Sharing of Electrons in Molecules: Characterization of Hydrogen Bonds

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The behaviors of the electrons in binary complexes formed from HF, H_2O, and NH_3 as well as in the complex formed between HF and CH_4 are analyzed at the single electron level in order to characterize the nature of intermolecular bonding in dimers that may contain hydrogen bonds. The analysis uses the quantitative measures of the degree to which a single electron is shared between two points ζ and ζ', the sharing index $I(\zeta; \zeta')$, and the underlying sharing amplitude $\langle\zeta; \zeta'\rangle$, as well as the derived quantities, bond indices, self-sharing indices, delocalization indices, and volume−point sharing indices. The bond indices, together with the delocalization indices and the self-sharing indices, give a gross dissection of the sharing of an electron between the volumes associated with atoms and between molecules. These indices give a preliminary indication of the variety of the strengths of sharing in the complexes, but they do not necessarily distinguish between bonding and antibonding sharing. It is the sharing amplitude which indicates the wide variety of types of intermolecular sharing in the complexes, the sharing ranging from covalent to antibonding in the complexes studied. By comparing the sharing in two conformations of the complexes between two given molecules, such as the complexes $HOH-NH_3$ and H_2NH-OH_2 involving water and ammonia, the difference between the sharing in complexes in which the bonding is, according to the acid−base nature of the moieties, conducive to proton transfer (the natural order) and in which the bonding is not conducive to proton transfer (the unnatural order) can be determined. In general the intermolecular sharing is found to be larger in the conformation conducive to proton transfer, with the sharing amplitude with the fixed point on the bridge proton clearly indicating that in the natural conformation a covalent bond (although weak in some cases) is formed to the proton acceptor in contrast to the unnatural conformation in which the sharing amplitude indicates a non- or antibonded behavior to the proton acceptor. The electron shared from the proton acceptor is also found to be more delocalized over the bridge proton and the proton donor in the natural conformation than in the unnatural conformation. We propose that the term "hydrogen bond" should be restricted to those bonds which involve a bridge proton between the moieties forming the complex and for which the sharing amplitude from the bridge proton to the proton acceptor has the characteristics of a covalent bond. We suggest that the other complexes, which are locally stable, should not be considered to be hydrogen-bonded. The weakest covalent intermolecular sharing is found in FH−FH while the strongest is in $FH-NH_3$, the value of the intermolecular sharing in the latter being almost the same as between the fluorine and the bridge proton in the complex. The weakest antibonding (in terms of sharing) is found in H_3CH-FH, and the strongest antibonding in the NH_3 dimers.

I. Introduction

Hydrogen bonds are ubiquitous in nature,[1] yet the behavior of electrons in complexes containing hydrogen bonds is incompletely understood.[2] By "behavior of electrons" we include not just behavior as measured by quantities such as electron densities, bonding energies, vibrational frequencies and intensities, and shifts in magnetic resonance frequencies but also those aspects which are more directly related to the wavelike behavior of electrons such as the localization and delocalization of the electrons as well as the characteristic nodal patterns of waves. The behaviors of electrons in which we are interested are associated with the wavelike aspects of electrons and are described by sharing indices and sharing amplitudes.[3−5] These not only indicate the way in which atoms are bonded together but also give the distinctive wavelike (nodal) properties of a single electron in a molecule.

Questions regarding the nature of hydrogen bonding are not new.[6] Some studies of hydrogen bonds have been based on analyses of the results of calculations of the electronic energy of hydrogen-bonded moieties. Typically, such analyses have involved partitioning schemes by which various contributions to the energy are separated from the total energy. The classic study is that by Umeyama and Morukuma[7] in which the energy is partitioned into electrostatic, polarization, exchange, and charge-transfer interactions, together with a coupling term which accounts for the discrepancy between the sum of these four interactions and the total self-consistent field energy. Such calculations, although useful as a guide for understanding the various models that are used in molecular mechanics, suffer from the defects that the partitioning schemes are in fact arbitrary in the assignments of the various components of energy and that the schemes are generally restricted to an analysis of wave

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functions that ignore effects due to the correlation of the electrons. Correlation, however, is important in determining the behavior of even a single electron in a many electron system.[3−5] Although rooted in calculated wave functions our approach to a description of the behavior of electrons differs from those based on energy partitioning in that it involves an analysis based on a quantitative measure of the sharing of an electron between two points in space. It is an analysis of the behavior of an electron in a many electron system and not of the energy of a system. Unlike energy decomposition schemes, the analysis used in the present paper is invariant to transformations of the orbitals used in the construction of the wave function and to choice of basis set as long as the basis set is sufficiently complete. Most importantly, the sharing analysis is applicable to correlated wave functions, the type of wave functions used in the present study.

That hydrogen bonding involves at least some change in the electronic structures of the moieties taking part in hydrogen bonding is clear from the changes in infra-red and Raman spectra upon hydrogen bond formation.[8] Changes in force constants and frequency shifts must be accompanied by some change in electronic structure. There are also proton chemical shifts attributable to changes in electron density upon hydrogen bond formation.[9] What the change in electron behavior is, however, is not completely delineated by the spectroscopic manifestations of the change. For example, the questions of whether the electrons in the vicinity of the bridge proton become more or less delocalized, or whether the bonding from the bridge toward the proton acceptor is of a covalent nature or of a nonbonded, or even of an antibonded, nature are not answered. Our interest is related to these questions—namely, we address the question of the changes in the behavior of an electron when two moieties are hydrogen-bonded. More specifically, we ask whether the electrons in the regions of the hydrogen bond have the characteristic features of covalent bonds or of the interactions between closed shell species, what the degree of delocalization of an electron from one moiety to the other is, and what the changes in the internal sharing are.

In the present paper we consider both hydrogen-bonded and non-hydrogen-bonded binary complexes formed between the molecules HF, NH_3, and H_2O, and between CH_4 and FH. Two configurations of the ammonia dimer are considered, that considered by Dill, Allen, Topp, and Pople[10] and that considered by Tao and Klemperer.[11] At the outset we give the basin−basin sharing indices between the various atomic basins into which the complexes can be divided according to the Bader criterion.[12] We next give some volume−point sharing indices for the complexes. We then proceed to an analysis of the sharing amplitudes with the fixed point chosen to be on the bridge proton in the hydrogen bond. The penultimate section weaves together the threads that are developed in the first section in order to give a coherent picture of the behavior of an electron in the complexes, while the final section gives a summary of the main results. This last section may consulted to get the flavor of the results of the paper without going through the details.

The preceding paper, which analyzes the characteristics of sharing in the hydrides of the first row of eight elements, should be consulted both for a quick review of the basis of the sharing analysis and for the characteristics of sharing in a variety of bonds in species containing no bridge protons.

With the exception of one of the calculations pertaining to the ammonia dimers, the results reported below are based on MP2 calculations performed by the GAUSSIAN 92 suite of programs at the 6-31++G** level of approximation using frozen cores.[13] The atomic overlap integrals needed for the bond indices and the volume−point sharing indices were calculated by using the programs EXTREM and PROAIM[14] and ATOMICI.[15]

II. Basin−Basin Sharing Indices in Complexes with Bridge Protons

The sharing of an electron between two basins A and B basins is measured by the sharing index I_{AB}. Twice the sharing index (TBSI) is the sum $I_{AB} + I_{BA}$. For interbasin sharing, this index is the total interbasin sharing index (TIBSI) B_{AB}, which measures the amount an electron is shared between the two basins A and B. When the indices are the same we simply have twice the self-sharing of an electron in a basin. It is important to recall that the sharing indices are normalized to the total number of electrons in the molecule.

In this section we consider the sharing in complexes with bridge protons. There are two questions to be addressed. The first is how the internal sharing indices in each molecule forming the complex change upon formation of the complex. The second is what the intermolecular sharing from the basins of one molecule to the basins of the other molecule is. Included in the latter is the total intermolecular sharing. The answer to the first question requires a comparison with the basin−basin sharing indices given in the preceding paper.

At the outset it must be recognized that in this section we consider only the basin−basin sharing indices. These do not do not give the finest details of the sharing. The full details of the characteristics of hydrogen-bonded complexes will not be apparent until the sharing amplitudes are considered.

With the exception of the last complex considered in this section, the ammonia dimer in the conformation of Tao and Klemperer, the two sum rules giving the average number of electrons in a basin[5] indicate that the procedures by which the surfaces are determined and the integrations carried out probably give TBSI's accurate to three decimal places.

We first consider the intermolecular sharing in two complexes, the first being the $H_3CH{-}FH$ complex, which is not typical of a hydrogen-bonded complex, and the second being FH−FH, which traditionally is considered to be a hydrogen-bonded complex. (In general the formulas of the complexes are written to indicate which proton serves as the bridge proton, with the dash indicating the purported hydrogen bond. For example, the complex between methane and hydrogen fluoride is written as $H_3CH{-}FH$. The proton on the methane that serves as the bridge proton is adjacent to the dash "−" which in turn is adjacent to hydrogen fluoride. Fluorine is adjacent to the bridge proton.) After analyzing the bonding in these two complexes, we proceed to consider other binary complexes formed from HF, H_2O, and NH_3.

The basin−basin sharing indices of the complex $H_3CH{-}FH$ at the calculated minimum of the energy are given in Table 1. (The basin−basin sharing indices are elements of a symmetric matrix. Note that the row and column indices on the sharing indices are given to the left and at the top of the table. Only the diagonal and lower left elements of the symmetric matrix are given.) The geometry of the complex is shown in Figure 1. The hydrogens labeled H1 to H4 have their primary bonds to the carbon, while H5 has its primary bond to the fluorine. H4 is the bridge hydrogen between the methane and the fluorine. The basin−basin sharing indices in isolated methane are given in Table 4 of ref 5, while those in isolated hydrogen fluoride are found in Table 7 of the same reference. There are a number

TABLE 1: Sharing Indices in H_3CH-FH

TBSI; basin\basin	H1	H2	H3	C	H4	F	H5
H1	1.070						
H2	0.039	1.070					
H3	0.039	0.039	1.067				
C	0.872	0.872	0.872	8.334			
H4	0.037	0.037	0.037	0.862	1.009		
F	0.001	0.001	0.001	0.006	0.019	18.992	
H5	0.000	0.000	0.000	0.000	0.001	0.439	0.109
self-sharing − core	0.535	0.535	0.534	2.167	0.504	7.496	0.055
delocalization index	0.494	0.494	0.493	1.742	0.496	0.233	0.220
no. basin electrons[a]	1.028	1.028	1.027	5.909	1.000	9.729	0.274
$(HF)-(HCH_3)$ sharing	0.027						

[a] From sharing index sum rule.

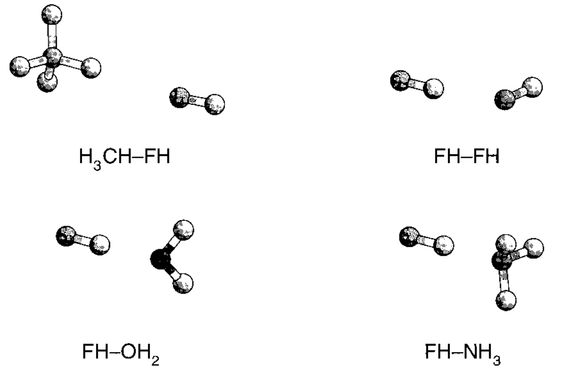

Figure 1. Orientations of the complexes H_3CH-FH, FH−FH, $FH-OH_2$, and $FH-NH_3$ used for the analysis of the sharing of an electron.

TABLE 2: Sharing Indices in FH−FH

TBSI; basin\basin	F1	H1	F2	H2
F1	19.079			
H1	0.378	0.087		
F2	0.052	0.045	18.953	
H2	0.001	0.001	0.417	0.098
self-sharing − core	7.539	0.043	7.476	0.049
delocalization index	0.215	0.212	0.257	0.209
no. basin electrons[a]	9.755	0.255	9.733	0.258
(FH)−(FH) sharing	0.098			

[a] From sharing index sum rule.

of minor changes in the intramolecular interbasin sharing indices upon formation of the dimer: the sharing indices from C to H1, H2, and H3 are slightly larger than the carbon hydrogen sharing indices in CH_4, while the index from C to the bridge hydrogen is about 1% smaller than the carbon−hydrogen bond index in isolated CH_4. There is a 2% decrease in the F to H5 sharing index as compared to the sharing in free HF. There are also slight changes in the self-sharing indices: the self-sharing indices of C, H1, H2, and H3 are increased slightly over the values in CH_4 while the other self-sharing indices are decreased slightly from those in the isolated molecules. Of greater interest for the discussion below are the sharing indices between the two moieties. The total interbasin sharing index (denoted by “bond index” below) between the bridge hydrogen and the fluorine is 0.019, about one-half the value of that between the hydrogens in methane, which are slightly anti-bonded,[5] but five times the bond index of 0.004 in He_2 at its calculated minimum of energy. We note that the bond index between the carbon and the fluorine is very small, being but 0.006. The total bond index between CH_4 and HF is also small, 0.027. The significance of the sizes of these intermolecular sharing indices will be apparent in the discussion of the FH−FH dimer.

A check of the total numbers of electrons in CH_4 and HF indicates that in addition to there being little sharing between the two molecules there is also extremely little transfer of electrons from one moiety to the other.

The basin−basin sharing indices of the classic hydrogen-bonded complex FH−FH are given in Table 2 with the geometry of the complex shown in Figure 1. The indices for isolated HF are given in Table 7 of ref 5. We first note that the primary sharing indices between the hydrogens and the fluorines undergo larger changes upon formation of the complex than the primary bond indices in the CH_4-FH complex. The primary bond index (the total interbasin sharing index) in the F1H1 molecule has decreased by 0.063 from the value of 0.441 in the monomer, a 15% decrease. This decrease indicates a significant reorganization of electronic structure in the proton donor. The primary bond index in the proton acceptor has decreased by 0.024, a 5% decrease from the bond index in free HF. The self-sharing index on F1 (the atom that donates the proton) is larger than in an isolated FH by about 0.03, while the self-sharing index on F2 (the atom that is the proton acceptor) is smaller by about the same amount. The self-sharing index of the bridge proton decreases by 20% to 0.043. The self-sharing index of the other hydrogen in the complex is also less than in the free molecule. These changes in the internal sharing in the moieties making up the complex are all larger than those found in the H_3CH-FH complex.

Of greater significance are the sharing indices between the fluorine of the proton acceptor and the hydrogen and the fluorine of the proton donor. The bond index between F2 and H1 is 0.045, while the index between F2 and F1 is slightly larger, 0.052. Each of these is separately larger by a factor of about 2 than the *total* intermolecular sharing index of 0.027 in the methane−hydrogen fluoride complex. The sharing between F1 and F2 in $(FH)_2$ is about eight times as large as the sharing between the carbon and the fluorine in H_3CH-FH. In FH−FH, the sharing from F1 to F2 is a bit larger than that between H1 and F2, the rough equality of the indices indicating that the sharing of an electron from the fluorine in the proton acceptor FH is delocalized over both the hydrogen and fluorine basins in the proton donor FH. The total bond index between the two hydrogen fluorides is 0.097, or about one-fourth the value of the bond index between the proton and the fluorine in isolated hydrogen fluoride and about three times the value of the (secondary) bond index between two hydrogens in methane.

The sharing between the hydrogen fluorides is placed in a better perspective when it is noted that the number of electrons in the hydrogen basin in an isolated hydrogen fluoride is but 0.276 as compared to 1.022 in each hydrogen basin in isolated methane. Of the 0.276 electrons in the hydrogen basin in HF, only 0.059 electrons, representing 20% of the electrons in the basin, are shared to points within the basin, the rest being shared with the fluorine. In methane, the self-sharing index of each hydrogen basin is 0.530 with the result that somewhat more than 50% of the electrons in a hydrogen basin are shared to points within the basin. The hydrogen basin in HF therefore has fewer electrons available for sharing to the other hydrogen fluoride in the dimer than has a proton in methane, yet the bond index between the proton in FH and the other FH molecule is significantly larger than the bond index between the proton in H_3CH and the FH molecule.

Another comparison that can be made is with the bond index in LiH given in ref 5. The total bond index between the two HF moieties, 0.097, is about 46% of the Li−H bond index in LiH. The intermolecular sharing in the hydrogen fluoride dimer is not inconsiderable. Now LiH, from the basin charges,

TABLE 3: π-Electron Contribution to Sharing Indices in FH−FH

TBSI; basin\basin	F1	H1	F2	H2
F1	3.973			
H1	0.011	0.000		
F2	0.006	0.003	3.968	
H2	0.000	0.000	0.012	0.000
π self-sharing − π core	1.986	0.000	1.984	0.000
π delocalization index	0.009	0.007	0.010	0.006
no. π basin electrons[a]	1.995	0.007	1.994	0.006
(FH)−(FH) π-sharing	0.009			

[a] From sharing index sum rule.

TABLE 4: Sharing Indices in FH−OH_2

TBSI; basin\basin	F	H1	O	H2	H3
F	19.130				
H1	0.343	0.082			
O	0.083	0.080	17.126		
H2	0.002	0.001	0.560	0.190	
H3	0.002	0.001	0.560	0.007	0.190
self-sharing − core	7.565	0.041	6.563	0.095	0.095
delocalization index	0.215	0.213	0.642	0.285	0.285
no. basin electrons[a]	9.780	0.254	9.205	0.380	0.380
(FH)−(OH_2) sharing	0.169				

[a] From sharing index sum rule.

contains a dominantly ionic bond. That the intermolecular sharing in the hydrogen fluoride dimer is not ionic is apparent when it is noted that in spite of the changes in the sharing indices and, in particular, in spite of the relatively large sharing between the moieties, the total numbers of electrons associated with F1H1 and F2H2 are 10.01 and 9.99, respectively. As in the previous complex there is little transfer of electrons from one moiety to the other upon formation of the hydrogen bond.

There are also some changes in the delocalization indices of the atoms upon formation of the dimer. The delocalization indices of the basins in isolated HF are 0.221.[5] The delocalization indices of fluorine and hydrogen in the proton donor of the complex are slightly lower, 0.215 and 0.212, respectively. The delocalization index of the acceptor fluorine (F2) increases to 0.257, a change of 0.035 from the free molecule, while that of the terminal hydrogen (H2) is reduced to 0.209. This increase in the delocalization index of the proton acceptor occurs in spite of the decrease in the average number of electrons in the acceptor basin. (In this regard it should be noted that the sum rule

$$\bar{N}_A = I_{AA} + \Delta_A$$

holds between the average number of electrons in the volume V_A and the self-sharing index I_{AA} and the delocalization index Δ_A of volume V_A. These three quantities are not independent.) Is this increase in the delocalization of the electrons on the proton acceptor a general phenomenon in the other hydrogen-bonded complexes?

Before considering other complexes, we give a further dissection of the sharing in the hydrogen fluoride dimer. The dimer is found to be very close to planar when a full geometry optimization is carried out. What is the π-contribution to the sharing? By enforcing planarity on the geometry, the π-contribution to the bond indices can be ascertained using symmetry arguments. This contribution to the sharing indices of FH−FH is given in Table 3. The π-contribution to intermolecular bond indices is less than about 10% of the sum of the total bond indices. The bonding between the two hydrogen fluorides is therefore mainly through the σ-structures. Also apparent from the table is the dearth of π-contribution to the internal bond index in hydrogen fluoride itself.

What the bond indices do not answer is the question of the type of sharing between the moieties. Is the structure of the sharing of an electron of a covalent type as between the hydrogen and the fluorine in HF, of a nonbonding type as between the two heliums in He_2, or of an antibonding type as in the $^1\Sigma_g$ state arising from the $1\sigma_u^{*2}$ configuration of H_2?[5] Although the volume−point indices given in section III give some hint of the type of bonding involved in the sharing between the moieties, it is the analysis of the sharing amplitudes given in section IV which is definitive in characterizing the sharing.

The sharing indices in the complex FH−OH_2 are given in Table 4. The geometry of the complex is shown in Figure 1. Consider first the bonds internal to each moiety. The internal bond index in hydrogen fluoride is less than that in the hydrogen fluoride dimer, 0.343 rather than 0.378, and is a significant 22% less than the index of 0.441 in free hydrogen fluoride. This change indicates a larger reorganization of the electronic structure of FH in FH−OH_2 than in FH−FH. In the internal hydrogen−oxygen bonds there is a decrease of 0.033 from the value of the bond index in an isolated water molecule. This represents but a 5% change in this sharing. The pattern that is emerging is that the internal electronic structure of the proton donor is changed more than the internal structure of the proton acceptor upon complex formation.

The bond index between the oxygen in H_2O and the hydrogen in HF is 0.080, while that between the oxygen and fluorine is 0.083, both larger than the similar intermolecular indices in the hydrogen fluoride dimer. Again, the sharing from the heavy atom on the proton acceptor, the water molecule, is spread about equally over the whole hydrogen fluoride molecule. These values together with the total intermolecular bond index of 0.169, which is one-half the value of the internal fluorine hydrogen sharing in this complex, indicate both significant delocalization of the sharing involved in hydrogen bonding and significant sharing between the molecules in this complex.

The changes in the bond indices given above are accompanied by changes in the delocalization indices of the atoms. The delocalization indices of each atom in HF, as well as the hydrogens in water, all decrease from the free molecule values, while the delocalization index of oxygen, the proton acceptor, increases. The decreases in HF are similar to those in the proton donor molecule in the hydrogen fluoride dimer. The increase in the oxygen delocalization index over the free molecule value is 0.045, a bit larger than the increase in the delocalization index of the acceptor in the hydrogen fluoride dimer.

Relative to the self-sharing indices of the heavy atoms in the isolated molecules, the self-sharing index of the fluorine (the proton donor) is increased by hydrogen bond formation while that of the oxygen is decreased.

The number of electrons in hydrogen fluoride is 10.034 while there are 9.965 in water, a transfer of about 0.03 electrons to the HF. As in the case of the hydrogen fluoride dimer, there is little physical transfer of electrons from one moiety to the other upon formation of the complex in spite of the increase in the delocalization between the moieties.

Table 5 contains the sharing indices in FH−NH_3, and the geometry is shown in Figure 1. The internal bond index between the fluorine and the hydrogen in the complex is 0.327, a 26% decrease from the index in isolated hydrogen fluoride, a larger decrease than found in FH−OH_2. There is a decrease of roughly $3^1/_2$% in the internal nitrogen to hydrogen bond indices in the NH_3 end of the complex. The pattern found above that

TABLE 5: Sharing Indices in FH−NH$_3$

TBSI; basin\basin	F	H1	N	H2	H3	H4
F	19.157					
H1	0.328	0.091				
N	0.115	0.120	13.781			
H2	0.003	0.002	0.748	0.413		
H3	0.003	0.002	0.748	0.014	0.413	
H4	0.003	0.002	0.748	0.014	0.014	0.413
self-sharing − core	7.578	0.045	4.891	0.207	0.207	0.207
delocalization index	0.225	0.227	1.240	0.391	0.391	0.391
no. basin electrons[a]	9.804	0.272	8.131	0.598	0.598	0.598
(FH)−(NH$_3$) sharing	0.249					

[a] From sharing index sum rule.

changes in the internal bond index to the bridge hydrogen in the proton donor are larger than the changes in the proton acceptor continues.

The intermolecular bond indices from the nitrogen to the hydrogen and to the fluorine are 0.120 and 0.115, respectively. The nitrogen bond index to the bridge hydrogen is bit larger than that to the fluorine, unlike in the previous two complexes. What is more remarkable is the size of the total sharing between the two moieties, 0.249, a value that is 75% of the internal HF bond index in the complex. The intermolecular sharing upon hydrogen bond formation is now sizable relative to the internal sharing between the hydrogen and the fluorine in HF. In fact, the intermolecular bond index in the hydrogen fluoride ammonia complex is larger than the bond index between the hydrogen and a fluorine in the ion (FHF)$^-$ considered below.

The changes in the delocalization indices of the atoms differ from those in the previous complexes. The delocalization index of the proton acceptor (nitrogen) is larger in the complex than in free NH$_3$ by the amount 0.077, a larger increase than found above in the other complexes, and is accompanied by a small increase in the delocalization indices of both the hydrogen and the fluorine in the proton donor, HF. The increases in the delocalization indices in HF are counter to the previous examples. The trend that remains is in the changes of delocalization indices of the proton acceptor upon complex formation—the change increases in the series fluorine, oxygen, nitrogen.

Again the self-sharing indices of the heavy atoms relative to those of the isolated molecules have changed in a fashion consistent with the trends established above—the self-sharing index of the atom that is the proton donor has increased while that of the atom that is the proton acceptor has decreased.

The numbers of electrons on the hydrogen fluoride and on the ammonia in the complex are 10.076 and 9.923, indicating that 0.076 electrons have been transferred from the ammonia molecule upon hydrogen bond formation. The number of electrons transferred from the molecule that is the proton acceptor to the proton donor increases along the present series of molecules.

The next complex considered is the (FHF)$^-$ ion, found to be linear with the proton centered between the fluorines. The bond indices are given in Table 6 with the geometry of the ion depicted in Figure 2. The fluorine−hydrogen bond indices are 0.224, each being about half the bond index in isolated HF, twice the intermolecular hydrogen−nitrogen and the fluorine−nitrogen bond indices in FH−NH$_3$ but less than the total intermolecular bond index in FH−NH$_3$. As an aside, the value of the FH bond index of 0.224 may be compared to the total intermolecular bond index of 0.249 in the FH−NH$_3$ complex, clearly indicating the large amount of sharing between the molecules in the latter complex.

TABLE 6: Sharing Indices in (FHF)$^-$

TBSI; basin\basin	F1	H	F2
F1	19.322		
H	0.224	0.089	
F2	0.181	0.224	19.322
self-sharing − core	7.661	0.045	7.661
delocalization index	0.203	0.224	0.203
no. basin electrons[a]	9.864	0.269	9.864

[a] From sharing index sum rule.

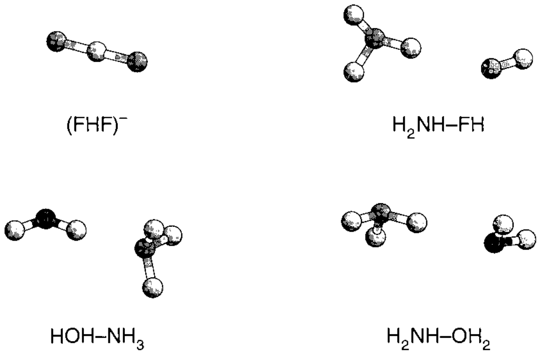

Figure 2. Geometries of the complexes (FHF)$^-$, H$_2$NH−FH, HOH−NH$_3$, H$_2$NH−OH$_2$ used for the analysis of the sharing of an electron.

There is considerable sharing between the two fluorines. The fluorine−fluorine bond index of 0.181, only 20% less than the hydrogen−fluorine index, indicates a considerable amount of delocalization of the electron from one end fluorine to the other. In the hydrogen-bonded complexes so far considered, this delocalization of an electron from the atom that is the proton acceptor to the fluorine on which the proton resides is a common theme. (In (FHF)$^-$, fluorines are considered as donors and acceptors.)

Before continuing to the other complexes, we summarize what has been found so far. The sharing between hydrogen fluoride and methane in the H$_3$CH−FH complex is relatively small. There are only slight changes in the intramolecular sharing indices compared to the indices in the isolated molecules. In the series, FH−FH, FH−OH$_2$, and FH−NH$_3$, the changes in the internal sharing indices in the proton donor FH from the value in isolated FH increase along the series. The changes, ranging from 15% to 26%, indicate a significant reorganization of the internal electronic structure of the proton donor. At the same time the intermolecular sharing increases. In each of the last three complexes, the sharing from the heavy atom of the proton acceptor is delocalized over the proton donor, FH. The intermolecular bond index in the complex FH−FH is 0.097, that in FH−NH$_3$ is 0.249. This value in the latter molecule, together with the change in the internal sharing indices in the complex upon hydrogen bond formation, indicates that not only is there significant change in the internal electronic structure of the proton donor but there is also a significant change in the one-electron behavior external to the moieties upon hydrogen bond formation between hydrogen fluoride and ammonia. The size of the intermolecular bond index, larger than the bond index in LiH and larger than the fluorine to hydrogen bond index in (FHF)$^-$, itself indicates that more than electrostatics is involved in the hydrogen bonding in this complex. There is significant bonding between the moieties, and there is significant delocalization of the electron from the proton acceptor atom to the entire proton-donating FH molecule. In the FH−FH complex, π-electrons make little contribution to the intermolecular sharing. The changes in the self-sharing indices of the heavy atoms follow a consistent pattern in that the self-sharing index of the

TABLE 7: Sharing Indices in H_2NH-FH

TBSI; basin\basin	H1	F	H2	N	H3	H4
H1	0.106					
F	0.433	18.975				
H2	0.000	0.032	0.396			
N	0.000	0.021	0.733	13.965		
H3	0.000	0.001	0.015	0.779	0.454	
H4	0.000	0.001	0.015	0.779	0.016	0.454
self-sharing − core	0.053	7.487	0.198	4.983	0.227	0.227
delocalization index	0.217	0.244	0.398	1.157	0.406	0.406
no. basin electrons[a]	0.270	9.732	0.595	8.139	0.632	0.632
$(HF)-(HNH_2)$ sharing	0.056					

[a] From sharing index sum rule.

atom which is the proton donor increases while that of the atom which is the proton acceptor decreases relative to the values in the isolated molecules. The changes in the heavy atom self-sharing indices are all larger than in the H_3CH-FH complex. The changes in the delocalization indices of the proton acceptor upon formation of the complex increase in the series, fluorine, oxygen, nitrogen, indicating increasing delocalization of an electron shared from the proton acceptor.

The strengths of the hydrogen bond increases along the series $FH-FH$, $FH-OH_2$, and $FH-NH_3$. The intermolecular bond indices as well as the number of electrons transferred from one moiety to the other upon hydrogen bond formation in the last three complexes are found to parallel the strengths of the hydrogen bonds. The internal fluorine to hydrogen bond indices in the proton donor are found to decrease along this series.

With the exception of H_3CH-FH in the complexes considered above, hydrogen fluoride is the proton donor, acting as an acid. What happens when HF is a proton acceptor? The sharing indices in the complex $HF-HNH_2$ in which ammonia is the proton donor are given in Table 7, and the geometry is shown in Figure 2. For the most part there are but slight changes in the internal bond indices of the molecules upon hydrogen bond formation. The exception is the bond index from the nitrogen to the bridge proton (H2 in the table), which decreases from 0.775 to 0.733, a decrease of 0.042, which represents but a 5% drop in value.

The bond index between H2 (the proton "donated" by the ammonia) and the fluorine is 0.032 while the index between the nitrogen and the fluorine is 0.021. The sharing from the fluorine is spread over both the H2 proton and the heavy atom in the proton donor, the nitrogen. This is similar to the $FH-NH_3$ complex in which the sharing from the nitrogen is spread out over both the bridge proton and the heavy atom in the proton donor, the fluorine. Unlike the $FH-NH_3$ complex, the sharing between the atom that is the proton acceptor (fluorine) and the bridge hydrogen is 50% larger than the sharing between the two heavy atoms. There is also a considerable difference between the two complexes in the amount of sharing from the entire proton acceptor to the entire proton donor molecule. In the present complex, $HF-HNH_2$, the total intermolecular sharing is 0.056, as compared to 0.249 in $FH-NH_3$. These differences in the intermolecular sharing indices correlate quite nicely with the relative acidities (basicities) of HF and NH_3; HF is an acid relative to NH_3.

Also of note is that the delocalization index of the fluorine, the proton acceptor, is 0.024 larger than in the free HF molecule. This change is smaller than any of the previous increases in the delocalization indices of fluorine when acting as a proton acceptor. The small change in this complex is in line with the idea that hydrogen fluoride is the acid of this pair of molecules.

Do these differences in the sharing indices, together with the correlation of the relative acidities of the partners, extend to other pairs of molecules, such as the complexes formed between water and ammonia? Tables 8 and 9 give the sharing indices for $HOH-NH_3$ and H_2NH-OH_2, the first complex having the moieties in a position for facile proton transfer from the water to the ammonia, and the second complex having the moieties oriented so as to facilitate a transfer of a proton from the ammonia to the water.

TABLE 8: Sharing Indices in $HOH-NH_3$

TBSI; basin\basin	H1	O	H2	N	H3	H4	H5
H1	0.228						
O	0.609	17.334					
H2	0.006	0.478	0.158				
N	0.002	0.070	0.085	13.809			
H3	0.000	0.002	0.002	0.759	0.426		
H4	0.000	0.002	0.002	0.762	0.015	0.432	
H5	0.000	0.002	0.002	0.763	0.015	0.015	0.433
self-sharing − core	0.114	6.667	0.079	4.904	0.213	0.216	0.216
delocalization index	0.309	0.581	0.287	1.221	0.396	0.398	0.398
no. basin electrons[a]	0.422	9.248	0.366	8.124	0.609	0.614	0.615
$(HOH)-(NH_3)$ sharing	0.168						

[a] From sharing index sum rule.

TABLE 9: Sharing Indices in H_2NH-OH_2

TBSI; basin\basin	H1	H2	N	H3	O	H4	H5
H1	0.462						
H2	0.017	0.462					
N	0.784	0.784	14.002				
H3	0.014	0.014	0.703	0.363			
O	0.001	0.001	0.032	0.051	17.143		
H4	0.000	0.000	0.001	0.001	0.583	0.206	
H5	0.000	0.000	0.001	0.001	0.583	0.007	0.206
self-sharing − core	0.231	0.231	5.001	0.182	6.572	0.103	0.103
delocalization index	0.408	0.408	1.153	0.392	0.626	0.296	0.296
no. basin electrons[a]	0.639	0.639	8.154	0.574	9.198	0.399	0.399
$(H_2NH)-(OH_2)$ sharing	0.089						

[a] From sharing index sum rule.

Consider the $HOH-NH_3$ complex. The bond indices are given in Table 8, and the geometry is shown in Figure 2. The bond index from oxygen to the nonbridge hydrogen of water in the complex is 0.609, a slight increase from the value of 0.593 in an isolated water molecule. On the other hand, the bond index from oxygen to the bridge hydrogen decreases from the value in isolated free water by 19%, to a value of 0.478. There are also decreases in the internal nitrogen−hydrogen bond indices in the NH_3 moiety. The self-sharing indices behave in a fashion similar to those discussed above: the self-sharing index of the oxygen (the proton donor) increases upon hydrogen bond formation, while the self-sharing index of nitrogen (the proton acceptor) decreases. The delocalization indices of the oxygen and of the bridge hydrogen are less than those indices in the free water molecule, while the delocalization index of the nitrogen is 0.062 larger than that in free ammonia. These changes are in line with those of the previous complexes.

The total sharing between H_2O and NH_3 is large, the intermolecular bond index being 0.167. The intermolecular sharing is primarily from the nitrogen to the bridge hydrogen and the oxygen, the bond indices being 0.085 and 0.070, respectively. As found for the previous complexes, the sharing from the atom that is the proton acceptor is delocalized over both the bridge proton and the proton donor.

The change in the oxygen−bridge proton bond index upon complex formation and the large intermolecular bond index again indicate significant restructuring of electronic behavior upon complex formation.

TABLE 10: Sharing Indices in HOH−OH$_2$

TBSI; basin\basin	H1	O1	H2	O2	H3	H4
H1	0.222					
O1	0.603	17.310				
H2	0.006	0.497	0.161			
O2	0.001	0.056	0.066	17.137		
H3	0.000	0.001	0.001	0.573	0.199	
H4	0.000	0.001	0.001	0.573	0.007	0.199
self-sharing − core	0.111	6.655	0.080	6.568	0.099	0.099
delocalization index	0.305	0.579	0.285	0.635	0.291	0.291
no. basin electrons[a]	0.416	9.234	0.366	9.203	0.390	0.391
(HOH)−(OH$_2$) sharing	0.127					

[a] From sharing index sum rule.

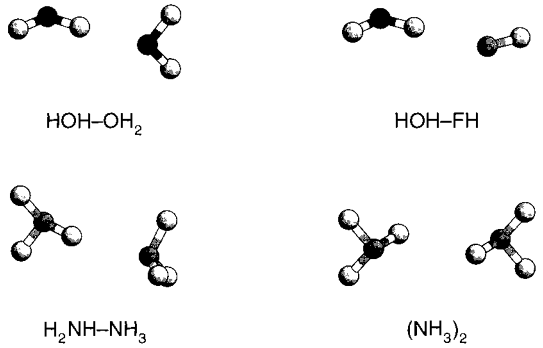

Figure 3. Geometries of the complexes HOH−OH$_2$, HOH−FH, H$_3$N−HNH$_2$, and (NH$_3$)$_2$ used for the analysis of the sharing of an electron. The ghost orbitals in (NH$_3$)$_2$ are centered midway between the "bridge" protons.

The bond indices in H$_2$NH−OH$_2$ are given Table 9 with the geometry of the complex shown in Figure 2. The changes in the sharing indices upon formation of H$_2$NH−OH$_2$ from the monomers follow the trends given above but in general with smaller values. The bond index from nitrogen to the nonbridge hydrogens in the complex are 0.784, an increase of 0.009 in contrast to the change of 0.016 in the preceding complex. The nitrogen to bridge hydrogen bond index decreases from 0.775 to 0.703, a decrease of about 9% in contrast to the 19% decrease in the oxygen to the bridge hydrogen upon formation of HOH−NH$_3$. (In both cases, the change is in the bond index from the atom that is the proton donor to the bridge hydrogen.) There are similar changes in the other internal bond indices.

The total sharing between the molecules is 0.089, 53% of the value in HOH−NH$_3$ when water is the proton donor. The sharing in H$_2$NH−OH$_2$ from the heavy atom that is the proton acceptor (oxygen in this case) is spread over the bridge proton and the other heavy atom. As in the case of the complex HF−HNH$_2$ in which HF is asked to act as a base, the intermolecular sharing in H$_2$NH−OH$_2$ from the oxygen to the bridge proton is larger than the sharing between the oxygen and the nitrogen. The differences in the sharing found between the two complexes formed from ammonia and water again correlate quite nicely with the relative acidities of the two molecules.

The bond indices in complex HOH−OH$_2$ are given in Table 10, with the geometry shown in Figure 3. The changes in internal bond indices upon formation of the complex are the following: the bond index from O1 to H1 (the terminal hydrogen on the proton donor) increases, while the bond index from oxygen to the bridge proton decreases by 16%, a slightly larger decrease than the analogue in the FH−FH dimer; there are small decreases in the other primary bond indices in the proton acceptor; there is a 20% decrease in the self-sharing index of the bridge proton, small decreases in the self-sharing indices of the terminal hydrogens of the proton acceptor, and an increase in the self-sharing index of the terminal hydrogen of the proton donor.

TABLE 11: Sharing Indices in HF−HOH

TBSI; basin\basin	H1	F	H2	O	H3
H1	0.103				
F	0.426	18.969			
H2	0.001	0.038	0.177		
O	0.000	0.034	0.536	17.259	
H3	0.000	0.001	0.007	0.597	0.217
self-sharing − core	0.052	7.484	0.089	6.629	0.108
delocalization index	0.214	0.249	0.290	0.583	0.302
no. basin electrons[a]	0.265	9.734	0.379	9.213	0.410
(HF)−(HOH) sharing	0.073				

[a] From sharing index sum rule.

The total intermolecular bond index is 0.127, a value that is 21% of the value of the oxygen−hydrogen bond index in isolated water. The oxygen−oxygen bond index is 0.056, while the oxygen-bridge proton bond index is 0.066, these being of comparable values. The sharing of the electrons from the proton acceptor is again spread out over the heavy atom and the bridge hydrogen of the proton donor.

The behavior of the delocalization indices follows the patterns established above: the delocalization index of the oxygen that is the proton acceptor increases upon complex formation from 0.594 to 0.635, while the delocalization indices of the other oxygen and the bridge proton decrease upon complex formation.

The sharing indices of the complex HF−HOH are given in Table 11 with the geometry shown in Figure 3. The internal bond indices and the self-sharing indices all change upon formation of the complex in a fashion similar to that found in H$_2$NH−OH$_2$. For example, the bond index from the proton donor to the bridge hydrogen is $9^1/_2$% smaller than in isolated HOH, compared to the 22% change of the primary bond index to the bridge proton in FH−OH$_2$. The intermolecular sharing indices also follow the pattern found above: the sharing from fluorine to the donor molecule is spread over both the bridge proton and the oxygen, with the sharing to the bridge proton being somewhat larger (0.004 or 12%) than the sharing to the oxygen. (There is a similar situation in th FH−NH$_3$ complex, but the difference is but 4%.) The total intermolecular bond index is 0.073 as compared to 0.169 in FH−OH$_2$. Again, the difference in the pattern of sharing between the two complexes HF−HOH and FH−OH$_2$ fits nicely with the relative acid−base properties of HF and H$_2$O.

The last complexes considered in this section are two dimers formed from ammonia: the configuration H$_3$N−HNH$_2$ studied by Dill, Allen, Topp, and Pople,[10] in which one ammonia is a proton donor and the other ammonia is the proton acceptor, and the configuration studied by Tao and Klemperer,[11] in which the two ammonia molecules are antiparallel. This latter is indicated by (NH$_3$)$_2$. The values of the sharing indices of these two configurations are given in Tables 12 and 13. The geometries of the complexes are shown given in Figure 3. The basin−basin sharing indices for H$_3$N−HN$_2$ are based on a frozen core 6-31++G** calculation using the geometrical constraints indicated in ref 10. The length of the hydrogen bond is the only variable in the geometry optimization. The sharing indices for (NH$_3$)$_2$, on the other hand, are based on a single point MP2 frozen core calculation using the basis set [7s5p3d,4s1p]-{3s3p2d}, the last set being the orbitals centered between the two ammonia molecules as given in ref 11. The orbitals on the ghost atom are not contracted. The results of calculations of the sharing in (NH$_3$)$_2$, given in this section and in section

TABLE 12: Sharing Indices in $H_3N{-}HNH_2$

TBSI; basin\basin	H1	H2	H3	N1	H4	N2	H5	H6
H1	0.440							
H2	0.016	0.435						
H3	0.016	0.016	0.435					
N1	0.770	0.767	0.767	13.842				
H4	0.001	0.001	0.001	0.064	0.348			
N2	0.001	0.001	0.001	0.039	0.685	14.024		
H5	0.000	0.000	0.000	0.002	0.014	0.789	0.468	
H6	0.000	0.000	0.000	0.002	0.014	0.789	0.017	0.468
self-sharing − core	0.220	0.218	0.218	4.921	0.174	5.012	0.234	0.234
delocalization index	0.402	0.400	0.400	1.205	0.390	1.152	0.410	0.410
no. basin electrons[a]	0.622	0.618	0.618	8.126	0.564	8.164	0.644	0.644
$(NH_3){-}(HNH_2)$ sharing	0.113							

[a] From sharing index sum rule.

TABLE 13: Sharing Indices in $(NH_3)_2$

TBSI; basin\basin	N1	H1	H2	H3	N2	H4	H5	H6
N1	13.870							
H1	0.738	0.413						
H2	0.778	0.015	0.459					
H3	0.778	0.015	0.017	0.459				
N2	0.037	0.034	0.001	0.001	13.868			
H4	0.033	0.003	0.001	0.001	0.739	0.414		
H5	0.001	0.001	0.000	0.000	0.778	0.015	0.459	
H6	0.001	0.001	0.000	0.000	0.778	0.015	0.016	0.459
self-sharing − core	4.935	0.207	0.229	0.229	4.934	0.207	0.229	0.229
delocalization index	1.184	0.403	0.406	0.406	1.184	0.404	0.406	0.406
no. basin electrons[a]	8.118	0.610	0.635	0.635	8.118	0.611	0.635	0.635
no. basin electrons[b]	8.118	0.610	0.635	0.635	8.118	0.611	0.635	0.635
$(NH_3){-}(NH_3)$ sharing	0.117							

[a] From sharing index sum rule. [b] From diagonal sum.

IV, demonstrate the flexibility of the present procedure of analysis when dealing with arbitrary basis sets.

The values of the sharing indices for the Dill, Allen, Topp, and Pople configuration of the ammonia dimer are given in Table 12. The self-sharing index of the bridge hydrogen decreases upon the formation of the dimer, as does the self-sharing index of the nitrogen that is the proton acceptor. The self-sharing index of the nitrogen that is the proton donor increases upon formation of the complex. The trends are in agreement with those found for the previous complexes.

The value of the intermolecular bond index is 0.113. This is larger than the intermolecular bond indices in the complexes $H_3CH{-}FH$, $HF{-}HNH_2$, $HF{-}HOH$, $H_2NH{-}OH_2$, and $FH{-}FH$, and smaller than those in $HOH{-}OH_2$, $HOH{-}NH_3$, $FH{-}OH_2$, and $FH{-}NH_3$. (The ordering of the lists is from the complex with the smallest intermolecular bond index to the largest intermolecular bond index.) Leaving aside $H_3CH{-}FH$, in the first group the proton donors, with the exception of that in FH−FH, are being asked to behave counter to the relative acidities of the moieties. In the second group, the proton donors are asked to behave in concert with the relative acidities of the moieties. Is the Dill, Allen, Topp, and Pople configuration of the ammonia dimer more like a member of the first group or more like a member of the second group? On the basis of the total intermolecular bond index, the Dill, Allen, Topp, and Pople configuration of the ammonia dimer would be placed between FH−FH and the second group, that is, as a proper hydrogen bond. However, aside from FH−FH (if placed in the first group), a feature that is common to the complexes of the first group and to the Dill, Allen, Topp, and Pople configuration of the ammonia dimer is that the sharing from the atom that is the proton acceptor to the atom that is the proton donor is less than the sharing from the acceptor to the bridge hydrogen. With the minor exception of $FH{-}NH_3$, which has a large intermolecular bond index, this is not the case for the members of the second group, nor for the hydrogen−fluoride dimer. On the basis of this finer dissection of electron sharing from the proton acceptor to the bridge proton and to the proton donor, the ammonia dimer should be placed in the first group. At this stage we must recall that the bond indices themselves do not fully characterize the type of sharing between moieties. For example, in H_2 at the Hartree−Fock level, the bond index in the ${}^1\Sigma_g$ state arising from the $1\sigma_u^{*2}$ configuration is the same as the bond index in the ${}^1\Sigma_g$ state arising from the $1\sigma_g^2$ configuration. The difference between these two states is not apparent from the bond indices but is apparent from the sharing amplitudes. A more detailed analysis of the type of intermolecular sharing in the ammonia dimer, as well as in the other complexes, is given in section IV where the sharing amplitudes are considered. A definitive statement about the proper ordering of the complexes is made in section V.

The basin−basin sharing indices, as well as certain other quantities, for the Tao−Klemperer configuration of the ammonia dimer are given in Table 13. As previously noted, the calculations for this configuration were carried out with the basis set [7s5p3d,4s1p]-{3s3p2d}, the last set being the set on a ghost atom located at the center of symmetry of the complex. The position of the ghost atom is at the center of gravity of the dimer, that is, midway between the "bridge" protons in Figure 3. The two nitrogens and the hydrogens labeled H1 and H4 are in a plane. The hydrogens H1 and H4 are the protons in positions to be donated to N2 and N1, respectively. It is this complex for which the sharing index sum rules[5]

$$\bar{N}_A = \sum_B I_{AB}$$

and the diagonal sum rule

$$\bar{N}_{\mathrm{A}} = \sum_m \nu_m(\varphi_m,\varphi_m)_{\mathrm{A}}$$

disagreed to a significant degree when using the default values of the parameters in PROAIM[16] and when no hand-editing of the surface files was performed. When the surfaces were visualized, there was found to be a large amount of leakage through the surfaces in the sense tubes were found to extend into the adjacent basins. These tubes are probably a result of the inadequate coverage of the surfaces by the paths used to determine the surfaces.[17] In order to get the sum rules to agree to 0.001, we have found it necessary to modify the default parameters used in the determination of the surfaces. We increased the number of paths and the number of orientations sampled on the unit spheres (thereby decreasing the breadth of the tubes) and hand-edited the surfaces so as to remove any remaining tubes. In addition to the visual criterion just mentioned, the average kinetic energies in a basin were calculated using the alternative forms

$$-\frac{1}{2}\int_{\mathrm{basin}} \mathrm{d}\zeta[\nabla^2\rho(\zeta;\,\zeta')|_{\zeta'=\zeta}]$$

and

$$\frac{1}{2}\int_{\mathrm{basin}} \mathrm{d}\zeta[\nabla\cdot\nabla'\rho(\zeta;\,\zeta')|_{\zeta'=\zeta}]$$

These two evaluations of the average kinetic energy should be the same for precisely determined Bader basins.

For the hydrogen basins the two evaluations of the average kinetic energy agreed to within 2.0×10^{-5} hartrees for the nonplanar hydrogen basins and to within 1.8×10^{-3} hartrees for the planar hydrogen basins. These values should be compared to the differences of 3.6×10^{-5} hartrees found for the hydrogen basins in the isolated ammonia monomer. The nonplanar values are in quite satisfactory agreement. The planar values are about 2 orders of magnitude worse, but we used these basins as cleaned up. The overlap integrals for the nitrogen basins were still not satisfactory. To improve these, we resorted to a bit of subterfuge. There is a bond critical point at the ghost atom. A clean surface separating the monomers was found from this critical point. The monomer overlap integrals were determined. The average numbers of electrons for the monomers as found from the sharing index sum rule are 9.999 52 and 9.999 65, while those found from the diagonal sum rule are 9.999 60 and 9.999 68. These are in quite decent agreement. The differences between the two evaluations of the average kinetic energy for the monomer basins in the complex are 6×10^{-3} hartrees and 4×10^{-3} hartrees. These differences are of the same order as the difference for the two evaluations of the average kinetic energy in the isolated monomer. The error here is probably partly due to the truncation, by the integration algorithm, of the volume integrated over. We deemed the overlap integrals for monomers in the complex to be satisfactory. In order to determine the overlap integrals for the nitrogen basins, we invoked the sum rules

$$(\varphi_m,\,\varphi_n)_{\mathrm{NH}_3} = (\varphi_m,\,\varphi_n)_{\mathrm{N}} + \sum_{i=1}^{3}(\varphi_m,\,\varphi_n)_{\mathrm{H}_i}$$

holding for each monomeric unit, to determine the $(\varphi_m,\,\varphi_n)_{\mathrm{N}}$ in that monomer. The nitrogen overlap integrals so determined were used to determine the sharing indices. The overall accuracy of the procedure is indicated by the agreement of the average kinetic energy of an electron in a basin as calculated by two different procedures and by the agreement of the sharing index sum and the diagonal sum giving the average number of electrons in the individual basins. The latter are equal to within 0.0001.

The sharing indices behave as is by now expected. The self-sharing of H1 and H4 is less in the complex than in the isolated molecules, and there is a slight increase in the self-sharing indices of the nitrogens—these act a bit as proton donors and proton acceptors in this configuration. The value of the internal bond index from N1 to H1 is a bit less than the value found in the isolated molecule, as is the bond index from N2 to H4.

The total intermolecular bond index is 0.117. slightly larger than that found for the Dill, Allen, Topp, and Pople configuration. (The sharing in these two complexes is not directly comparable because of the difference in basis sets used in the calculations.) This intermolecular bond index is practically equally divided between the three pairs of atoms, N1−N2, N1−H4, and N2−H1. The comments given above regarding the ordering of the complexes apply here also.

Thus far we have found that the intermolecular sharing of electrons in the complexes formed between hydrogen fluoride, water, and ammonia is larger than that between the complex formed between methane and hydrogen fluoride. The sharing ranges from relatively small, but not negligible, in HF−HOH, which has an intermolecular bond index of 0.073, to large in $\mathrm{FH{-}NH_3}$, which has an intermolecular bond index of 0.249. For the most part, the sizes of the intermolecular bond indices are in good correspondence with the relative acidities of the molecules making up the complexes, the intermolecular bond index of HF−HOH being less than that of $\mathrm{FH{-}OH_2}$, for example. The bond indices from the proton acceptor to the proton donor and the bridge hydrogen also reflect the relative acidities of the molecules making up a complex. The internal bond indices and the self-sharing indices also change upon complex formation in consistent ways, the bond index between the proton donor and the bridge hydrogen decreasing upon complex formation while the self-sharing index of the proton donor increases. In the complexes with hydrogen bonds, the bond indices indicate a significant delocalization of the sharing from the proton acceptor to the bridge proton and to the atom that is the proton donor. The changes in the internal sharing indices of the proton donor upon complex formation indicate that there is a considerable reorganization of the electronic structure of the donor in the complexes that are traditionally considered to contain hydrogen bonds.

III. Basin−Point Sharing Indices

The basin−basin sharing indices in a molecule give information somewhat at the level of information given by a Lewis dot structure, but with the very important distinctions that the basin−basin sharing indices are quantitative and that the concept of sharing provided by the sharing indices is not that the electron is physically shared by being between the two nuclei that are bonded, as implied by Lewis dot structures, but that the wave describing the electron is physically spread over all the atoms constituting the molecule or the complex.

The basin−point sharing index, being a detailed description of the sharing emanating from a basin, microscopically describes the delocalization of an electron. In this section we consider the basin−point sharing indices of three complexes, the first being $\mathrm{HF{-}HCH_3}$, the second FH−FH, and the third $\mathrm{FH{-}NH_3}$. The first complex serves as a calibration for the other two, this

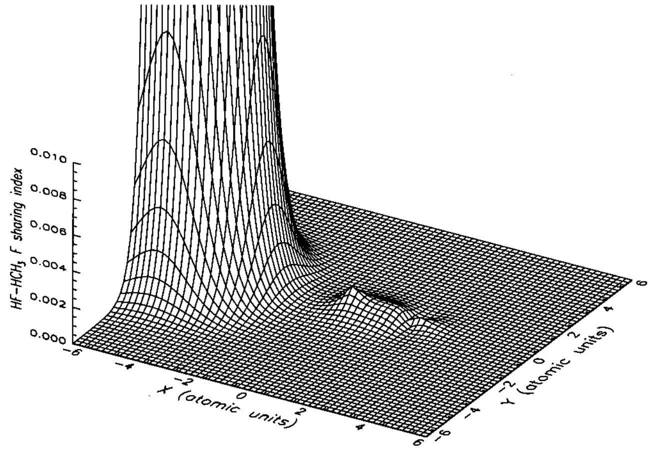

Figure 4. Cut of the basin−point sharing index in the complex H_3-CH−FH. The principal basin is the fluorine basin.

first complex indicating the nature of the sharing between two closed shell and non-hydrogen-bonded-species. The second two complexes illustrate, first, how the sharing in hydrogen-bonded species differs from the sharing in closed shell molecules and, second, the delocalized nature of the sharing from the proton acceptor.

A slice of the basin−point sharing index from the fluorine basin in the complex HF−HCH_3 is shown in Figure 4. (The various complexes depicted in Figures 1−3 have the same orientation used for the figures in this and the subsequent section.) The plane of the figure contains the fluorine nucleus, below the intense peak at the left of the figure; the bridge proton on the methane, below the low peak immediately to the right of the intense peak; and the carbon nucleus, sitting essentially in the cleft between the two rightmost peaks. The vertical scale (greatly enlarged compared to the figures below) is chosen so that the sharing features in the vicinity of the carbon−hydrogen bond are easily seen. Between the intense left-hand peak and the proton is a range in which the sharing index is very small. This is an indication that between the molecules there may be a node in the underlying sharing amplitudes when one point of the amplitude is fixed in the region of the fluorine basin. The structure in the region of the carbon−hydrogen bond is also worth noting. The major peak in this region surrounds the proton, in agreement with the results of section II in which it was found that there is greater sharing between the fluorine and the bridge proton than between the fluorine and the carbon. The sharing index is relatively flat between the proton and the carbon nucleus. Near the carbon nucleus are the remnants of a node which is similar to the node of an sp hybrid. Aside from this node, which is intrinsic to the hybrid orbital on carbon, there is no other indication of a nodal structure between the proton and the carbon nucleus. The sharing structure in the hydrogen−carbon region is, aside from some relative scaling of the regions at the hydrogen and at the carbon ends, quite similar to the basin−point sharing index from a proton basin toward the carbon in methane given in ref 5. The structure is also, with some relative scaling, similar to the square of a valence bond wavefunction describing a carbon−hydrogen bond.

We turn now to the hydrogen fluoride dimer. In the previous section we found that the bond indices from the fluorine that is the proton acceptor in FH−FH to the other fluorine and to the bridge hydrogen in the other molecule are of comparable size. What is the spatial distribution of this sharing from the proton acceptor? More detail about the distribution of this sharing can be gleaned from the basin−point sharing index. A slice of the basin−point sharing index with the basin containing the fluorine that is the proton acceptor is given in Figure 5. The plane of the slice contains the four nuclei. The fluorine that is the proton acceptor is at the left of the figure under the main peak, the bridge proton is under the minor peak just to the right of the main peak, and the fluorine that is the proton donor is under the cleft between the two rightmost peaks. The primary basin contains a large part of the main peak.

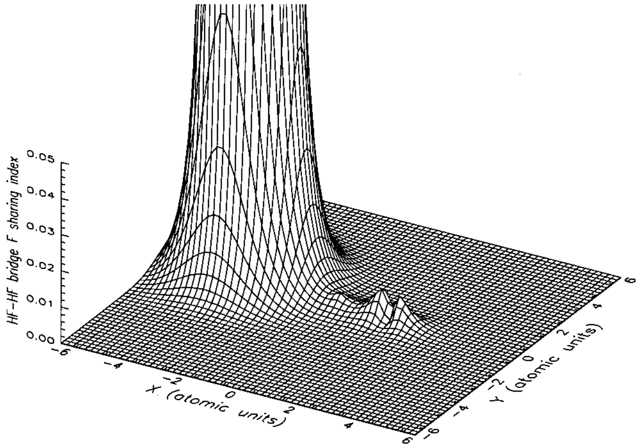

Figure 5. Cut of the basin−point sharing index in the complex FH−FH. The principal basin is the fluorine basin, which is the proton acceptor.

Within the primary basin the basin−point sharing index resembles the shape of the electron density of a fluorine atom. In the vicinity of the bridge proton the basin−point sharing index resembles the square of a hydrogenic 1s orbital, while in the vicinity of the terminal fluorine the sharing index resembles the square of a 2p orbital. The remnants of the node of the 2p orbital lie between the two rightmost peaks. The basin−point sharing index between the primary basin and the bridge hydrogen resembles that of a covalent bond between the two hydrogens in H_2, albeit at a smaller scale and with the sharing index being greatly skewed toward the primary basin, which contains by far the larger number of electrons. The basin−point sharing in the region lying between the bridge proton and the terminal fluorine (at the right) also resembles that of a covalent bond, but with the height of the saddle point in the figure being lower than the height of the saddle point between the primary basin and the bridge proton.

Are these saddle points remnants of nodes in the amplitudes or are they simply manifestations of a weak covalent sharing structure? It must be recalled that the nodes in the sharing amplitudes appear only as remnants of nodes in the volume−point sharing indices,[4] so that a definitive judgment as to whether the saddle structures are remnants of nodes or are weak covalent structures cannot be decided solely on the basis of the basin−point sharing indices. It is necessary to look at the sharing amplitudes. What is clear from the figure is that the sharing of an electron from the fluorine atom on the left is delocalized over the entire hydrogen fluoride molecule on the right.

Differences of the basin−point sharing index in this complex from that in HF−HCH_3 are apparent from a perusal of Figures 4 and 5. First note the difference in the vertical scale of the two figures. The sharing from the proton acceptor in the hydrogen fluoride dimer is, as anticipated from the basin−basin sharing indices, much larger than that in the HF−HCH_3 complex, is more delocalized over the companion molecule than in the methane complex, and has a different structure than that of the methane complex. It is quite clear that the behavior of

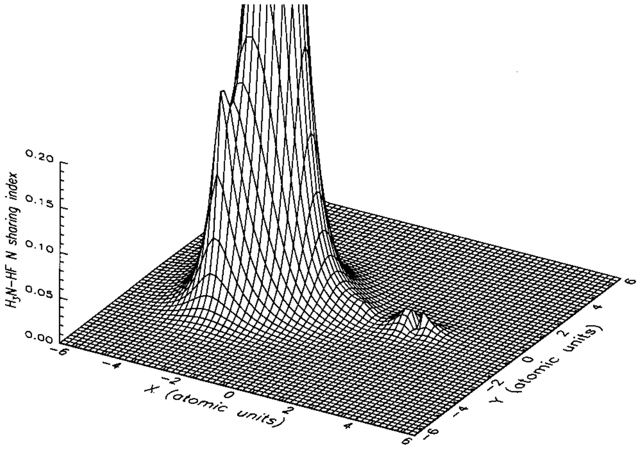

Figure 6. Cut of the basin–point sharing index in the complex FH–NH_3. The principal basin is the nitrogen basin.

the electrons in the region of hydrogen bonding is quite different in these two complexes.

The basin–point sharing index from the nitrogen atom in the complex H_3N–HF is given in Figure 6. Again note the change in the vertical scale. The following nuclei are in the plane of the cut. The nitrogen nucleus is under the large peak, the bridge proton is under the shoulder to the right of the main peak, and the fluorine is in the the cleft between the two rightmost peaks. A second proton on the ammonia is located under the nub on the side of the main peak at $x = -3$ au.

The sharing from the nitrogen atom to the bridge proton is greater than in the hydrogen fluoride dimer—the sharing to the bridge proton does not exhibit the saddle of Figure 5 between the proton acceptor and the bridge proton. Indeed, there is a portion of the basin–point sharing index on the downward slope to the right of the main peak that is in the volume ascribed to the bridge proton. This may be seen from the electron density of the ammonia–hydrogen fluoride complex that is given in Figure 7. The plane of the figure is the same as that used for the sharing index in Figure 6. The dividing surface been the two moieties intersects the plane of the cut close to the line for which $x = 0$. When this line is followed on the surface of the sharing index in Figure 5, the line is found to be considerably to the left of the bridge proton. Quite clearly, the sharing from the nitrogen to the bridge proton should be described as covalent even though the bond index is less than that from the nitrogen to one of the protons in isolated ammonia.

Again there is a saddle between the bridge proton and the fluorine nucleus, this saddle possibly being due to the remnants of a node of the sharing amplitude in this region. As in the case of the HF–HF dimer, the size and shape of the basin–point sharing index in the region of the donor hydrogen fluoride molecule indicates that the sharing from the nitrogen that is the proton acceptor is delocalized over the entire HF donor molecule.

IV. Sharing Amplitudes

The sharing amplitudes, $\langle \zeta; \zeta' \rangle$, give the most detailed description of the behavior of an electron in a many electron system. In this section we consider the sharing amplitudes for a number of complexes, some of which are hydrogen-bonded and some of which are not. The sharing amplitudes depend on two sets of coordinates, or on eight variables in general. Because for singlet states the dependence of $\langle \zeta; \zeta' \rangle$ on the spin variables σ and σ' is simply $\delta_{\sigma\sigma'}$, we have essentially six variables to deal with. In the figures in this section we fix one coordinate, say ζ'. This coordinate is called the fixed point. Typically the fixed point is chosen to be on the bridge proton. The other coordinate, ζ, is considered as the variable. In the figures, the variable point is restricted to lie in a plane. In the figures the fixed point is indicated by a star enclosed in a circle, while the locations of the nuclei in the plane and the perpendicular projections of the out-of-plane nuclei are indicated by the filled circles. Nodes are indicated by the solid lines that are not the grid lines.

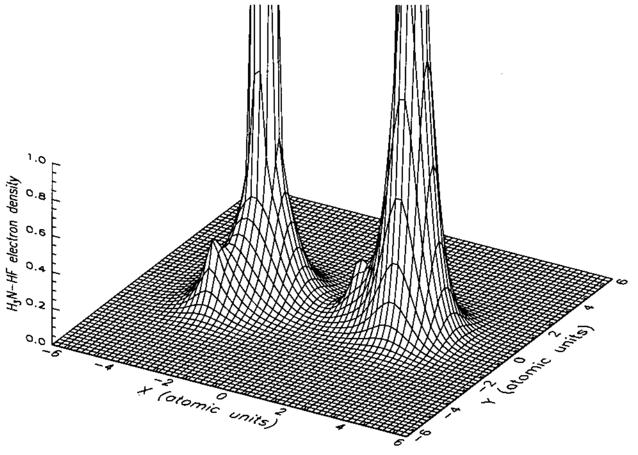

Figure 7. Cut of the electron density in the complex FH–NH_3. Contrast the electron density in the region between the nitrogen and the bridge proton with the volume–point sharing index in the same region given in Figure 6.

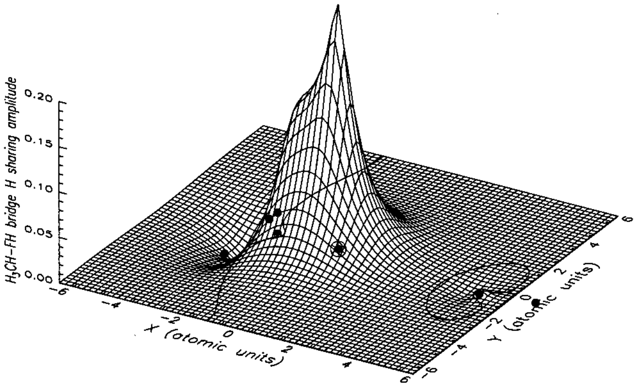

Figure 8. Cut of the sharing amplitude in the complex H_3CH–FH with the fixed point on the bridge proton.

We first give brief descriptions of the sharing amplitudes in the four complexes H_3CH–FH, FH–FH, FH–OH_2, and FH–NH_3 and then give a more detailed description of the differences in the amplitudes by constructing, out of some simple atomic orbitals, amplitudes which mimic those found in these complexes. This allows us to take over much of the language used in the more usual descriptions of electron behavior, such as used in molecular orbital descriptions and/or valence bond descriptions of bonding.

The sharing amplitude in the complex H_3CH–FH with the fixed point on the bridge proton is given in Figure 8. The plane of the figure contains the fluorine and its proton, the bridge proton and the carbon nucleus, and almost one other proton in methane. The (almost) in-plane proton in methane is the leftmost filled circle. The top two filled circles are the projections of the positions of two of methane's protons onto the plane. The carbon nucleus is at the filled circle to the right of the three circles having the most negative values of x. The

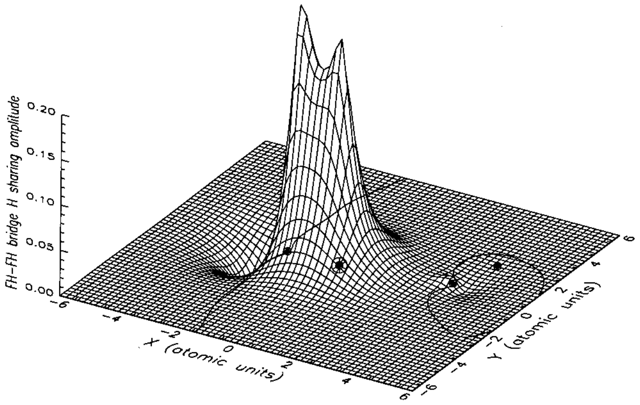

Figure 9. Cut of the sharing amplitude in the FH−FH dimer with the fixed point on the bridge proton.

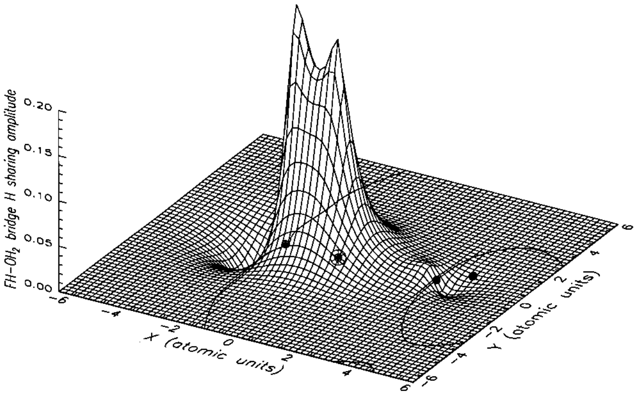

Figure 10. Cut of the sharing amplitude in the complex FH−OH_2 with the fixed point on the bridge proton.

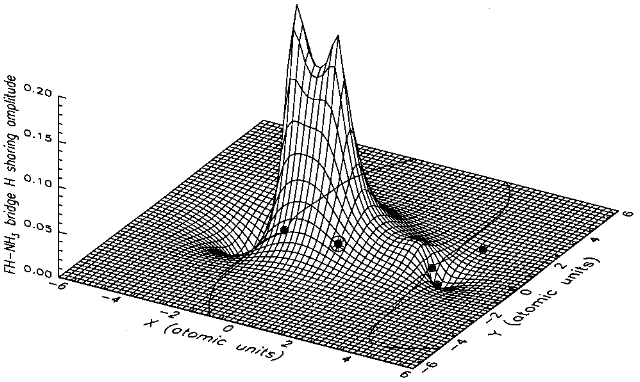

Figure 11. Cut of the sharing amplitude in the FH−NH_3 complex with the fixed point on the bridge proton.

other filled circles, reading from left to right, are the bridge proton, the fluorine nucleus, and (off the grid) the proton in FH.

There is no need to discuss the sharing amplitude from the fixed point back toward the rest of the methane molecule because the amplitude in the region of the methane is essentially the same as that found in the isolated methane molecule given in ref 5. It is the sharing amplitude from the bridge proton toward the hydrogen fluoride which indicates the intermolecular sharing characteristics of an electron in this complex. There is a closed nodal line (which in three dimensions is a closed surface) between the fixed point on the bridge proton and the fluorine nucleus. Near the fluorine nucleus, the nodal line has an indentation so the fluorine nucleus is not enclosed by the node. There is a minimum in the sharing amplitude to the left of the fluorine nucleus, the amplitude rising as the fluorine nucleus is approached. The location of the nodal line, between the two nuclei, is important for it is similar to the nodal line in the complex He_2, which, although having a different shape, lies between the fixed point located on a helium nucleus and the other helium nucleus. (The difference in shape is related to the differences in the orbitals which may be used to mimic the sharing structures of the two complexes.) As will be shown below, the node can be reproduced by a combination of a 1s orbital on the bridge proton with a predominantly antibonding 2p orbital on the fluorine nucleus. The location and, indeed, the shape of this node therefore indicates that the sharing between the bridge proton of methane and the hydrogen fluoride molecule has a weak antibonding character and is not of a covalent character.

The nature of the sharing is brought out more clearly by comparing the sharing amplitude in the methane−hydrogen fluoride complex with the sharing amplitude in the hydrogen fluoride complex given in Figure 9. All nuclei in FH−FH are in the plane. The fixed point is on the bridge proton. Again, the sharing amplitude from the bridge proton toward the left is similar to the sharing amplitude found in isolated hydrogen fluoride. The sharing amplitude in the region toward the other hydrogen fluoride molecule is quite different from that in Figure 8. In the hydrogen fluoride dimer, the closed nodal line is to the right of the second fluorine nucleus. There is an indentation of the nodal line near the fluorine. The structure of the sharing amplitude in the vicinity of the second fluorine nucleus is reminiscent of a type of 2s2p hybrid, with the hybrid bonding to the bridge hydrogen. The important conclusion at this stage is that the sharing of an electron from the bridge proton to the hydrogen-bonded hydrogen fluoride is similar to the sharing in a covalent bond, albeit a weak one. The sharing amplitude is remarkably similar (although not identical) to the amplitude from the proton toward the fluorine in isolated hydrogen fluoride. A more detailed analysis of the form of the sharing amplitude is given later.

Figure 10 gives a slice of the sharing amplitude from the bridge proton in the FH−OH_2 complex. The fluorine nucleus, the proton in HF, and the oxygen nucleus are in the plane of the slice. Beginning at the left of the figure, the solid dots are the fluorine nucleus, the bridge proton from FH, the oxygen nucleus, and the perpendicular projection of the two protons of water.

The structure of the sharing amplitude to the right of the fixed point, extending into the region of the water molecule, is significantly different from the sharing amplitude in the hydrogen bond region of the hydrogen fluoride dimer. First, there is more sharing between the bridge proton and the water molecule than between the bridge proton and the second HF in Figure 9. Second, the secondary peak to the left of the oxygen nucleus is larger in the present complex than in the previous complex. Third, the nodal line, which is mainly to the right of the oxygen nucleus, now passes extremely close to, or perhaps through, the oxygen nucleus. There is no indentation about the heavy nucleus as in Figure 9. The structure of the node in the vicinity of oxygen nucleus is akin to the node of a pure 2p orbital. From the perspective of sharing amplitudes, the hydrogen bond in FH−OH_2 has a definite covalent character.

A slice of the sharing amplitude from the bridge proton in the complex FH−NH_3 is given in Figure 11. The fluorine nucleus, the bridge proton, the nitrogen, and one of the ammonia protons are in the plane of the slice. From left to right, the solid dots represent the fluorine nucleus, the bridge proton, the nitrogen nucleus, the perpendicular projections of two of ammonia's protons, and the third ammonia proton. The sharing amplitude from the bridge proton to the ammonia molecule has the full characteristics of a covalent bond, including the nodal line that passes just to the hydrogen fluoride side of the nitrogen nucleus, just as occurs from a proton in isolated ammonia.[5] The secondary peak near the oxygen is also larger than the secondary peak in Figure 10, which in turn is larger than the secondary peak in Figure 9.

The four figures above give a sequence of complexes that begins with non-hydrogen-bonded $H_3CH{-}FH$ and then proceeds through a series of complexes with increasingly stronger hydrogen bonds. A brief description of the type of sharing from the bridge proton to the purported proton acceptor was given. Here we give a semiquantitative analysis of the type of intermolecular sharing involved in the complexes, using terminology that is familiar from valence bond and/or molecular orbital descriptions of bonding.

The sharing amplitude can be written in terms of the natural spin orbitals $\varphi_n(\zeta)$ as

$$\langle\zeta;\,\zeta'\rangle = \sum_n \varphi_n(\zeta)\,\nu_n^{1/2}\,\varphi_n^*(\zeta')$$

where ν_n is the occupation number of the n^{th} orbital. For fixed ζ', the sharing amplitude $\langle\zeta;\,\zeta'\rangle$, as a function of ζ, can also be considered to be a one-electron orbital. The idea in this section is to express the sharing amplitude with ζ' fixed in terms of some set of (atomic) orbitals. We begin by expanding the natural spin orbitals $\varphi_n(\zeta)$ in terms of some basis set, say $\phi_i(\zeta)$, as

$$\varphi_n(\zeta) = \sum_i \phi_i(\zeta)a_{in}$$

The sharing amplitude is then a linear combination of the new basis orbitals

$$\langle\zeta;\,\zeta'\rangle = \sum_i \phi_i(\zeta)\sum_n a_{in}\nu_n^{1/2}\,\varphi_n^*(\zeta') = \sum_i \phi_i(\zeta)\,b_i(\zeta')$$

with

$$b_i(\zeta') = \sum_n a_{in}\nu_n^{1/2}\,\varphi_n^*(\zeta')$$

We choose the $\phi_i(\zeta)$ to be a set of localized (atomic) orbitals. We also recognize that it is the amplitude $\langle\zeta;\,\zeta'\rangle$ which is endowed with meaning rather than the individual orbitals $\phi_i(\zeta)$. Nonetheless, it is these localized orbitals which allow us to make contact with more usual terminology.

In Figures 8, 9, 10, and 11, the sharing amplitudes with the fixed point on the bridge proton are mimicked by linear combinations of six orbitals: $\phi_{1s}(\zeta)$, a 1s orbital centered on the bridge proton (the location of the fixed point); $\phi_{a;2s}(\zeta)$, a 2s orbital centered on the proton acceptor; $\phi_{a;2p}(\zeta)$ an in-plane 2p orbital centered on the proton acceptor; $\phi_{d;2s}(\zeta)$, a 2s orbital centered on the proton donor; $\phi_{d;2p}(\zeta)$, an in-plane 2p orbital centered on the proton donor; and $\phi_{d;1s;dif}(\zeta)$, a diffuse 1s orbital on the proton donor, used for reasons given shortly. The amplitude in this region is written as

$$\phi_{1s}(\zeta)a_{1s} + \phi_{a;2s}(\zeta)a_{a;2s} + \phi_{a;2p}(\zeta)a_{a;2p} + \phi_{d;2s}(\zeta)a_{d;2s} + \phi_{d;2p}(\zeta)a_{d;2p} + \phi_{d;1s;dif}(\zeta)a_{d;1s;dif}$$

with the orbitals (normalized to unity) of the forms

$$\phi_{1s}(\zeta) = (a^3/\pi)^{1/2}\,\mathrm{e}^{-ar_p}$$

$$\phi_{h;2s}(\zeta) = \{b_h^5/[\pi(3 - 3b_hc_h + b_h^2\,c_h^2)]\}^{1/2}(r_h - c_h)e^{-b_hr_h}$$

$$\phi_{h;2p}(\zeta) = (d_h^5/\pi)^{1/2}\,x_h\,e^{-d_hr_h}$$

and with the coefficients $b_i(\zeta')$ replaced by the a_i. h, as a general subscript in the list of functions, is set to a in order to denote the heavy atom which is the proton acceptor and to d in order to denote the proton donor. r_p is the distance from the proton to the point ζ, r_h is the length of the vector $\mathbf{r}_h$ from the heavy atom nucleus to the point ζ, and x_h is the component of $\mathbf{r}_h$ that lies along the direction from the heavy nucleus to the proton. The choice of the phases of the 2s and 2p orbital should be carefully noted. The 2s orbital is positive for large values of r_h, and the 2p orbital is negative when x_h is negative.

It may be noted that the combination of orbitals used in the formation of the sharing amplitude with the fixed point on the bridge proton is a generalization of the set of orbitals used by Pimentel and McClellan[18] in a rather simplified molecular orbital description of hydrogen bonds.

Initially the orbital exponents are chosen a bit arbitrarily. We begin by using effective charges found by a slight modification of Slater's rules[19] for the isolated atoms; the effective charge of the 2s orbital is chosen to be slightly larger than that of the 2p so that the asymptotic behavior of the node in fluorine noted in ref 5 is reproduced.[20] Similar differences are introduced in the exponents of the 2s and 2p orbitals of the other heavy atoms. The same orbital exponents of fluorine are used for fluorine as a proton acceptor and as a proton donor. c_h, which gives the location of the 2s node, is chosen such that $\phi_{2s}(\zeta)$ is orthogonal to the 1s orbital with an effective charge of e_h (chosen by Slater's rules) on the heavy atom. This gives $c_h = 3/(b_h + e_h)$. The coefficients of the orbitals, together with the orbital exponents except e_h, are varied until the structure of the sharing amplitude in the neighborhood of the heavy atom nuclei is *qualitatively* reproduced. In addition, we find it necessary to include a diffuse "anti-1s" contribution, $\phi_{d;1s;dif}(\zeta)$, on fluorine as a proton donor in order to reproduce the location of the node near the donor by countering the long-range behavior of the proton 1s orbital. The parameters referring to hydrogen fluoride as a proton donor are fixed for all complexes. The parameters used in Figures 12, 13, 14, and 15 are collected in Table 14. The orbital exponents in the table are indicated by z with an identifying subscript. X_a and X_d give the x coordinate of the proton acceptor and the proton donor.

When Figures 12, 13, 14, and 15 are compared to the corresponding figures given above, it is found that the complete nodal structures from the regions of the proton acceptors to the edges of the figures are not reproduced. This disagreement is probably attributable to the fact that we are attempting to mimic the amplitudes in the hydrogen bond regions with a very limited set of orbitals. Near the proton acceptor there is qualitative agreement of the nodes between the mimicry and the figures from the MP2 calculations. The overall shapes of the sharing amplitudes are also in reasonable agreement. The nodal line that runs near the fluorine (as the proton donor) is reproduced rather well when a diffuse 1s orbital with a negative coefficient is centered on the nucleus (see the values of $a_{d;1s;dif}$ in Table 14).

Our main interest here is with the coefficients of the orbitals on the proton acceptors, denoted by $a_{2s;acceptor}$ and $a_{2p;acceptor}$ in Table 14. Recall that the 2s orbitals are positive far from the

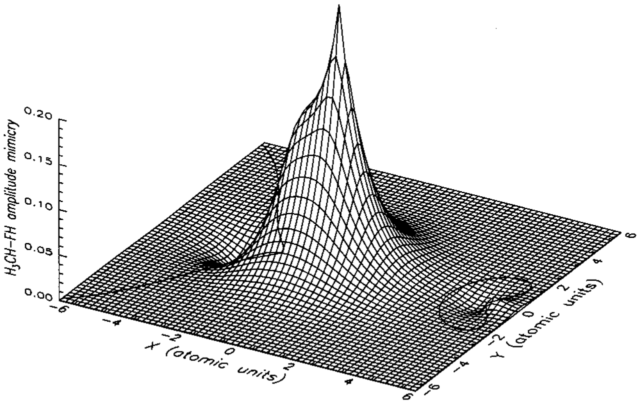

Figure 12. Cut of the sharing amplitude that mimics the amplitude of the complex CH_4−FH in the region between the bridge proton and the fluorine. The fixed point is on the bridge proton. The mimicry parameters are in Table 14.

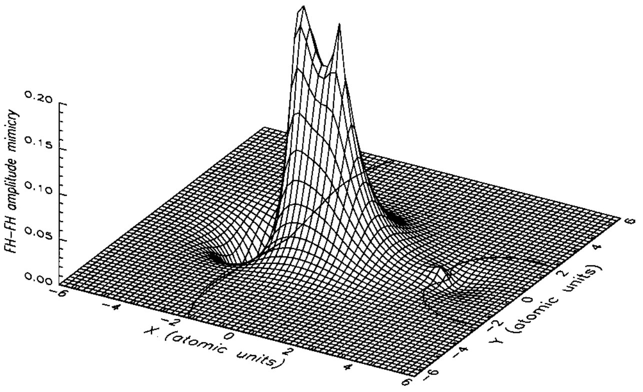

Figure 13. Cut of the sharing amplitude that mimics the amplitude of the complex FH−FH in the region between the bridge proton and the fluorine. The fixed point is on the bridge proton. The mimicry parameters are in Table 14.

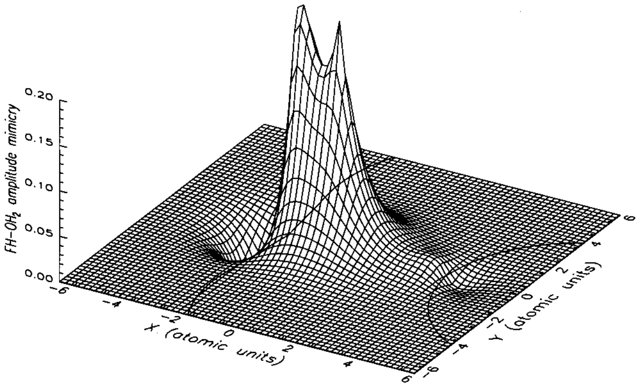

Figure 14. Cut of the sharing amplitude that mimics the amplitude of the complex FH−OH_2 in the region between the bridge proton and the fluorine. The fixed point is on the bridge proton. The mimicry parameters are in Table 14.

nuclear center and the 2p orbitals are negative when x_h is negative. The data for the complex H_3CH−FH is given in column 1 of Table 14. The coefficient of the bridge proton, $a_{1s;bridge}$, is positive. With the phase chosen for the orbital, the contribution of the proton 1s orbital to the sharing amplitude is everywhere positive. The coefficient of the 2s orbital on fluorine, $a_{2s;acceptor}$, is negative, indicating that at large distances from the fluorine nucleus the contribution of this orbital to the amplitude is negative—that is, in conventional terms the combination of the proton 1s orbital with the fluorine 2s orbital is antibonding. The coefficient of the fluorine 2p orbital is positive, indicating, with the phase convention that the 2p orbital is negative toward the bridge proton, that the combination of the fluorine 2p and the bridge proton 1s orbital is also antibonding. The fluorine 2s and 2p orbitals form an $sp^{1.9}$ hybrid orbital with the (negative) major lobe pointing toward the bridge proton, again substantiating the antibonding nature of the electron sharing between methane and hydrogen fluoride.

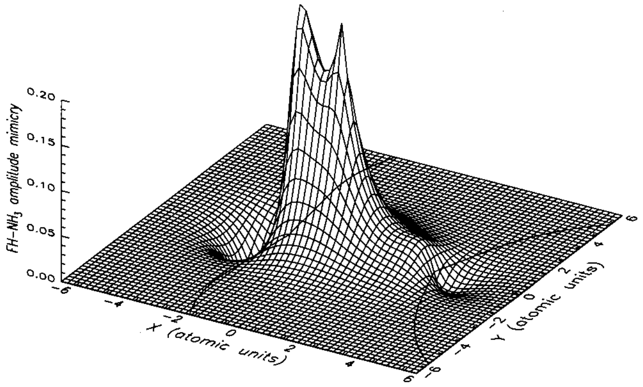

Figure 15. Cut of the sharing amplitude that mimics the amplitude of the complex FH−NH_3 in the region between the bridge proton and the fluorine. The fixed point is on the bridge proton. The mimicry parameters are in Table 14.

TABLE 14: Mimicry Parameters[a]

	H_3CH−FH	FH−FH	FH−OH_2	FH−NH_3
$a_{1s;bridge}$	0.337	0.263	0.263	0.263
$a_{2s;donor}$	0.123	0.035	0.035	0.035
$a_{2p;donor}$	0.197	0.296	0.296	0.296
$a_{2s;acceptor}$	−0.0069	−0.0078	0.001	0.0097
$a_{2p;acceptor}$	0.0095	−0.0081	−0.035	−0.041
$a_{1s;anti;donor}$	0.000	−0.077	−0.076	−0.076
X_d	−2.051	−1.761	−1.779	−1.820
X_a	5.084	3.510	3.589	3.162
$z_{1s;bridge}$	1.2	1.3	1.3	1.3
$z_{1s;anti;donor}$	1.1	1.1	1.1	1.1
$z_{1s;donor}$	5.7	8.7	8.7	8.7
$z_{2s;donor}$	1.75	2.7	2.7	2.7
$z_{2p;donor}$	1.6	2.5	2.5	2.5
$z_{1s;acceptor}$	8.7	8.7	7.7	6.7
$z_{2s;acceptor}$	2.7	2.7	2.3	2.1
$z_{2p;acceptor}$	2.5	2.5	2.0	1.8

[a] *a*, orbital coefficient; *X*, location of nucleus; *z*, orbital exponent.

The sharing in the methane−hydrogen fluoride complex differs qualitatively from that in the hydrogen fluoride dimer. The coefficients for FH−FH are given in column 2 of Table 14. In FH−FH the coefficients of both acceptor orbitals are negative, with the coefficient of the 2p orbital being somewhat larger than the coefficient of the 2s orbital. The 2s orbital is antibonding to the bridge proton while the 2p orbital is bonding. It is clear from Figures 9 and 13 that the overall combination produces a bonding contribution to the sharing amplitude in the region between the bridge proton and the proton acceptor. The bonding orbital on the fluorine can be looked at as hybrid $sp^{1.1}$ orbital with its major negative lobe pointing away from the bridge proton, the bonding (in terms of sharing) being to the minor positive lobe of the hybrid.

The sharing in the hydrogen bond region of the hydrogen fluoride−water complex is mimicked by a coefficient of the 2s orbital on oxygen that is essentially zero and a negative coefficient of the 2p orbital on oxygen. The negative contribution of $a_{2p;acceptor}$ indicates that there is bonding from the bridge proton to the proton acceptor through the 2p oxygen orbital, with essentially no contribution from the 2s orbital. The lack of contribution of the 2s orbital on the proton acceptor is

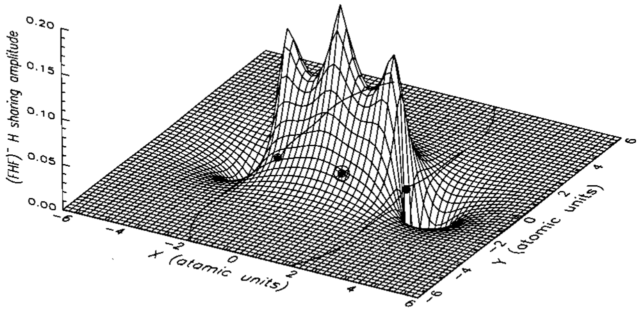

Figure 16. Cut of the sharing amplitude in the $(FHF)^-$ ion with the fixed point on the proton.

apparent in Figure 10 when it is recognized that the node in the sharing amplitude passes through the oxygen nucleus.

The last mimicry is that of the sharing amplitude in the $FH-NH_3$ complex, given in Figure 15. This is to be compared to Figure 11. The coefficient of the contribution of the 2s orbital on nitrogen is positive and that of the 2p orbital is negative. Although the contribution of the 2p is the greater, both orbitals give a bonding contribution to the sharing amplitude in the region between the bridge proton and the proton acceptor. The picture is that the nitrogen hybrid orbital that contributes to the sharing amplitude with the fixed point on the bridge proton is an sp hybrid with its positive major lobe pointing toward the bridge proton.

The systematic changes in the sharing amplitude from the bridge proton to the proton acceptor in these complexes is clear. The hybrid orbital on the proton acceptor in the hydrogen fluoride−methane complex is antibonding, the hybrid orbital on the proton acceptor in the hydrogen fluoride dimer is bonding but with the major lobe negative and pointing away from the bridge proton, the hybrid orbital on the proton acceptor in the hydrogen fluoride−water complex is essentially pure p, and the hybrid orbital on the proton acceptor in the hydrogen fluoride−ammonia complex is an sp orbital (mostly p) with the major lobe positive and pointing toward the bridge proton. These changes correlate nicely with the changes in the bond indices given in Tables 1, 2, 4, and 5.

One of the ideas that arises from the primitive molecular orbital description of hydrogen bonding given by Pimentel and McClellan[18] is that the electrons involved in the bonding are delocalized over the entire hydrogen-bonding region. The present description of hydrogen bonds by the sharing quantities fleshes out this idea in a quantitative manner even when effects that have their origins in the correlation of the electrons are included. The mimicry of the sharing amplitudes with the fixed points on the bridge proton essentially completes the program that began by describing hydrogen bonds in terms of orbitals, not in terms of the original constructs of molecular orbitals, but in terms of a rather different picture of the behavior of a single electron in a many electron system, which, nonetheless, retains some of the forms of previous descriptions.

A cut of the sharing amplitude in the $(FHF)^-$ ion with the fixed point on the proton is given in Figure 16. The plane of the cut contains all three nuclei. The shape of the sharing amplitude toward the fluorine nuclei is reminiscent of the sharing amplitude from the proton toward the fluorine in the hydrogen fluoride monomer, with the difference that the maxima near the fluorines are, relative to the peak at the proton, lower than the corresponding maxima in HF. This agrees with the bond indices between the proton and the fluorine(s) in the two species. Quite clearly, the sharing from the bridge proton to the fluorines in $(HFH)^-$ is to be classified as covalent.

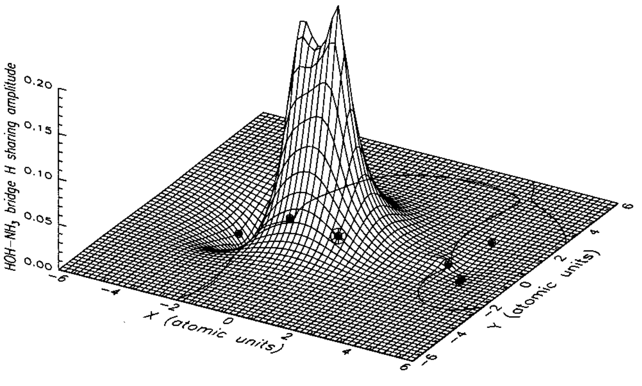

Figure 17. Cut of the sharing amplitude in the $HOH-NH_3$ complex. The fixed point is on the bridge proton.

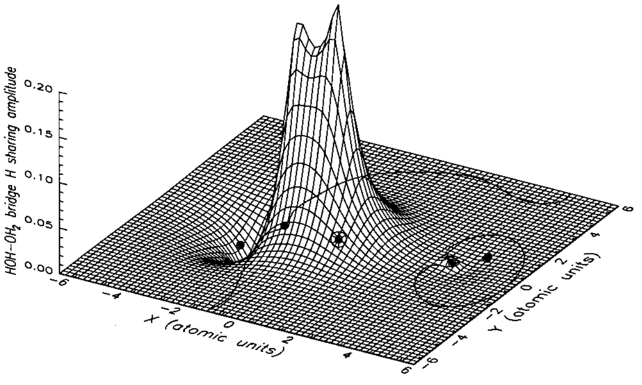

Figure 18. Cut of the sharing amplitude in the complex $HOH-OH_2$. The fixed point is on the bridge proton.

The analyses above lead us to a classification of these complexes into two types. We shall consider complexes to be hydrogen-bonded when the sharing from the bridge proton to the proton acceptor has the characteristics of a covalent bond, that is, the sharing is of the type exemplified by the dimers $FH-FH$, $FH-OH_2$, and $FH-NH_3$. [The $(FHF)^-$ ion also fits this pattern.] Complexes with the sharing from the bridge proton to the proton acceptor of the antibonding type, as in H_3CH-FH, are not considered to be hydrogen-bonded.

With the above as background, we now turn to the rest of the complexes. In the following, the fixed point is chosen to be on the bridge proton.

The bond indices in Table 8 indicate that there is considerable sharing of an electron between water and ammonia in the complex $HOH-NH_3$. A cut of the sharing amplitude in this complex is given in Figure 17. The water molecule is at the left in the figure, while ammonia is at the right with the nitrogen facing the bridge proton. The oxygen nucleus, the proton, and the nitrogen nucleus are in the plane, as is the second water proton and one of the other protons in ammonia (at a positive value of y). From the bridge proton to and including the nitrogen nucleus the sharing amplitude is positive, indicating that the bonding in this region is predominantly covalent. The curvature of the node about the nitrogen nucleus can be interpreted in terms of the semiquantitative dissection of the amplitudes given above. The 2p orbital on nitrogen gives a bonding contribution to the sharing amplitude while the 2s orbital gives an antibonding contribution. The major contribution is from the 2p orbital with the result that the net sharing is bonding. We classify this as a hydrogen-bonded complex.

A cut of the sharing amplitude in the water dimer $HOH-OH_2$ is given in Figure 18. The three nuclei in the water molecule at the left are in the plane of the figure, as is the

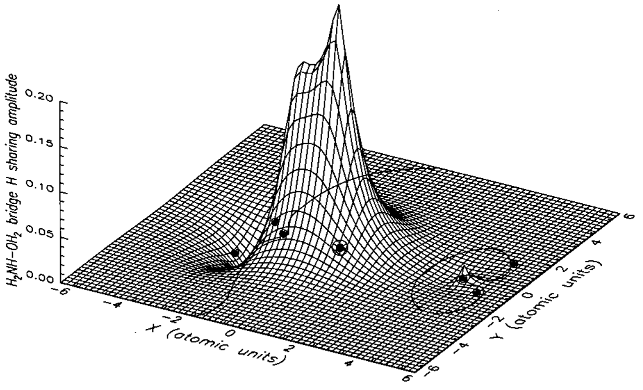

Figure 19. Cut of the sharing amplitude in the complex H_2NH-OH_2. The fixed point is on the bridge proton.

oxygen nucleus in the water on the right. The plane of the cut bisects the HOH angle in this second water molecule. The sharing amplitude from the bridge proton to the oxygen that is the proton acceptor is positive, indicating that the sharing amplitude is bonding in this region. As in Figure 17, the shape of the node near the proton acceptor indicates a dominant bonding contribution from the 2p orbital on the proton acceptor and a smaller antibonding contribution from the 2s orbital. The shapes of the nodes near the proton acceptors differ in Figures 17 and 18. The indentation near the proton acceptor in Figure 18 is much more pronounced than the indentation if Figure 17. The difference indicates that the contribution from the 2s orbital in the water dimer is larger than in the complex containing ammonia. This difference in structure correlates well with the bond indices between the bridge protons and the proton acceptors of 0.085 and 0.066 in $HOH-NH_3$ and $HOH-OH_2$ (Tables 8 and 10) and with the relative ease with which water donates a proton to the nitrogen in ammonia and to the oxygen in water. In each case, however, the sharing amplitude indicates covalent bonding in the region of the hydrogen bond, and we classify the complexes as being hydrogen-bonded.

Water tends to donate a proton to ammonia and not vice versa. Tables 8 and 9 give the values of 0.085 and 0.051 for the bond indices between the bridge proton and the proton acceptors in $HOH-NH_3$ and H_2NH-OH_2, so the sharing from the bridge proton to the proton acceptor is larger in the first complex. What does the form of the sharing amplitude indicate about the sharing when the molecules are constrained so that ammonia is in a position to donate a proton to water? A cut of the sharing amplitude from the bridge proton in the complex H_2NH-OH_2 is given in Figure 19. The plane of the cut contains the bridge proton, the nitrogen nucleus (to the left of the bridge proton), and the oxygen nucleus (to the right of the bridge proton). The form of the sharing amplitude in the region of the proton acceptor differs considerably from that in the $HOH-NH_3$ complex given in Figure 17. In fact the node in the region of the proton acceptor is much more like that in the methane–hydrogen fluoride complex given in Figure 8. The analysis of the sharing amplitude in that case applies equally here, although the intermolecular sharing is larger in the present complex. The node in the sharing amplitude between the proton donor and the proton acceptor indicates that the sharing is antibonding, in agreement with the empirical finding that water donates a proton to ammonia. This complex is not hydrogen-bonded.

This behavior of the nodal structure is also found in the complexes HOH–FH, in which hydrogen fluoride is asked to be a base, and in $HF-HNH_2$, in which ammonia is asked to be an acid. The cuts of the sharing amplitudes with the fixed points on the bridge protons are given in Figures 20 and 21, respectively. The plane of the cut in Figure 20 contains all the nuclei with HOH on the left and FH on the right. In Figure 21, the plane of the cut contains the nitrogen nucleus, the bridge proton, the fluorine nucleus, and the proton on fluorine. In each of these figures the sharing amplitude from the fixed point on the bridge proton to the proton acceptor has the characteristic shape of antibonding. Again, the shape of the sharing amplitude is in agreement with empirical findings of the relative proton-donating abilities of the molecules. These complexes are not hydrogen-bonded.

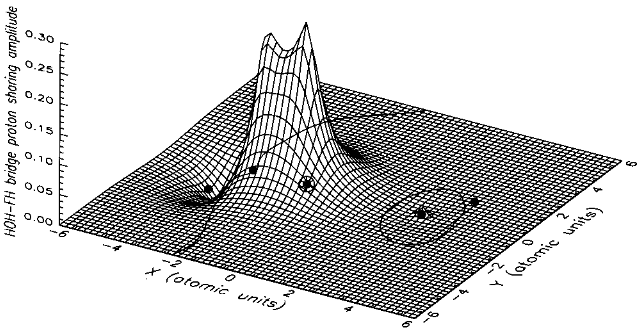

Figure 20. Cut of the sharing amplitude in the complex HOH–FH. The fixed point is on the bridge proton.

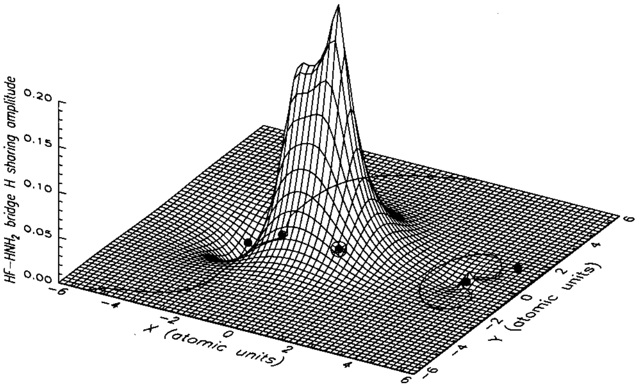

Figure 21. Cut of the sharing amplitude in the complex H_2NH-FH. The fixed point is on the bridge proton. Note that ammonia is at the left in the figure and hydrogen fluoride is at the right.

The correlation of the nodal structures in the region between the bridge proton and the purported proton acceptor with the relative acidities of the molecules leads us to suggest that proton transfer is facile when there is no extrinsic nodal structure between the bridge proton and the proton acceptor. We suggest that the characteristic extrinsic nodal structure between the proton acceptor and the bridge proton, as found in the methane–hydrogen fluoride complex as well as in the H_2NH-OH_3, HOH–FH, and $HF-HNH_2$ complexes, is indicative of antibonding and is antithetical to proton transfer. If this is more general, then the sharing amplitudes give an invariant way of predicting a class of reactions.

The final item considered in this paper is the nature of the bonding in the ammonia dimer, a subject of some controversy.[11] The complexes considered here are the dimers in two configurations, one in the configuration (H_3N-HNH_2) considered by Dill, Allen, Topp, and Pople[10] and the other in the symmetrical configuration found by Klemperer and Tao.[11] The calculation of the wavefunction for the Dill, Allen, Topp, and Pople configuration was at the MP2, 6-31++G** level of approximation using frozen cores, while the calculation for the Klemperer and Tao configuration was done using their basis set, which includes contributions from a ghost atom located at the center of gravity of the dimer. The cuts of the sharing amplitudes are

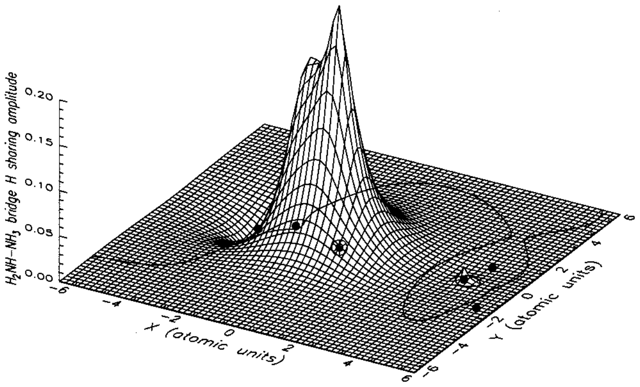

Figure 22. Cut of the sharing amplitude in the Dill, Allen, Topp, and Pople conformation of the complex H_3N-HNH_2. The fixed point is on the bridge proton.

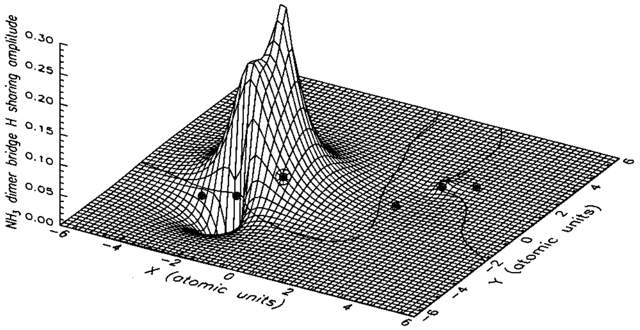

Figure 23. Cut of the sharing amplitude in the complex $(NH_3)_2$. The fixed point is on one of the bridge protons.

given in Figures 22 and 23, respectively. In each complex, the sharing amplitude has a node between the bridge proton and the proton acceptor.

Consider first Figure 22. The two nitrogens as well as the bridge proton are in the plane of the cut. The two nonbridge protons in the left-hand ammonia are out of the plane. The projections of their positions on the plane are the leftmost solid circle. The solid circle near $x = 5.6$, $y = -1.8$ is the in-plane proton from the other ammonia. The nitrogen in this ammonia is at the point with the minor mountain peak. The other solid circle is the projection of the positions of the other two protons onto the plane. The fixed point is on the bridge proton. The sharing amplitude at the nitrogen that is the proton acceptor is positive. There is a circular (in the plane) node close to the nitrogen nucleus. This node is to be considered as intrinsic to the nitrogen, being primarily from the 2s orbital on the nitrogen. (The small distortion from being centered on the nucleus can be ascribed to a small admixture of a 2p orbital centered on the nitrogen nucleus.) There is an additional node further from the nitrogen nucleus. This node is not intrinsic to the nitrogen. Between the inner node and the outer, the amplitude is negative. We take these characteristics to indicate that the sharing amplitude from the bridge proton to the proton acceptor is weakly antibonding—the structure of the sharing amplitude in the region between the nitrogen acceptor and the bridge proton is not similar to that found in the species above, which are commonly considered to hydrogen bond, but rather is similar to the amplitude in He_2 in ref 5.

The sharing amplitude for the configuration of Klemperer and Tao is given in Figure 23. The basis set used has contributions from a ghost atom situated at the center of symmetry of the complex. (See Figure 3 for the geometry of the complex.) The two nitrogen nuclei (one to the lower left of the bridge proton, the other near the weak 2p type structure about it), the bridge proton, and the proton at $x \approx 2$, $y = 0$ are in the plane of the cut. The other solid circles are projections of the other protons. The ammonia molecules are oriented such that their permanent dipoles are antiparallel. Between the bridge proton and all the nuclei of the proton acceptor there is a node. As in the case of the above ammonia dimer, this is reminiscent of the node that is between the heliums in He_2. On this basis, the sharing from the bridge proton to the proton acceptor molecule must be classified as weakly antibonding.

It should be noted that the total intermolecular sharing index in each of the ammonia dimers is larger than in the hydrogen fluoride dimer. In spite of this, the sharing amplitudes indicate that there is not what we would classify as a hydrogen bond in the ammonia dimers. This also illustrates that the basin−basin sharing indices should not be interpreted in isolation.

V. Discussion

With the determination of the type of sharing from the bridge protons, we can weave together the threads from the previous sections. We combine the types of sharing found in section IV with the values of the basin−basin sharing indices of section II so as to order the complexes on the basis of the strength and type of intermolecular sharing.

Throughout, it is important to recognize that the analysis of the type of sharing which exists between and within the molecules forming the complexes is dependent on the total wave function only and not upon the individual orbitals chosen to form the wave function. This frees the analysis of the behavior of an electron in a many electron system from the arbitrariness inherent in the choice of the individual orbitals used to construct the wave function.

In Table 15 the complexes are ordered by two criteria. The complexes having a sharing amplitude from the bridge proton which is of the antibonding type to the acceptor molecule are listed before those having a bonding type of sharing. Within the antibonding complexes those with the greater total intermolecular sharing are listed before those with lesser intermolecular sharing. Within the bonding complexes, the molecules with the larger total intermolecular sharing are listed after those with the lower total intermolecular sharing. The net result is that the entries in Table 15 are ordered with the complexes having the most antibonding type of intermolecular sharing at the top and the complexes having the most bonding type of intermolecular sharing at the bottom. The table gives the type of sharing from the bridge proton to the proton acceptor, the total intermolecular bond indices, the bond indices from the proton acceptor to the bridge proton, the bond indices from the proton acceptor to the proton donor, and the percent change in internal bond from the proton donor to the bridge proton upon complex formation from the isolated molecules.

There are some systematics that can be gleaned from the table. Reading from bottom to top, the complexes with FH as the proton donor have, in order, NH_3, OH_2, and FH as the proton acceptors. The same ordering holds when the proton donor is HOH. (We do note that the intermolecular sharing from the bridge proton in HOH−FH is antibonding. Hydrogen fluoride is not a base in water.) This sequence is the order of increasing electronegativity of the atom that is the proton acceptor. When H_2NH is the proton donor (the antithetical to bonding situation), the ordering of the proton acceptors (again reading from bottom to top) is reversed: it is FH, OH_2, and NH_3.

With two exceptions, the total intermolecular bond indices, B_{intermol}, of the complexes that are bonding are larger than the indices of the antibonding complexes. The exceptions are the

TABLE 15: Intermolecular Sharing Indices

complex	type of sharing	$B_{\text{intermolecular}}$	$B_{\text{acceptor-bridge proton}}$	$B_{\text{acceptor-donor}}$	% $\Delta B_{\text{donor-bridge proton}}$[a]
$(NH_3)_2$[b]	antibonding	0.117	0.034[c]	0.037	5[d]
H_2NH-NH_3	antibonding	0.113	0.064	0.039	12
H_2NH-OH_3	antibonding	0.089	0.051	0.032	9
HOH−FH	antibonding	0.073	0.038	0.034	4
H_2NH-FH	antibonding	0.056	0.032	0.021	5
H_3CH-FH	antibonding	0.027	0.019	0.006	1
FH−FH	bonding	0.098	0.045	0.052	15
$HOH-OH_2$	bonding	0.127	0.066	0.056	16
$HOH-NH_3$	bonding	0.168	0.085	0.070	19
$FH-OH_2$	bonding	0.169	0.080	0.083	22
$FH-NH_3$	bonding	0.249	0.120	0.115	26
$(FHF)^-$	bonding		0.222[c]	0.181	

[a] Percent change in proton donor to bridge proton bond index upon complex formation. [b] Special basis set with ghost atom. [c] There are two acceptor-bridge proton indices with this index. [d] There are two donor-bridge proton bonds having this change.

TABLE 16: Intermolecular Sharing Matrix

donor\ acceptor	NH_3		OH_2		FH	
H_2NH	anti	0.113	anti	0.089	anti	0.056
HOH	syn	0.168	syn	0.127	anti	0.073
FH	syn	0.249	syn	0.169	syn	0.098

ammonia dimers in which the values of B_{intermol} are 0.015 and 0.019 larger than the value in the hydrogen fluoride dimer but less than the values in the other “bonding” complexes. In spite of this, the sharing amplitude in the ammonia dimers is characteristic of antibonding rather than bonding.

Before continuing to the other entries in Table 15 we note that the interrelationships of the total interbasin sharing in this set of molecules are brought out more clearly by arranging the total intermolecular sharing indices in the form of a matrix. This is given in Table 16. The proton donors play the role of the row indices, while the proton acceptors play the role of the column indices. The column indices are in the order in which the heavy elements are arranged in the periodic table, and the row indices are arranged such that the atomic numbers of the heavy elements increase toward the bottom of the table. The entries serving as matrix elements contain the notation anti or syn, indicating sharing that is of the antibonding type or that is of the bonding type, together with the value of the total intermolecular sharing index.

The antibonding complexes are found to occupy the upper right part of the matrix, the bonding the lower left. All of the complexes involving ammonia as the proton donor are antibonding insofar as the bridge proton to acceptor molecule is concerned. In general a proton donor is antibonding to those acceptors that lie to its right in the periodic table. The total intermolecular sharing indices decrease in going to the right along a row. The total intermolecular sharing indices increase in going down a column. Thus for a given donor molecule the total intermolecular sharing decreases with increasing atomic number of the acceptor heavy atom. For a given acceptor molecule the total intermolecular sharing increases with increasing atomic number of the donor heavy atom. Because of the connection between the electronegativities of the heavy atoms and their atomic numbers for this series, these trends may be rephrased in terms of electronegativities rather than atomic numbers.

Turning back to Table 15, the bond indices between the proton acceptor and the bridge proton, $B_{\text{acceptor-bridge proton}}$, follow the general trend set by B_{intermol}, including the larger indices for both ammonia dimers when the two bonds in $(NH_3)_2$ are counted. The bond indices, $B_{\text{accept-donor}}$, between the atom that is the proton acceptor and the atom that is the proton donor in the bonding complexes are all larger than those in the antibonding complexes. Apparent also from the table is the greater delocalization of the sharing of the electron from the proton acceptor over the bridge proton and the proton donor in the bonding complexes as contrasted to the antibonding complexes.

The intermolecular bond indices in the bonding complexes indicate that significant sharing of electrons develops between the molecules upon hydrogen bond formation. Furthermore, the sizes of the indices between the proton acceptor and the bridge proton, and between the proton acceptor and the proton donor, indicate that the sharing from the proton acceptor is spread over the heavy atom and bridge proton of the proton donor molecule.

The largest changes in the internal bond indices upon complex formation are found in the bond index between the proton donor and the bridge proton. The right-hand column of Table 15 gives the percent change in the internal bond index $B_{\text{donor-bridge proton}}$ between the proton donor and the bridge proton upon complex formation. The percent changes in $B_{\text{donor-bridge proton}}$ in the complexes having a bonding type of sharing run from 15% in the FH−FH dimer to 26% in $FH-NH_3$. The percent changes in the other complexes, running from 1% in the complex containing methane to 12% in the Dill, Allen, Topp, and Pople configuration of the ammonia dimer, are all less than any of the changes in the bonding complexes. These percent changes in $B_{\text{donor-bridge proton}}$ [with the minor exception of that in $HF-HNH_2$ and noting that there are changes in both moieties of the $(NH_3)_2$ dimer] also follow the trends set by the total intermolecular bond index. The conclusion is that there are significant changes in the internal bond indices that accompany the development of the intermolecular sharing in the hydrogen-bonded complexes upon complex formation. In turn, these changes indicate that the behavior of the electrons within a molecule undergoes significant modification upon complex formation. The (percent) changes are less in the complexes that, by the present criteria, are not hydrogen-bonded.

VI. Summary

At the fundamental level, the behavior of a single electron in a many electron system is quantitatively described by the sharing amplitude and the point−point sharing index. The volume−point and volume−volume sharing indices, both arising from the point−point sharing index by suitable integration over prescribed volumes, are coarser grained measures of the sharing of an electron between a point and a volume and between two volumes. The bond index between two basins (or volumes) is the total sharing between those two basins. The sharing amplitude is the quantity which is as close as can be gotten to a wave function for a single electron in a many electron system. Reference should be made to the preceding paper[5] for an analysis of electron behavior in some simple hydrides in order to get an idea of the trends in species containing typical single bonds. Our remarks below are confined for the most part to the complexes considered in this paper.

The total intermolecular bond index in the complex H_3CH-FH is small, being 0.027 as compared to the bond indices of 0.896 in H_2, 0.211 in LiH, and 0.441 in HF. The complex H_3CH-FH (and He_2 in the previous paper[5]) serves as the prototype of non-hydrogen-bonded complexes. The total intermolecular bond indices in FH−FH, $FH-OH_2$, and $FH-NH_3$ are larger, being 0.098, 0.169, and 0.249. These three complexes typify hydrogen-bonded complexes, with the intermolecular sharing ranging from relatively weak to quite strong. The sharing in these three complexes and in $HOH-OH_2$ and $HOH-NH_3$, all typically classified as containing hydrogen bonds, has the following characteristics: (1) the sharing from the proton acceptor is delocalized over both the bridge proton and the proton donor; (2) the intermolecular sharing increases with the strength of the hydrogen bond; (3) there is significant internal and external reorganization of the behavior of an electron upon hydrogen bond formation; (4) the values of the intermolecular bond indices correlate very nicely with the relative acid−base strengths of the moieties. Leaving aside the ammonia dimers for now, the intermolecular bond indices in the above hydrogen-bonded complexes are larger than the bond indices in the complexes H_2NH-OH_2, HOH−FH, and H_2NH-FH in which the proton donor is asked to behave counter to their relative acid−base strengths.

The intermolecular bond indices in all the complexes are smaller than in the strongly covalent bonds of H_2 and CH_4. The total intermolecular bond index in $FH-NH_3$ is, however, 75% of the value of the FH bond index in the complex and larger than the bond index in LiH, indicating a large amount of delocalization of an electron between the moieties.

The two ammonia dimers have total intermolecular bond indices that are larger than that in the FH−FH dimer but smaller than those in the other hydrogen-bonded dimers. On this basis, these complexes might be classified as hydrogen-bonded; however, on the basis of the other intermolecular bond indices (proton acceptor to bridge proton and proton acceptor to proton donor), the ammonia dimers could be classified as non-hydrogen-bonded complexes. The coarse-grained measure of sharing provided by the bond indices does not suffice to give a clean classification of intermolecular bonding in these complexes. It is the sharing amplitudes which provide the key for the proper classification of the complexes.

The volume-point sharing indices given for the complexes H_3CH-FH, FH−FH, and $FH-NH_3$ in section III provide a more detailed dissection of the sharing of an electron. In this paper, the basin−point sharing indices are all from the basin containing the proton acceptor. In the first complex the two moieties exhibit closed shell behavior, with exceedingly low values of sharing in the region between the moieties and low values in the regions of the carbon and the bridge proton of methane. The two hydrogen-bonded complexes show the difference between two hydrogen-bonded complexes having quite different intermolecular bond indices and, when compared to H_3CH-FH, illustrate the difference between non-hydrogen-bonded complexes and hydrogen-bonded complexes. There is little delocalization from the fluorine in H_3CH-FH to the CH− portion of the methane molecule. There is significant delocalization from the acceptor fluorine basin over the proton donor FH in FH−FH and considerable delocalization from the nitrogen basin in $FH-NH_3$ over the FH molecule. In the latter, the volume−point sharing index from the nitrogen basin towards the bridge proton appears in all respects as a fully formed covalent bond that is only somewhat weaker (in terms of sharing) than the internal bond in HF. There is sufficient detail in the volume−point indices to indicate that the sharing in the region of the bridge proton is s-type (i.e., mimicked by an s orbital) and the sharing in the region of the fluorine that is the proton donor is dominantly p-type.

The sharing amplitudes give the most detailed information about the behavior of a single electron in a many electron system. These amplitudes not only show distinct differences between the hydrogen-bonded and the non-hydrogen-bonded complexes but also show the variations in sharing among the hydrogen-bonded and non-hydrogen-bonded complexes.

These differences can be illustrated by a reconstruction of the sharing amplitudes in terms of traditional constructs such as particular sp hybrids or in terms of particular combinations of s and p orbitals. As an indication of some of the results we find, we give here an abbreviated and qualitative description, in terms of orbitals, of the structure of the sharing amplitudes from the fixed point on the bridge proton toward the acceptor fluorine in H_3CH-FH, FH−FH, $FH-OH_2$, and $FH-NH_3$. The full details are found in section IV. Choose the conventions that the 2s orbital on the acceptor fluorine is positive at large distances from the fluorine and that the 2p orbital on the acceptor fluorine is positive toward the bridge proton. The 1s orbital on the proton is chosen to be positive. The constants *a*, *b*, and *c* below are chosen to be positive. One point of the sharing amplitude is fixed at the bridge proton. The sharing amplitude from the bridge proton to the region of the fluorine in H_3CH-FH can be mimicked by the combination $a1s - b2s - c2p$. This is akin to a totally antibonding combination of orbitals. In FH−FH, the combination of orbitals that mimic the sharing amplitude in the region of the proton acceptor is $a1s - b2s + c2p$, which is antibonding between the 1s and the 2s orbitals and bonding between the 1s and the 2p orbitals. (The overall sharing pattern and values of the coefficients indicate that the bonding is weakly covalent.) The combination of orbitals in $FH-OH_2$ is $a1s + c2p$, which is bonding between the 1s and the 2 p orbital with no contribution from the 2s orbital, while the combination of orbitals in $FH-NH_3$ is $a1s + b2s + c2p$, which is bonding between the 1s and both the 2s and the 2p orbitals. In somewhat more picturesque terms, what we have in H_3CH-FH is sharing between a positive hydrogen 1s orbital on the bridge proton and an sp hybrid on fluorine, which has its major lobe negative and pointing toward the bridge proton. In FH−FH the major lobe of the sp hybrid is negative and pointing away from the bridge proton that has a positive 1s orbital. The bonding is to the minor lobe of the sp hybrid, or to the backside (which is positive) of the hybrid 2s2p orbital. In $FH-OH_2$ there is no contribution of the 2s orbital on the oxygen, the only sharing being through the 2p orbital that is positive toward the bridge proton. Finally in $FH-NH_3$ the sharing is to the major lobe of the sp hybrid on the fluorine that is positive and points toward the bridge proton containing a positive 1s orbital. The intermolecular sharing amplitude from the bridge proton toward the proton acceptor in this complex indicates that the hydrogen bond is fully covalent.

The sharing amplitudes for complexes $HOH-NH_3$ and $HOH-OH_2$ indicate covalent intermolecular bonding between the moieties, while the patterns of the amplitudes in the complexes HOH−FH, H_2NH-OH_2, and HOH−FH are characteristic of antibonding between the moieties. The sharing amplitudes from the bridge protons in the two conformations of the ammonia dimer, the configuration considered by Dill, Allen, Topp, and Pople[10] and the configuration considered by Tao and Klemperer,[11] indicate that there is antibonding between the moieties in spite of the fact that the total intermolecular bond indices are larger than that in FH−FH. Thus we have covalent bonding patterns in the complexes FH−FH, FH−OH_2, FH−NH_3, HOH−NH_3, and HOH−OH_2. In HOH−FH, H_2NH−OH_2, HOH−FH, and the two ammonia dimers the sharing amplitude indicates antibonding, as found in the non-hydrogen-bonded complex H_3CH−FH and in He_2.[5]

It is also noted in section IV that the patterns of the sharing amplitudes are found to be correlated with the relative acid/base properties of the moieties involved in the complexes and give a classification of electron behavior into hydrogen-bonded “interactions” and non-hydrogen-bonded “interactions”.

A characteristic feature of all the complexes that have a covalent type of sharing structure from the bridge proton to the proton acceptor is that the complexes are in conformations that are appropriate for a facile proton transfer from one molecule to the other, in concert with the relative acidities of the moieties. A feature of the complexes having an antibonding type of structure is that, although the molecules are aligned for such facile proton transfer, the transfer of the bridge proton is contrary to the relative acidities of the molecules in the complexes. Thus, at least for the present complexes, the type of sharing, bonding and antibonding, from the bridge proton to the proton acceptor correlates nicely with the relative ease of transfer of the bridge proton.

As a result of these considerations, we have stated in section IV that “We shall consider complexes to be hydrogen-bonded when the sharing from the bridge proton to the proton acceptor has the characteristics of a covalent bond, that is, the sharing is of the type exemplified by the dimers FH−FH, FH−OH_2, and FH−NH_3. [The $(FHF)^-$ ion also fits this pattern.] Complexes with the sharing from the bridge proton to the proton acceptor of the antibonding type, as in H_3CH−FH, are not considered to be hydrogen-bonded.”

The ammonia dimers illustrate that there can be a fair amount of delocalization of an electron from one molecule to the other in spite of the antibonding nature of the sharing indicated by the sharing amplitude. The delocalization is still less than that in all but one of the present complexes, yet it reminds us that the bond indices by themselves should not be taken as a complete characterization of the type of sharing.

In the present paper, we have considered only the simplest of complexes that may exhibit hydrogen bonds. There are many questions that can be raised. What is the bonding in more complicated dimers and in multimers? A simple question is the question of the details of the sharing in the formamide dimer in which the oxygen which is the proton acceptor has a double bond to the neighboring carbon. Is the sharing the same in the formaldehyde oxime dimer? What is the sharing in complexes in which aromatic rings are involved? Is the sharing between hydrogen fluoride and acetylene of the bonding or of the antibonding variety? How are intramolecular hydrogen bonds to be characterized? These questions lead to questions of the characterization of hydrogen bonding in biological structures. The present method of analysis gives a consistent and systematic procedure for characterizing the behavior of an electron in such hydrogen-bonded systems.

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(16) The version of PROAIM actually used is called VECSURF. VECSURF contains modifications written by J. Cioslowski to (1) facilitate vectorization and (2) supply some default parameters to the routines.

(17) In the Tao and Klemperer dimer,[11] there are the usual bond critical points between the nitrogen and the protons in each ammonia molecule. There is also a bond critical point between the molecules at the origin of the ghost atom. The surfaces from the in-plane NH bond points intersect the surface emanating from the bond critical point that lies at the ghost atom. The numerical algorithms used for the determination of the surfaces of the basins and the subsequent integrations have difficulty with the basins adjoining the surface that separates the two molecules. The electron density in the region between the molecules is low and elongated along the plane of reflection formed by the two nitrogens and the bridge protons. The net results are (1) the paths defining the surfaces as found numerically from the bond critical point located between the molecules do not span the surface, the surface resulting from the algorithm being a narrow sheet with long axis perpendicular to the plane of reflection, and (2) the paths determining the other surfaces of basins adjacent to this surface are poorly determined by the numerical algorithm.

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(20) See Figure 4 of ref 5.