	7.11000000	−6.3305736
	P	1 1.00				
		0.3670360	−6.3305736			
	P	1 1.00				
		0.0756940	−6.3305736			
	P	1 1.00				
		0.0237230	−6.3305736			
	D	4 1.00				
		7.9947300	−6.3305736			
		2.7847730	−6.3305736			
		1.2097440	−6.3305736			
		.5053930	−6.3305736			
	d	1 1.00				
		0.1988510	1.0000000			
	d	1 1.00				
		0.0660000	1.0000000			
As	As 0			As 0		
	s	3 1.00		as-28-mwb 4 28		
		3.43147400	0.14816600			
		1.89686600	−0.44989000		1	
		0.29444900	0.69568300	2	1.00000000	0.00000000
	S	1 1.00				
		0.11189600	1.00000000		1	
	S	1 1.00		2	3.612625	53.965620
		0.03729866	1.00000000			
	P	3 1.00			1	
		1.29644700	−0.36995400	2	3.907926	88.949088
		0.94997100	0.37321400			
		0.25442100	0.60030400		1	
	P	1 1.00		2	1.926467	22.420288
		0.08759300	1.00000000			
	P	1 1.00			1	
		0.02919766	1.00000000	2	1.773434	−4.704815
	D	1 1.00				
		0.29300000	1.00000000			

are discussed in section 4. Finally, section 5 contains some concluding remarks.

2. Theoretical Background

According to the HSAB principle, hard−hard/soft−soft interactions are more favorable in comparison to the corresponding hard−soft/soft−hard counterparts, provided that other quantities such as strength remain unaltered. To determine which reaction is more favorable, corresponding reaction energies are generally compared.

Reaction energies for the various reactions studied are corrected for the basis set superposition error (bsse) through the commonly used counterpoise method[17] as well as for the bsse nuclear relaxation as proposed by Lendvay and Mayer.[18] The usual reaction energy (ΔE_0) for the $[Ag(XH_3)]^+$ complex formation and the reaction energies corrected for the bsse by the counterpoise method[17] (ΔE_1) and the Lendvay−Mayer nuclear relaxation[18] (ΔE_2) are given by

$$\Delta E_0 = E_{[Ag\cdots XH_3]^+} - E_{Ag^+} - E_{XH_3} \tag{4}$$

$$\Delta E_1 = E_{[Ag\cdots XH_3]^+} - E^*_{Ag^+(XH_3)} - E^*_{XH_3(Ag)} \tag{5}$$

and

$$\Delta E_2 = \Delta E_1 + [E'_{XH_3} - E_{XH_3}] \tag{6}$$

where the various energy quantities used in expressions 4−6 represent the following:

(i) $E_{[Ag\cdots XH_3]^+}$: total energy of the complex $[Ag\cdots XH_3]^+$
(ii) E_{Ag^+}: total energy of the isolated Ag^+ soft acid
(iii) E_{XH_3}: total energy of the optimized XH_3 base (isolated)
(iv) $E^*_{Ag^+(XH_3)}$: total energy of the Ag^+ in the presence of the basis set of XH_3 (in the configuration adopted in the complex)
(v) $E^*_{XH_3(Ag)}$: total energy of the XH_3 in the presence of the basis set of Ag (in the configuration adopted in the complex)
(vi) E'_{XH_3}: total energy of the XH_3 in the configuration adopted in the complex excluding at all the Ag atom.

Note that the energy difference in the last parenthesis of ΔE_2 (eq 6) must be positive.[18]

Similarly, for the $[FH\cdots XH_3]$ complex formation, the corresponding reaction energies are written as

$$\Delta E_0 = E_{[FH\cdots XH_3]} - E_{HF} - E_{XH_3} \tag{7}$$

$$\Delta E_1 = E_{[FH\cdots XH_3]} - E^*_{FH(XH_3)} - E^*_{XH_3}(FH) \tag{8}$$

$$\Delta E_2 = \Delta E_1 + [E'_{XH_3} - E_{XH_3}] \tag{9}$$

$$\Delta E_3 = \Delta E_2 + [E'_{HF} - E_{HF}] \tag{10}$$

(i) $E_{[FH\cdots XH_3]}$: total energy of the complex $[FH\cdots XH_3]$
(ii) E_{HF}: total energy of the isolated HF hard acid
(iii) E_{XH_3}: total energy of the optimized XH_3 base (isolated)
(iv) $E^*_{FH(XH_3)}$: total energy of the HF in the presence of the basis set of XH_3 (in the configuration adopted in the complex)
(v) $E^*_{XH_3(FH)}$: total energy of the XH_3 in the presence of the basis set of HF (in the configuration of adopted in the complex)
(vi) E'_{XH_3}: total energy of the XH_3 in the configuration adopted in the complex excluding at all the Ag atom.
(vii) E'_{HF}: total energy (single-point) of the isolated HF hard acid (excluding XH_3)

Solvent effects were incorporated through the Onsager (dipole)[19] and the point charge (PCM)[20] models. The PCM method depends very strongly on the cavity radius. The Onsager method is, on the other hand, rather primitive. The level of theory used for the electronic structure calculation dictates the amount of correlation involved in it, e.g., HF, MP2, MP4SDTQ, DFT/B3LYP, etc. Similarly, the dependence on basis set may be analyzed by systematically, improving the quality of the basis set, say, by using the Dunning's basis set.[21] Influence of the pseudopotential may be gauged by considering pseudopotential on selective atoms in the molecules.

3. Computational Details

For all the bases XH_3 (X=N, P, As) and their complexes with Ag^+ and HF, computations are carried out using the B3LYP/6-311+G** level of theory[22,23] with the Gaussian 98 Revision A9 package of programs.[24] Geometries are optimized using the DFT/B3LYP method[23] within the Berny algorithm,[25] and the frequency calculation is performed using the OPT=VeryTight and Integral (Grid=Ultra Fine) options.[24] Ab Initio pseudopotential calculations are performed for the molecules containing heavier elements, As and/or Ag^+.

Both pseudopotential and basis set[26] used for Ag^+ and As are given in Table 1. Reaction energies are calculated using eqs 4−10, which take care of counterpoise bsse correction and nuclear relaxation effects. Hardness values are calculated as the HOMO−LUMO gaps (eq 9). Frequency calculations are done mainly to decide whether a structure is the true minimum energy

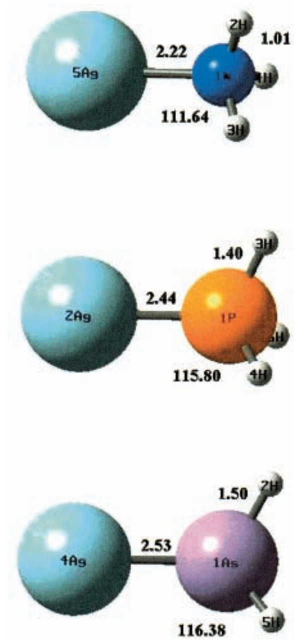

Figure 1. Structure of the $[Ag\cdots XH_3]^+$ complexes.

TABLE 2: B3LYP Optimized Geometries for the $[Ag-XH_3]^+$ Complexes (C_{3V})

N	P	As
H,1,B1	Ag,1,B1	H,1,B1
H,1,B2,2,A1	H,1,B2,2,A1	H,1,B2,2,A1
H,1,B3,2,A2,3,D1	H,1,B3,2,A2,3,D1	Ag,1,B3,2,A2,3,D1
Ag,1,B4,2,A3,3,D2	H,1,B4,2,A3,3,D2	H,1,B4,2,A3,4,D2
variables	variables	variables
B1 = 1.019	B1 = 2.441	B1 = 1.501
B2 = 1.019	B2 = 1.406	B2 = 1.501
B3 = 1.019	B3 = 1.406	B3 = 2.526
B4 = 2.218	B4 = 1.406	B4 = 1.501
A1 = 107.15	A1 = 115.81	A1 = 101.76
A2 = 107.15	A2 = 115.81	A2 = 116.38
A3 = 111.70	A3 = 115.81	A3 = 101.76
D1 = −114.73	D1 = 120.0	D1 = −127.59
D2 = 122.64	D2 = −120.0	D2 = −127.59

structure with no imaginary frequency. All the species belong to the C_{3V} point group of symmetry (except HF, which is of $C_{\infty V}$ symmetry). Solvent effects are incorporated through the Onsager (dipole) and PCM methods with the corresponding gas-phase geometries for both sets of complexes. For the Onsager methodology,[19] volume calculations are performed initially to determine the cavity radius. The PCM method[20] also depends very strongly on the radius of the cavity, which is, however, difficult to define for the complexes. Solution phase calculations are done using B3LYP method[23] with no ZPE and the dielectric constant of water.

Basis set dependence is judged by the single-point calculations on the B3LYP/6-311+G** geometries[21] with the pseudopotential and basis set for Ag^+ as in Table 1 and Dunning's correlation consistent basis set[21] for other atoms.

4. Results and Discussion

Various geometrical parameters calculated at the B3LYP/6-311+G** level of the theory for the complexes $[Ag\cdots XH_3]^+$ in form of a **Z** matrix are reported in the Table 2, and the corresponding structures are depicted in Figure 1. Table 2 also contains the geometries of XH_3 (X = N, P, As) molecules.

TABLE 3: B3LYP Total Energies, ZPEs, and Hardness Values for the Isolated, Fully Optimized Species

species	E, au	ZPE, au	η, au
Ag^+	−146.6775	0.0	0.1197
NH_3	−56.5826	0.0342	0.1406
PH_3	−343.1733	0.0239	0.1370
AsH_3	−8.0088	0.0217	0.1374
$[Ag\cdots NH_3]^+$	−203.3360	0.0383	0.1020
$[Ag\cdots PH_3]^+$	−489.9239	0.0269	0.1001
$[Ag\cdots AsH_3]^+$	−154.7535	0.0246	0.0966

TABLE 4: B3LYP Single-Point Energies, ZPEs, and Hardness Values for the XH_3 Bases in the Conformations Which Are Adopting in the $[Ag\cdots XH_3]^+$ Optimized Complexes

species	E', au	ZPE, au	η, au
NH_3	−56.5826	0.0341	0.1410
PH_3	−343.1676	0.0241	0.1251
AsH_3	−8.0015	0.0222	0.1235

TABLE 5: B3LYP Total Energies, ZPEs, and Hardness Values for the Ag^+ and XH_3 Species, Including the BSSE Corrections (Single-Point Calculations in the Presence of the (X) Basis Set in the Conformations Adopted in the $Ag\cdots XH_3$ Optimized Complexes)

species	E*, au	ZPE, au	η, au
$Ag^+(NH_3)$	−146.6778	0.0	0.1197
$Ag^+(PH_3)$	−146.6778	0.0	0.1197
$Ag^+(AsH_3)$	−146.6778	0.0	0.1197
$NH_3(Ag)$	−56.5841	0.0341	0.1291
$PH_3(Ag)$	−343.1685	0.0241	0.1210
AsH3(Ag)	−8.0017	0.0222	0.1174

TABLE 6: B3LYP Total Energies and Hardness Values (au) for All Stationary Points, Both at the Dipole and PCM Solvent Models

	Diploe		PCM	
species	E	η	E	η
Ag^+	−146.6775	0.1197	−146.8047	0.1163
NH_3	−56.5843	0.1440	−56.5913	0.1457
PH_3	−343.1736	0.1378	−343.1744	0.1384
AsH_3	−8.0088	0.1375	−8.0092	0.1378
$[Ag\cdots NH_3]^+$	−203.3362	0.1011	−203.4414	0.1011
$[Ag\cdots PH_3]^+$	−489.9240	0.1016	−490.0203	0.1024
$[Ag\cdots AsH_3]^+$	−154.7541	0.0938	−154.8454	0.1022

The B3LYP total energies, ZPEs, and η values for the isolated fully optimized species are given in Table 3. It may be noted that the complex $[Ag\cdots AsH_3]^+$ is more stable than $[Ag\cdots H_3As]^+$ by 14.0 kcal/mol and the latter is not a true minimum since it has two imaginary frequencies (doubly degenerate −157.5i cm^{-1}). It is apparent that Ag^+ is softer than all three XH_3 molecules and the η values of $[Ag\cdots NH_3]^+$ and $[Ag\cdots PH_3]^+$ are comparable. Corresponding quantities required for the bsse correction including nuclear relaxation effect (E* and E') are presented in Tables 4 and 5. It is obvious that the effect of bsse on η is much more dramatic than on the total energy or the ZPE.

Table 6 provides the B3LYP total energies and η values for various species in aqueous solution modeled by dipole and PCM methods, respectively. The effect is generally not very prominent but is more conspicuous in the PCM model.

Result of the single-point calculation with B3LYP/6-311+G** level optimized geometries and Dunning's basis set on all atoms but Ag^+ (pseudopotential and basis set as in the Table 1) are reported in Table 7.

Table 8 presents the reaction energies (kcal/mol) associated with all three reactions: $Ag^+ + XH_3 \rightarrow [Ag(XH_3)]^+$; X = N, P, As. Influence of various factors on reaction energies are analyzed below.

TABLE 7: B3LYP Results Using Some of the Dunnings Correlation-Consistent Basis Sets

species	cc-pVDZ[a]	cc-pVTZ[a]	cc-pVQZ[a]	cc-pVQZ[b]
NH_3	−56.5535	−56.5846	−56.5913	−56.5914
PH_3	−343.1599	−343.1800	−343.1850	−343.1850
$[Ag..NH_3]^+$	−203.3172	−203.3404	−203.3452	−203.3449
$[Ag..PH_3]^+$	−489.9116	−489.9310	−489.9363	−489.9365

[a] Single-point calculation using the optimized B3LYP/6-311+G** geometries in Tables 2 and 3 and pseudopotential and basis set for Ag shown in Table 1. [b] Fully optimized geometries at this level of theory (for Ag pseudopotential and basis set, as in Table 1)

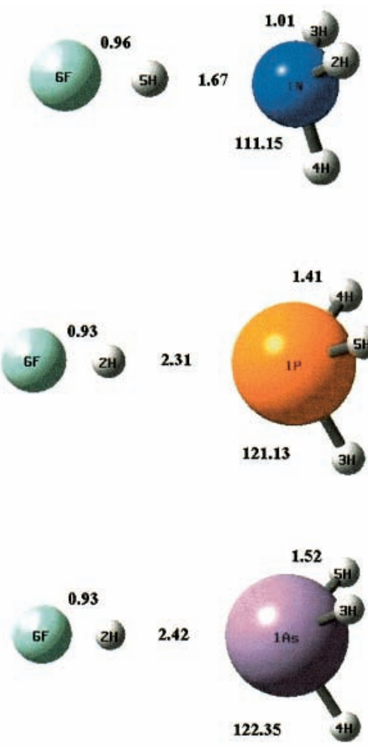

Figure 2. Structure of the $[FH\cdots XH_3]$ complexes.

A. Influence of Pseudopotential. Here two columns (1 and 2) represent reaction energies (with ZPE) obtained from two types of calculations. While in the former set, the pseudopotential is taken for Ag^+ and As only, the latter set includes pseudopotentials in all atoms except hydrogen. From the results, it is clear that the pseudopotentials do not introduce any error. Here ZEP does not account for more than 5% of the binding energy.

B. Correlation Effects. Three columns provide the reactions energies (with ZPE) calculated at the HF, MP2, and B3LYP levels of theory. As expected,[9] for Ag^+ being a soft acid with a highly polarizable core, the in−out correlation is very important. It is also clear that for a qualitative description, MP2 or B3LYP would serve the purpose.

C. Solvent Effects. Two columns present reaction energies (without ZPE) calculated at the B3LYP level with Onsager and PCM models with the dielectric constant of water. It is seen that the solvent (both dipole and PCM models) does not change the preference order. Recently, it has been also observed[22] that the solvent has a negligible affect on hardness and Fukui functions. However, it is important to notice that one is comparing neutral molecules where solvent effects are expected to be small. Surely, the effect will be large for reactions

TABLE 8: Reaction Energy (kcal/mol)

	pseudopotential		correlation effect (with ZPE)			solvent effect		basis set superposition error		
species	1	2	HF	MP2	B3LYP	Onsager	PCM	ΔE_0	ΔE_1	ΔE_2
$[Ag\cdots NH_3]^+$	−45.0	−45.3	−33.5	−41.7	−45.0	−46.7	−28.4	−45.0	−43.8	−43.9
$[Ag\cdots PH_3]^+$	−44.0	−43.8	−28.8	−38.2	−44.0	−45.8	−25.8	−44.0	−46.9	−43.2
$[Ag\cdots AsH_3]^+$	−40.3	−40.3	−26.1	−34.1	−40.3	−42.5	−19.8	−40.3	−44.9	−40.0

TABLE 9

	cc-pVDZ[a]	cc-pVTZ[a]	cc-pVQZ[a]	+ZPE	+ZPE + bsse
$Ag(NH_3)^+$	−54.1	−49.1	−47.9	−45.3	−44.2
$Ag(PH_3)^+$	−46.5	−46.1	−46.3	−44.4	−43.6

[a] Calculations without ZPE and without bsse. The last calculations are so big that we cannot do ZPE and bsse. But assuming that both effects are additive, we can add the results obtained at the beginning for ZPE and the last one for bsse.

TABLE 10: B3LYP Optimized Geometries for the $[FH\cdots XH_3]$ Complexes (C_{3V})

$FH\cdots NH_3$	$FH\cdots PH_3$	$FH\cdots AsH_3$
N	P	As
H,1,B1	H,1,B1	H,1,B1
H,1,B2,2,A1	H,1,B2,2,A1	H,1,B2,2,A1
H,1,B3,2,A2,3,D1,0	H,1,B3,2,A2,3,D1,0	H,1,B3,2,A2,3,D1,0
H,1,B4,2,A3,4,D2,0	H,1,B4,2,A3,3,D2,0	H,1,B4,2,A3,3,D2,0
F,1,B5,2,A4,4,D3,0	F,1,B5,3,A4,5,D3,0	F,1,B5,3,A4,5,D3,0
variables	variables	variables
B1 = 1.016	B1 = 2.320	B1 = 2.427
B2 = 1.016	B2 = 1.417	B2 = 1.521
B3 = 1.016	B3 = 1.417	B3 = 1.521
B4 = 1.674	B4 = 1.417	B4 = 1.521
B5 = 2.636	B5 = 3.258	B5 = 3.361
A1 = 107.79	A1 = 121.13	A1 = 122.34
A2 = 107.79	A2 = 121.13	A2 = 122.36
A3 = 111.31	A3 = 121.13	A3 = 122.35
A4 = 111.34	A4 = 121.12	A4 = 122.34
D1 = 116.10	D1 = 119.99	D1 = 120.00
D2 = 121.93	D2 = −120.00	D2 = 120.00
D3 = 121.90	D3 = −131.84	D3 = −132.82

involving small ions. The effect of solvent on chemical potential and hardness has been addressed by Pearson some time ago.[27] One can see also that Ag^+ prefers to bind to NH_3 rather than PH_3 even in aqueous solution. This seems to be due to the greater basicity of NH_3.

D. Basis Set Superposition Error. The commonly used counterpoise correction[17] is used to take care of the basis set superposition error (bsse), and the Lendvay−Mayer[18] technique is used to tackle the bsse nuclear relaxation. The respective binding energies ΔE_0, ΔE_1, and ΔE_2 (eqs 4−6) are also presented in Table 8. It is easily discernible that the trend depends on the bsse correction. It may be noted that while ΔE_1 provides the proper HSAB order,[10] ΔE_2 values for $[Ag(NH_3)]^+$ and $[Ag(PH_3)]^+$ are very close, and their difference is not very meaningful.

To be sure that the trends indeed change with the basis set, we systematically improve the quality of the basis set by using the Dunning's basis set.[21] The calculations were done only for N and P complexes because of the size of the basis set. Table 9 reports the binding energies for $[Ag(XH_3)]^+$, X = N and P, with cc-pVDZ, cc-pVTZ, and cc-pVQZ basis sets. The last calculations are so large that we cannot calculate ZPE or bsse. But assuming that both effects are additive, we can add the result obtained for ZPE and bsse and also present them in Table 9. Since the differences are so small, one can at most say that the stability of these complexes are comparable.

TABLE 11: B3LYP Total Energies, ZPEs, and Hardness Values for the Isolated, Fully Optimized Species in the Phase

species	E, Au	ZPE, au	η, au
FH	−100.4824	0.0093	0.2129
NH_3	−56.5826	0.0342	0.1406
PH_3	−343.1733	0.0239	0.1370
AsH_3	−8.0088	0.0217	0.1374
$[FH\cdots NH_3]$	−157.0877	0.0484	0.1567
$[FH\cdots PH_3]$	−443.6645	0.0363	0.1456
$[FH\cdots AsH_3]$	−108.4974	0.0337	0.1427

TABLE 12: B3LYP Single-Point Energies, ZPEs, and Hardness Values for the XH_3 Bases in the Conformations Adopted in the $[FH\cdots XH_3]$ Optimized Complexes

species	E', au	ZPE, au	η, au
NH_3	−56.5826	0.0081	0.2064
PH_3	−343.1729	0.0088	0.2105
AsH_3	−8.0084	0.0089	0.2322
$FH(NH_3)$	−100.4808	0.0342	0.1407
$FH(PH_3)$	−100.4821	0.0241	0.1342
$FH(AsH_3)$	−100.4520	0.0289	0.1346

TABLE 13: B3LYP Total Energies for the FH and XH_3 Species, Including the BSSE Corrections: Single-Point Calculations in the Presence of the (E) Basis Set in the Conformations Adopted in the $FH\cdots XH_3$ Optimized Complexes

species	E^*, au	η, au
$FH(NH_3)$	−100.4812	0.1976
$FH(PH_3)$	−100.4824	0.1979
$FH(AsH_3)$	−100.4824	0.1987
$(FH)NH_3$	−56.5839	0.1389
$(FH)PH_3$	−343.1735	0.1345
$(FH)AsH_3$	−8.0085	0.1341

TABLE 14: B3LYP Total Energies and Hardness (Both in au) with Different Solvent Models (H_2O)

species	PCM	η	dipole	η
FH	−100.4934	0.2285	−100.4856	0.2209
NH_3	−56.5913	0.1457	−56.5844	0.1443
PH_3	−343.1744	0.1427	−343.1735	0.1378
AsH_3	−8.0092	0.1378	−8.0088	0.1375
$[FH\cdots NH_3]$	−157.1043	0.1620	−157.0979	0.1640
$[FH\cdots PH_3]$	−443.6711	0.1472	−443.6695	0.1477
$[FH\cdots AsH_3]$	−108.5030	0.1442	−108.5013	0.1433

To check whether Ag^+ prefers to bind to a soft base when there is a competition between Ag^+ and a typical hard acid like HF vis a vis the validity of HSAB principle and MHP, we also repeat the calculations for HF reacting with the same set of bases, viz., XH_3 (X = N, P, As). While the geometrical parameters are given in Table 10, Figure 2 presents the corresponding structures. All the complexes belong to C_{3V} symmetry and the minimum-energy structure, as authenticated by zero imaginary frequency. Corresponding total energy, hardness and reaction energies, including bsse correlations and solvent effects are presented in Tables 11 to 15. As was pointed out earlier,[9,16] the trends do not change in case of interactions

TABLE 15: B3LYP Reaction Energies (kcal/mol)

reaction process	ΔE_0 (without ZPE)	ΔE_0 (with ZPE)	ΔE_1 (without ZPE)	ΔE_2 (without ZPE)	ΔE_3 (without ZPE)	PCM	dipole
$FH + NH_3 = [FH\cdots NH_3]$	−14.3	−11.2	−14.2	−14.2	−13.2	−12.3	−17.5
$FH + PH_3 = [FH\cdots PH_3]$	−5.54	−3.61	−5.39	−5.17	−5.03	−2.07	−6.48
$FH + AsH_3 = [FH\cdots AsH_3]$	−3.95	−2.27	−4.08	−3.87	−3.77	−0.27	−4.34

with a hard acid when different methods of calculation with various basis sets are performed. The HSAB principle is valid in all cases. This relative robustness of hardness is an unmistakable signature of the MHP.[15] Calculation of corresponding quantities for a soft species is, however, very much dependent on the level of theory and the quality of basis set used.

Pearson[4] pointed out that the HSAB principle is better understood via the exchange reaction $AB + CD = AC + BD$ rather than the binary complex formation reaction $A + B = AB$. It is quite gratifying to note that in case we take the data from Tables 3 and 11, Ag^+ prefers to bind to PH_3, while HF prefers to bind to NH_3, as expected from HSAB principle, viz.

$$[Ag(NH_3)]^+ + FH\cdots PH_3 = FH\cdots NH_3 + [Ag(PH_3)]^+ \quad (11)$$

E (au)	−203.336	−443.664	−157.088	−489.924
η (au)	0.102	0.146	0.157	0.100

It is easily discernible that the exchange reaction 11 is energetically favorable in the forward direction. Even the η values reveal that the hardest species lie in the product side and the average hardness of the products is greater than the average hardness of the reactants,[28] a joint vindication of the MHP and the HSAB principle.

5. Concluding Remarks

For the interactions involving hard acids such as HF, the DFT/B3LYP methods with a reasonably good basis set is adequate, whereas the effects of correlation and nuclear relaxation are important for the reactions of the soft acid, Ag^+.

For the analyzed reactions, the solvent does not change the trend, and pseudopotentials do not introduce any error. While the zero-point energy is roughly 5% of the binding energy, the quality of the basis set is shown to have a drastic effect on the Ag^+ reaction energies. The basis set superposition error must be corrected upon in order to get a proper trend in the reactions of the soft acid. Since the binding energy of the complexes $Ag(NH_3)^+$ and $Ag(PH_3)^+$ are so similar, one has to resort to the exchange reactions to validate the HSAB and maximum hardness principle.

Acknowledgment. P.K.C. would like to thank C.S.I.R., New Delhi, for financial assistance. Part of this work has been supported by FONDECYT (Fondo para el Desarrollo de la Ciencia y la Tecnologia) Grants 1010649, 2000092, 2000085, and 2990030. E.C. thanks Postgrado y Postítulo (U. de Chile) under Grants PG/05/1999 and PG/26/2000. B.G., E.C., and J.C.S. thanks DAAD (Deutsches Akademischer Austauschdienst) for Ph.D. fellowships. We thank Mr. B. Maiti for his help in the preparation of the manuscript.

References and Notes

(1) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533.
(2) Pearson, R. G. *J. Chem. Educ.* **1965**, *581*, 643.
(3) (a) Pearson, R. G. In *Theoretical Models of Chemical Bonding*, Part 2; Maksie, Z. B. Ed.; Springer-Verlag: Berlin, 1990; pp 45−76. (b) Sen, K. D., Mingos, D. M. P., Eds. In *Chemical Hardness: Structure and Bonding*; Springer-Verlag: Berlin, 1993; Vol. 80, pp 11−25. (c) Chattaraj, P. K. *J. Indian Chem. Soc.* **1992**, *69*, 173. (d) Pearson, R. G. *Hard and Soft Acids and Bases*; Dowden-Hutchinson and Ross: Stroudsberg, PA, 1973.
(4) Pearson, R. G. *Chemical Hardness*; Wiley: New York, 1997.
(5) Parr, R. G.; Pearson, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 7512.
(6) Nalewajski, R. F. *J. Am. Chem. Soc.* **1984**, *106*, 944.
(7) Chattaraj, P. K.; Lee, H.; Parr, R. G. *J. Am. Chem. Soc.* **1991**, *113* (3), 1855.
(8) Chattaraj, P. K.; Cedillo, A.; Parr, R. G. *Int. J. Quantum Chem. Soc.* **2000**, *77*, 403.
(9) Chattaraj, P. K.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1994**, *116* (6), 1067.
(10) Huheey, J. E. *Inorganic Chemistry*; Harper and Row: New York. 1972.
(11) (a) Williams, R. J. P.; Hale, J. D. *Struct. Bonding (Berlin)* **1966**, 1249. (b) Edwards, J. O. *J. Am. Chem. Soc*. **1954**, *76*, 1540. (c) Yingst, A.; McDaniel, D. H. *Inorg. Chem*. **1967**, *3*, 55. (d) Hancock, R. D.; Marsicano, F. *Inorg. Chem*. **1980**, *19*, 2709. (e) Hancock, R. D.; Martell, A. E. *J. Chem. Educ.* **1996**, *73*, 654.
(12) Klopman, G. *J. Am. Chem. Soc*. **1968**, *90*, 223.
(13) Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*; Oxford University Press: Oxford, 1989.
(14) Pearson, R. G. *Proc. Natl. Acad. Sci. U.S.A.* **1986**, *83*, 8440.
(15) (a) Pearson, R. G. *J. Chem. Educ.* **1987**, *64*, 561. (b) Parr, R. G.; Chattaraj, P. K. *J. Am. Chem. Soc.* **1991**, *113*, 3, 1854. (c) Pearson, R. G *Acc. Chem. Res.* **1993**, *26*, 250. (d) Chattaraj, P. K. *Proc. Indian Natl. Sci. Acad.—Part A* **1996**, *62*, 1133. (e) Ayers, P. W. ; Parr, R. G. *J. Am. Chem. Soc.* **2000**, *122*, 2010. (f) Chattaraj, P. K.; Liu, G. H.; Parr, R. G. *Chem. Phys. Lett*. **1995**, *237*, 171
(16) Chattaraj, P. K.; Nath, S. *Ind. J. Chem., Sect. A* **1994**, *33*, 842.
(17) Boys, S. B.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.
(18) Lendvay, G.; Mayer, I. *Chem. Phys. Lett.* **1998**, *297*, 36.
(19) Kirkwood, J. G. *J. Chem. Phys*. **1934**, *2*, 351.
(20) (a) Miertus, S.; Scrocco, E.; Tomasi, J. *Chem. Phys*. **1981**, *55*, 117. (b) Miertus, S.; Tomasi, J. *Chem. Phys*. **1982**, *65*, 239. (c) Cossi, M.; Barone, V.; Cammi, R.; Tomasi, *J. Chem. Phys. Lett*. **1996**, *255*, 327.
(21) Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys*. **1993**, *98*, 1358.
(22) Fuentealba, P.; Cedillo, A. *J. Chem. Phys.* **1999**, *110*, 9807.; Fuentealba, P.; Pérez, P.; Contreras, R. *J. Chem. Phys.* **2000**, *113*, 2544.
(23) (a) Becke, A. D. *Phys. Rev. A* **1998**. 38, 3098. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785; Miechlich, B.; (c) Savin, A. Stoll, H.; Preuss, H. *Chem. Phys. Lett*. **1989**, *157*, 200.
(24) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.9; Gaussian, Inc.: Pittsburgh, PA, 1998.
(25) (a) Schlegel, H. B. *J. Comput. Chem.* **1982**, *3*, 214. (b) Schlegel, H. B. In *New Theoretical Concepts for Understanding Organic Reactions*; Bertran, J., Ed.; Kluwer: Dordrecht, The Netherlands, 1989; p 33. (c) Schlegel, H. B. In *Modern Electronic Structure Theory*; Yarkony, D. R., Ed.; World Scientific Plublishing: Singapore, 1995).
(26) Andrea, D.; Haeussermann, U.; Dolg, M.; Stoll, H. and Preuss, H. *Theor. Chim. Acta* **1990**, *77*, 123.
(27) Pearson, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 6109.
(28) (a) Datta, D. *Inorg. Chem*. **1992**, *31*, 2797. (b) Ghanty, T. K.; Ghosh, S. K. *J. Phys. Chem.* **1996**, *100*, 12, 295.