

position. In a positive ion  $\rho$  will be diminished and the empirical value of  $z_A z_B$  will be less.<sup>18</sup> Obviously the Platt model cannot account for an increase in this parameter, and it has been shown that the model is poor for metallic hydride ions.<sup>18</sup>

### Conclusion

Tables IV, VI, and VII contain data for elements whose  $z$  values are not given in Tables I or II. From the data, and by comparison to neighboring elements,  $z$  values can be estimated for Mn, Zn, Ga, Cd, In, Hg, and Tl. A periodic chart (Figure 1) of the elements can now be shown in which effective nuclear charges,  $z$ , are given for 63 of the elements. By interpolation, a number of  $z$  values for other elements can be estimated but are not shown in the chart.

Hopefully, the effective charges can be useful in several ways. For example, the vibrational frequencies of diatomic molecules such as  $\text{CO}_2$ , or even  $\text{Fe}_2$ , could be predicted. Frequencies for heteronuclear molecules can be predicted, if suitable corrections are made for ionic character and  $\pi$  bonding. Finally, the compressibilities of metals can be estimated, at least for cubic solids.

Since the effective charges are also equal to the number of bonding electrons for the atom, they should be related to bond energies. Indeed, a rough correlation with the heats of atomization of the metals is immediately obvious. However, there are individual variations which show that the relationship is not simple. At the very least, a size factor must also be considered.

The most important use of the  $z$  values lies in their possible application to the force constants for polyatomic molecules. A model in which each nucleus is represented by an effective positive charge leads to the central force field. At one time it was thought that such a force field was of limited value. However, more recent work shows that, properly used, the central force field is the same as the general valence force field.<sup>19</sup> For example, in a three-atom case, the three internuclear distances are not independent variables. Instead one must use two of these distances and the included angle.

The screened nucleus model allows all of the constants of the general valence force field to be evaluated quite readily. Unfortunately there is no theoretical reason to believe that a

single effective charge for each nucleus will be valid for every set of displacement coordinates. It is quite likely that the bending mode will require a different value of  $z$  from stretching modes. Also only positive interaction constants can be calculated from the model, whereas it is known that in some cases such constants are negative.

In spite of these misgivings it seems worthwhile to try to use the screened nucleus model in polyatomic cases. Using an empirical approach, as in this work, the factors which determine  $z$  in various cases may become clear.

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## A General Analysis of Noncovalent Intermolecular Interactions

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**Abstract:** We present ab initio calculations on a wide variety of intermolecular complexes, including "van der Waals" molecules, H-bonded complexes of varying strength, "charge-transfer" complexes, ionic associations, radical complexes, and three-body interactions. We use the Morokuma component analysis and electrostatic potentials in order to help us analyze the interaction energy and minimum energy structure of such complexes. We present a simple approach to use the electronic structure of the monomers that make up the complex, in order to predict the structure and interaction energy of the complex in the absence of detailed calculations or experiments.

Attempts to understand intermolecular interactions go back nearly as far as the theories of chemical bonding, the first postulate of the hydrogen bond coming from G. N. Lewis's lab

around 1920.<sup>1</sup> Subsequent simple theoretical models by Pauling,<sup>2</sup> among others, showed that electrostatic models could qualitatively reproduce observed H-bond energies. In 1954,

however, Tsubomura<sup>3</sup> and Coulson<sup>4</sup> used perturbation theory to estimate the contributions of different energy components to the energy of the hydrogen bond connecting two water molecules. These two studies indicated that exchange repulsion and charge-transfer energies as well as electrostatic were all of comparable magnitude, and that the success of the earlier electrostatic theories was apparently due to a (near) cancellation between the attractive (charge transfer) and repulsive (exchange repulsion) terms. Pimentel and McClellan<sup>5</sup> in 1960 listed the H-bond phenomena that an electrostatic model could not account for: (1) the many fold increase in intensity of the proton donor A-H stretching band upon H-bond formation; (2) the lack of correlation between H-bond strength and dipole moment of the base; (3) the lowered IR intensity of the in-plane bending mode of the proton donor upon H-bond formation; (4) the fact that hydrogen halide crystals were "zig-zag" rather than forming linear chains; (5) frequency shifts in electronic transitions; (6) relative stabilities of cis and trans *o*-halophenols. Recently, however, quantum mechanical studies by a number of workers<sup>6,7</sup> have again focused attention on the electrostatic properties of the hydrogen bond.

On the other hand, "charge-transfer" complexes were first analyzed by Mulliken<sup>8</sup> using a quantum mechanical two-determinant "charge-transfer" model. Subsequently, theoretical studies by Hanna<sup>9</sup> and Lefevre and Stiles<sup>10</sup> suggested that polarization and dispersion were more important than charge transfer in determining the interaction energy and geometry of the benzene-I<sub>2</sub> complex. Recent work by Lathan and Morokuma<sup>11</sup> provide further support that the ground state structure and properties of many "charge-transfer" complexes are predominantly determined by electrostatic forces. Historically, it is possible to understand why the first models for H bonds were electrostatic, since the predominant interest in studying these H-bonded complexes was in their *structural* properties. The interest in "charge-transfer" complexes came about because of their *spectral* properties and thus it made sense to suggest a simple "charge-transfer" model for these phenomena. We attempt in this paper to relate "charge transfer" and "H bonds" within a single picture which incorporates many other noncovalent complexes as well. Bent<sup>12</sup> has attempted a similar analysis in a recent comprehensive review of donor-acceptor interactions. Most of his examples were based on crystal data, whereas we now have data available from precise theoretical and experimental gas-phase studies. However, as we shall see, many of his conclusions were very perceptive and closely related to ours.

An important development in the 1950's was Buckingham's recognition<sup>13</sup> that considering just the charge and dipole moment of a molecule is not sufficient to allow one to understand its intermolecular interactions. For example, the lattice energy of dry ice was shown to have an important contribution from that molecule's quadrupole moment.

Recently, the advent of large-scale computational facilities have led to two important types of applications of quantum mechanics to a large number of complexes. Especially noteworthy were applications of perturbation theory<sup>6</sup> and SCF calculations. In the latter category, the method developed by Morokuma<sup>7</sup> to decompose the interaction energy into components has been of the greatest utility in elucidating intermolecular interactions. This method has been applied by Morokuma to H bonds (in ground and excited states), to donor-acceptor complexes (often called "charge-transfer" complexes),<sup>11</sup> and to proton affinities.<sup>14</sup> Recently, Umeyama and Morokuma<sup>15</sup> have completed an extensive study on component analysis of a wide variety of H-bonded systems. Their very nice paper parallels ours in some aspects and we will draw heavily on the results of their study in this paper. We have recently found component analysis to be very useful in comparing proton affinities, Li<sup>+</sup> affinities, and H bonds.<sup>16</sup>

Previously we examined a wide variety of H-bonded complexes, in the hopes of understanding the key features which determine H-bond structures and relative energies. We found that the electrostatic potential<sup>17</sup> was a very useful index that not only allowed us to determine qualitative feature of H bond structure, but to rank different H-bonded complexes in terms of their energies.

It is the purpose of this study to extend that approach<sup>17</sup> to analyze closed-shell intermolecular interactions ranging all the way from very weak complexes (Ne...HF) to very strong (NH<sub>4</sub><sup>+</sup>...F<sup>-</sup>), utilizing SCF calculations, the Morokuma component analysis, electrostatic potentials, and simple model calculations. We also consider non-closed-shell interactions and three-body complexes. In this way, we hope to elucidate the key features which determine complex structure and energies for noncovalent interactions. We conclude by proposing a simple predictive approach which allows one to understand many of the key features of intermolecular complex formation and to predict some of the properties of such complexes prior to detailed calculations or experiment.

### Computational Details

This study utilized the 431G basis set<sup>18</sup> and the program GAUSSIAN 70<sup>19</sup> for the SCF calculations and the Morokuma component analysis. The electrostatic potentials were evaluated using the MOLE<sup>20</sup> properties package.

A brief review of the Morokuma component analysis<sup>7</sup> is in order here, since we make extensive use of it in this paper. By using Hartree product and Hartree-Fock products of initial and converged density matrices for interacting pairs (or triples, etc.), the total SCF interaction energy ( $\Delta E$ ) can be decomposed into electrostatic ( $\Delta E_{ES}$ ), which is the Hartree product interaction energy between the charge distributions of the isolated molecules, polarization ( $\Delta E_{POL}$ ), which represents the charge redistribution energy within fragments, charge transfer ( $\Delta E_{CT}$ ), which represents the energy gained by allowing charge transfer between fragments and exchange repulsion ( $\Delta E_{EX}$ ), which represents the Pauli exchange repulsion between fragments. Kitaura and Morokuma<sup>21</sup> have recently further decomposed "charge transfer" into charge transfer plus a coupling term, but we follow the original definition in this paper.

Experimental monomer geometries were used here with the exception of NH<sub>3</sub> and (CH<sub>3</sub>)<sub>3</sub>N, where we used the geometries previously described.<sup>16</sup> In the intermolecular interaction, the monomer geometries were kept rigid. Table I contains the total energies of the monomers used in this study.

### Results and Discussion

Before we proceed further, we need to define what we mean by noncovalent complexes. Noncovalent complexes are those in which: (1) there are the same number of electron pairs in the isolated molecules as in the complex, and (2) no new *types* of covalent bonds are formed upon complexation. Criterion 2 eliminates from our consideration such interactions as BH<sub>3</sub> → B<sub>2</sub>H<sub>6</sub>. In BH<sub>3</sub> dimerization, the *nature* of the covalent bonding changes, even though the number of electron pairs stays the same.

We divide our study of closed-shell dimeric complexes into three general areas: very weak complexes, moderate strength complexes, and strong complexes. In a fourth section, we examine the concept of nonadditivity in closed-shell intermolecular interactions. In a fifth section, we discuss open shell-closed shell noncovalent interactions and, in a sixth section, propose a simple, general model for understanding noncovalent interactions.

**I. Very Weak Complexes.** Here we focus on complexes with interaction energy  $\leq 1$  kcal/mol. The weakest "closed-shell"

**Table I.** Total Energies of Molecules Studied

Molecule	$E_T$ , au	Molecule	$E_T$ , au
H <sub>2</sub>	-1.126 74	Ne	-128.522 35
N <sub>2</sub>	-108.753 67	HCN	-92.731 30
Cl <sub>2</sub>	-917.923 30	HNC	-92.716 41
F <sub>2</sub>	-198.458 40	CO <sub>2</sub>	-187.327 93
HF	-99.887 26	SO <sub>2</sub>	-546.351 33
LiF	-106.822 19	Li <sup>+</sup>	-7.233 21
ClF	-558.209 38	Be <sup>2+</sup>	-13.605 72
H <sub>2</sub> O	-75.907 39	NH <sub>4</sub> <sup>+</sup>	-56.458 70
NH <sub>3</sub>	-56.102 59	F <sup>-</sup>	-99.247 82
HCl	-459.563 10	Cl <sup>-</sup>	-459.026 41
H <sub>2</sub> S	-398.203 19	N(CH <sub>3</sub> ) <sub>3</sub>	-173.005 90
H <sub>3</sub> P	-342.025 16	BH <sub>4</sub> <sup>-</sup>	-26.924 36
H <sub>2</sub> NCHO	-168.677 22	Li <sub>2</sub>	-14.862 88

**Table II.** Component Analysis of the Ne...HF Interaction (kcal/mol)

	Ne...HF		
	$R(\text{Ne}\cdots\text{F})$ , Å		
	3.0	3.3	3.6
$\Delta E$	0.02	-0.23	-0.19
$\Delta E_{\text{ES}}$	-0.18	-0.05	-0.02
$\Delta E_{\text{POL}}$	-0.03	-0.00	0.01
$\Delta E_{\text{CT}}$	-0.05	-0.40	-0.23
$\Delta E_{\text{EX}}$	0.28	0.22	0.07

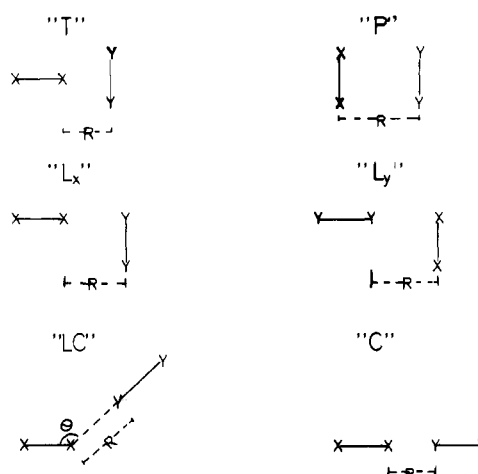
	Ne...FH		
	$R(\text{Ne}\cdots\text{F})$ , Å		
	2.7	3.0	3.3
$\Delta E$	0.06	-0.06	-0.03
$\Delta E_{\text{ES}}$	-0.05	-0.02	-0.02
$\Delta E_{\text{POL}}$	0.01	0.01	0.01
$\Delta E_{\text{CT}}$	-0.23	-0.12	-0.05
$\Delta E_{\text{EX}}$	0.33	0.07	0.03

interaction is that between He atoms. This has been studied extensively by perturbation theory approaches and by large scale ab initio methods.<sup>22</sup> It appears that the attraction is due entirely to dispersion forces, with a well depth  $\sim 0.025$  kcal/mol for (He)<sub>2</sub>.<sup>20</sup>

The next type of complex, which has recently received a lot of attention in elegant experiments by Klemperer and co-workers, involves an interaction between a rare gas atom and a polar molecule. Among such complexes which have been studied are ArClF,<sup>23</sup> ArHCl,<sup>24</sup> and ArOCS.<sup>25</sup> In each case, the rare gas atom appears to favor the most electropositive site on the polar molecule, with a T-shaped structure being found for ArOCS.

Rather extensive theoretical studies on NeHF and NeH<sub>2</sub>O are in the literature<sup>26</sup> and these calculations also suggest a specific interaction between the positive end of the polar molecule and the rare gas atom. As a calibration point for our calculations on stronger complexes, we chose to study Ne...HF and to examine the energy components involved in the interaction. The results are summarized in Table II.<sup>27</sup> The total interaction energy is in rather good agreement with the results of Losonczy et al.<sup>26</sup> and give us confidence in our use of a rather limited basis set. As we expect, the electrostatic energy favors a Ne...HF configuration over the Ne...FH. Based on the Ne...Ne dispersion attraction ( $\sim 0.07$  kcal/mol),<sup>28</sup> we expect the Ne...HF dispersion attraction to be  $\sim 0.14$  kcal/mol,<sup>29</sup> but it is unlikely to be directional enough to favor the Ne...FH structure over Ne...HF. The fact that experiments on the

## STRUCTURES CONSIDERED

**Figure 1.** Diatomic structures considered in the geometry searches.**Table III.** Component Analysis of the (H<sub>2</sub>)<sub>2</sub> and (N<sub>2</sub>)<sub>2</sub> Interactions (kcal/mol)

	"P"	"T" <sup>a</sup>	"C"
(H <sub>2</sub> ) <sub>2</sub> Structures			
$\Delta E$	0.014	-0.013	0.002
$\Delta E_{\text{ES}}$	0.005	-0.007	0.008
$\Delta E_{\text{POL}}$	0	0	0
$\Delta E_{\text{CT}}$	-0.005	-0.011	-0.008
$\Delta E_{\text{EX}}$	0.014	0.005	0.002
$R_{\text{min}}$ , Å	(3.5) <sup>b</sup>	3.5	(3.5) <sup>b</sup>
(N <sub>2</sub> ) <sub>2</sub> Structures			
$\Delta E$	0.24	-0.25	0.13
$\Delta E_{\text{ES}}$	0.19	-0.19	0.24
$\Delta E_{\text{POL}}$	0.00	-0.01	-0.01
$\Delta E_{\text{CT}}$	-0.18	-0.18	-0.17
$\Delta E_{\text{EX}}$	0.24	0.13	0.08
$R_{\text{min}}$ , Å	(3.6) <sup>b</sup>	3.6	(3.6) <sup>b</sup>

<sup>a</sup> The "L" structure was higher in energy than the "T" structure and was not a local minimum in the energy surface. <sup>b</sup> No minimum in the surface, so a calculation at this  $R$  is reported for component comparison.

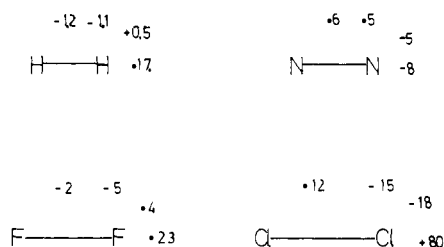
ArHCl complex<sup>24</sup> find that it has an Ar...HCl structure (*not* Ar...ClH) is additional support for this conclusion.

The electrostatic potential at 4 au from Ne (we have used this reference point as a measure of "basicity") is  $< 0.0001$  au; thus, on the scale we developed,<sup>17</sup> the attraction between Ne and HF would be expected to be extremely small, which it appears to be.

A more interesting set of interactions are those involving homonuclear diatomics. Here we study (H<sub>2</sub>)<sub>2</sub>, (N<sub>2</sub>)<sub>2</sub>, (Cl<sub>2</sub>)<sub>2</sub>, and H<sub>2</sub>-N<sub>2</sub>.

For (H<sub>2</sub>)<sub>2</sub>, we have studied four limiting structures: a "T" shaped structure, an "L" structure, a collinear structure (C), and a parallel (P) structure (Figure 1). The interaction between H<sub>2</sub> molecules is very weak and the T-shaped dimer is, as expected from point quadrupole models, the most stable in the SCF calculations (Table III) and the only one bound with respect to two H<sub>2</sub>.<sup>30</sup> The (H<sub>2</sub>)<sub>2</sub> dispersion attraction is of the same magnitude as that of He<sub>2</sub> and it is relatively isotropic, with ratios of 0.96, 0.90, and 1.07 for T, C, and P structures.<sup>28</sup> Thus it is likely that the SCF calculations (and the electrostatic energy) contain the essential features of the directionality of the H<sub>2</sub> interaction. The well depth is so shallow, however, that the complex is very floppy. Kochanski<sup>31</sup> has published a very

## REPRESENTATIVE ELECTROSTATIC POTENTIALS



**Figure 2.** Electrostatic potentials at 5 au in various diatomics. This distance is the distance referred to in the C, LC ( $\theta = 60^\circ$ ), L, and T structures in Figure 1. Units are  $10^4$  au.

**Table IV.** Component Analysis Results for  $(\text{Cl}_2)_2$  (kcal/mol)

	Structure (see Figure 1)				
	C	T	L	LC ( $\theta = 75^\circ$ )	LC ( $\theta = 60^\circ$ )
$\Delta E$	0.09	-0.02	-0.13	-0.19	-0.18
$\Delta E_{\text{ES}}$	0.18	0.05	-0.04	-0.09	-0.07
$\Delta E_{\text{POL}}$	-0.01	0.00	0.00	0.00	0.00
$\Delta E_{\text{CT}}$	-0.15	-0.22	-0.24	-0.25	-0.24
$\Delta E_{\text{EX}}$	0.07	0.15	0.15	0.15	0.13
$R_{\text{min}}, \text{\AA}$	(3.9) <sup>a</sup>	4.0	3.9	3.8	3.8

<sup>a</sup> No minimum energy found for this approach.

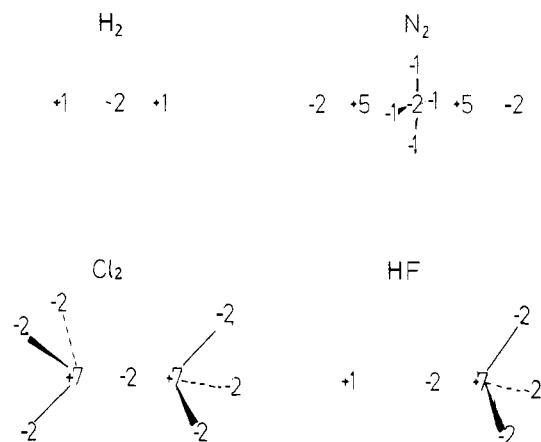
precise (Hartree-Fock plus dispersion) calculation on the interaction of two  $\text{H}_2$  molecules. Dispersion attraction contributes substantially to the absolute binding of  $(\text{H}_2)_2$ , but, as found here, the T structure is clearly the lowest energy structure.

The calculations on the  $\text{N}_2$  dimer (Table III) find it to have a T structure, in essential agreement with experiment. The dispersion attraction for  $(\text{N}_2)_2$ <sup>32</sup> is expected to be  $\sim 0.1$  kcal/mol, with ratios of dispersion energies of 1.02, 1.32, and 0.88 for T, C, and P structures.<sup>28</sup> Thus it is clear that this correction to the SCF calculated surface will not change its qualitative features.

The  $\text{Cl}_2$  dimer is a very interesting case. According to a simple point quadrupole model,<sup>13</sup> all homonuclear dimers should have a T-shaped minimum. This is not the relative orientation found in solid  $\text{Cl}_2$ ,<sup>33</sup> nor is it the one most consistent with the supersonic nozzle beam data.<sup>34</sup> The structure most consistent with this data is an "L" structure. Our SCF calculations find the minimum energy for  $(\text{Cl}_2)_2$  to be close to an L-type structure (Table IV), with the angle between  $\text{Cl}_2$  molecules  $70^\circ$  rather than  $90^\circ$  (this is an "LC" structure, see Figure 1). Again, the dispersion attraction<sup>35</sup> will be maximum for the collinear (C) configuration, but not likely to cause the minimum energy to be the collinear structure. It is likely to decrease the  $\theta$  value between  $\text{Cl}_2$  molecules to  $<70^\circ$ .

How can we rationalize these results. Once again we turn our attention to electrostatic potential maps (Figure 2). As one can see in the figure, the most positive locations of the potential for  $\text{H}_2$  are along the bond axis, the most negative areas are perpendicular to this molecule, bisecting the H-H bond. For  $\text{N}_2$ , the situation is reversed, with the negative potential along the axis and the positive potential perpendicular to the axis. This is consistent with the fact that the quadrupole moment of  $\text{N}_2$  is negative and that of  $\text{H}_2$  positive. However, for both molecules, a T-shaped structure would be predicted, to bring the most positive end of one molecule toward the most negative end of the other.

## MODEL CHARGE DISTRIBUTIONS



**Figure 3.** Model electron distributions which can represent the charge distribution in some of the diatomics.

**Table V.** Results of  $\text{N}_2$ - $\text{H}_2$  Surfaces

	Structure <sup>a</sup>				
	P	P <sub>R</sub>	C	T (X = H)	T (X = N)
$\Delta E$	-0.03	-0.01	-0.15	-0.05	0.08
$\Delta E_{\text{ES}}$	-0.03	-0.01	-0.10	0.04	0.03
$\Delta E_{\text{POL}}$	0.00	0.00	-0.01	0.00	0.00
$\Delta E_{\text{CT}}$	-0.02	-0.02	-0.14	-0.13	-0.03
$\Delta E_{\text{EX}}$	0.02	0.02	0.10	0.04	0.08
$R_{\text{min}}, \text{\AA}$	3.9	3.9	3.2	3.5	(3.5) <sup>b</sup>

<sup>a</sup> See Figure 1; the two T structures are not identical for  $X \neq Y$ .

<sup>b</sup> No minimum found for this structure.

$\text{Cl}_2$ , is, however, different. The most positive potential is along the bond axis. The most negative potential is almost straight above a Cl atom, but inclined at  $\sim 15^\circ$  relative to the axis, almost exactly where one would expect, given the SCF calculated minimum energy structure for  $(\text{Cl}_2)_2$ .

Based on the electrostatic potential,  $(\text{F}_2)_2$  would be expected to have a similar structure to  $(\text{Cl}_2)_2$ , and the SCF calculations by Umeyama and Morokuma<sup>36</sup> do indeed find its minimum to be close to an "L" structure.

How can we rationalize the nature of these electrostatic potentials in terms of the electronic structure of the diatomics?  $\text{H}_2$  has the majority of charge in the bonding area between the hydrogens and relatively little "outside" the hydrogens along the bond axis; thus it has a positive region along the axis and a negative region perpendicular to it.  $\text{N}_2$  has its most negative region in the direction of the lone pairs along the axis; obviously buildup of charge in the  $\pi$  regions is still not sufficient to prevent this region from being relatively electropositive. As one goes from  $\text{N}_2$  to  $\text{F}_2$ , one adds four  $\pi$  electrons into  $\pi^*$  orbitals, which buildup charge on the ends of the  $\pi$  orbitals (at the F), but not in the center. Thus, the most negative region occurs not along the axis bisecting the bond, but on either end.

The take home lesson here is as follows: knowing *sign* and *magnitude* of the quadrupole moment are not sufficient to allow one to predict the directionality of the interaction potential involving that molecule. A *point quadrupole model*<sup>37</sup> is *inadequate*, but a *finite quadrupole model* which reflects the key features of the molecule's charge distribution is *adequate*. We illustrate such models for  $\text{H}_2$ ,  $\text{N}_2$ , and  $\text{Cl}_2$  in Figure 3 ( $\text{F}_2$  would be similar to  $\text{Cl}_2$ ).

In view of the fact that  $(\text{N}_2)_2$  and  $(\text{H}_2)_2$  both have a T structure and these molecules have opposite sign quadrupole

**Table VI.** Counterpoise Correction to N<sub>2</sub>-H<sub>2</sub> Structures (kcal/mol)

Structure	$\Delta E^a$	$\Delta E(\text{corr})^a$
C	-0.15	-0.08
T (X = H)	-0.05	0.00
P	-0.03	0.00
P <sub>R</sub>	-0.01	0.01

<sup>a</sup> At  $R_{\text{min}}$  of Table IV.

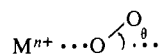
monents, we expected the minimum energy structure of H<sub>2</sub>-N<sub>2</sub> to be collinear (C). Indeed our SCF calculations found this result, as illustrated in Table V. Dispersion energy would be expected to further stabilize the C structure relative to the others.<sup>28</sup>

With this 431G basis, we have found nontrivial (~1 kcal/mol) stabilization for H<sub>2</sub>O when only the orbitals of a second H<sub>2</sub>O<sup>17</sup> are placed at the minimum energy H-bond location. Thus, we tried to correct our H<sub>2</sub>-N<sub>2</sub> surfaces for this effect and the "corrected" interaction energies are presented in Table VI. The magnitude of the interaction energies are changed, but not the fact that the collinear (C) structure is significantly more stable than other structures.

What structure would one predict for N<sub>2</sub>-Cl<sub>2</sub> or H<sub>2</sub>-Cl<sub>2</sub>? In view of the fact that the most positive and negative regions of H<sub>2</sub> and N<sub>2</sub> have similar magnitude electrostatic potentials, but that the positive locations in Cl<sub>2</sub> are much larger in magnitude than the negative, we expect these dimers to have collinear structures as well. Dispersion effects would be expected to reinforce this preference.

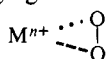
Other diatomics of interest include CO, O<sub>2</sub>, and O<sub>2</sub><sup>-</sup>. Although we have not done any calculations on these molecules in this paper, our previous analysis of N<sub>2</sub>, F<sub>2</sub>, and Cl<sub>2</sub> allows us to note the following: Since CO is isoelectronic to N<sub>2</sub>, it also should have its most negative electrostatic potential along the bond axis. In addition, the most negative potential should be on the carbon end, because the carbon nuclear charge does not "cancel" the negative potential due to the electrons as effectively as does the O nucleus. This is consistent with the calculated interaction geometry of H<sup>+</sup> with CO (C protonation is favored)<sup>38</sup> as well as with the fact that *most* metal complexes have the linear structure M<sup>n+</sup>...C≡O. Back-bonding and charge transfer are clearly of importance in these interactions, but the qualitative structural features appear to be consistent with the predictions of this simple model.

As one adds electrons to N<sub>2</sub> and moves from ten valence electron diatomics to 12 (O<sub>2</sub>), 13 (O<sub>2</sub><sup>-</sup>), and 14 (F<sub>2</sub>, Cl<sub>2</sub>), the most negative location of the electrostatic potential shifts from the bond axis (N<sub>2</sub>) to nearly perpendicular to this axis (F<sub>2</sub>). Thus, one might expect that O<sub>2</sub> and O<sub>2</sub><sup>-</sup> would interact with cations (and metal complexes) in a "nonlinear" fashion, e.g.,



where  $\theta$  is likely to be <75° (the minimum electrostatic potential for F<sub>2</sub>), but >0° (the minimum electrostatic potential for N<sub>2</sub>). Such a structure is apparently the minimum energy for the Fe-O<sub>2</sub> interaction in hemoglobin.<sup>39</sup>

Cotton and Wilkinson<sup>40</sup> cite examples of metal complexes where the oxygen is bridging



and this is not out of line with the observation that for F<sub>2</sub> (Figure 2), the whole "π" region has a negative electrostatic potential. However, we must emphasize caution with respect to such a simple analyses of complex formation, since (O<sub>2</sub>)<sub>2</sub>

**Table VII.** Component Energies for (HF)<sub>2</sub> and (HCl)<sub>2</sub> as a Function of  $\theta$  (kcal/mol)

	$(HF)_2^a$				
	$\theta$				
	0	30	37.5	45	60
$\Delta E$	-7.44	-7.71	-7.79	-7.82	-7.59
$\Delta E_{\text{ES}}$	-8.36	-8.67	-8.76	-8.78	-8.50
$\Delta E_{\text{POL}}$	-0.67	-0.60	-0.56	-0.52	-0.45
$\Delta E_{\text{CT}}$	-2.46	-2.79	-2.95	-3.14	-3.55
$\Delta E_{\text{EX}}$	4.04	4.35	4.48	4.63	4.90

	$(HCl)_2^b$			
	$\theta$			
	45	60	75	90
$\Delta E$	-1.67	-1.95	-2.01	-1.71
$\Delta E_{\text{ES}}$	-1.65	-1.83	-1.75	-1.33
$\Delta E_{\text{POL}}$	-0.10	-0.09	-0.07	-0.05
$\Delta E_{\text{CT}}$	-0.84	-1.08	-1.30	-1.46
$\Delta E_{\text{EX}}$	0.92	1.04	1.11	1.14

<sup>a</sup>  $R(\text{F}\cdots\text{F}) = 2.69 \text{ \AA}$ , FH...F linear; see also ref 15 for a study of this complex. <sup>b</sup>  $R(\text{Cl}\cdots\text{Cl}) = 4.05 \text{ \AA}$ , ClH...Cl linear.

is apparently a P-shaped dimer.<sup>40</sup> This is hard to rationalize from the above unless: (1) specific electron pairing (*covalent*) effects are operative in (O<sub>2</sub>)<sub>2</sub> and overcome the electrostatic energy (which would be expected to favor an L or LC structure), or (2) the electrostatic interaction is so weak (the experimental quadrupole moment of O<sub>2</sub> is only -0.39 B) a P-shaped structure is favored because it minimizes repulsion effects.

Janda et al.<sup>42</sup> have shown that (benzene)<sub>2</sub> is polar, consistent with an important role of quadrupole-quadrupole attractions. It has been pointed out to us that the sign of the quadrupole moment in hexafluorobenzene<sup>43</sup> is opposite to that of benzene, and, thus, one might expect a stacked structure to be most stable for the C<sub>6</sub>H<sub>6</sub>-C<sub>6</sub>F<sub>6</sub> heterodimer. Based on our above analysis, the knowledge of the relative signs of the quadrupole moments<sup>37</sup> may not be sufficient to predict the minimum energy structure; further theoretical work on the charge distribution and electrostatic potential of C<sub>6</sub>F<sub>6</sub> as well as possible experimental studies of the C<sub>6</sub>H<sub>6</sub>-C<sub>6</sub>F<sub>6</sub> complex are probably in order. There is experimental evidence favoring the "stacked" C<sub>6</sub>H<sub>6</sub>-C<sub>6</sub>F<sub>6</sub> "heterodimer" in benzene solution.<sup>44</sup>

**II. Moderate Strength Complexes.** We examine a large number of complexes here, considering H-bonded complexes and non-H-bonded complexes, most of which are in the energy range 1-20 kcal/mol.

(a) **H Bond Directionality.** We and others have been interested in H bond directionality for many years. In an earlier paper in 1972<sup>45</sup> we suggested that the  $\sigma$ - $\pi$  orbital energy differences might hold the key to the charge-transfer energy and the reason that (HF)<sub>2</sub> is not collinear, as a dipole-dipole model would predict. More recently, we noted<sup>17</sup> that at least part of this directionality was evident at the electrostatic level. In fact F. van Duijneveldt pointed out to us that for (HF)<sub>2</sub>, if one considers the electrostatic potential *gradient* rather than just the potential, one predicts a minimum energy angle  $\theta$  quite near that found with the complete SCF calculation. The Morokuma energy decomposition method allows us to evaluate the energy components as a function of  $\theta$  and assess their roles in determining  $\theta$ . The results for (HF)<sub>2</sub> are presented in Table VII.<sup>46</sup> They indicate that, almost exactly, the minimum energy  $\theta$  occurs where predicted by the electrostatic energy alone. The

charge-transfer energy does increase with increasing  $\theta$ , but it is mainly balanced by a nearly corresponding increase in exchange repulsion and a very slight decrease in polarization energy (see also ref 15).

How general is this result? We now consider variations in the dimers  $(\text{HCl})_2$  and  $(\text{H}_2\text{O})_2$ <sup>46</sup> and refer to our earlier study<sup>16</sup> on such a variation for  $\text{HF}\cdots\text{HNNH}_2$  and  $\text{CH}_3\text{F}\cdots\text{HNNH}_2$ .  $(\text{HCl})_2$  has a much larger minimum energy  $\theta$  than  $(\text{HF})_2$  and here we see (Table VII) that the electrostatic energy minimum is at a smaller  $\theta$  ( $65^\circ$ ) than the SCF calculated ( $70^\circ$ ). In this case, the charge-transfer energy does increase the  $\theta$  beyond that predicted by the electrostatic energy, but not by a very large amount (see Note Added in Proof).

In the water dimer Umeyama and Morokuma<sup>15</sup> find the minimum SCF energy ( $\theta = 37^\circ$ ) to be again nearly exactly that predicted by the electrostatic component with the exception of O $\cdots$ O distance variation. Hankins et al.<sup>47</sup> pointed out that their finding of  $\theta \neq 0$  for the water dimer appeared largely due to the tendency to relieve repulsions between the three waters not involved in the hydrogen bond. The configuration with the external proton cis had a far less attractive electrostatic energy.<sup>15</sup> Thus, it appears that this tendency for the proton donor  $\text{H}_2\text{O}$  to keep its external H trans to the proton acceptor H's is at least as important as any intrinsic lone pair directionality. This trans-cis isomerism mainly influences the electrostatic component of the energy.

Finally, we refer to our study of  $\text{CH}_3\text{F}\cdots\text{HNNH}_2$  (C-H in same plane as N-H).<sup>14</sup> Here the minimum energy  $\theta$  is  $70^\circ$ , whereas the minimum in the electrostatic energy is at  $\theta > 90^\circ$ . The increased electrostatic attraction (probably between the N: and the C-H) at  $\theta = 90^\circ$  is compensated for by increased exchange repulsion at this angle.

What do these results tell us about the nature of H bond directionality? In contrast to what we suggested earlier,<sup>45</sup> the key appears to be the electrostatic energy. This energy has its minimum not at  $\theta = 0$  (for HF or HCl as a proton acceptor) as a simple dipole picture would imply, but at  $\theta \neq 0$ . This can be rationalized by noting that a quadrupole-quadrupole interaction model for  $(\text{HF})_2$  favors  $\theta = 90^\circ$  and that the observed minimum is a compromise between the minimum energy favored by dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole interactions.<sup>17</sup> Another way to rationalize it is to use a more realistic (but still simple) model of the charge distribution of HF or HCl (Figure 3). This model reflects the fact that the  $\pi$  electrons are less tightly bound and extend further from the F than the  $\sigma$ ; they are thus in a better position to interact strongly with an approaching proton donor. Even though our earlier analysis was incorrect in its focus on the charge-transfer energy, the use of orbital energy differences as measure of "lone pair" directionality is still useful. Comparing the difference between the highest occupied  $\sigma$  and  $\pi$  orbitals of HF ( $\Delta = 0.107$  au) and HCl ( $\Delta = 0.137$  au), and the difference between the highest occupied  $b_1$  and  $a_1$  orbitals of  $\text{H}_2\text{O}$  ( $\Delta = 0.058$  au), we were able to rationalize the relative directionality<sup>45</sup> of the lone pairs of these proton acceptors. Using HF or HCl as proton donors, because these have no external atom repulsions, we see that  $\text{H}_2\text{O}$  as proton acceptor favors a proton donor approach at a small angles ( $0$ – $10^\circ$ ), HF favors  $\theta \sim 40^\circ$ <sup>48</sup> and HCl and  $\text{H}_2\text{S}$  favor  $\theta = 70^\circ$ . Proton donors with external atoms (e.g., HOH, HNNH<sub>2</sub>, HSH, and HPH<sub>2</sub>) increase the minimum energy  $\theta$  beyond these values because, with external atoms trans, the larger  $\theta$ , the further these atoms are apart, and the smaller the repulsion.

If one considers different acids,  $\text{H}^+$ ,  $\text{Li}^+$ , and HF, approaching HF as the electron donor, as we did previously,<sup>16</sup> we see that the electrostatic potential maps are very useful for understanding the directionality of these interactions.  $\text{H}^+$  approaches within 1 Å of the HF, at which distance the electrostatic potential has a minimum at  $\theta = 45^\circ$ ; this is close to

**Table VIII.** Energy Components for  $\text{HCN}\cdots\text{HF}$  and  $\text{HNC}\cdots\text{HF}$  (kcal/mol)

	$\text{HCN}\cdots\text{HF}^a$	$\text{HNC}\cdots\text{HF}^b$
$\Delta E$	-8.64	-9.29
$\Delta E_{\text{ES}}$	-8.86	-9.38
$\Delta E_{\text{POL}}$	-1.08	-1.64
$\Delta E_{\text{CT}}$	-1.96	-3.76
$\Delta E_{\text{EX}}$	3.27	5.49

<sup>a</sup>  $R(\text{N}\cdots\text{F}) = 2.99$  Å. <sup>b</sup>  $R(\text{C}\cdots\text{F}) = 2.99$  Å.

the SCF calculated minimum energy angle for  $\text{H}_2\text{F}^+$ .  $\text{Li}^+$ , on the other hand, approaches only to 1.75 Å from the F and, at this distance, the electrostatic potential and the SCF energy have their minimum at  $\theta = 0$ . For HF, the minimum energy F $\cdots$ H distance  $R(\text{F}\cdots\text{H}) \sim 1.8$  Å; however, since HF, unlike  $\text{Li}^+$ , is dipolar, we must use the electrostatic potential gradient. Placing a partial plus charge at 1.8 Å to represent the H, and a corresponding partial minus charge at 2.7 Å to represent F, and varying  $\theta$ , one predicts  $\theta \sim 45^\circ$ , near the SCF calculated minimum energy for  $(\text{HF})_2$ .

**(b) The Relative Interaction Energies for  $\text{HCN}\cdots\text{HF}$  and  $\text{HNC}\cdots\text{HF}$ .** One interesting exception to our correlation between electrostatic potential and H bond energy<sup>17</sup> was  $\text{HCN}\cdots\text{HF}$  and  $\text{HNC}\cdots\text{HF}$ . We suggested that the latter complex has a much greater charge-transfer energy to compensate for its less negative electrostatic potential at 4 au from the negative end of the molecule. We used this greater charge-transfer energy to rationalize why  $\Delta E(\text{HNC}\cdots\text{HF})$  is greater than  $\Delta E(\text{HCN}\cdots\text{HF})$ . Again, energy components are an excellent handle on this question and the results are presented in Table VIII. To our surprise, the electrostatic energy is greater for  $\text{HNC}\cdots\text{HF}$ , paralleling the relative total interaction energies. There is greater charge transfer in  $\text{HNC}\cdots\text{HF}$ , as we suggested, but also significantly greater exchange repulsion (recall the way these two components canceled each other out in the analysis of the directionality of  $(\text{HF})_2$ ).

Again, a simple electrostatic model can rationalize these results: Imagine the proton acceptors sitting in the field of HF. For HNC, both N and C are somewhat negative (according to Mulliken populations) and are able to interact attractively with the positive end of HF. On the other hand, in HCN, the carbon is net positive and will interact repulsively with HF. This effect appears to outweigh the fact that HCN causes a slightly greater electrostatic potential at the proton of HF than does HNC (see later discussion in VIb).

**(c) Energy Components for First and Second Row Hydrides.** We applied the Morokuma component analysis to a series of the hydrides we studied earlier<sup>17</sup> in order to look for generalizations about the contributions of each of the components to the H bond energy. We chose HF and HCl as reference proton donors and acceptors and examined the complexes  $\text{HF}\cdots\text{Y}$ ,  $\text{Y}\cdots\text{HF}$ ,  $\text{HCl}\cdots\text{Y}$ , and  $\text{Y}\cdots\text{HCl}$ , where  $\text{Y} = \text{HF}$ ,  $\text{H}_2\text{O}$ ,  $\text{H}_3\text{N}$ ,  $\text{HCl}$ ,  $\text{H}_2\text{S}$ , and  $\text{H}_3\text{P}$ ; the results are presented in Tables IX and X. Umeyama and Morokuma have carried out a similar study for the hydrides HF,  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ , and  $\text{CH}_4$ .<sup>15</sup>

It is clear that the largest source of attraction in all but two cases ( $\text{HCl}\cdots\text{H}_2\text{PH}_2$  and  $\text{HF}\cdots\text{H}_2\text{PH}_2$ ) is electrostatic. In all cases but one ( $\text{HF}\cdots\text{HOH}$  vs.  $\text{HF}\cdots\text{HCl}$ ) the total interaction energy in a given row is in the same order as the electrostatic energy. In most of the very strong complexes, the electrostatic energy is substantially greater than the total interaction energy and there is a large ( $>5$  kcal/mol) exchange repulsion. In many of the weaker complexes, the  $\Delta E_{\text{ES}}$  is almost equal to the total interaction energy. The ratio of the relative attraction due to charge transfer and electrostatic is different depending on the row of the periodic table of the proton donor and acceptor. If both are first row, the average ratio is 0.38. If both are second

**Table IX.** Energy Components for HF...HA and B...HF Interactions (kcal/mol)

	HF...HX <sup>a,b</sup> HA =					
	HF <sup>b</sup>	HOH <sup>b</sup>	HNH <sub>2</sub> <sup>b</sup>	HCl	HSH	HPH <sub>2</sub>
$\Delta E$	-7.82	-5.40	-3.53	-4.47	-2.35	-0.98
$\Delta E_{ES}$	-8.78	-5.49	-2.88	-6.44	-2.26	-0.53
$\Delta E_{POL}$	-0.52	-0.21	-0.08	-0.34	-0.17	-0.05
$\Delta E_{CT}$	-3.14	-2.52	-2.05	-2.82	-1.27	-1.04
$\Delta E_{EX}$	4.63	2.82	1.48	5.13	1.34	0.64
$R, \text{\AA}$	2.69	2.94	3.22	3.37	3.68	4.05
$\theta$	45	60	75	39	55	76

	X...HF <sup>c</sup> B =					
	HF <sup>b</sup>	H <sub>2</sub> O <sup>b</sup>	H <sub>3</sub> N <sup>b</sup>	HCl	H <sub>2</sub> S	H <sub>3</sub> P
$\Delta E$	-7.82	-13.22	-16.29	-3.44	-5.76	-6.90
$\Delta E_{ES}$	-8.78	-16.70	-24.97	-3.17	-5.70	-6.68
$\Delta E_{POL}$	-0.52	-1.31	-1.90	-0.16	-0.32	-0.56
$\Delta E_{CT}$	-3.14	-2.92	-4.58	-1.80	-2.66	-3.27
$\Delta E_{EX}$	4.63	7.71	15.17	1.69	2.92	3.61
$R, \text{\AA}$	2.69	2.69	2.69	3.40	3.40	3.40
$\theta$	45	0	0	71	68	0

<sup>a</sup> All dimer geometries from ref 17; for HF...HSH was incorrect in that reference. <sup>b</sup> See also ref 15 for a study of this complex. <sup>c</sup> All dimer geometries from ref 17 except  $R(F...X)$  standardized for first-row bases ( $R = 2.69 \text{\AA}$ ) and for second ( $R = 3.4 \text{\AA}$ ).

**Table X.** Energy Components for HCl...HA and B...HCl Interactions (kcal/mol)

	HCl...HA HA =					
	HF	HOH	HNH <sub>2</sub>	HCl	HSH	HPH <sub>2</sub>
$\Delta E$	-3.44	-2.48	-1.55	-2.01	-1.10	-0.44
$\Delta E_{ES}$	-3.17	-2.01	-1.07	-1.75	-0.87	-0.23
$\Delta E_{POL}$	-0.16	-0.07	-0.02	-0.07	-0.03	-0.01
$\Delta E_{CT}$	-1.80	-1.25	-0.74	-1.30	-0.73	-0.41
$\Delta E_{EX}$	1.69	0.85	0.28	1.11	0.53	0.22
$R, \text{\AA}^a$	3.42	3.70	4.10	4.05	4.40	4.80
$\theta^a$	71	82	80 <sup>a</sup>	70	75	87

	B...HCl B =					
	HF	H <sub>2</sub> O	H <sub>3</sub> N	HCl	H <sub>2</sub> S	H <sub>3</sub> P
$\Delta E$	-4.47	-8.18	-10.75	-2.01	-3.45	-4.32
$\Delta E_{ES}$	-6.44	-11.70	-17.59	-1.75	-3.09	-3.66
$\Delta E_{POL}$	-0.34	-1.01	-1.66	-0.07	-0.17	-0.28
$\Delta E_{CT}$	-2.82	-3.15	-5.21	-1.30	-2.03	-2.61
$\Delta E_{EX}$	5.13	7.69	13.72	1.11	1.83	2.24
$R, \text{\AA}^a$	3.20	3.20	3.20	4.05	4.05	4.05
$\theta^a$	39	13	0	70	71	0

<sup>a</sup> Note that there is an error for HCl...HNH<sub>2</sub> in ref 17; otherwise these values are from this reference, except for our choosing a constant  $R$  for B...HCl where B = base from a given row.

row, the average ratio is 0.95; if the proton donor is first row and the proton acceptor second, the ratio is 0.57; and finally, if the proton acceptor is first row and the proton donor second, the ratio is 0.71. This confirms our suggestion<sup>45</sup> that charge-transfer effects are relatively more important for the second row than the first. This fact was also rationalized by Allen.<sup>49</sup> We have carried out a statistical analysis on these 20 hydride H bonds to see which energy component is best correlated with the total interaction energy  $\Delta E$ . The correlation coefficient ( $r^2$ ) for  $\Delta E_{ES}$  is 0.96, for  $\Delta E_{POL} = 0.90$ ,  $\Delta E_{CT} = 0.76$ , and  $\Delta E_{EX} = 0.84$ ,  $r^2$  for  $\Delta E_{ES} + \Delta E_{EX} = 0.98$ . Thus, the energy component which most closely parallels  $\Delta E$  is  $\Delta E_{ES}$ .

As has been noted before,<sup>17</sup> for a given proton donor, when one changes the proton acceptor, the minimum energy X...Y distance stays the same (for a given row of the periodic table). That is why we used the same  $R(F...B)$  distance in our comparison of the energy components for H<sub>3</sub>N...HF, H<sub>2</sub>O...HF, and HF...HF. We now carried out a more limited comparison with a given proton acceptor (HF) and considering different proton donor (HF, HOH, HOH<sub>2</sub>) at the same  $R$  ( $R = 2.94 \text{\AA}$ ), even though this is not the minimum energy  $R$ . (Since Umeyama and Morokuma<sup>15</sup> carried out a more extensive comparison and analysis of the energy components in hydride H bond at fixed  $R$ , we refer the reader to their Table XVII.

Table XI. Energy Components for (LiF)<sub>2</sub>, (HF)<sub>2</sub>, and LiF-HF (kcal/mol)

	(LiF) <sub>2</sub> <sup>a</sup>		(HF) <sub>2</sub> <sup>b</sup>	
	Linear <sup>c</sup>	Cyclic <sup>d</sup>	Linear <sup>e</sup>	Cyclic <sup>f</sup>
$\Delta E$	-45.34	-62.42	-7.82	-6.86
$\Delta E_{ES}$	-46.28	-85.02	-8.78	-6.66
$\Delta E_{POL}$	-3.24	-7.07	-0.52	-0.28
$\Delta E_{CT}$	-8.11	-18.34	-3.14	-3.48
$\Delta E_{EX}$	-12.29	-48.01	4.63	3.55

	LiF...HF <sup>g</sup>		HF...LiF <sup>h</sup>		
	$\theta = 0$	$\theta = 30^\circ$	$\theta = 0$	$\theta = 30^\circ$	$\theta = 45^\circ$
$\Delta E$	-22.02	-21.58	-19.50	-19.33	-18.80
$\Delta E_{ES}$	-28.23	-26.61	-17.83	-18.22	-18.20
$\Delta E_{POL}$	-2.19	-2.06	-2.49	-2.18	-1.85
$\Delta E_{CT}$	-8.17	-9.89	-3.87	-4.09	-4.40
$\Delta E_{EX}$	16.57	16.98	4.68	5.15	5.65

<sup>a</sup> See also ref 15, Table XX; these authors evaluated the energy components for the  $D_{2h}$  structure of the dimer, whereas we forced rigid monomer geometries ( $C_{2h}$  symmetry) on the molecule. <sup>b</sup> See also ref 15, Table XX. <sup>c</sup>  $R(F\cdots F)_{\min} = 3.28 \text{ \AA}$ ;  $\theta_{\min} = 0$ . <sup>d</sup>  $R(F\cdots F)_{\min} = 2.22 \text{ \AA}$ ;  $\theta_{\min} = 52^\circ$ . <sup>e</sup>  $R(F\cdots F)_{\min} = 2.69 \text{ \AA}$ ;  $\theta_{\min} = 42^\circ$ . <sup>f</sup>  $R(F\cdots F)_{\min} = 2.55 \text{ \AA}$ ;  $\theta_{\min} = 55^\circ$ . <sup>g</sup>  $R(F\cdots F)_{\min} = 2.44 \text{ \AA}$ ;  $\theta_{\min} = 0$ . <sup>h</sup>  $R(F\cdots F)_{\min} = 3.44 \text{ \AA}$ ;  $\theta_{\min} = 0$ .

## GEOMETRIES OF XF DIMERS

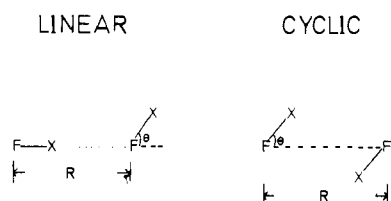


Figure 4. Parameters optimized in XF dimers.

Their choice of  $R$  was slightly different than ours; the relative energy components are nearly identical.) At this  $R$ , which is optimum for HFHOH, the order of interaction energies is similar to that found with minimum energy geometries, but the polarization plus charge-transfer energies are nearly identical for all three (in fact,  $\Delta E_{CT} + \Delta E_{POL}$  is largest for the weakest interaction). This is in line with our previous suggestion, based on Mulliken population changes, that for a fixed proton acceptor and  $R(A\cdots B)$ , the charge redistribution effects (polarization plus charge transfer) were insensitive to proton donor.<sup>17</sup> The key component in determining proton donor strength with a fixed acceptor at a fixed  $R$  is clearly the exchange repulsion, with  $\Delta E_{ES}$  also significant. This is consistent with a simple picture of the proton donor: H—A. The more ionic this bond (the closer the electron pair to A) the less exchange repulsion a base feels on approaching H and the greater the B...H attraction. This relates nicely to the "bond dipole" analysis by Allen.<sup>49</sup> On the other hand, changing the proton acceptor with a given proton donor (see B...HF interactions in Table IX) has a very large effect on the charge redistribution energies.

**(d) Relative Energies of Linear and Cyclic Structures of Dipolar Molecules.** Another question in which we have had previous interest is why (LiF)<sub>2</sub> and other alkali halides have a minimum energy cyclic geometry and (HF)<sub>2</sub> and other hydride dimers have a minimum energy linear geometry ( $\theta$  not necessarily = 0, but with the A—H bond pointing directly at the proton acceptor B).<sup>50</sup> We hoped that energy components would shed some light on this so we optimized the energy for linear and cyclic geometries (Figure 4) of (LiF)<sub>2</sub> and the cyclic geometry of (HF)<sub>2</sub> and also examined some structures of HFLiF and LiFHF. These results are summarized in Table XI. Comparing (LiF)<sub>2</sub> and (HF)<sub>2</sub>, we see that the minimum energy

geometry in both cases ((LiF)<sub>2</sub> cyclic and (HF)<sub>2</sub> linear,  $\theta = 45^\circ$ ) is that in which the electrostatic energy is lower.<sup>51</sup>

Umeyama and Morokuma<sup>15</sup> have independently compared the energy components for linear and cyclic (HF)<sub>2</sub> and (LiF)<sub>2</sub> and noted that the minimum energy structure of each is that which optimizes the electrostatic energy.

We thus decided to carry out some very simple model calculations just using an atom-centered partial charge representation of the monomers (LiF and HF). Varying the monomer bond distance and dipole, we found that for a given  $R(F\cdots F)$  the linear structure<sup>51</sup> was always favored. However, if one now includes repulsion in a hard-sphere manner,  $R(F-F) < 3.0 \text{ \AA}$  is excluded for the linear structure, but the cyclic structure allows shorter F—F distances and thus the cyclic geometry can be lower in energy than the linear (Table XII).

These results stimulated us to study by SCF calculations the cyclic LiF dimer at the minimum energy  $R(F\cdots F)$  found for the linear structure. Sure enough, at this distance ( $R(F\cdots F) = 3.2 \text{ \AA}$ ), the electrostatic energy ( $-39 \text{ kcal/mol}$ ) and total interaction energy ( $-44.5$ ) were higher than that found for the linear structure.

Reversing the situation and studying (HF)<sub>2</sub> at  $R(F\cdots F)$  much less than optimum for both cyclic and linear dimers (we chose  $R(F\cdots F) = 2.2 \text{ \AA}$ , since this is the minimum energy  $R(F\cdots F)$  in cyclic (LiF)<sub>2</sub>), led to the result that the electrostatic energy was lower for the linear structure ( $\Delta E_{ES} = -15.89$  (linear),  $-13.23$  (cyclic)) as expected from our electrostatic model calculations, but the total interaction energy is lower for the cyclic structure ( $-2.94 \text{ kcal/mol}$ ) than the linear ( $0.34 \text{ kcal/mol}$ ) due to less exchange repulsion.

At the equivalent F...F distance ( $R = 2.2 \text{ \AA}$ ) the electrostatic energy for (HF)<sub>2</sub> is far less attractive than that for (LiF)<sub>2</sub>. Thus our explanation for the difference between (HF)<sub>2</sub> and (LiF)<sub>2</sub> is as follows: LiF dimer involves sufficient electrostatic attraction that, in the cyclic dimer, the two monomers are able to penetrate to a far smaller F...F distance than that predicted from van der Waals radii. In (HF)<sub>2</sub>, the electrostatic energy is insufficient to allow such a penetration.

An interesting side point emerges from our study of the LiF...HF and HF...LiF linear dimers. The LiF...HF dimer has its minimum energy and minimum electrostatic energy at  $\theta = 0$ ; for the HF...LiF dimer, the electrostatic energy is lower at  $\theta = 30^\circ$  than  $\theta = 0$ , but the total interaction energy (due to less exchange repulsion and more polarization) is minimum at  $\theta = 0$ . This is further strong evidence that it is the Lewis base



**Table XII.** Simple Partial Charge Energies of Linear vs. Cyclic Structures (kcal/mol)

HF <sup>a</sup>			LiF <sup>a</sup>		
R	Linear	Cyclic	R	Linear	Cyclic
1.9	-16.6	-10.3 (45) <sup>c</sup>	2.3	<i>d</i>	-150 (15) <sup>c</sup>
2.2	-10.0	-5.9 (52)	2.8	<i>d</i>	-55 (35)
2.6	-5.7	-3.2 (56)	3.3	-43	-27 (45)
3.6	-2.1	-1.1 (70)	4.3	-17	-10 (55)

<sup>a</sup> Atom-centered partial charges chosen to reproduce experimental HF (or LiF) dipole moments; bond distance of monomer used is the experimental value; results are insensitive to use of 431G calculated dipole moment. <sup>b</sup>  $R = R(\text{F-F})$ , Å. <sup>c</sup> Optimized cyclic  $\theta$  at given  $R$  in parentheses. <sup>d</sup>  $R(\text{F}\cdots\text{Li}) < R(\text{Li-F})$  in monomeric LiF.

**Table XIII.** Interaction Energies and Geometries of Complexes of LiF, HF, and ClF<sup>a</sup>

Base	HF		LiF		ClF	
	R	$-\Delta E$	R	$-\Delta E$	R	$-\Delta E$
H <sub>3</sub> N	2.67	16.2	2.03	30.5	2.7	8.0
(CH <sub>3</sub> ) <sub>3</sub> N	2.70	1.58	(2.03) <sup>b</sup>	29.7		
H <sub>2</sub> NCHO	2.73	13.0	1.82	30.6	(2.7) <sup>c</sup>	5.9

<sup>a</sup> Minimized with respect to  $R$  ( $\theta$  chosen from H<sub>2</sub>CO for formamide). <sup>b</sup> Not optimized. <sup>c</sup> Not optimized because  $R(\text{Cl}\cdots\text{N}) \approx R(\text{Cl}\cdots\text{F})$  from FCINH<sub>3</sub> and FCIFH complexes; thus  $R(\text{Cl}\cdots\text{O})$  would be expected to be the same.

which is crucial in determining the directionality of the electrostatic energy in these interactions. The electrostatic energy in HF $\cdots$ LiF reflects the fact that the optimum direction for a dipole to approach HF is  $\theta \neq 0$ , even for a molecular as dipolar as LiF ( $\mu = 6.5$  D); for LiF as Lewis base, the F is much more like F<sup>-</sup> and less "directional" and  $\theta = 0$  is favored. Even though the other energy components still cause  $\theta = 0$  to be the optimum total interaction energy in HFLiF, the overall potential is far flatter for increasing  $\theta$  than the corresponding potential in LiF $\cdots$ HF (see Note Added in Proof).

On the basis of the above reasoning, we would generalize as follows: dimers involving monomers with small bond dipoles, such as the set of hydrides mentioned above and such non-H-bonded complexes as (ClF)<sub>2</sub> should have minimum energy linear structures; molecules with much larger dipole moments, such as alkali halides and hydrides,<sup>52</sup> should have minimum energy cyclic structures. Umeyama and Morokuma<sup>15</sup> came to similar conclusions on why (LiF)<sub>2</sub> was cyclic and (HF)<sub>2</sub> linear.

We decided to test this hypothesis theoretically for ClF dimer. The minimum energy linear structure has  $R(\text{F}\cdots\text{F}) = 4.5$  Å,  $\theta = 45^\circ$ , and  $-\Delta E = 1.9$  kcal/mol; the minimum energy cyclic structure had  $R(\text{F}\cdots\text{F}) = 4.4$  Å,  $\theta = 60^\circ$ , and  $-\Delta E = 0.4$  kcal/mol. This prediction would be easy to test experimentally by supersonic nozzle beam techniques.<sup>23-25</sup>

(e) **HF, LiF, and ClF as Lewis Acids.** We have noted<sup>16</sup> that one of the interesting differences between H<sup>+</sup> and HF as Lewis acids and Li<sup>+</sup> as a Lewis acid are that the former two are stronger acids toward amines than amides; whereas, the Li<sup>+</sup> is a stronger acid toward amides than amines. We showed this was due to differences in exchange repulsion.<sup>16</sup> We now attempt to extend this generalization to LiF as a Lewis acid. As one can see from Table XIII, the B $\cdots$ LiF distance is shorter for amides than amines and, as we expect from our previous studies,<sup>16</sup> LiF interacts more strongly with amides than amines.

What do we expect for ClF acting as Lewis acid? In view of our results for FCl $\cdots$ NH<sub>3</sub> and FCl $\cdots$ FH surfaces, which showed (see below) almost identical  $R(\text{Cl}\cdots\text{B})$  minimum energy distances, we expect  $R(\text{Cl}\cdots\text{O}=\text{C})$  for the FCl $\cdots$ formamide interaction to be similar to  $R(\text{Cl}\cdots\text{N})$  and  $R(\text{Cl}\cdots\text{F})$  and this in-

**Table XIV.** Energy Components of H<sub>2</sub>O $\cdots$ CO<sub>2</sub> Interactions

	H <sub>2</sub> O $\cdots$ CO <sub>2</sub>	OCO $\cdots$ HOH
	( $R = 2.65$ Å)	( $R = 3.1$ Å, $\theta = 15^\circ$ )
$\Delta E$	-5.62	-3.04
$\Delta E_{\text{ES}}$	-7.82	-3.65
$\Delta E_{\text{POL}}$	-0.51	-0.32
$\Delta E_{\text{CT}}$	-1.09	-0.98
$\Delta E_{\text{EX}}$	3.79	1.91

teraction to be significantly weaker than the FCl $\cdots$ NH<sub>3</sub> interaction. This is the case, as we can see in Table XIV.

Thus, of the three Lewis acids, HF, LiF, and ClF, LiF is the "odd" one (with respect to relative acidity toward amines and amides). Our interpretation of this is as follows: a base approaching LiF is able to penetrate quite close to the LiF, since the "first" exchange repulsion it encounters is the Li inner shell. Both HF and ClF have valence electron pairs located on the X-F bond which interact strongly with the approaching base and which are the crucial factors in determining the amount of exchange repulsions and the minimum energy  $R$ .

(f) **H Bond Structure vs. Non-H-Bond Structure.** In a further attempt to ascertain what makes the H bond unique, we decided to examine complexes where there is an opportunity to form an H bond, but a different structure is preferred.

There are two such examples which have received recent attention. Jonsson et al.<sup>53</sup> studied CO<sub>2</sub> $\cdots$ H<sub>2</sub>O with ab initio calculations and found the non-H-bonded structure H<sub>2</sub>O $\cdots$ CO<sub>2</sub> more stable than the H-bonded HOH $\cdots$ OCO. Klemperer and co-workers<sup>54</sup> have characterized the ClFHF complex as "anti-H-bonded" HF $\cdots$ ClF rather than H-bonded ClF $\cdots$ HF.

We repeated Jonsson's search using the 431G basis in order to ascertain which energy component was the dominant one in determining the minimum energy structure. Table XIV clearly shows that the greater electrostatic energy in the H<sub>2</sub>O $\cdots$ CO<sub>2</sub> structure is key.

In ClF $\cdots$ HF, we found to our surprise that the H-bonded structure was calculated to be somewhat more stable ( $-\Delta E(\text{FHFC}) = 4.62$  kcal/mol;  $-\Delta E(\text{HFCIF}) = 3.36$  kcal/mol), inconsistent with Klemperer's experiments. Again,

H<sub>3</sub>N—SO<sub>2</sub> STRUCTUREFigure 5. Description of angle  $\theta$  in H<sub>3</sub>N...SO<sub>2</sub>.

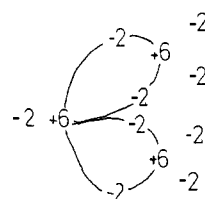
Table XV. Product of Electrostatic Potentials

X	Product $\times 10^6$ (HX...ClF) <sup>a</sup>	Product $\times 10^6$ (ClF...HX) <sup>a</sup>
F	-936	-924
OH	-1534	-620
NH <sub>2</sub>	-1950	-357
Cl	-416	-714
SH	-676	-399
PH <sub>2</sub>	-754	-105

<sup>a</sup> Reference electrostatic potential of Lewis acid times reference electrostatic potential of Lewis base.

however, the more stable structure has the lower electrostatic energy. During the course of this study, we learned that Umeyama and Morokuma<sup>36</sup> had studied the FCl...HF surface at both 431G and 431G\*\* levels. They found similar results to ours at the 431G level, but the extended basis (431G\*\*) suggested the ClF...HF to be less stable than HF...ClF by 0.1 kcal/mol. It is clear that within the accuracy of the best calculations, the two structures are close in energy. We thus asked ourselves: How surprising is it that the FCl...HF complex has the anti-H-bonded structure? Both Lucchese and Schaefer<sup>55</sup> and Umeyama and Morokuma<sup>36</sup> have studied FCINH<sub>3</sub> theoretically, *but only* the anti-H-bonded structure H<sub>3</sub>N...ClF, not the H-bonded structure ClF...HNH<sub>2</sub>. Their choice was reasonable, since NH<sub>3</sub> is such a good base and poor acid. We carried out a 431G potential surface for FCl...NH<sub>3</sub> ( $\Delta E = -8.01$  kcal/mol) and H<sub>2</sub>NH...FCl ( $\Delta E = -1.76$  kcal/mol) varying the A...B distance and, for H<sub>2</sub>NH...FCl, the NFCl angles. Once again the lower energy structure has the more negative  $\Delta E_{ES}$ . It is clear that FCl...NH<sub>3</sub> should have an anti-H-bonded structure.

Is there any way to generalize these results to other Lewis acids and bases? We have proposed a method,<sup>17</sup> which, when given the electrostatic potential at reference points near a molecule, will allow one to predict the relative ability of this molecule to function as a proton donor and acceptor. We also derived least-squares equations which best fit the data for proton donation to a reference base (NH<sub>3</sub>) and proton acceptance from a reference acid (HF). Later in the same article we pointed out that if one assumes that the H bond energy is some product function of proton donor ability and proton acceptor ability, one could use these electrostatic potential values to *order* relative complex forming energies, and, given one absolute energy, could predict the remaining. We would now like to apply this method to FCl; the only problem is how to choose the reference point at which the electrostatic potential should be chosen. We chose the reference points for proton donors A-H at approximately the position that a typical base atom would be located (2 Å) in its minimum energy geometry. Since for both FCl...FH and FCl...NH<sub>3</sub> the minimum energy Cl...B distance is  $\sim 2.7$  Å, we used this reference point from the Cl, at which the electrostatic potential was 0.026 au. The electrostatic potential at 2.12 Å from F (our previous reference point for first row Lewis bases) was -0.021 au. Note how well the electrostatic potential predicts that ClF is a significantly weaker Lewis base than HF; the potential near the F of HF is

SO<sub>2</sub> CHARGE MODELFigure 6. Model SO<sub>2</sub> electron distribution.Table XVI. Energy Components for H<sub>3</sub>N...SO<sub>2</sub><sup>a</sup> Interaction (kcal/mol)

	$\theta$			
	60°	75°	90°	120°
$\Delta E$	-8.96	-11.38	-11.36	-3.61
$\Delta E_{ES}$	-17.18	-18.58	-19.52	-19.94
$\Delta E_{POL}$	-1.80	-1.90	-1.87	-1.37
$\Delta E_{CT}$	-6.94	-5.21	-4.47	-2.19
$\Delta E_{EX}$	15.16	14.31	14.50	19.89

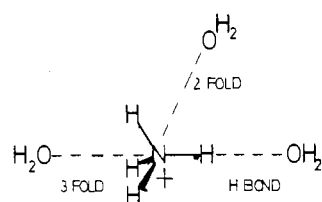
<sup>a</sup>  $R(N...S) = 2.7$  Å.

-0.036; these relative potentials compare well with the predicted relative interaction energies with HF as Lewis acid ( $\Delta E(\text{HF}...HF) = -7.8$  kcal/mol;  $\Delta E(\text{ClF}...HF) = -4.6$  kcal/mol).

Our simple analysis assumes that the relative energies of ClF...HX and HX...ClF should be related to the product of the reference electrostatic potentials. Table XV presents the values of these products for X = F, OH, NH<sub>2</sub>, Cl, SH, and PH<sub>2</sub>. The fact that the anti-H-bonded structure is clearly favored for ClF interacting with all but HF and HCl is noteworthy. The fact that HF slightly favors anti-H-bond structure is fortuitously in agreement with the most accurate calculations and experimental observations, since the 431G calculations suggested the opposite order. However, HCl is predicted to be the only hydride which should hydrogen bond to FCl. We hope this prediction will be tested experimentally.

A final non-H-bonded complex recently studied by Lucchese and Schaefer is H<sub>3</sub>N...SO<sub>2</sub>.<sup>56</sup> Once again, only the anti-H-bonded geometry, H<sub>3</sub>N...SO<sub>2</sub>, was studied and it is clear from an examination of the electrostatic potential at 2.7 Å from the S (0.038 au) and 4 au from the O (-0.040 au), that this structure would be favored over the H-bonded H<sub>2</sub>NH...OSO with the relative  $\Delta E$ 's in the ratio  $[0.038 \times (-0.075)]/[0.017 \times (-0.040)]$ . This complex is especially intriguing, because the minimum in the geometry occurs with the SO<sub>2</sub> axis almost perpendicular ( $\theta = 83^\circ$ ) (see Figure 5) to the threefold axis of NH<sub>3</sub>. The most positive electrostatic potential for SO<sub>2</sub> at 2.7 Å from S occurs at 75° off the C<sub>2v</sub> axis, nearly  $\perp$  to the molecular plane, and, as one can see from the energy component analysis (Table XVI), the electrostatic energy has its minimum in  $\theta$  rather close to the actual minimum energy geometry. This is one of the most dramatic examples which demonstrates that: (1) the minimum in the surface is close to that predicted by the electrostatic energy; (2) this minimum is very far from what a dipole-dipole calculation would predict; rather a more sophisticated picture of the charge distribution (see Figure 6 for such a distribution for SO<sub>2</sub>) can qualitatively rationalize the observed results.

We now examine whether CO<sub>2</sub> or SO<sub>2</sub> (discussed above) would be expected to form an H bond with any of the six hydrides we have analyzed with FCl. The reference electrostatic potentials for CO<sub>2</sub> are -0.024 au (4 au from O) and 0.020 au (5 au = 2.65 Å from C, roughly where the water O sites in the minimum energy geometry of H<sub>2</sub>O...CO<sub>2</sub>. Constructing a table

NH<sub>4</sub><sup>+</sup>–H<sub>2</sub>O STRUCTURESFigure 7. Structures considered for NH<sub>4</sub><sup>+</sup>...OH<sub>2</sub>.Table XVII. Product of Electrostatic Potentials for HX...CO<sub>2</sub> and HX...SO<sub>2</sub> Interactions

HX	Product × 10 <sup>6</sup>			
	OCO...HX	HX...CO <sub>2</sub>	OSO...HX	HX...SO <sub>2</sub>
HF	-1056	-720	-1760	-1368
H <sub>2</sub> O	-936	-1180	-1200	-2242
NH <sub>3</sub>	-408	-1500	-680	-2850
HCl	-816	-320	-1360	-608
H <sub>2</sub> S	-456	-520	-760	-988
H <sub>3</sub> P	-120	-580	-200	-1102

Table XVIII. Energy Components for Li<sup>+</sup>...OH<sub>2</sub> and Be<sup>2+</sup>...OH<sub>2</sub>

	Li <sup>+</sup> ...OH <sub>2</sub> (R = 1.80 Å) <sup>a</sup>	Be <sup>2+</sup> ...OH <sub>2</sub> (R = 1.59 Å) <sup>b</sup>
	ΔE	-47.89
ΔE <sub>ES</sub>	-51.13	-124.91
ΔE <sub>POL</sub>	-7.75	-44.73
ΔE <sub>CT</sub>	-1.73	-2.49
ΔE <sub>EX</sub>	12.72	28.43

<sup>a</sup> R = R(Li-O) minimum energy, θ = 0; see also ref 58. <sup>b</sup> R = R(Be-O) minimum energy, θ = 0.

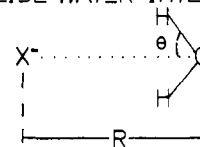
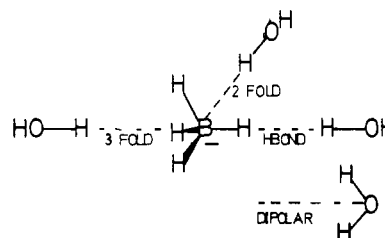
such as Table XVI for HX...CO<sub>2</sub> vs. OCO...HX and HX...SO<sub>2</sub> vs. OSO...HX is now trivial (Table XVII). The results for CO<sub>2</sub> are consistent with our and Jonsson et al.'s<sup>53</sup> calculations; many of the remaining entries are predictions we hope will be tested.

**III. Strong Complexes. (a) Cation-Neutral Complexes.** We present results for Li<sup>+</sup>...OH<sub>2</sub> and Be<sup>2+</sup>...OH<sub>2</sub> surfaces<sup>57</sup> in Table XVIII. The surfaces indicate that the major contribution to these interactions in the electrostatic and that the total energy minimizes at the θ = 0, C<sub>2v</sub> geometry expected from simple electrostatic considerations. This has been previously found by Noell and Morokuma.<sup>58</sup>

We also decided to examine Be<sup>2+</sup> interacting with NH<sub>3</sub>, trimethylamine, and formamide; we wished to see if it, like Li<sup>+</sup>, would interact more strongly with amides.<sup>16</sup> This turned out to be the case, and, similar to the result for Li<sup>+</sup>-base interactions, the Be<sup>2+</sup>-formamide minimum energy distance is significantly shorter than the Be<sup>2+</sup>-NH<sub>3</sub> minimum energy distance. The interaction energy (-ΔE) for the Be<sup>2+</sup>-amide interaction is greater in magnitude than for Be<sup>2+</sup>-NH<sub>3</sub>, due to the fact that the exchange repulsion is smaller in this case (Table XIX).

NH<sub>4</sub><sup>+</sup>...OH<sub>2</sub> is a more complex case; one could imagine that the OH<sub>2</sub> could approach directly toward a proton (onfold), toward a twofold axis of NH<sub>4</sub><sup>+</sup>, or toward a threefold axis (Figure 7). The results, presented in Table XX, indicate the significant preference for the onfold approach (moving the water hydrogens so that the NH...OH<sub>2</sub> group has C<sub>s</sub> rather than C<sub>2v</sub> symmetry results in an increase in energy) as reflected in the electrostatic energy as well. (See also the studies by Pullman on NH<sub>3</sub><sup>+</sup> solvation.<sup>59</sup>)

## HALIDE-WATER INTERACTIONS

Figure 8. Parameters optimized in X<sup>-</sup>...HOH interaction.BH<sub>4</sub><sup>-</sup>–H<sub>2</sub>O STRUCTURESFigure 9. Structures considered for BH<sub>4</sub><sup>-</sup>...OH<sub>2</sub>.Table XIX. Energy Components for Be<sup>2+</sup>-Base Interactions (kcal/mol)

	Base		
	NH <sub>3</sub>	N(CH <sub>3</sub> ) <sub>3</sub>	H <sub>2</sub> NCHO
ΔE	-164	-191	-197
ΔE <sub>ES</sub>	-158	-138	-130
ΔE <sub>POL</sub>	-49	-110	-119
ΔE <sub>CT</sub>	-5	8	16
ΔE <sub>EX</sub>	48	48	35
R <sub>min</sub> , Å	1.64	(1.64) <sup>a</sup>	1.48

<sup>a</sup> R not optimized.

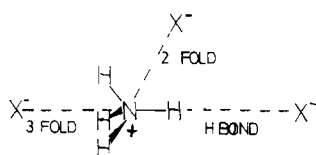
Table XX. Energy Components for NH<sub>4</sub><sup>+</sup>...OH<sub>2</sub> Structures (kcal/mol)

	Structure		
	H bond	Twofold	Threefold
ΔE	-27.3	-21.8	-20.4
ΔE <sub>ES</sub>	-34.1	-24.9	-21.8
ΔE <sub>POL</sub>	-4.1	-2.0	-1.7
ΔE <sub>CT</sub>	-5.0	-1.5	-1.2
ΔE <sub>EX</sub>	5.9	6.6	4.3
R(N...O) <sub>min</sub> , Å <sup>a</sup>	2.68	2.69	2.65

<sup>a</sup> Minimum energy N...O distance.

**(b) Anion-Neutral Complexes.** We have earlier pointed out<sup>60</sup> that a simple atom-centered electrostatic model could rationalize the fact that both F<sup>-</sup>...HOH and Cl<sup>-</sup>...HOH have C<sub>s</sub> symmetry with θ ≠ 0 and for the Cl<sup>-</sup>...HOH complex θ is significantly larger than that for F<sup>-</sup>...HOH. We have thus examined the F<sup>-</sup> and Cl<sup>-</sup>...HOH interactions as a function of θ (Figure 8) employing energy component analysis (Table XXI). As one can see, the minimum energy occurs near the minimum in the electrostatic energy.

Again BH<sub>4</sub><sup>-</sup>...H<sub>2</sub>O is more complex case; we have considered six approaches: the water can approach toward a B-H bond, toward the twofold axis, and along a threefold axis; the water geometry is either O-H pointing in, or dipolar (Figure 9, Table XXII). The energy component calculations show that the lowest energy is the one with the lowest ΔE<sub>ES</sub>. For the O-H approach, exchange repulsion plays an important role.

NH<sub>4</sub><sup>+</sup>...X<sup>-</sup> STRUCTURESFigure 10. Structures considered for NH<sub>4</sub><sup>+</sup>...F<sup>-</sup> and NH<sub>4</sub><sup>+</sup>...Cl<sup>-</sup>.Table XXI. Energy Component Calculations for X<sup>-</sup>...H<sub>2</sub>O as a Function of  $\theta$  (Figure 8) (kcal/mol)

	F <sup>-</sup> ...H <sub>2</sub> O ( $R = 2.48 \text{ \AA}$ )		
	$\theta$		
	0°	7°	14°
$\Delta E$	-39.33	-40.12	-39.75
$\Delta E_{ES}$	-36.98	-37.82	-37.20
$\Delta E_{POL}$	-5.15	-4.92	-4.51
$\Delta E_{CT}$	-18.09	-17.85	-17.00
$\Delta E_{EX}$	20.89	20.48	18.95
	Cl <sup>-</sup> ...H <sub>2</sub> O ( $R = 3.15 \text{ \AA}$ )		
	$\theta$		
	14°	20°	26°
$\Delta E$	-21.00	-21.00	-20.79
$\Delta E_{ES}$	-19.37	-19.38	-19.18
$\Delta E_{POL}$	-1.83	-1.67	-1.49
$\Delta E_{CT}$	-7.07	-6.68	-6.22
$\Delta E_{EX}$	7.28	6.73	6.10

(c) **Cation-Anion Interactions.** For NH<sub>4</sub><sup>+</sup>...F<sup>-</sup> and NH<sub>4</sub><sup>+</sup>...Cl<sup>-</sup> interactions, one could imagine three reasonable approaches (Figure 10), as indicated in Table XXIII, the anion approach directly toward a hydrogen is the lowest energy and has the lowest electrostatic energy.

**IV. Many-Body Interactions.** The above analysis so far has only focused on two-body interactions; now we attempt to understand many-body effects with the energy component analysis. We consider (H<sub>2</sub>O)<sub>3</sub>, Li<sup>+</sup>(OH<sub>2</sub>)<sub>2</sub>, and F<sup>-</sup>(H<sub>2</sub>O)<sub>2</sub> in various geometries.

The three structures of the water trimer (Figure 11) were first clearly analyzed by Hankins et al.,<sup>47</sup> the nonadditivity of the sequential trimer found to be "attractive" and the nonadditivity of the double donor or double acceptor repulsive. We have earlier suggested, on the basis of comparisons of the electrostatic potential of H<sub>2</sub>O and (H<sub>2</sub>O)<sub>2</sub> that the relative nonadditivities could be understood at the electrostatic level.<sup>17</sup> For example, in

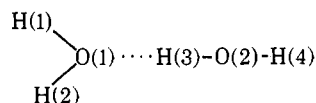


Figure 11. Structures of water clusters considered in this study.

Table XXII. Energy Components for BH<sub>4</sub><sup>-</sup>...H<sub>2</sub>O Interactions (kcal/mol)

	Structure		
	H bond	Twofold	Threefold
OH <sup>-</sup> ... Approach			
$\Delta E$	-7.27	-12.29	-11.86
$\Delta E_{ES}$	-19.69	-12.46	-10.85
$\Delta E_{POL}$	-5.64	-1.52	-1.46
$\Delta E_{CT}$	-3.70	-2.54	-1.50
$\Delta E_{EX}$	-21.77	4.22	1.96
$R(B-O)_{min}$	4.1	3.5	3.4
Approach			
$\Delta E$	-9.40	-20.38	-14.26
$\Delta E_{ES}$	-19.22	-21.77	-13.39
$\Delta E_{POL}$	-2.68	-1.69	-0.79
$\Delta E_{CT}$	-0.82	-1.20	-1.47
$\Delta E_{EX}$	13.31	4.29	1.40
$R(B-O)_{min}$	3.8	3.2	3.4

<sup>a</sup> See Figure 9 for structures.

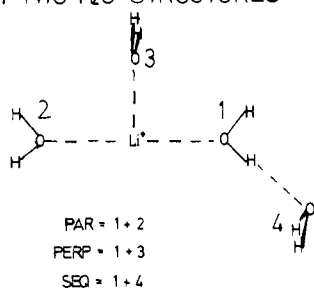
Table XXIII. Energy Components for NH<sub>4</sub><sup>+</sup>...X<sup>-</sup> Interactions (kcal/mol)<sup>a</sup>

	Structure		
	H bond	Twofold	Threefold
X = F			
$\Delta E$	-163.37	-145.3	-143.0
$\Delta E_{ES}$	-18.4	-147.4	-142.7
$\Delta E_{POL}$	-8.3	-4.17	-3.7
$\Delta E_{CT}$	-35.6	-15.9	-13.7
$\Delta E_{EX}$	61.6	22.2	17.0
$R_{min}, \text{ \AA}$	2.30	2.25	2.20
X = Cl			
$\Delta E$	-124.3	-116.8	-116.0
$\Delta E_{ES}$	-125.6	-121.0	-120.0
$\Delta E_{POL}$	-4.0	-2.7	-2.4
$\Delta E_{CT}$	-19.4	-10.2	-8.8
$\Delta E_{EX}$	24.6	17.1	15.3
$R_{min}, \text{ \AA}$	2.88	2.77	2.74

<sup>a</sup> See Figure 10 for structures.

the electrostatic potential near H(1) and H(2) is more positive than that in H<sub>2</sub>O monomer and that near H(4) less positive. That is why the sequential trimer, where the third water acts as a proton acceptor and approaches H(1) or H(2), is more stable than the double donor trimer, where the third water (a proton acceptor) approaches H(4). We thus examined energy components for the nonadditivity effects and these are presented in Table XXIV (Figure 10). Note that we have already subtracted all effects due to two-body interactions and are only considering the three-body (nonadditivity) effects.<sup>61</sup> As one can see, the *nonadditivities* are qualitatively explicable at the

electrostatic level, although there are important contributions from all components for the double proton donor and an important contribution from charge transfer for the double proton acceptor. The latter effect is quite reasonable, since the central water is less capable of transferring charge to a second water if it is already functioning as an electron donor to one. We can imagine forming a sequential trimer in two ways: (a) bringing

Li<sup>+</sup>-TWO H<sub>2</sub>O STRUCTURESFigure 12. Structures of Li<sup>+</sup>(H<sub>2</sub>O)<sub>2</sub> clusters considered in this study.Table XXIV. Nonadditivities of Water Trimers<sup>a</sup> (kcal/mol)

	Double donor	Double acceptor	Sequential <sup>b</sup>	Sequential <sup>c</sup>
$\Delta E$	0.99	0.99	-1.50	-1.14
$\Delta E_{ES}$	0.22	0.45	-0.84	-0.73
$\Delta E_{POL}$	0.25	0.05	-0.24	-0.09
$\Delta E_{CT}$	0.13	0.52	0.25	-0.75
$\Delta E_{EX}$	0.39	-0.01	-0.67	0.43

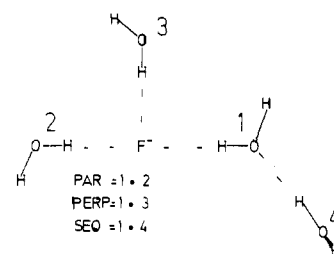
<sup>a</sup> See Figure 11; for the waters donating a proton to the central water,  $\theta = 54.73^\circ$ ; for the waters functioning as proton acceptor  $\theta = 37^\circ$ ;  $R(O\cdots O) = 2.85 \text{ \AA}$  in all cases. <sup>b</sup> Adding a proton acceptor water to H(1) (see text). <sup>c</sup> Adding a proton donor water to O(2) (see text); these two sequential geometries differ slightly, thus their  $\Delta E$ 's are different.

a proton-acceptor water up to H(1) or H(2) or (b) bringing a proton donor up to O<sub>2</sub>. Although both ways of looking at it give similar (attractive) nonadditivities and electrostatic contributions to the nonadditivity, in possibility (a), there is a large *decrease* in exchange repulsion, due to the H(1)-O(1) bond having its electron pair pushed further toward the O; in possibility (b) there is a large increase in charge-transfer attraction, because O<sub>2</sub> is much more electron rich when H(3)-O(2)-H(4) acts as a proton donor to H(1)-O(1)-H(2) than when isolated. These effects are also explicable using the model developed by Allen,<sup>49</sup> whose focus is on the ionization potential of the electron donor and the bond dipole of the proton acceptor.

For Li<sup>+</sup>(OH<sub>2</sub>)<sub>2</sub> (Figure 12) and F<sup>-</sup>(OH<sub>2</sub>)<sub>2</sub> (Figure 13) (Table XXV) we considered three types of structures: Perpendicular ( $\perp$ ), parallel ( $\parallel$ ) and sequential (S).

The sequential structures we examined were similar to that for (H<sub>2</sub>O)<sub>3</sub>, with a central water functioning as a proton donor (to F<sup>-</sup> or to H<sub>2</sub>O) and an electron donor (to H<sub>2</sub>O or to Li<sup>+</sup>). In each case, we examined the nonadditivity for coordinating a second water to the ion-water complex. In each case, the electrostatic nonadditivity was an important contribution (Table XXV). In analogy with the two sequential (H<sub>2</sub>O)<sub>3</sub> cases discussed above, when the second coordination sphere H<sub>2</sub>O approached a lone pair of the inner shell water (F<sup>-</sup> $\cdots$ H<sub>2</sub>O $\cdots$ HOH), there was a substantial charge-transfer contribution to the nonadditivity. When the second coordination sphere water approached an O-H bond of the inner shell water (Li<sup>+</sup> $\cdots$ OH<sub>2</sub> $\cdots$ OH<sub>2</sub>), there was a substantial (decrease in) exchange repulsion contribution to the nonadditivity.

The nonadditivities for  $\perp$  and  $\parallel$  structures are not only quite different for F<sup>-</sup>(H<sub>2</sub>O)<sub>2</sub> than for Li<sup>+</sup>(H<sub>2</sub>O)<sub>2</sub>, but the angular dependence ( $\perp$  vs.  $\parallel$ ) is very different. We have earlier suggested<sup>57</sup> that there must be an important contribution of the nonadditivity of the exchange repulsion to explain the difference in the nonadditivities of Li<sup>+</sup>(H<sub>2</sub>O)<sub>2</sub> and Li<sup>+</sup>(H<sub>2</sub>O)<sub>2</sub> $\perp$ . Exchange repulsion does indeed turn out to be the single largest contributor to this difference, with a significant contribution from polarization as well. The F<sup>-</sup>(H<sub>2</sub>O)<sub>2</sub> nonadditivities are

F<sup>-</sup>-TWO H<sub>2</sub>O STRUCTURESFigure 13. Structures of F<sup>-</sup>(H<sub>2</sub>O)<sub>2</sub> clusters considered in this study.Table XXV. Nonadditivities of Li<sup>+</sup>(H<sub>2</sub>O)<sub>2</sub> and F<sup>-</sup>(H<sub>2</sub>O)<sub>2</sub><sup>a</sup>

	Perpendicular	Parallel	Sequential
Li <sup>+</sup> (H <sub>2</sub> O) <sub>2</sub>			
$\Delta E$	5.88	2.54	-3.96
$\Delta E_{ES}$	1.14	1.18	-1.94
$\Delta E_{POL}$	2.45	1.37	-0.72
$\Delta E_{CT}$	0.79	0.24	0.05
$\Delta E_{EX}$	1.50	-0.25	-1.35
F <sup>-</sup> (H <sub>2</sub> O) <sub>2</sub>			
$\Delta E$	7.95	8.04	-4.39
$\Delta E_{ES}$	2.50	4.04	-2.06
$\Delta E_{POL}$	2.09	1.03	-0.85
$\Delta E_{CT}$	3.41	3.95	-1.95
$\Delta E_{EX}$	-0.05	-0.98	0.47

<sup>a</sup> F<sup>-</sup> $\cdots$ HOH kept at  $R(F\cdots O) = 2.48 \text{ \AA}$ ,  $\theta = 0^\circ$ . Li<sup>+</sup> $\cdots$ OH<sub>2</sub>, C<sub>2v</sub> structure,  $R(Li\cdots O) = 1.80 \text{ \AA}$ , sequential water at optimum location for water dimer  $R(O\cdots O) = 2.85 \text{ \AA}$ ,  $\theta = 37^\circ$ .

much larger than those for Li<sup>+</sup>(H<sub>2</sub>O)<sub>2</sub>, and there are important contributions to this difference in both electrostatic and charge-transfer components. The most intriguing fact here is the surprising angular *independence* of the nonadditivity of F<sup>-</sup>(H<sub>2</sub>O)<sub>2</sub>, with the nonadditivity for the  $\perp$  structure similar to that for the  $\parallel$  structure. As one can see, the *greater repulsive* nonadditivity contributions of the electrostatic component to the  $\parallel$  structure is by far the largest contributor to making the total nonadditivity for the  $\parallel$  structure almost as great as that for the  $\perp$  structure. Again, we can rationalize this with a model picture of the F<sup>-</sup> $\cdots$ HOH charge distribution.

F<sup>-</sup> has a triply degenerate highest occupied orbital, but the approaching O-H bond lowers the energy of and removes electron density from the orbital  $\parallel$  to the F<sup>-</sup> $\cdots$ OH bond. The remaining orbitals to the axis are less affected and thus considering only electrostatic effects, a second water will prefer to approach  $\perp$  to the first. By comparing the electrostatic potential (4 au from F<sup>-</sup>) surrounding F<sup>-</sup> and HOH $\cdots$ F<sup>-</sup> (along  $\perp$  (-0.221) and  $\parallel$  (-0.231) to the OH $\cdots$ F<sup>-</sup> axis), we can rationalize that: (1) a second water sees a less negative potential than the first when approaching F<sup>-</sup>; and (2) the second H<sub>2</sub>O would prefer (just considering HOH $\cdots$ F<sup>-</sup> electrostatic attraction) to approach *perpendicular* to the OH $\cdots$ F<sup>-</sup> axis.

**V. Open Shell-Closed Shell Complexes.** Relatively few open shell-closed shell complexes have been studied by theoretical methods. Two theoretical studies of open shell-closed shell complexes are of special interest here.

Noble and Korzeborn<sup>62</sup> studied the F $\cdots$ HF potential surface. They found that bringing a linear F-H toward a F atom was repulsive in a  $^2\Sigma$  state, but attractive ( $\Delta E = -1.5 \text{ kcal/mol}$ ) for the  $^2\Pi$  state. This is rationalized if we evaluate the electrostatic potential for the F atom forcing the unpaired electron to be localized in one of the p orbitals. In the  $^2\Sigma$  state of FH $\cdots$ F, the F-H approaches the "positive" side of the F atom; in the

Table XXVI. Electrostatic Potential near Li and F

Li		F (singly occupied p <sub>z</sub> )			
X <sup>a</sup>	ESPOT <sup>b</sup>	X <sup>a</sup>	ESPOT <sup>b</sup>	Z <sup>a</sup>	ESPOT <sup>b</sup>
3.0	0.069	3.0	-0.0107	3.0	0.0232
3.5	0.041	3.5	-0.0071	3.5	0.0144
3.78	0.031	4.0	-0.0048	4.0	0.0096
4.0	0.024	4.5	-0.0034	4.5	0.0068
4.5	0.014	5.0	-0.0025	5.0	0.0049
5.0	0.008	5.5	-0.0019	5.5	0.0037
5.5	0.005	6.0	-0.0014	6.0	0.0028
6.0	0.003				

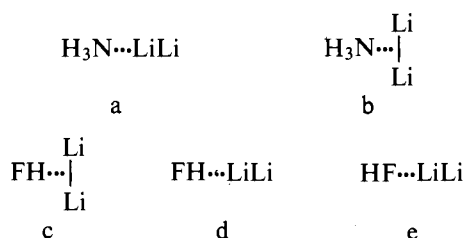
<sup>a</sup> Distance from atom in atomic units; X refers to X axis, Z refers to Z axis. <sup>b</sup> Electrostatic potential at that point in atomic units.

<sup>2</sup>Π state, the F-H approaches the "negative" side (Table XXVI).

Nicely and Dye<sup>63</sup> studied Li...NH<sub>3</sub> and found a surprisingly strong attraction ( $\Delta E = -15$  to  $-20$  kcal/mol, depending on basis set). We decided to evaluate the electrostatic potential as a function of distance from the Li atom (Table XXVI). At 2 Å (roughly the minimum in the Li...NH<sub>3</sub> surface), the electrostatic potential is (0.031 au) of the same order of magnitude as the electrostatic potential 2 Å from the proton of HF (0.044; see Table VI of ref 17). Although it is likely that polarization and charge transfer will contribute substantially to this attraction, it is worth comparing this Li electrostatic potential at 2 Å with the corresponding potential for Ne (<0.0001) or H (0.005)

The fact that the potentials are significantly smaller for F than Li can partially rationalize the much greater strength of the Li...NH<sub>3</sub> than the F...HF (<sup>2</sup>Π) interaction. It also rationalizes the weak attraction found in the F...NH<sub>3</sub> (<sup>2</sup>A) interaction.<sup>64</sup> However, the Li...NH<sub>3</sub> interaction is ~15 times stronger than the F...HF (<sup>2</sup>Π), whereas the magnitude of the electrostatic potential for Li is only ~5 times that of F (along the direction of the doubly occupied orbital).

In view of the fact that we do not yet have the capability of carrying out Morokuma component analyses for open shell systems, we decided to analyze the properties of intermolecular interactions involving Li<sub>2</sub>. Our reason for choosing this model system is as follows: Unlike Li...NH<sub>3</sub>, H...NH<sub>3</sub> has no energy minimum in its ground state surface,<sup>65</sup> leading us to conclude that the much greater polarizability of Li than H (~21 vs. 0.5 Å<sup>3</sup>)<sup>66</sup> could play a role in its unusual properties. Li<sub>2</sub> has a polarizability approximately equal to that of two Li atoms<sup>67</sup> and thus has this "unusual" property. We evaluated the electrostatic potential near Li<sub>2</sub> along the bond axis and perpendicular to it. We then carried out ab initio calculations on the following potential surfaces:



in each case varying the intermolecular separation, and, in the HF...Li<sub>2</sub> complex, the HF...Li<sub>2</sub> angle. The results of these calculations are summarized in Table XXVII. They suggest that even though the high polarizability of Li<sub>2</sub> is very important in these interactions, electrostatics is at least as important, since those structures which have a repulsive (positive) electrostatic energy (structures b and d) have no minima in their

Table XXVII. Li<sub>2</sub> Properties and Interactions

R <sup>b</sup>	Electrostatic Potential <sup>a,b,c</sup>	
	Along bond axis	⊥ to center of bond
3.5	0.072	-0.020
4.25	0.045	-0.023
5.0	0.030	-0.020

ΔE	Energy Components for Interactions <sup>d</sup>				
	-25.0	1.1	-15.0	3.4	-3.2
ΔE <sub>ES</sub>	-41.8	0.9	-23.4	4.3	-4.7
ΔE <sub>POL</sub>	-28.5	-0.7	-21.0	-2.2	-2.7
ΔE <sub>CT</sub>	19.4	-1.7	10.9	-0.3	-1.2
ΔE <sub>EX</sub>	25.9	2.6	18.5	1.6	5.4
R <sub>min</sub> , Å	2.0	(4.0) <sup>e</sup>	1.8	(2.7) <sup>e</sup>	2.8

<sup>a</sup> See Figure 1 and 2. <sup>b</sup> In atomic units. <sup>c</sup> Quadrupole moment calculated =  $13.0 \times 10^{26}$  esu Å<sup>2</sup>; recommended value =  $13.8 \times 10^{26}$  esu Å<sup>2</sup> (see ref 38). <sup>d</sup> In each case, R is the distance indicated by the dotted lines in the figures. <sup>e</sup> No energy minimum found for this approach. <sup>f</sup>  $\theta_{\min} = 45^\circ$ .

potential surface. By comparing the electrostatic potentials for Li and Li-Li (along bond axis), we deduce that the electrostatic energy term plays a larger role in the diatomic interactions, but should play a nonnegligible role in the atom as well. This "electrostatic" Li-NH<sub>3</sub> attraction would not show up in a multiple expansion, but would be a "penetration" term, with the NH<sub>3</sub> lone pair penetrating near the Li nucleus and "feeling" a rather large amount of unshielded nuclear charge.

**VI. A Simple Approach to Noncovalent Complexes.** What we attempt to do in this section is to suggest an extension of our approach<sup>17</sup> for hydrogen bonding that can qualitatively predict the strength, geometry, and spectroscopic properties of noncovalent complexes prior to explicit calculations or experiments. We have used some of these ideas previously in this manuscript (e.g., in our prediction of the interaction energies of FCl...HX complexes).

(a) **Structure and Energetics of Complexes.** Earlier<sup>17</sup> we found that the interaction energy ( $\Delta E$  in kcal/mol) of proton donors with H<sub>3</sub>N as base was related to the electrostatic potential (in au) near the proton (POTA) by

$$-\Delta E = 325 \times (\text{POTA}) \quad (1)$$

Using HF as a proton donor, we found that the interaction energy ( $\Delta E$ ) HF...electron donor interactions are fit well with the equation

$$-\Delta E = -201 \times (\text{POTB}) \quad (2)$$

where POTB is the electrostatic potential near the Lewis base. Now combining these two equations and making use of the fact that the H<sub>3</sub>N...HF interaction has a  $-\Delta E$  of 16.3 kcal/mol, we derive

$$-\Delta E = -4020 \times (\text{POTA}) \times (\text{POTB}) \quad (3)$$

We now attempt to determine if this equation is general for the noncovalent interactions involving Lewis acids and bases considered in sections I-III; it has been "derived" originally from H bond surfaces.

As test cases, we use (Cl<sub>2</sub>)<sub>2</sub>, CO<sub>2</sub>...H<sub>2</sub>O, SO<sub>2</sub>...NH<sub>3</sub>, Li<sup>+</sup>...OH<sub>2</sub>, F<sup>-</sup>...H<sub>2</sub>O, NH<sub>4</sub><sup>+</sup>...F<sup>-</sup>, and F...HF (<sup>2</sup>Π). This list contains examples of the various types of complex mentioned in previous sections. In Table XXVIII, one can see that eq 3 is rather successful in predicting the interaction energies of a wide variety of complexes. Only for (Cl<sub>2</sub>)<sub>2</sub> is the percent error more than 25%.

Thus, we feel this approach has clear promise of being predictive. For example, using POTB for NH<sub>3</sub> and POTA for Cl<sub>2</sub>,

**Table XXVIII.** Comparison of Predictions of Equation 3 and 431G Calculations

Complex <sup>a</sup>	POTA <sup>a</sup>	POTB <sup>a</sup>	$-\Delta E$ (eq 3) <sup>b</sup>	$-\Delta E$ (431G) <sup>b</sup>
(Cl <sub>2</sub> ) <sub>2</sub>	0.008	-0.002	-0.1	-0.2
O <sub>2</sub> C...OH <sub>2</sub>	0.020	-0.059	-4.7	-5.6
H <sub>3</sub> N...SO <sub>2</sub>	0.038	-0.075	-11.5	-11.4
F...H <sub>2</sub> O	0.030	-0.250	-30.2	-39.3
Li <sup>+</sup> ...OH <sub>2</sub> <sup>d</sup>	0.265	-0.059	-62.9	-47.2
H <sub>4</sub> N <sup>+</sup> ...F <sup>-</sup>	0.185	-0.250	-186	-163
F...HF (2II)	0.044	-0.005	-0.9	-1.2 <sup>e</sup>

<sup>a</sup> In atomic units. <sup>b</sup> In kcal/mol. <sup>c</sup> Considered just minimum energy geometry of complex, as discussed in text. For example, for O<sub>2</sub>C...OH<sub>2</sub>, this is the approach with the water O approaching the CO<sub>2</sub> carbon. For F...H<sub>2</sub>O, used  $\theta = 0$  geometry. <sup>d</sup> Used reference potential at 2 Å from Li<sup>+</sup>. <sup>e</sup> Estimated from tabulated results in ref 62.

we predict an interaction energy of -2.4 kcal/mol for H<sub>3</sub>N...Cl<sub>2</sub>; this is close to the value found by Lucchese and Schaefer (-2.38) using a double  $\zeta$  basis.<sup>55</sup>

Let us briefly summarize how this approach can be used with molecules not discussed here or in ref 17: (1) Evaluate the electrostatic potential surrounding the molecule. In the negative regions evaluate the potential 4 au from first-row basis (Li-Ne) and 5 au from second-row bases (Na-Ar). Use the angular variable which gives the most negative electrostatic potential at that distance. For electrophiles, use the same procedure, except a reference distance of 2 Å for H bonding protons and 5 au (2.7 Å) for both first and second row electrophiles (recall we found a very similar minimum energy distance for S<sup>+</sup>...X<sup>-</sup> in O<sub>2</sub>S...NH<sub>3</sub> and C<sup>+</sup>...X<sup>-</sup> in O<sub>2</sub>C...OH<sub>2</sub>; thus our choice of a similar reference position for first and second row electrophiles seems justified). (2) Use the reference potentials in the negative and positive regions of various molecules to determine the energies (eq 3) and structures (recall, for example, our comparison of  $\Delta E(\text{CO}_2\cdots\text{H}_2\text{O})$  and  $\Delta E(\text{O}_2\text{C}\cdots\text{OH}_2)$  in Table VII) of noncovalent complexes.

**(b) Choice of Reference Point for Electrostatic Potential or Electrostatic Potential Gradient.** Up to now (here and in ref 17) we have used a particular choice of points to evaluate and compare the electrostatic potential for different molecules. We now attempt to show that the qualitative analysis we have described in section a is not very sensitive to the choice of reference potential. For some of the Lewis bases we have previously discussed, we evaluated the electrostatic potential throughout the lone pair region. In Table XXIX, we compare the electrostatic potential at a number of locations as well as evaluating the electrostatic potential gradient at our previously defined reference position. As noted before, the electrostatic potential gradient should be a more precise estimate of the relative strengths of interaction of bases with *dipolar* Lewis (B... $\delta^+$ HX $\delta^-$ ). The reason for this is that the H interacts attractively with the electrostatic potential of B, but X interacts repulsively. Thus, the larger the electrostatic potential gradient the greater the differential interaction of B with H and X.

It is clear from Tables XXIX and XXX that in comparing the electrostatic potential of a number of bases, the relative magnitudes are insensitive to whether one uses the minimum ESPOT values, the ESPOT at the appropriate van der Waals radii, or the ESPOT at the reference points we described in a. However, the ESPOT gradient, unlike ESPOT, does successfully rationalize the fact that for (HF)<sub>2</sub>,  $\theta \neq 0$ . In addition (see Table XXX), the ESPOT gradient correctly orders the relative energies of HCN...HF and HNC...HF, consistent with the discussion earlier in this paper. H<sub>2</sub>CO...HF is still out of line relative to HCN...HF and HNC...HF, but this is due to our choice of a fixed *R* (for a given row) to compare the gra-

**Table XXIX.** Some Representative Electrostatic Potentials and Electrostatic Potential Gradients for Lewis Bases (in atomic units)

Molecule	Angle <sup>a</sup>	ESPOT (min) <sup>b</sup>	ESPOT (van der Waals) <sup>c</sup>	ESPOT (ref) <sup>d</sup>	ESPOT gradient (ref) <sup>e</sup>	
H <sub>3</sub> N	0	-0.176	-0.140	-0.075	0.0287	
	H <sub>2</sub> O	0	-0.137	-0.110	-0.059	0.0204
		30	-0.135	-0.107	-0.056	0.0200
		45	-0.130	-0.101	-0.052	0.0191
		60	-0.115	-0.091	-0.045	0.0176
HF	75	-0.095	-0.076	-0.036	0.0149	
	0	-0.067	-0.064	-0.036	0.0108	
	30	-0.071	-0.067	-0.035	0.0109	
	45	-0.073	-0.068	-0.033	0.0108	
	60	-0.070	-0.064	-0.028	0.0101	
H <sub>3</sub> P	75	-0.059	-0.057	-0.022	0.0085	
	0	-0.060	-0.057	-0.029	0.0105	
	H <sub>2</sub> S	0	-0.037	-0.037	-0.023	0.0066
		30	-0.044	-0.044	-0.025	0.0077
		60	-0.055	-0.051	-0.026	0.0091
75		-0.052	-0.048	-0.023	0.0086	
HCl	90	-0.038	-0.037	-0.017	0.0061	
	0	-0.013	-0.007	-0.012	0.0019	
	30	-0.018	-0.015	-0.014	0.0031	
	60	-0.029	-0.027	-0.016	0.0049	
	75	-0.028	-0.026	-0.014	0.0049	
90	-0.020	-0.018	-0.009	0.0037		

<sup>a</sup> The angle relative to the dipolar axis where the electrostatic potential or gradient was evaluated. <sup>b</sup> The electrostatic potential minimum for a given base (and given angle) (in atomic units). <sup>c</sup> The electrostatic potential at the appropriate van der Waals radius (for HF, 1.35; H<sub>2</sub>O, 1.40; H<sub>3</sub>N, 1.50; HCl, 1.80; H<sub>2</sub>S, 1.85; H<sub>3</sub>P, 1.90 Å). <sup>d</sup> The electrostatic potential at the reference position we previously chose<sup>17</sup> (2.12 Å for N, O, and F and 2.65 Å for Cl, S, and P). <sup>e</sup> The electrostatic potential *gradient* at the reference position. Evaluated for a finite dipole of length 1 au extending from the reference position to the reference position plus 1 au.

**Table XXX.** Comparison of Relative Electrostatic Potentials Gradients and Interaction Energies for Some Lewis Bases

Base	ESPOT (ref) <sup>a</sup>	ESPOT gradient (ref) <sup>b</sup>	$\Delta E(\text{Base}\cdots\text{HF})$ <sup>d</sup>
H <sub>3</sub> N	1.000	1.000	1.000
H <sub>2</sub> O	0.787	0.711	0.822
HCN	0.667	0.564	0.546
H <sub>2</sub> CO	0.653 (0.750) <sup>c</sup>	0.543 (0.662)	0.613
HNC	0.627	0.582	0.571
HF	0.480	0.383	0.479
H <sub>3</sub> P	0.386	0.366	0.423
H <sub>2</sub> S	0.346	0.317	0.356
H <sub>2</sub> CS	0.320	0.300	0.374
HCl	0.213	0.177	0.209
HCP	0.053	0.045	0.129

<sup>a</sup> Relative magnitude of electrostatic potential at reference position<sup>17</sup> and at optimum  $\theta$  (in atomic units). <sup>b</sup> Relative magnitude of electrostatic potential gradient at reference position at optimum  $\theta$  (in atomic units). <sup>c</sup> ESPOT or ESPOT gradient for H<sub>2</sub>CO at 0.93 of reference distance; see text for explanation of this choice of distance. <sup>d</sup> Relative interaction energies of bases with HF; see ref 17.

dients. If one corrects for the difference in calculated minimum energy *R* (see parentheses in Table XXX) H<sub>2</sub>CO...HF is correctly "predicted" to have a more negative  $\Delta E$  than HCN...HF or HNC...HF.

The only ordering not correctly predicted by the ESPOT gradient is H<sub>2</sub>S...HF vs. H<sub>2</sub>CS...HF. We thus carried out component analysis calculations on H<sub>2</sub>CS...HF and

**Table XXXI.** Energy Components for H<sub>2</sub>CS...HF and H<sub>2</sub>CO...HF Interactions

	H <sub>2</sub> CS...HF <sup>a</sup>	H <sub>2</sub> CO...HF <sup>b</sup>
$\Delta E$	-6.33	-9.94
$\Delta E_{ES}$	-5.45	-12.09
$\Delta E_{POL}$	-0.50	-1.39
$\Delta E_{CT}$	-3.26	-2.85
$\Delta E_{EX}$	2.89	6.39

<sup>a</sup>  $R = 3.40$ ,  $\theta = 68^\circ$ ; ref 17 incorrectly had  $\Delta E = -6.1$  kcal/mol.

<sup>b</sup>  $R = 2.73$ ,  $\theta = 40^\circ$ .

H<sub>2</sub>CO...HF and these are presented in Table XXXI. The electrostatic energy is indeed less negative for H<sub>2</sub>CS...HF than H<sub>2</sub>S...HF, and the greater  $-\Delta E$  is mainly due to the greater charge-transfer energy in H<sub>2</sub>CS...HF than H<sub>2</sub>S...HF. One is tempted to relate this to the less bound HOMO of H<sub>2</sub>CS (-0.345 au) compared to H<sub>2</sub>S (-0.383 au), but the same relative HOMO relation holds for H<sub>2</sub>CO (-0.439 au) and H<sub>2</sub>O (-0.500 au), where the charge-transfer energies for interaction with HF are nearly identical. This is another example where charge-transfer effects appear to be relatively more important for second than first row electron donors.

A similar comparison of choices of ESPOT and ESPOT gradient for the proton donors previously discussed (ref 17, Table VI) also indicates that the relative ranking of these Lewis acids is not particularly sensitive to choice of reference point (Table XXXII). The prediction of relative acid strength toward NH<sub>3</sub> is quite good, with the exception of HCN and HCF<sub>3</sub>, which are predicted (via ESPOT) to be significantly better Lewis acids than the  $\Delta E$  indicates. This is not surprising in view of our previous discussion on the importance of exchange repulsion in determining Lewis acidity. Umeyama and Morokuma<sup>15</sup> found that this term (along with the electrostatic) was by far the biggest factor in why CH<sub>4</sub> was a much weaker Lewis acid than the other first-row hydrides.

**(c) A Qualitative Approach to Analyzing the Structure and Energetics of Noncovalent Complexes.** How does one derive the electrostatic potentials for new molecules? If we carry out a 431G ab initio calculations on these molecules, one can use eq 3 directly. For other basis sets, one can recalculate the numerical term in eq 3 by evaluating the electrostatic potential for one reference acid (HF) and base (NH<sub>3</sub>) with that basis set. However, if one wants to use eq 3 in a general way, one would like to avoid the use of detailed calculations and be able to evaluate the potentials at trivial cost. Earlier in this paper, we suggested a way to do just that: determine a simple electron distribution for the molecule, using nuclei and electron pairs such as described in Figures 3 and 6, use experimental properties such as dipole and higher moments to locate electron pairs, then use these charge distributions to evaluate the electrostatic potential at the reference points. Such charge distributions, in addition to exchange repulsion and dispersion terms, have been extensively used in studies of the properties of amide crystals and water liquid. What our results suggest is that such charge distributions can be employed to evaluate the electrostatic potentials. One can then use these electrostatic potentials to analyze the directionality of noncovalent interactions of such a molecule and, with some experimental or accurate ab initio  $\Delta E$ 's, to develop an equation like 3 suitable for qualitative predictions of interaction energies. We are currently working on an appropriate and general "recipe" for charge placement, using van der Waals radii, electronegativity, and dipole moments to locate the charges. The preliminary results are encouraging. The electrostatic properties predicted from such charge distributions closely parallel those of Tables XXIX and XXX. The purpose of such an analysis is to be able

**Table XXXII.** Comparison of Electrostatic Potentials, Potential Gradients, and Interaction Energies for Some Lewis Acids

Lewis acid (A)	ESPOT (van der Waals) <sup>a</sup>	ESPOT (ref) <sup>b</sup>	ESPOT gradient (ref) <sup>c</sup>	$-\Delta E$ - (H <sub>3</sub> N...A) <sup>d</sup>
FH	0.103	0.044	-0.0147	16.3
HOH	0.076	0.030	-0.0103	8.9
H <sub>2</sub> NH	0.054	0.017	-0.0063	4.3
ClH	0.085	0.034	-0.0109	10.8
HSH	0.050	0.019	-0.0060	4.4
H <sub>2</sub> PH	0.022	0.005	-0.0014	1.2
NCH	0.090	0.039	-0.0123	9.7
CNH	0.096	0.038	-0.0134	13.1
PCH	0.054	0.019	-0.0070	4.6
H <sub>3</sub> CH	0.018	0.003	-0.0015	1.1
F <sub>3</sub> CH	0.077	0.036	-0.0104	7.6

<sup>a</sup> Electrostatic potential along A-H line at 1.2 Å from proton. <sup>b</sup> Electrostatic potential along A-H line at 2 Å from proton. <sup>c</sup> Electrostatic potential gradient at 2 Å from proton using reference position and reference plus 1 au. <sup>d</sup> Interaction energy of H<sub>3</sub>N with the different Lewis acids.

to develop an equation (eq 3) for all types of chemical structures; i.e., to predict the directionality and relative strengths of noncovalent interactions. Such a charge distribution would not have the capability of predicting the complete structure of noncovalent complexes without inclusion of repulsive terms.

The energy component calculations presented by Umeyama and Morokuma<sup>11,14,15</sup> and here can be useful in the construction of electrostatic plus repulsion plus dispersion empirical potential functions. As suggested above, if the electrostatic term contains the correct "directionality" of the total interaction energy, then the exchange repulsion and dispersion should be relatively nondirectional. If charge transfer is not included in the empirical functions, then the magnitude of the exchange repulsion can be decreased or the electrostatic term increased to compensate for it. Since charge transfer has a distance dependence closer to that of the exchange repulsion, the former choice appears to be more logical.

What simple qualitative picture of the structure and energies of noncovalent complexes emerges from the component analyses calculations discussed here and by Umeyama and Morokuma?<sup>11,14,15</sup> Up to this point, we have focused on electrostatic properties and have been able to elucidate *energies* and *directionality* of noncovalent complexes. To rationalize the minimum energy distance between molecules, we must consider exchange repulsion. We have earlier noted, that for H bonds AH...B, the minimum energy A...B distance  $R$  is mainly a function of A-H; for a given A-H and B = first row (N, O, F), all complexes have nearly the same  $R$ ; for B = second row (Cl, S, and P), all complexes have nearly the same  $R$ , which is  $\sim 0.6$  Å longer than the first-row  $R$  (see also ref 49 for a nice analysis of this result).

Based on the Morokuma component analysis for B...HCl and B...HF, we can see that this near equality is due to a cancellation of effects. Considering B = H<sub>3</sub>N, H<sub>2</sub>O, and HF, the N lone pair extends out furthest; one might expect it to "bump into" the H-F bond pair and thus cause  $R(N...F)$  to be significantly larger than  $R(F...F)$ . However, this greater exchange repulsion is compensated for by the greater ability of the amine to polarize the H-X bond and move it more toward the X, thus allowing the amine to approach closer to the H-X than a simple "hard sphere" model would allow.

Further support for this view comes from our previous analysis of Li<sup>+</sup> affinities.<sup>16</sup> Using an extremely nonpolarizable Lewis acid like Li<sup>+</sup> leads to  $R(N-Li^+) > R(O-Li^+) > R(F-Li^+)$ , consistent with the relative "sizes" of the Lewis



bases. Because an amide C=O can penetrate closer to Li<sup>+</sup> than an amine can, the amide interaction energy with Li<sup>+</sup> is larger, despite its smaller electrostatic potential. A comparison of the amide and amine surfaces with Li<sup>+</sup> at the minimum energy *R* for the amide found all the attractive energy components favoring the amine and only the exchange repulsion made the Li<sup>+</sup> affinity greater for the amide than the amine.<sup>16</sup>

We have tried to argue above why Li<sup>+</sup> (and extremely nonpolarizable Lewis acids) are special cases. Our choice of reference points for evaluating the electrostatic potential and the use of an "effective" hard sphere repulsion allows us to build a general, simple picture which should be least correct for the most nonpolarizable Lewis acids.

For a given acid A-H, the minimum energy distance is very different for A=F, O, N, or C, probably due to the location of the electron pair in the A-H bond. This difference in location will affect the bond dipole<sup>49</sup> as well as exchange repulsion terms. The minimum energy of the complex is mainly determined by the distance between the lone pair on B and the bond pair of A-H. One of the most dramatic examples of this is the comparison<sup>15</sup> of H<sub>3</sub>N...HCH<sub>3</sub> (*R*(C...N) = 4.0 Å) and H<sub>3</sub>N...HCF<sub>3</sub> (*R*(C...N) = 3.4 Å). Clearly, the fluorine pulls the H-C electron pair closer to the fluorine and shortens the C...N distance. A systematic comparison of the location of the localized orbitals for the isolated molecules and the noncovalent complex could lead to a more detailed insight into the way the location and polarizability of the Lewis acid pairs affect the properties of the noncovalent complex.

**(d) Spectral Properties of Complexes.** What about the spectroscopic effects of complex formation, most extensively documented for H bonds and charge-transfer complexes. We suggest that many are qualitatively explicable within this picture. The downfield NMR chemical shift of the H-bonded proton appears to be mainly due to the fact that the exchange repulsion between the B lone pair and the A-H bond pair causes the proton to lose charge on H bond formation (charge redistribution effects appear to decrease this deshielding).<sup>68</sup>

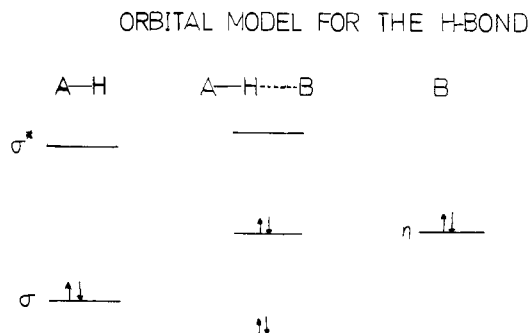
The infrared red shift of the A-H stretch and the magnitude of the A...B stretching frequency correlate qualitatively with the strength of the H bond and are explicable with a very simple electrostatic approach. One would expect similar effects for other noncovalent non-H-bonded complexes.

Large IR intensity changes upon stretching the A-H bond in the presence and absence of an H-bonded base B do appear to require charge redistribution effects (polarization and charge transfer) for their explanation, but in the few cases examined theoretically (see ref 69, Table VII) for a given A-H bond, varying the base B they *correlate* with POTB and  $-\Delta E$  (eq 3).

Let us now consider electronic spectral properties of complexes. There are basically two phenomena of interest: First, changes of intramolecular excitation upon complex formation have been widely studied theoretically on C=O...H hydrogen bonds. It appears from the results of Iwata and Morokuma<sup>70</sup> and Del Bene<sup>71</sup> that the *spectral shifts* can be understood on the basis of the difference of the charge distribution (electrostatic potential) in ground and excited states.

Thus, we expect that, knowing the charge distribution of molecular excited states, we can predict the *structure* and *energy* of complex formation in a manner exactly analogous to our analysis (eq 3) for ground-state complex formation.

Charge-transfer *transitions* can also be understood on the basis of the charge distribution and *electronic structure* of the *isolated molecules*: in a complex A...B, if B has a high-lying occupied orbital and A has a low-lying virtual orbital, then one expects a relatively low-energy electronic transition in the AB complex, but not in the isolated molecules. The energy of such a transition will be influenced in a predictable way by addition of groups on A or B that change the orbital energies of these



**Figure 14.** Simple three-center, four-electron H-bond model.

molecules. The key point is that the qualitative features of the phenomena are explicable on the basis of the electronic structure and orbital energies of the isolated molecules. One can thus use the electrostatic potential in both the Lewis acid and base to predict relative charge-transfer transition energies.

**(e) Simple Orbital Descriptions of Noncovalent Complexes.** One might consider H bonds within the framework of a simple orbital model (Figure 14) such as that proposed by Herzberg.<sup>72</sup> The stability of the H bond would arise from the fact that the *n*- $\sigma^*$  interaction is more stabilizing than the *n*- $\sigma$  is destabilizing. We suggest that many of the key features of the H bond might be evident even if one *removes* the  $\sigma^*$  orbital from the basis set, and retains only the *destabilizing* *n*- $\sigma$  interaction. The *electrostatic attraction* would *overcome* this *destabilizing* interaction. There is a neat way to test this hypothesis, in view of Brunck and Weinhold's development<sup>73</sup> of a localized bond orbital (LBO) model, where anti bonds (e.g.,  $\sigma^*$ ) can be removed from the basis set. Since semiempirical methods yield such unreliable energy components, one would need to test our hypothesis by carrying out *ab initio* calculations on noncovalent complexes with and without the  $\sigma^*$  orbital in the basis set.

**(f) Summary.** Our results suggest that the basic energetic, structural, and spectroscopic features of the intermolecular complex formation can be understood by focusing on the properties (electrostatic potentials and orbital energies) of the isolated fragments. Since the electrostatic is the *longest* range term in the intermolecular potential, it makes good sense to emphasize it in this approach, which is necessarily a *simple*, first-order treatment. It should be emphasized that one must include exchange repulsion in some way to correctly describe the distance dependence of the intermolecular potential. A more refined treatment would add energy terms to eq 3 in an order consistent with perturbation theory approaches to intermolecular forces.<sup>6</sup>

Of the six objections to an electrostatic *model* noted in the introduction, we have discussed 1-5 above. (Elsewhere<sup>74</sup> we have shown why 6 cannot be used to test an electrostatic model.) It appears that only IR intensity changes (1 and 3) require going beyond an electrostatic model to estimate *their* magnitude. Even for these it appears that chemical trends (e.g., dependence of A-H enhancement on base B) can be satisfactorily rationalized using relative electrostatic potentials. The lack of correlation of H-bond strength with dipole moment (2) is true, but does not invalidate the electrostatic model, since the *electrostatic* interaction energy often doesn't correlate with the dipole moments of the monomers. Above, we have shown that it is the reference electrostatic potential which is the relevant property to correlate with  $\Delta E$  and this correlation holds quite well. Above, we have shown that the structure of HX crystals (and dimers) (4) is explicable at the electrostatic level and have pointed out that electronic spectral shifts (5) are a consequence of the electrostatic properties of the molecules in ground and excited states and do not invalidate a simple elec-

trostatic model to examine structure and energies of complexes.

Let us stress again that the use of an electrostatic model does not imply that charge redistribution and exchange repulsion effects in noncovalent bonding are negligible. Morokuma component analyses discussed here and elsewhere<sup>11,13-15</sup> have shown them to be important. In fact, Umeyama and Morokuma<sup>14</sup> have shown that the methyl substituent effect on the proton affinities of amines is predominantly due to differences in the polarization energy; these authors caution against indiscriminate use of electrostatic potential maps. We have tried to show above that *many* structural, energetic, and spectral features of noncovalent interactions can be understood with an electrostatic viewpoint without having to invoke charge redistribution and dispersion effects.

**VII. Sources of Error in Our Calculations and Caveats on the Application of Equation 3.** The energy component calculations reported here all have used a 431G basis set, which tends to overestimate interaction energies. There is some evidence<sup>70</sup> to suggest that while the magnitude of the energy components and the interaction energies do change significantly in going from the STO-3G to the 431G basis, most qualitative trends are common to both basis sets. More extended basis set (e.g., 431G\*) component analysis are limited,<sup>13,15,33</sup> but suggest that the main effect of polarization functions is to bring the calculated polarities into more reasonable agreement with experiment. In fact, both we (analyzing ion-H<sub>2</sub>O interactions)<sup>60</sup> and Umeyama and Morokuma (analyzing (H<sub>2</sub>O)<sub>2</sub> and (HF)<sub>2</sub>)<sup>15</sup> have shown that one can *scale* the calculated interaction energies using the calculated and experimental monomer dipole moments. Such scaling leads to surprisingly good agreement with experiment and near Hartree-Fock calculations. Umeyama and Morokuma<sup>15</sup> also showed that by far the largest effect of adding polarization functions to the basis set was to decrease the electrostatic energy, the other energy components remaining approximately the same. This suggests (although it has not been proved) that the electrostatic energy will be optimum at a larger  $\theta$  with more extended basis sets. For example in (HF)<sub>2</sub>, the accurate theoretical calculations<sup>48</sup> and experiments predict  $\theta \approx 60^\circ$  rather than  $\theta \approx 40^\circ$  found with the "double  $\zeta$ " basis. We predict that the electrostatic potential and its gradient will have their minimum at a larger  $\theta$  for the more extended basis sets than the minimum found with the double  $\zeta$  basis.

Our use of a fixed geometry model for the monomers is probably not a cause of *large* errors for those complexes which are relatively weakly (<10 kcal/mol) bound<sup>75,76</sup>. Based on more extensive studies, it is probably not a large error in many anion-neutral and cation-neutral interactions.<sup>60</sup> Our calculations on NH<sub>4</sub><sup>+</sup>...X<sup>-</sup> (X = F and Cl) were artificial and were used to test the hypothesis that the lowest energy approach was that predicted by the electrostatic approach; H<sub>3</sub>N...HF is by far the more stable form of NH<sub>4</sub>F in the gas phase. In cases (e.g., F<sup>-</sup> + HF and H<sub>3</sub>O<sup>+</sup> + H<sub>2</sub>O) where the complex has a very different structure than a simple "linear combination" of the structural parameters of the isolated monomers, one expects eq 3 to underestimate the interaction energy.

The use of the magnitude of the negative electrostatic potential to predict relative proton affinities of a series of bases has been surprisingly successful, considering that charge transfer plus polarization are larger than electrostatic in the typically very strong ( $\Delta E > 100$  kcal/mol) interactions. However, in those cases of significant structural reorganization (e.g.,  $\pi$  bases),<sup>16</sup> the relative proton affinities are much higher than predicted by the simple model (recall also the Umeyama and Morokuma<sup>14</sup> analysis of the methylamine basicities). For example, the electrostatic potential near CH<sub>4</sub> is small and positive; this molecule *still* has a *substantial* proton affinity. Even He has a nontrivial ( $\sim 40$  kcal/mol) proton affinity,<sup>78</sup>

which eq 3 would not predict. Thus, for actual  $\Delta E$  estimates of proton affinities, a more refined version of eq 3, including some representation of charge redistribution effects, is required.

Our simple approach assumes that for a series of bases, they will rank in the same order, no matter what the reference acid. This is not always the case; we have tried to argue here and elsewhere why Li<sup>+</sup> and Li-X compounds<sup>16</sup> are anomalous. Beautiful work by Beauchamp and co-workers<sup>79</sup> on H<sup>+</sup>, Li<sup>+</sup>, and Ni(C<sub>5</sub>H<sub>5</sub>)<sup>+</sup> does indeed suggest that it is Li<sup>+</sup> which is most different from the other two. There are also some interesting " $\pi$  bonding" effects in particular Ni(C<sub>5</sub>H<sub>5</sub>)<sup>+</sup> interactions which our "first-order" model does not treat (e.g., MeCN as base); this is not surprising in view of the strength ( $-\Delta E \sim 50$  kcal/mol) and complexity of the Ni(C<sub>5</sub>H<sub>5</sub>)<sup>+</sup>-ligand interaction.

In the cases discussed above, we have either treated dispersion energy in a very simple, empirical fashion (weak complexes) or neglected it (moderate and strong complexes). There is some strong justification for this, even though the number of examples where dispersion energy has been explicitly and accurately calculated is limited. Kochanski<sup>31</sup> has studied the interaction energy for various configurations of (H<sub>2</sub>)<sub>2</sub> and found that the inclusion of dispersion energy did not change the qualitative conclusion that the "T" configuration was significantly more stable than "C" or "P". Matsuoka et al.<sup>80</sup> studied the (H<sub>2</sub>O)<sub>2</sub> surface using configuration interaction techniques and concluded that dispersion energy stabilized the linear, cyclic, and bifurcated structures of (H<sub>2</sub>O)<sub>2</sub> by -1.1, -1.2, and -0.9 kcal/mol, respectively, thus leaving a negligible effect on their *relative* stabilities. Very weak interactions between molecules with very little polarity such as hydrocarbons or rare gas atoms are not very directional and specific; our approach does not deal with them. In such cases, simple empirical models<sup>28</sup> which combine dispersion attraction and exchange repulsion will allow one to treat such phenomena.

Let us emphasize again that all the energy components are nontrivial for moderate strength and strong noncovalent complexes. The fact that the electrostatic component contains as much information as it does about directionality and relative magnitudes of noncovalent interactions is surprising, but encourages us to develop simple approaches using the electrostatic properties of molecules to analyze such interactions. The electrostatic *potentials* and their *gradients* are not the same as the electrostatic energy, and are, unlike the energy components, a property of a given molecule. Thus, one can use the electrostatic potential and its gradient in equations like 3. We have noted before<sup>17</sup> that the electrostatic potentials near Lewis bases can give qualitative insight into the magnitude of not only the electrostatic energy, but also the charge transfer and exchange terms when one compares the interactions of a series of Lewis bases with a Lewis acid.

**VIII. Conclusions and Future Issues.** In this paper, our main conclusions are: (1) The electrostatic energy and electrostatic potential are very useful guides to qualitative and semiquantitative predictions of the energies and shapes of noncovalent complexes. The electrostatic energy does an excellent job of predicting the directionality of many interactions, including Cl<sub>2</sub>...Cl<sub>2</sub>, HF...HF, HCl...HCl, F<sup>-</sup>...HOH, and Cl<sup>-</sup>...HOH.

(2) The geometries of complexes are often different than those of "simple" electrostatic models; for example, (Cl<sub>2</sub>)<sub>2</sub> has an "L" rather than the "T" structure predicted from a point quadrupole model, (HF)<sub>2</sub> and (HCl)<sub>2</sub> deviate from the linear structure that a simple atom-centered partial charge model would predict, and F<sup>-</sup>...HOH and Cl<sup>-</sup>...HOH do not have the simple C<sub>2v</sub> structure predicted by an anion-point dipole model.

We find that these differences are due to the crudeness of the electrostatic models, *not* to the fact that an *electrostatic*

model is inadequate (charge redistribution effects need *not* be invoked for many of the complexes studied here, although in the previous section we suggested situations where they may play a nonnegligible role).

(3) The simplest electrostatic model that incorporates the key features of the results of our calculations is one which explicitly includes electron pairs (e.g., for HF, Figure 3). Alternative approaches involve consideration of higher moments (an appropriate dipole plus quadrupole model could give a correctly "zig-zag" HF dimer), but these would be harder to apply and develop for all but the smallest molecules.

(4) Li<sup>-</sup> functioning as an electrophile is anomalous when compared to H<sup>-</sup> or Cl<sup>-</sup>. We feel this is due to the fact that bases approaching Li do not experience their major exchange repulsion from the valence electron pair.

(5) These results provide strong support for the use of the form of empirical potential function (using electron pairs and nuclei) used by Lennard-Jones and Pople<sup>81</sup> and Rahman and Stillinger<sup>82</sup> on water interactions and recently generalized by Shipman and Scheraga.<sup>83</sup>

(6) We propose a simple, predictive approach for use in analyzing the properties of noncovalent complexes.

Future directions that this work might take include refining this "first-order" model with a limited number of very accurate calculations on selected molecules as well as development of simple second-order models. As we indicated in section VII, the model proposed here is likely to fare more poorly when considering molecules which contain atoms below Ar in the periodic table because of "back-bonding effects" (such as observed in Ni(C<sub>5</sub>H<sub>5</sub>)<sup>+</sup>)<sup>79</sup> as well as the greater polarizability of heavier atoms (e.g., charge-transfer complexes involving I<sub>2</sub>).

It would also be of interest to study non-closed-shell complexes such as those involving O<sub>2</sub>, Li, and F with the Morokuma component analysis.

**Note Added in Proof.** A possible rationale for the near cancellation of the angular dependence of the exchange repulsion and charge transfer in (HF)<sub>2</sub> is as follows: The charge transfer term depends on the overlap between the lone pair of the electron donor and the antibonding orbital(s) of the electron acceptor S<sub>1p,σ\*</sub>; the exchange term depends on the overlap between the lone pair orbital and the bonding orbital(s) of the electron acceptor, S<sub>1p,σ</sub> (see ref 6). The distance dependence of S<sub>1p,σ\*</sub> and S<sub>1p,σ</sub> will be quite different, due to the different nodal structure of σ and σ\*. Increasing θ at a fixed R(F-F) will make the lone pair (1p) have more p character, stick out further from the F, and have a greater overlap with both the bonding and antibonding orbitals of the electron acceptor. Thus, both S<sub>1p,σ</sub> and S<sub>1p,σ\*</sub> will increase with increasing θ and so will the exchange repulsion (repulsive term) and charge transfer (attractive term). The fact that the angular dependences for these terms and the angular dependence for the polarizability (which favors θ = 0 because α<sub>||</sub> > α<sub>⊥</sub> for HF) almost exactly numerically cancel each other for (HF)<sub>2</sub> is somewhat fortuitous, as the other examples we present show. Particularly interesting is H-F...Li-F, which has a smaller minimum energy θ than that predicted from the electrostatic energy alone partly because the magnitude of the exchange repulsion goes up much more steeply with increasing θ than does the charge transfer (compare the components in Tables VII and XI). One might "predict" a smaller θ in H-F...LiF than HF...HF, due to the larger dipole moment of LiF, but one would be "correct" for the wrong reasons; the fact that θ is smaller in HF...LiF than HF...HF is not an electrostatic effect but due both to the greater polarizability of Li-F and the greater exchange repulsion of the F lone pair with the Li inner shell.

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## The Use of Population Optimized Basis Functions. 1. Determination of Optimum Basis Functions and Their Use in a Semiempirical Method for Atomic State Energies

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**Abstract:** Direct optimization of the exponents in minimum Slater type orbital basis sets on atoms with fractional closed shell populations provided a series of optimum exponents for atoms in molecule-like states. These optimum exponents were very well fit by an empirical linear relation based on the populations themselves. The calculated optimum exponents were used in a new semiempirical atomic orbital method to calculate the energies of a large number of states of atoms and ions.

### (I) Introduction

Atomic orbital basis sets are very widely used in molecular orbital methods because they provide a simple uniform foundation for these methods. It is clear that regardless of the form used to represent atomic orbitals, the "size" of an orbital will vary with the effective nuclear charge. Changes in molecular electronic distribution affect the apparent nuclear charge, so

the optimum mathematical representation of atomic orbitals varies with the distribution of electrons in any molecule.

Variation of atomic orbital size with electronic distribution is included implicitly in extended basis set LCAO-MO calculations<sup>1</sup> and has been included explicitly in minimum basis set calculations by direct minimization<sup>2,3</sup> or by the use of a modified form of Slater's rules<sup>4</sup> to predict optimum exponents<sup>5</sup> for Slater orbital basis sets.