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Sharing Analysis of the Behavior of Electrons in Some Simple Molecules

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The behavior of the electrons in the simple hydrides of the first row of eight elements, LiH, BeH_2, BH_3, CH_4, NH_3, H_2O, and HF, together with H_2 and the complex He_2, is described at the one-electron level within the conceptual framework provided by the sharing index $I(\zeta; \zeta')$, which gives a quantitative measure of the sharing of an electron between the two points ζ and ζ', and the underlying sharing amplitude $\langle\zeta; \zeta'\rangle$. With the exception of He_2, bond indices, self-sharing indices, delocalization indices, volume−point sharing indices, and sharing amplitudes are determined for the set of molecules from results of MP2/6-31++G** calculations. The calculations involving He_2 use a different basis set. The trends in all of these indices track the differences in the traditional electronegativities of the elements. The uniqueness of the carbon−hydrogen bond in methane among all the bonds described in this paper is associated with the equal participation of carbon and hydrogen in the sharing of an electron between the volumes associated with the atoms. The shapes of the sharing amplitudes can be described using much of the traditional language of bonding, such as hybrid orbitals and (partial) valence bond structures, in spite of the calculations including effects due to the correlation of electrons. The difference between covalent bonding and nonbonding (or weak antibonding) is illustrated by consideration of the complex He_2 formed between two closed shell atoms.

I. Introduction

That the chemistry of molecules is related to the behavior of the electrons in the molecules is beyond dispute. That the behavior of the electrons in molecules is described by a wave function (or more generally by a density matrix) is also beyond dispute. However, the description of electrons in an n electron system is complicated by the fact that $4n$ variables (three spatial and one spin for each electron) are required as a full set of arguments for the wave function. At an elementary level one would prefer to begin a description of the behavior of electrons in molecules by first describing the behavior of a single electron and then successively describing the behaviors of two, three, and more electrons, including a greater number of electrons in the description as one gains insight into the behavior of a lower number of electrons. In the case that the electronic wave function is formed from a single determinant of single particle orbitals, such as Hartree−Fock wave functions are constructed, some insight into the behavior of a single electron can be gained from the nature of the individual orbitals. There is a problem even at the level of this approximation, however. The orbitals are not unique, and it is the totality of the set of orbitals which describes the behavior of even a single electron. For wave functions that include correlation the problem is more severe because of the larger number of orbitals and the more complicated construction of the wave function from the orbitals.

The difficulty in describing the behavior of a single electron in a many electron system is mitigated by the quantitative measure of the sharing of a single electron between two points introduced in an earlier paper.[1] The fundamental quantity describing the sharing of an electron between the two points $\zeta \equiv (\mathbf{r}, \sigma)$ and $\zeta' \equiv (\mathbf{r}', \sigma')$ ($\mathbf{r}$ being the position vector and σ the spin variable) is the sharing amplitude, $\langle\zeta; \zeta'\rangle$. In a many electron system this amplitude is as close as one can get to a description of a single electron by a single particle wave function. The sharing amplitude is related to the point−point sharing index, $I(\zeta; \zeta')$, in a manner reminiscent of the relation between a wave function and a probability: $I(\zeta; \zeta') \equiv |\langle\zeta; \zeta'\rangle|^2$. This index is the quantitative measure of the sharing of an electron between the points ζ and ζ'.

Subsidiary measures of sharing may be obtained from the sharing index $I(\zeta; \zeta')$. The volume−point indices $I_A(\zeta)$ are found by integrating ζ' over the volume V_A. Volume−volume sharing indices, I_{AB}, between the two volumes V_A and V_B are formed by integrating ζ over the volume V_A and ζ' over the volume V_B. When the volume is an atomic basin, in the sense of Bader[2] for example, we refer to these as basin−point and basin−basin sharing indices. Both of these subsidiary indices have been used to describe the sharing in some simple molecules.[3,4] Thus far, however, the sharing amplitude $\langle\zeta; \zeta'\rangle$ has not been applied in a quantitative way to the description of the behavior of a single electron, the application given in ref 1 consisting of a qualitative description only of the amplitude in benzene.

The applications of the sharing indices given in ref 4 were limited to some simple hydrocarbons and the hydrogen molecule, all having covalent bonds, to lithium hydride, having a predominantly ionic bond, and to white phosphorus. There remain several questions yet to be addressed even at a simple level: Do the sharing indices, both the basin−basin and the basin−point indices, reflect the trends in bonding usually assumed by chemists as the rows in the periodic table are traversed? Do these indices vary in a way which mirrors the qualitative measures of the relative electronegativities of the

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atoms in a molecule and the placement of the elements in the periodic table? Are changes in features that are typically described in terms of hybrid orbitals, such as sp orbitals, apparent also in the sharing indices and amplitudes? Do the sharing amplitudes give any significant information about the bonding or about the chemical behavior of electrons in molecules? How are the various types of bonding, covalent to antibonding, reflected in the sharing indices and the sharing amplitude? In addition to these questions there remains the task of establishing standards against which the behavior of electrons in more complex molecules can be compared.

The present paper presents an analysis of the sharing of a single electron in a series of molecules in which the bonding is quite simple, varies in a systematic fashion, and is well understood. The paper therefore establishes a baseline against which bonding, as measured by the sharing amplitude and the sharing indices, in other molecules and complexes can be compared. More particularly, the present paper supplies the background for the analysis, given in the following paper, of the behavior of electrons in simple complexes containing hydrogen bonds.

The plan of this paper is as follows. In part II we give a brief description of the construction of the sharing amplitude and the sharing indices. Part III contains an analysis of the basin−basin sharing indices in the molecules H_2, LiH, He_2, CH_4, NH_3, H_2O, and HF. (For good measure we also include the entities BeH_2 and BH_3.) This sequence allows us to analyze the bond indices and self-sharing indices in molecules ranging from purely covalent molecules, typified by H_2 and CH_4, through polar-covalent molecules, to ionic molecules, represented by LiH, and nonbonded complexes, represented by He_2. The basin−point sharing indices for NH_3, H_2O, and HF are given in part IV. When taken with the basin−point sharing indices given in ref 4 this completes the experimentally known simple hydrides of the first row of eight elements in the periodic table. Part V presents the sharing amplitudes, most with one point fixed at a proton, for the sequence of molecules H_2, LiH, He_2, CH_4, NH_3, H_2O, and HF. This set of molecules illustrates the variation in the basin−point sharing indices and the sharing amplitudes in a simple series of hydrides and provides a standard for the monomers from which the hydrogen-bonded (and non-hydrogen-bonded) species in the following paper are formed.

One important aspect of the present procedure for analyzing the behavior of a single electron in a many electron system is the consistency of the various levels of description ranging from the basin−basin to the point−point level. This is, of course, the result of basing all the sharing indices on the fundamental quantity, the point−point sharing index, and the underlying sharing amplitude.

II. Background

The concept of the sharing of a single electron between two points in space is rooted in the fact that a pure state of a system is described by a wave function. The very idea of a wave is closely associated with the ability of being able to compare a structure over a set of points having some measure of delocalization. When considering the wavelike properties of a single electron in a many electron system, the electron should be pictured as being spread over some region in space. A quantitative measure of the spatial distribution of the wave representing a single electron in a many electron system is provided by the sharing index $I(\zeta;\zeta')$, this index being a measure that the wave is in the small volumes $d\zeta$ and $d\zeta'$ about the points ζ and ζ'.[1] (Other coordinates, such as the momentum coordinates, may also be used.) The sharing index itself is related to the sharing amplitude $\langle\zeta;\zeta'\rangle$ by $I(\zeta;\zeta') = |\langle\zeta;\zeta'\rangle|^2$, this relation being much like the relation between wave functions and probabilities. The sharing amplitude, which is the matrix square root of the single particle density matrix, is as close as one can get to a wave function for a single electron in a many electron system. One expression for the sharing amplitude is in terms of the natural spin orbitals $\varphi_m(\zeta)$ which diagonalize the single particle density matrix

$$\langle\zeta;\zeta'\rangle = \sum_m \varphi_m(\zeta)\, \nu_m^{1/2} \varphi^*{}_m(\zeta')$$

ν_m ($0 \le \nu_m \le 1$) is the occupation number of the mth natural spin orbital $\varphi_m(\zeta)$. For singlet states we note that the sharing amplitude is proportional to $\delta_{\sigma\sigma'}$, there being no sharing between opposite spins. This sharing amplitude is the fundamental quantity in our description of the behavior of a single electron in a many electron system. The sharing amplitude $\langle\zeta;\zeta'\rangle$ and the sharing index $I(\zeta;\zeta')$ are measures of the delocalization of a single electron.

An important sum rule which relates the point−point sharing index to the average electron density $\bar{N}(\zeta)$ at point ζ is

$$\bar{N}(\zeta) = \int d\zeta'\, I(\zeta;\zeta')$$

This sum rule in turn implies that the point−point sharing index satisfies the relation

$$\int d\zeta\, d\zeta'\, I(\zeta;\zeta') = N$$

N being the total number of electrons in the molecule. Because of this normalization to the total number of electrons in the molecules, we sometimes speak of the sharing of electrons, remembering that what is being described is a single electron property normalized to N.

From the point−point sharing index $I(\zeta;\zeta')$ we find two integrated sharing indices, the volume−point index

$$I_V(\zeta) \equiv \int_V d\zeta'\, I(\zeta;\zeta')$$

which gives a measure of the sharing of an electron between the volume V and the point ζ, and the volume−volume sharing index

$$I_{VV'} \equiv \int_V d\zeta \int_{V'} d\zeta' I(\zeta;\zeta')$$

which gives a measure of the sharing of an electron between the two volumes V and V' (which may overlap).

In our applications we typically choose the volume to be the volume of an atomic basin.[2] Let these be labeled A and B. We refer to these as atoms when the basins include nuclei. The bond index between the basins A and B is simply the total sharing between the two basins

$$B_{AB} = I_{AB} + I_{BA}$$

The self-sharing index, I_{AA}, is a measure of the degree to which an electron is localized within the volume V_A.[4] The valence $\mathcal{V}_A$ of a basin, defined by

$$\mathcal{V}_A = \sum_{C\neq A} B_{CA}$$

is a measure of the degree to which the electrons in the primary basin A are delocalized to basins outside the primary basin. It is, however, not quite the most useful measure. Rather, for reasons given below, we use the quantity

$$\Delta_{\mathrm{A}} = {}^{1}/_{2} V_{\mathrm{A}} = \sum_{\mathrm{C} \neq \mathrm{A}} I_{\mathrm{CA}}$$

which is proportional to the valence, as the measure of delocalization. This we dub the delocalization index.

Although we refer to B_{AB} as the bond index between the two basins A and B, we stress the fact that this bond index is a *quantitative measure* of the *sharing* of an electron between the *two distinct* basins and so is a measure of how an electron is *delocalized* between the basins. The bond index is *not* a measure of the electron density located in the *region between* the two atoms that are bonded.

There is also a sum rule relating the average number of electrons in the volume V_{A} to the basin−basin sharing indices

$$\bar{N}_{\mathrm{A}} = \sum_{\mathrm{B}} I_{\mathrm{AB}}$$

This we dub the "sharing index sum rule". The value of $\bar{N}_{\mathrm{A}}$ calculated by this means can be compared to that obtained from a direct calculation of

$$\bar{N}_{\mathrm{A}} = \int_{V_{\mathrm{A}}} \mathrm{d}\zeta\, \bar{N}(\zeta) = \sum_{m} \nu_m (\varphi_m, \varphi_m)_{V_{\mathrm{A}}}$$

using the diagonal elements of the atomic overlap matrices[2]

$$(\varphi_m, \varphi_n)V_{\mathrm{A}} \equiv \int_{V_{\mathrm{A}}} \mathrm{d}\zeta\, \varphi_m^{*}(\zeta)\, \varphi_n(\zeta)$$

and the occupation numbers. This provides a convenient and important check on the numerical accuracy of the calculations.

The simple sum rule

$$\bar{N}_{\mathrm{A}} = I_{\mathrm{AA}} + \Delta_{\mathrm{A}}$$

follows from the identification of the self-sharing index and the definition of the delocalization index. It is this division of the average number of electrons in the volume V_{A} into the number of electrons that are shared to points inside the volume V_{A} and those that are shared to points outside the volume which gives the indices I_{AA} and Δ_{A} their utility.

The self-sharing indices, I_{AA}, and the bond indices, B_{AB} (or the sharing indices I_{AB}), together with the delocalization index, Δ_{A}, give the coarsest measure of sharing. The values of the bond indices in some simple molecules have been found to agree with the intuitive ideas of chemists.[1,4] The self-sharing index gives the number of electrons in a basin that are not shared to points outside the specified basin, and the delocalization index gives the number of electrons that are shared outside the basin. A finer measure of the sharing structure is provided by the volume−point (atom−point) sharing indices. These may be considered as a representation of the microscopic valence structure of a basin. The finest detail of the sharing structure is given by the point−point sharing indices, these being akin to probabilities. The sharing amplitudes, on the other hand, have in most cases a rich nodal structure and provide information similar to that provided by a wave function.

The sharing amplitude $\langle \zeta; \zeta' \rangle$ for a fixed value of one of the indices, say ζ', can be considered as an orbital. As such it can be written as either a superposition of natural spin orbitals or as a superposition of more primitive orbitals centered, for example, on the nuclei. For fixed ζ', then, we can speak about the construction of the amplitude in such terms as the superposition of molecular orbitals or in terms of hybrid orbitals, always bearing in mind that it is the amplitude which is endowed with meaning and not the individual orbitals making up the amplitude.

TABLE 1: Sharing Indices in H_2

TBSI; basin\basin	H1	H2
H1	1.104	
H2	0.896	1.104
self-sharing − core	0.552	0.552
delocalization index	0.448	0.448
no. basin electrons[a]	1.000	1.000

[a] From sharing index sum rule.

TABLE 2: Sharing Indices in LiH

TBSI; basin\basin	Li	H
Li	3.989	
H	0.211	3.567
self-sharing − core	−0.006	1.784
delocalization index	0.105	0.105
no. basin electrons[a]	2.100	1.889

[a] From sharing index sum rule.

TABLE 3: Sharing Indices in He_2

TBSI; basin\basin	He1	He2
He1	3.996	
He2	0.004	3.996
self-sharing − core	1.998	1.998
delocalization index	0.002	0.002
no. basin electrons[a]	2.000	2.000

[a] From sharing index sum rule.

The results reported below are, with the exception of those pertaining to He_2, based on MP2 calculations done at the 6-31++G** level of approximation with frozen cores using the GAUSSIAN 92 suite of programs.[5] The calculation for He_2 uses the basis set of Diercksen and Sadlej.[6] The atomic overlap integrals were calculated by using the programs EXTREM and PROAIM[7] and ATOMICI.[8]

III. Basin−Basin Sharing Indices

We begin with an analysis of sharing in the simplest of nontrivial covalent molecules, H_2, proceed to an analysis of sharing in the ionic species LiH and in the nonbonded complex He_2, and then consider the sharing in the sequence of molecules CH_4, NH_3 H_2O, and HF, running the gamut in the latter sequence from a molecule having pure covalent bonds to a molecule having a polar-covalent bond. By this means we span the primitive types of bonding in simple, experimentally observed molecules and establish a foundation for the analysis given in the following paper of complexes involving hydrogen bonding. To complete the simple hydrides of the elements in the first row of eight of the periodic table we also consider the entities BeH_2 and BH_3.

Tables 1−3 give the basin−basin sharing indices in the molecules H_2, LiH, and He_2, all in their ground electronic states. In these tables the bond indices are arranged in the form of a matrix with the labels at the left and at the top of a table identifying the basins between which the sharing index is evaluated. Only the diagonal and left lower elements of the matrix are shown. The acronym "TBSI" in these and the following tables stands for twice basin sharing index. The off-diagonal terms of this index are numerically close in value to the classical bond indices in a number of molecules.[1,3,4] It is these off-diagonal elements which are referred to as bond indices in this paper. Again it is emphasized that the present measure of a bond index is in fact a measure of the sharing of an electron between two distinct regions of space and not of the electron density in the region between the two atoms.

The first two molecules were considered in ref 4 using the basis set 6-31G**. The values of the indices given in that reference differ a bit from those given here because of the different basis sets used in the calculations of the electronic wave functions. The differences are small (in the third decimal place), however, and no further comment will be made except to note that all comparisons in the present paper (with the one exception, He_2) are made using a common basis set. The effect on the basin−basin sharing indices when the frozen core stipulation is removed has also been found to be in the third decimal place.

The number of electrons in a hydrogen basin of H_2, as found from the sharing index sum rule, is 1.000, as is dictated by the symmetry of the molecule. This agreement gives an indication of the numerical accuracy of the integration routines in this molecule. The value the bond index is 0.90. The deviation from the classical value of 1.00 is in accord with the inclusion of correlation in the construction of the wave function[4] and with the behavior of the molecule upon dissociation. The self-sharing index of an electron in one of the hydrogen basins is 0.55, indicating that 0.55 electrons are not shared to points outside the basin. The delocalization index of one basin is 0.45, crudely the same as the self-sharing index. Roughly speaking, of the one electron in a hydrogen basin, one-half is shared within the basin and one-half is shared with points outside the basin. We take the hydrogen molecule to be the prototype of a covalent bond.

The values for the numbers of electrons in the basins of LiH clearly indicate a preponderance of ionic character. There are but 2.10 electrons in the lithium basin with 1.90 electrons in the hydrogen basin. These values indicate an almost complete transfer of the valence electron on the lithium atom to the hydrogen basin. The small value of 0.21 for the bond index, indicating little sharing between the lithium and the hydrogen basins as compared to that in H_2, is consistent with the dominant ionic nature of the bond. The self-sharing index of the lithium basin is 1.994. This indicates that two electrons (traditionally the 1s core electrons) in the lithium basin are not shared to points outside that basin. There remains but 0.10 of the valence electron in the lithium basin. The value of the delocalization index, 0.10, indicates that this electron is completely shared with the hydrogen.

Because of the nonsharing of the core electrons on lithium with points outside the basin, we subtract the number of core electrons from the self-sharing indices in the tables. The self-sharing indices in the tables therefore reflect the behavior of the valence electrons only. The numbers of electrons in the lithium and hydrogen basins, the self-sharing indices of the basins, and the bond index are all in accord with the differences in the traditional values of the electronegativities[9] of the two elements and with the traditional concept of the bonding in the molecule.

He_2 in its ground electronic state at its calculated equilibrium nuclear geometry (an internuclear distance of 5.66 au) is, like H_2, symmetrical. The small bond index of 0.004 indicates that there is little sharing of an electron between the two helium basins, in agreement with the traditional assessment that there is no chemical bond between the two atoms. A further analysis of the type of residual sharing in this complex is given in section V.

TABLE 4: Sharing Indices in CH_4

TBSI; basin\basin	C	H1	H2	H3	H4
C	8.320				
H1	0.870	1.060			
H2	0.870	0.038	1.060		
H3	0.870	0.038	0.038	1.060	
H4	0.870	0.038	0.038	0.038	1.060
self-sharing − core	2.160	0.530	0.530	0.530	0.530
delocalization index	1.740	0.492	0.492	0.492	0.492
no. basin electrons[a]	5.900	1.022	1.022	1.022	1.022

[a] From sharing index sum rule.

TABLE 5: Sharing Indices in NH_3

TBSI; basin\basin	N	H1	H2	H3
N	13.912			
H1	0.775	0.448		
H2	0.775	0.016	0.448	
H3	0.775	0.016	0.016	0.448
self-sharing − core	4.956	0.224	0.224	0.224
delocalization index	1.163	0.404	0.404	0.404
no. basin electrons[a]	8.119	0.628	0.628	0.628

[a] From sharing index sum rule.

TABLE 6: Sharing Indices in H_2O

TBSI; basin\basin	H1	O	H2
H1	0.214		
O	0.593	17.188	
H2	0.008	0.593	0.214
self-sharing − core	0.107	6.594	0.107
delocalization index	0.300	0.593	0.300
no. basin electrons[a]	0.407	9.186	0.407

[a] From sharing index sum rule.

TABLE 7: Sharing Indices in HF

TBSI; basin\basin	F	H
F	19.013	
H	0.441	0.110
self-sharing − core	7.507	0.055
delocalization index	0.221	0.221
no. basin electrons[a]	9.727	0.276

[a] From sharing index sum rule.

Tables 4−7 give the basin−basin sharing indices in the molecules CH_4, NH_3, H_2O, and HF. Although the bond indices of methane have been reported in ref 4, we give them here both for completeness and to indicate the effect of the basis set on the results of an MP2 approximation. As is the case for H_2 and LiH, the differences in the indices of methane calculated using the different basis sets are in the third decimal place.

The carbon and the hydrogen basins in CH_4 are very close to being electrically neutral. The values of the carbon−hydrogen bond indices are close to 0.87, quite close to the value of the bond index, 0.90, in H_2. The self-sharing indices of the hydrogens, 0.53, are also close to the values of 0.55 in the hydrogen molecule. In addition we note that the self-sharing index (minus the number of core electrons) in the carbon basin is 2.16, this value being close to four times the self-sharing in a hydrogen basin. When the self-sharing minus the number of core electrons on carbon is parceled out on a per hydrogen basis, we get 0.54 per bond to hydrogen. The delocalization index of the carbon basin is 1.74, or, on a per proton basis, 0.43. (In this case the delocalization index of carbon per bond is one-half the carbon−hydrogen bond index.) It is as though the sharing associated with each carbon−hydrogen bond is equally distributed between the carbon and the hydrogen basin, just as in the hydrogen molecule. The bonding in methane, as described by the basin−basin sharing indices and as given by more traditional analyses, is just as covalent as the bonding in the hydrogen molecule.

The bond indices between the hydrogen basins are small, the values being 0.038. These are in agreement with the traditional concept of the primary bonding in methane as being between the carbon and the hydrogens. The bonding between the hydrogens is secondary. A more detailed analysis of the type of sharing (bonding) between the hydrogens is given in section V. We do note that the valences (twice the delocalization indices) of the hydrogen basins are 0.98, close to the traditionally assumed valence of hydrogen. However, to get this valence for hydrogen, the contributions of the bond indices between the hydrogens must be included. On the other hand, the valence of the carbon basin is 3.48, less than the traditional value of 4. The reason for the valence being less than 4 is the same as the reason for the carbon−hydrogen bond indices (and the hydrogen−hydrogen bond index in H_2) being less than the canonical value of 1—the correlation between the electrons somewhat localizes a single electron having one coordinate of the sharing index within the carbon basin to have the other coordinate within that basin.

The next molecule to be considered is ammonia. Unlike the carbon basin in methane, which is electrically neutral, the nitrogen basin in ammonia has a charge of −1.12 with the hydrogen basins having the compensating positive charges of 0.37. The nitrogen−hydrogen bond indices in ammonia (the primary bond indices) are 0.78, distinctly smaller than the carbon−hydrogen bond indices in methane and in line with the difference in the electronegativities of nitrogen and carbon. The self-sharing index (minus the number of core electrons) of nitrogen is 4.96. As the following argument suggests, the increase in the self-sharing index over that of carbon in methane is in part attributable to the nonbonded pair of valence electrons on nitrogen, which is included in the nitrogen basin, and in part to the greater electronegativity of the nitrogen atom as compared to that of the carbon atom. If the contribution of the nonbonded valence electrons to the self-sharing index of nitrogen is taken to be 2.00, the self-sharing minus the number of core electrons and the number of nonbonding electrons is 2.96. If we suppose this to be parceled out equally among the three bonds to the hydrogens (this gives the residual self-sharing on nitrogen per bond to hydrogen), we get a value of 0.99 per bond to hydrogen. This is larger than the value of 0.54 obtained per hydrogen in methane and reflects the increase in the electronegativity of nitrogen from that of carbon. In agreement with this is the decrease in the self-sharing indices of hydrogen to 0.22 from the methane values of 0.59. We note that the values of the secondary bond indices, those between the hydrogens, have also decreased from the values in methane. Thus there is less sharing of an electron between the protons in ammonia than in methane.

The delocalization index of the nitrogen basin is 1.16 while that of a hydrogen basin is 0.40, both less than the corresponding indices of carbon and of the protons in methane. A part of the decrease of the delocalization index of nitrogen relative to the delocalization index of carbon in methane can be ascribed to the fewer bonds in ammonia. However, on a per bond basis, the delocalization index of the nitrogen basin follows the interbasin sharing indices, and a part of the decrease in the delocalization index must be ascribed to the greater electronegativity of nitrogen as compared to carbon.

TABLE 8: Sharing Indices in BeH_2

TBSI; basin\basin	H	Be	H
H	3.374		
Be	0.262	4.022	
H	0.087	0.263	3.375
self-sharing − core	1.687	0.011	1.687
delocalization index	0.175	0.262	0.175
no. basin electrons[a]	1.862	2.273	1.862

[a] From sharing index sum rule.

TABLE 9: Sharing Indices in BH_3

TBSI; basin\basin	B	H	H	H
B	4.385			
H	0.487	2.608		
H	0.497	0.132	2.608	
H	0.488	0.132	0.132	2.608
self-sharing − core	0.192	1.304	1.304	1.304
delocalization index	0.736	0.375	0.380	0.375
no. basin electrons[a]	2.928	1.679	1.684	1.679

[a] From sharing index sum rule.

The trends established above continue in water and in hydrogen fluoride. Consider water. The oxygen basin in water has a charge of −1.19 while the hydrogens have charges of 0.41. The primary bond indices have decreased to 0.59. The self-sharing index minus the number of core electrons and the number of nonbonded valence electrons is 2.59. On a per proton basis, this is 1.30, a considerable increase from that in ammonia. The self-sharing in a proton basin has decreased to 0.21. The secondary bond indices have also decreased. The delocalization indices of the hydrogens are smaller than those in ammonia, as is the delocalization index of oxygen relative to that of nitrogen.

In hydrogen fluoride, the charge of the fluorine basin is −0.73 while the charge of the hydrogen basin is 0.72. (There are only 0.28 electrons in the hydrogen basin.) We note that the fluorine basin is not as negative as the oxygen and nitrogen basins in water and ammonia. This is not surprising because the fluorine basin is almost saturated with electrons, having 9.73 electrons, or almost the full complement of the nearest rare gas. The self-sharing index of fluorine minus the numbers of core electrons (two) and nonbonded valence electrons (six) is 1.51, an increase over that of the oxygen basin in water. This increase in the value of the self-sharing index minus the numbers of core electrons and nonbonded valence electrons is in accord with the increase in the electronegativity of fluorine relative to oxygen. The self-sharing in the hydrogen basin, on the other hand, is 0.05, being quite small. The bond index of 0.44 (or the delocalization index of 0.22) together with the small value of the hydrogen self-sharing indicates that the electrons in the hydrogen basin are mainly involved in sharing with the fluorine basin.

For completeness Tables 8 and 9 give the sharing indices for the entities BeH_2 and BH_3. In terms of the self-sharing index of the beryllium basin and of the bond indices, beryllium hydride is quite similar to lithium hydride—the self-sharing of the beryllium basin is 2.01, very close to the number of core electrons on beryllium, while the bond index is 0.26, 0.05 larger than the bond index in LiH. As is the case in LiH, in BeH_2 there is almost complete transfer of the valence electrons on the heavy atom to the proton basins. What electron is not transferred is completely shared with the protons. Clearly, BeH_2 is ionic. Boron hydride, on the other hand, is a case intermediate between ionic and covalent. There is a considerable transfer of valence electrons from the boron atom to the proton basins. When apportioned among the three bonds to the protons, the self-sharing index of boron minus the number of core electrons is 0.064 per proton, a bit larger than the self-sharing index of hydrogen in hydrogen fluoride. The primary bond indices are 0.49, again a bit larger than the bond index in HF. On this basis, BH_3 is a polar-covalent molecule, in the same category as HF but with the hydrogens playing the role of the more electronegative element.

The secondary bond indices, those between the hydrogens, in BeH_2 and BH_3 are larger than those in the preceding compounds. The secondary bond index in BeH_2 is 0.086 while the secondary bond indices in BH_3 are 0.132. As a secondary index this latter is quite large, being 63% of the primary index in lithium hydride and 27% of the primary indices in BH_3 itself. The delocalization index of a hydrogen in BH_3 is 0.38. Thus the secondary sharing makes a substantial contribution to the delocalization index of a hydrogen in BH_3 (recall that there is sharing to two hydrogens and that the delocalization index is equal to the sum of the interbasin basin−basin sharing indices).

The behaviors of the sharing indices, when due account is taken of the nonbonded electrons, follow trends that mimic the electronegativities of the elements. The indices faithfully track the chemists' ideas of covalent and ionic bonding in this series of hydrides. In the series from lithium to fluorine, the bond indices increase from lithium to carbon, then decrease from carbon to fluorine. The self-sharing indices of the hydrogens decrease along the series from lithium to fluorine. The self-sharing indices of the heavy atom basins (minus the number of core electrons and nonbonded valence electrons) behave in the opposite fashion, the residual self-sharing indices of the heavy atom basins on a per bond basis increasing along the series from carbon to fluorine. The delocalization indices of the heavy atoms and of the hydrogens increase in a monotonic fashion from LiH to CH_4, then decrease in a monotonic fashion in going to HF.

The molecule that is unique in this series is methane. In the formation of the single bonds, hydrogen and carbon play equal roles, with the self-sharing indices of carbon (on a per hydrogen basis) and of hydrogen being the same. The primary bond indices in methane are the maximum in this series of hydrides. The bonds in the other hydrides considered here do not have this characteristic feature. However, the sharing indices in the other hydrides listed in the tables do fall into patterns that can be correlated with the traditional electronegativities of the atoms.

IV. Volume−Point Sharing Indices

The volume−point sharing indices give a more detailed dissection of the sharing than the basin−basin sharing indices. If the set of basin−basin sharing indices I_{AB} with the index B fixed and $A \neq B$ are considered to give the structure of the valence of basin B (or of the delocalization of electrons in basin B), the basin−point sharing indices give a microscopic view of this valence or delocalization. Although the volume−point sharing index in some aspects resembles the absolute value squared of a wave function, it must be kept in mind that $I_V(\zeta)$ is more akin to the diagonal element of a (partial) density matrix.[4] In general, density matrices are associated with impure states rather than pure states. This notwithstanding, we shall give qualitative descriptions of the shapes of these volume−point sharing indices in terms of such constructs as sp hybrids.

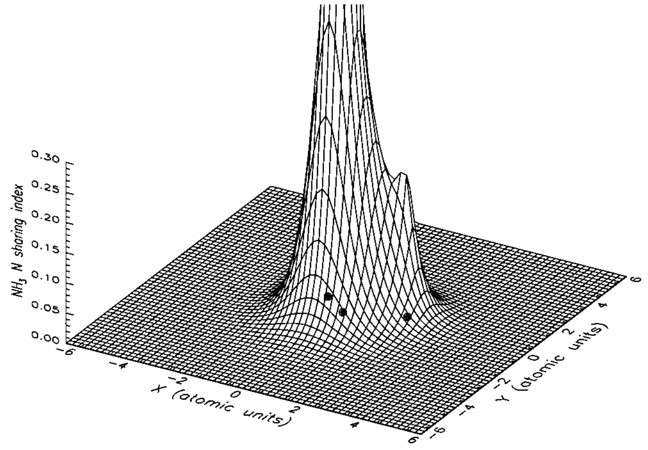

Figure 1. Volume−point sharing index from the nitrogen basin in NH_3. The plane of the cut contains the nitrogen nucleus and one of the protons and bisects the angle between the other two protons. The locations of the perpendicular projections of the nuclei onto the plane are indicated by solid circles. The primary basin surrounds the filled circle at the origin $(x, y) = (0, 0)$.

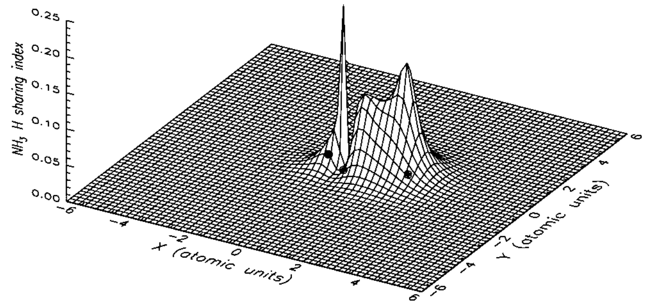

Figure 2. Volume−point sharing index from one of the hydrogen basins in NH_3. The position of the plane and the positions of the nuclei are the same as in Figure 1. The primary basin surrounds the rightmost filled circle.

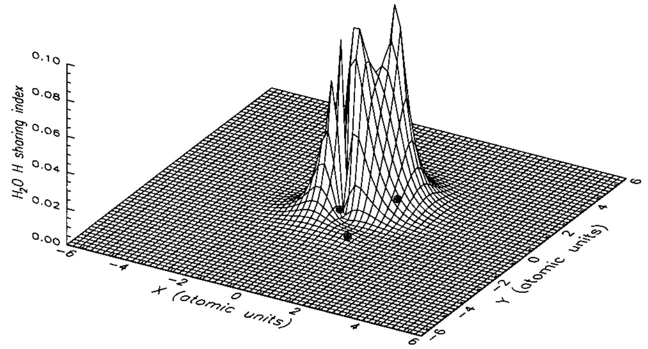

Figure 3. Volume−point sharing index from one of the protons in H_2O. The plane of the cut contains the oxygen and both protons. The primary basin surrounds the filled circle having positive values of x and y. There is an artifact in the left most structure in the figure. See the text.

Figures 1−4 are two dimensional cuts of the basin−point sharing index. The first is from the nitrogen basin in NH_3. The others, in sequence, are the indices from a proton basin in the molecules NH_3, H_2O, and HF. Similar figures for H_2, LiH, and CH_4 have been presented in ref 4. The three molecules presented here complete the description of the experimentally found simple hydrides of the first row of eight in the periodic table in terms of the basin−point sharing indices.

The basin−point sharing index from the nitrogen basin in ammonia is given in Figure 1. The plane of the cut contains the nitrogen nucleus and one of the protons, and bisects the angle between the other two protons. The perpendicular projections of the positions of the nuclei onto the plane are

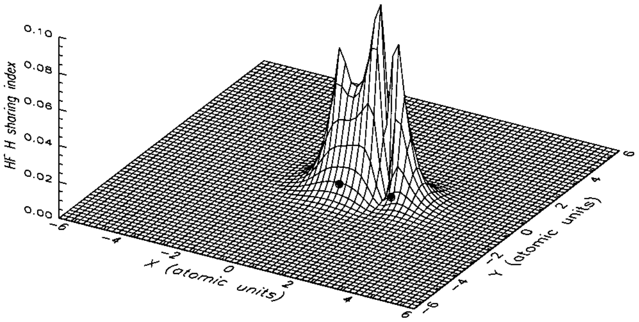

Figure 4. Volume−point sharing index from the proton in HF. The plane of the cut contains both nuclei. The primary basin surrounds the filled circle to the left.

indicated by the filled circles. The nitrogen nucleus (in the plane) is at $(x, y) = (0.00, -0.28)$, while the proton in the plane is at (1.79, 0.48). The point at (−0.89, 0.48) is the projection of both out of plane protons onto the plane.

Although qualitatively the sharing to the protons from the nitrogen basin resembles the corresponding sharing index for CH_4 (see Figure 6 of ref 4), there are readily noticeable differences. In ammonia the peak surrounding the in-plane proton is but a nub on the side of the sharing from the nitrogen basin, while in methane the peaks about the in-plane protons are quite distinct from the sharing peak about the carbon. In addition to this difference, the behavior of the slopes of the sharing indices along the straight lines drawn between the heavy nucleus and an in-plane proton differ in the two molecules, the basin−point sharing index in ammonia turning upward toward the minimum in a more leisurely fashion than in methane. It is as though the nitrogen is drawing the nitrogen basin−point sharing index away from the proton. This behavior may be looked upon as a result of the greater electronegativity of nitrogen as compared to the electronegativity of carbon.

The basin−point sharing index from the proton in NH_3 is given in Figure 2. The position of the plane and the positions of the nuclei are the same as in Figure 1. The primary basin surrounds the rightmost filled circle. The structure of the sharing close to the proton in the primary basin is similar to that of a 1s hydrogenic orbital. Toward the nitrogen nucleus is a deep valley which represents the remnants of a node, as will be apparent in the next section. The structure of the sharing index from a proton basin differs from that for methane, given in Figure 7 of ref 4, in that as the top of the ridge from the proton in the primary basin is followed toward the carbon nucleus, a secondary peak is found near the remnants of the node. In the case of methane, the ridge does not have the secondary peak but rather has a shoulder. As in the case of Figure 1, it is as though the nitrogen is drawing the sharing away from the proton. This difference in the basin−point sharing indices from the proton basins in methane and ammonia, again, is consistent with the difference in the electronegativities of carbon and nitrogen.

The basin−point sharing indices of H_2O and HF with the primary basin containing a proton are given in Figures 3 and 4. In each figure, the heavy nucleus and the proton(s) are in the plane of the cut. The primary basin in figure 3 contains the proton having positive values of both x and y. The primary basin in Figure 4 contains the proton that is to the left of the fluorine nucleus. (In Figure 3 there is an artifact which stems from the spacing of the points of the grid, 0.2 au, and the interpolation procedure used to construct the surface. A closer examination of the leftmost structure in the figure using a grid spacing of 0.05 au indicates that there is but one peak to the left of the deep cleft near the oxygen nucleus.) The trend established in CH_4 and NH_3 continues, with the secondary peak in the ridge extending from the primary basin toward the heavy nucleus increasing in size as the atomic number and the electronegativity of the heavy atom increases. Indeed, in HF the secondary peak is higher than the peak in the primary (proton) basin.

An effect associated with the increase in the atomic number which is not so visible in these plots is the shape of the remnants of the node that leads to the deep cleft near the heavy nucleus. The curvature of the floor of the valley is less in HF than in the preceding molecules. This change, which will be more apparent in the amplitudes given in the next section, can be rationalized by supposing that there is an increasing amount of 2p character in the sp hybrid on the heavy nucleus in the sequence from methane to hydrogen fluoride. As indicated above, however, the way given here of describing the changes in the shape of the volume−point sharing index in terms of single hybrid orbitals can only be approximate.

The differences in the shapes of the volume−point sharing indices given in ref 4 and in this paper coincide nicely with the qualitative measures of the relative electronegativities of the elements.

V. Sharing Amplitudes

The most detailed description of the sharing of a single electron is given by the point−point sharing index and the underlying sharing amplitude. It is the latter with which we will be concerned in this section. We consider the same group of molecules as considered above.

The one difficulty with the sharing amplitude is that it depends on eight variables, two sets of spatial variables and two spin variables. The restriction to a description of singlet states gives the spin dependence of the sharing amplitude $\langle \mathbf{r}, \sigma; \mathbf{r}'\sigma' \rangle$ as $\delta_{\sigma\sigma'}$. This reduces the number of essential variables to six, which is still difficult to visualize. We consider a drastically reduced set of points in visualizing the sharing amplitudes. One point, chosen to be $\mathbf{r}'$, is fixed at some convenient, and hopefully physically significant, point. This is called the fixed point. The other point, the movable point, is allowed to roam about three-dimensional space. Thus we attempt to visualize the behavior of the sharing amplitude between a fixed point and the rest of space. In the figures presented in this paper, we actually add one further constraint. The movable point is constrained to be in a specified plane. With a given fixed point we present two dimensional cuts of three-dimensional space.

A cut of the sharing amplitude in H_2 with the fixed point located on a proton is given in Figure 5. The positions of the protons are in the plane of the cut and are located at the solid circles. The fixed point is located at the star enclosed in a circle. In Figure 5 the fixed point coincides with the nucleus at the right. The x and y axes are the coordinates in the plane. The solid lines parallel to the x and to the y axes are grid lines at constant values of x and at constant values of y. On the vertical axis are the values of the sharing amplitude. The surface represents the values of the sharing amplitude as a function of the coordinates in the plane of the cut. In all the figures with the exception of the present one, the amplitudes are both positive and negative. The nodes of the amplitudes in the other figures are indicated by curved solid lines cutting across the grid lines. With the exception of Figure 17, the grid points from which the surfaces and lines are interpolated are at intervals of 0.2 au. As noted in section III, H_2 is our prototype for a covalent bond.

The features of the sharing amplitude of H_2 to be noted are: the two-humped structure, with the larger of the humps at the

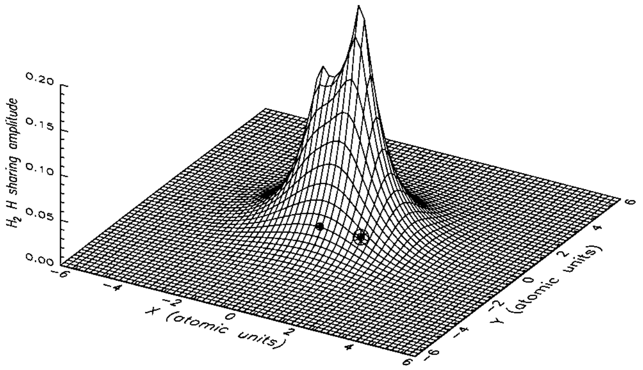

Figure 5. Cut of the sharing amplitude in H_2 from a fixed point. The plane of the cut contains the two protons which are at the positions of the solid circles. The fixed point is on the proton located at the star enclosed in a circle.

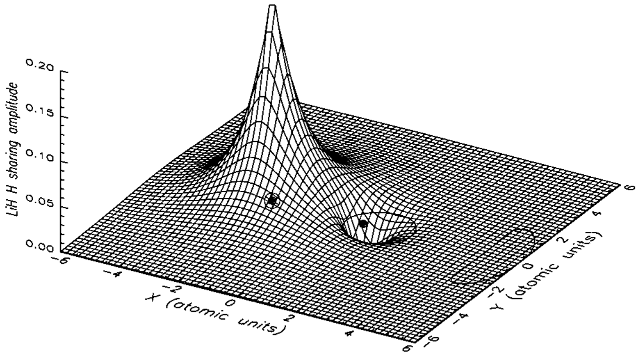

Figure 6. Cut of the sharing amplitude in LiH with fixed point at the proton. The plane of the cut contains both nuclei.

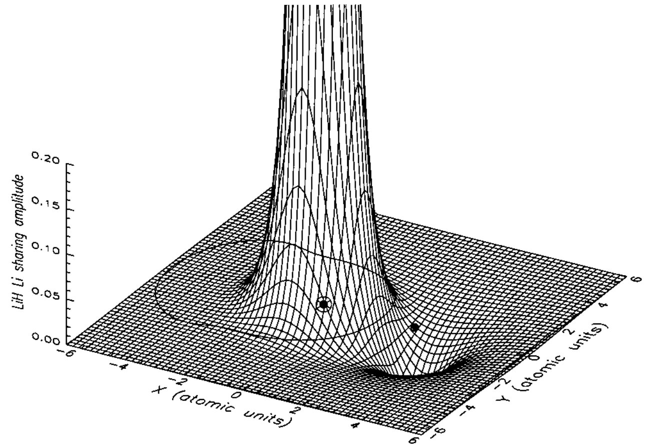

Figure 7. Cut of the sharing amplitude in LiH with the fixed point on the lithium nucleus. The plane contains both nuclei. For clarity, the orientation of the molecule is opposite to that in Figure 6.

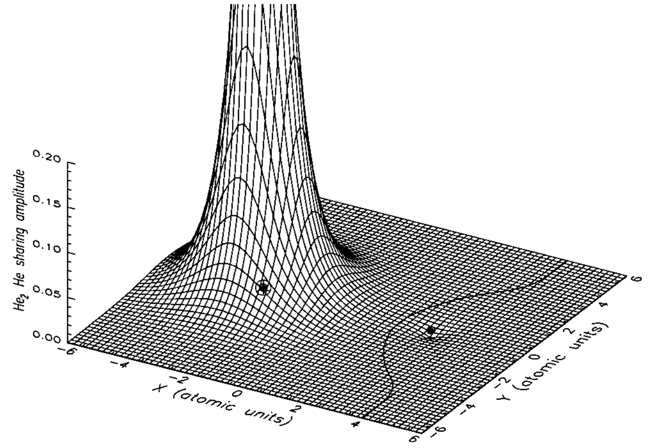

Figure 8. Cut of the sharing amplitude in He_2 with the fixed point on the left-hand nucleus. The plane of the cut contains both nuclei. Note the nodal line extending between the nuclei.

nucleus on which the fixed point is located; and the fact that the sharing amplitude in the ground electronic state of H_2 has no nodes. The structure of the sharing amplitude in the near vicinity of the proton with the fixed point mimics the shape of a 1s orbital centered on the fixed point. The structure about the second proton also mimics a 1s orbital, but with the center on the second proton and with diminished amplitude.

The fact that the sharing amplitude is not symmetrically disposed between the two protons is the result of including correlation in the construction of the ground-state wave function. Indeed, the sharing amplitude arising from the Hartree−Fock approximation to the ground-state wave function of H_2 is found to be symmetrical, as it must from the symmetry of the single determinant wave function. The asymmetry in the sharing amplitude when correlation is included is also apparent in the volume−point sharing index from one of the hydrogen basins, as shown in ref 4. As measured by the sharing amplitude (or of the sharing index), one of the effects of including correlation in the description of the ground state of H_2 as compared to a description by the Hartree−Fock ground state wave function is the increase in the localization of the electron to the vicinity of the fixed point.

The sharing amplitude of LiH with the fixed point at the proton is given in Figure 6. The plane of the cut contains both nuclei. First recall from the results given in section III that the valence electron from the lithium atom has been mainly transferred to the hydrogen atom (only 0.10 of the valence electron remains in the lithium basin) and that the sharing between the two basins is 0.21 so that the bonding is mainly of an ionic nature. The sharing amplitude is distinctly of a 1s character in the vicinity of the proton. About the lithium nucleus there is an almost circular node with center displaced away from the proton. This node can be interpreted in terms of a small contribution of a 2s orbital on the lithium atom to the sharing amplitude together with a smaller admixture of a lithium atom 2p orbital, which has lobes along the internuclear axis. The node surrounding the lithium nucleus, arising primarily from the lithium 2s orbital with the concomitant negative value of the amplitude at the lithium nucleus, is intrinsic to the electron structure of the lithium atom.

The sharing amplitude in LiH with the fixed point at the lithium nucleus is given in Figure 7. (For clarity in viewing the features of the sharing amplitude, the orientation of the molecule in Figure 7 is opposite to that in Figure 6.) The plane of the cut is the same as in Figure 6. Relative to the location of the node in Figure 6, the node surrounding the lithium nucleus in Figure 7 is pushed away from the lithium nucleus. There is a simple explanation of this difference. When the fixed point is on the lithium nucleus there are contributions from both the lithium 1s orbital and the lithium 2s orbital to the amplitude in the vicinity of the fixed point. Combined with the small amount of valence electron left in the lithium basin, the contribution from the 1s lithium orbital moves the node further from the lithium nucleus than with the fixed point on the proton when the main contribution to the amplitude in the vicinity of the lithium nucleus is from the 2s orbital on lithium. The sharing amplitude in He_2 with the fixed point at the left-hand nucleus is given in Figure 8. The basis set used for the calculation is that given in ref 6. The calculated equilibrium distance between the nuclei is 5.66 au. This distance is in good agreement with the results of the recent calculation of Williams et. al.[10] In agreement with the very small bond index of 0.004, which indicates very little sharing between the basins, the sharing amplitude is localized in the region of the fixed point. In addition there is a node between the fixed point and the other helium nucleus. The node has a minimum distance of about 1 au from the second nucleus.

The existence of the node in He_2 can be understood qualitatively by use of a simple model. Suppose that an adequate description of the ground electronic state of the complex is given by a single determinant wave function. Let the real normalized molecular spin orbitals, $\varphi_{s,\pm}$ with spin index s, be approximated by linear combinations of real 1s-type normalized atomic spin orbitals (of one sign), $\phi_{s,a}$, on the centers $a = 1,2$

$$\varphi_{s,\pm} = \frac{1}{\sqrt{2(1 \pm S)}}(\phi_{s,1} \pm \phi_{s,2})$$

where S (having a positive value) is the overlap integral between the two atomic orbitals. The atomic orbitals are chosen to be related by reflection in the plane perpendicular to, and passing through the midpoint of, the straight line connecting the nuclei. The sharing amplitude is

$$\begin{aligned}\langle\zeta;\zeta'\rangle &= \sum_s \{\varphi_{s,+}(\zeta)\varphi_{s,+}(\zeta') + \varphi_{s,-}(\zeta)\varphi_{s,-}(\zeta')\} \\ &= \frac{\delta_{\sigma,\sigma'}}{1-S^2}\{[\phi_1(\mathbf{r})\,\phi_1(\mathbf{r}') + \phi_2(\mathbf{r})\,\phi_2(\mathbf{r}')] - \\ &\qquad S[\phi_1(\mathbf{r})\,\phi_2(\mathbf{r}') + \phi_2(\mathbf{r})\,\phi_1(\mathbf{r}')]\}\end{aligned}$$

We suppose that the atomic orbitals, $\phi_{1,2}$, are mainly concentrated in the regions of the centers 1 and 2, respectively. Let $\sigma = \sigma'$. Fix $\mathbf{r}'$ on center 2 and with $\mathbf{r}$ trace a path from center 2 to center 1. The sharing amplitude when $\mathbf{r}$ is in the region of center 2 is essentially $[1/(1 - S^2)]\phi_2(\mathbf{r}')\ \phi_2(\mathbf{r}')$, a positive quantity. When $\mathbf{r}$ is in the region of center 1 the sharing amplitude is $-[S/(1 - S^2)]\phi_1(\mathbf{r})\ \phi_2(\mathbf{r}')$, a negative quantity. There is clearly a nodal surface lying between the two nuclei.

The smallness of the bond index, together with the node that lies between the nuclei and that is not intrinsic to the ground-state helium atom, is taken as a signature of nonbonding behavior. We expect that closed shell moieties that do not bond have behaviors similar to that found for He_2. We also expect that intermolecular nonbonded interactions, such as those associated with steric interactions, also have sharing amplitudes which, in the region of nonbonding, are similar to the structure in He_2.

The sharing amplitudes given above cover a range of bonding including covalent bonding, ionic bonding, and nonbonding. Antibonding, such as would be obtained in the $^1\Sigma_g$ excited state of hydrogen stemming from the $1\sigma_u^{*2}$ configuration, would give a sizable basin−basin sharing index and, with the fixed point on one of the protons, a sharing amplitude with a node between the two protons. The sharing amplitude would not be as localized about the fixed point as in the ground state of He_2. It is the value of the bond index together with the behavior of the sharing amplitude that gives the characterization of the type of bonding, whether it be bonding, nonbonding, antibonding, or some intermediate behavior.

We now turn to the sharing amplitudes in the sequence of molecules CH_4, NH_3, H_2O, and HF. We consider the first of these in some detail, setting the fixed point both on a proton and on the carbon nucleus. For the other molecules we set the fixed point only on a proton.

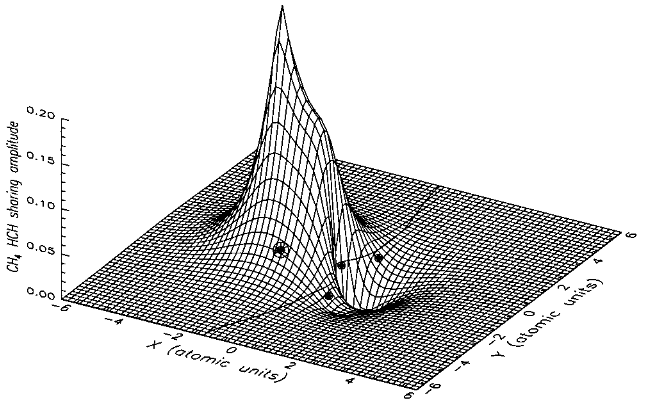

Figure 9. Cut of the sharing amplitude in CH_4 with the fixed point on a proton. The plane of the cut contains the fixed point, the carbon nucleus, and another proton.

The sharing amplitude in CH_4 with the fixed point on a proton and with the plane of sharing containing the fixed point, the carbon nucleus, and one other proton is given in Figure 9. The fixed point (star enclosed in a circle) overlays the proton at the left, the carbon nucleus is located at the midpoint of the xy plane (at $x = 0$, $y = 0$), and the other proton in the plane has a negative value of the y coordinate. The remaining point in the figure (positive value of the coordinate y) is the perpendicular projection of the other two protons onto the plane.

The sharing amplitude is positive in the vicinity of the fixed point. In the immediate vicinity of the fixed point, the sharing amplitude has the semblance of a hydrogenic 1s orbital. The amplitude decreases, with an upward curvature, as a line from the fixed point to the carbon nucleus is traversed. Near, but before arriving at, the carbon nucleus there is a precipitous decline in amplitude to negative values, there being a node that runs close to the carbon nucleus lying between the proton (fixed point) and the carbon nucleus. The amplitude continues to decline reaching a minimum beyond the carbon nucleus. To the right of the carbon nucleus, the amplitude increases.

The node (the curved line in the plane cutting across the grid lines) runs from negative values of y, between the fixed point and the carbon nucleus, to positive values of y. In the vicinity of the carbon nucleus the nodal line resembles that of some form of a 2s2p hybrid orbital, running between the fixed point and the carbon nucleus. The node associated with a pure 2p orbital would be a straight line in the plane of the figure, and the node associated with a pure 2s orbital would be a perfect circle in the plane. The nodes of the hybrids run between these extremes, which is what is observed in the figure. The node near the carbon nucleus is intrinsic to the carbon orbitals that contribute to this sharing amplitude; i.e., this node is intrinsic to the carbon atom.

Note that the nodal line passes between the fixed point and the other proton in the plane. By using the symmetry of the molecule, we infer that the nodal surface passes between the fixed point and all of the other protons. Figure 10, which gives the sharing amplitude in a plane containing three hydrogens with the fixed point on one of the hydrogens, corroborates this statement about the location of the node. In addition, this node is not intrinsic to a hydrogen atom in the ground state but rather is of the type found in He_2. A qualitative discussion of the existence of the node can be patterned after that given above for the helium complex.

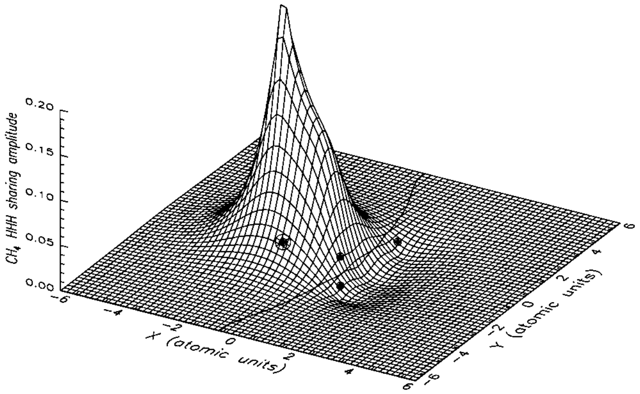

Figure 10. Cut of the sharing amplitude in CH_4 with the fixed point on a proton. The plane of the cut contains the fixed point and two other protons.

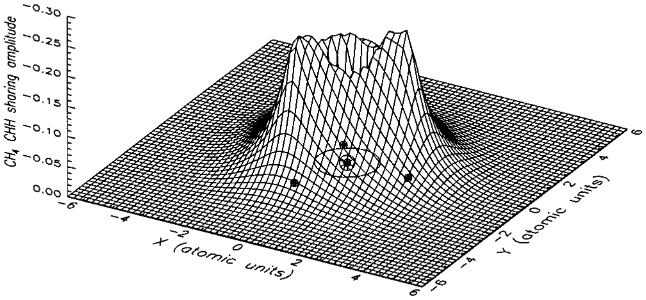

Figure 11. Cut of the sharing amplitude in CH_4 with the fixed point on the carbon nucleus. The plane of the cut contains the fixed point and two protons.

The type of bonding occurring between the hydrogens is the following. The hydrogen−hydrogen bond index is 0.038, larger than the value found in He_2, but small compared to the primary carbon−hydrogen bond index. The value of the bond index, together with the placement of the node between two protons, indicates that the bonding between the protons is slightly more antibonding than in the helium dimer. This antibonding between the protons contributes to the deviation of the nodal surface from that of a carbon 2s2p hybrid at large distance from the carbon; however, the similar type of behavior encountered below in hydrogen fluoride indicates that the presence of the protons is not the sole contribution to this deviation.

A surface plot of the sharing amplitude in CH_4 with the fixed point on the carbon nucleus is given in Figure 11. The plane of sharing in the figure contains, in addition to the fixed point, two protons. (The point having a negative value of x and a positive value of y lying close to the node is the perpendicular projection of the other two protons onto the plane of the figure.) Note that more negative values of the sharing amplitude are at the top of the figure. About the fixed point the amplitude is positive. There is a (roughly) circular node at 1 au from the carbon nucleus. The position of the node is more clearly identified in the contour plot given in Figure 12. Only the contours at intervals of 0.01 au and having values less than or equal to zero are shown in the contour plot. The structure of the sharing amplitude in the region of the carbon nucleus can be mimicked by a combination of 1s and 2s orbitals on the carbon nucleus. The two ridges beyond the node running away from the fixed point, more apparent in Figure 12 than in Figure 11, are clear indications of the sharing from the carbon to the protons. The ridges are relatively flat between the node and the proton, again indicating the equality of hydrogen and carbon in the sharing of an electron which was inferred from the basin−basin sharing indices in section III.

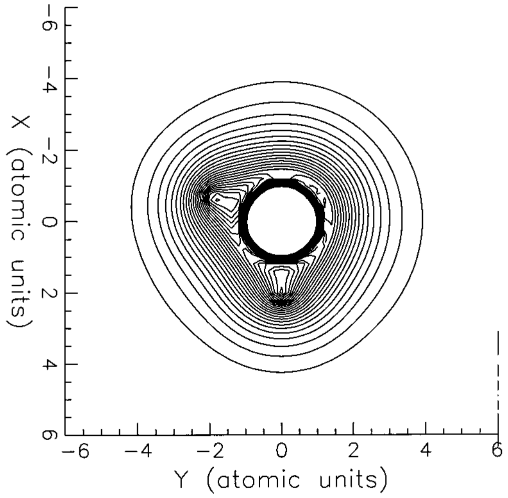

Figure 12. Contour map of the sharing amplitude given in Figure 11. The contours are at intervals of 0.01 au. Only contours with amplitudes having negative values are shown. Note that the ridges lying in the radial direction point to and encompass the protons.

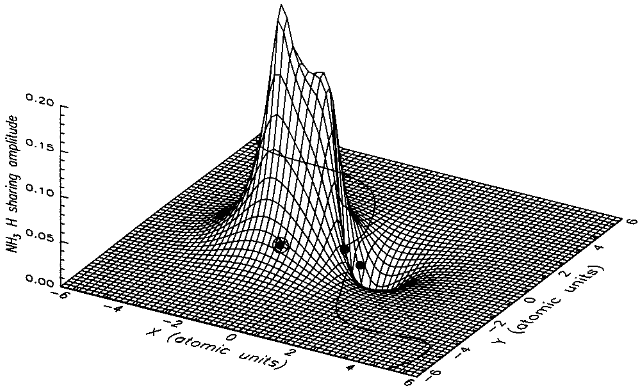

Figure 13. Cut of the sharing amplitude in NH_3 with the fixed point on a proton. The plane of the cut contains the fixed point and the nitrogen nucleus and bisects the angle between the nitrogen nucleus and the two protons not in the plane.

The sharing amplitude in NH_3 with the fixed point at a proton is given in Figure 13. The plane of the figure contains the fixed point and the nitrogen nucleus and bisects the angle between the nitrogen nucleus and the two protons not in the plane. The shape of the sharing amplitude is a bit like that in Figure 9, a maximum at the fixed point but now with a distinct secondary peak toward the nitrogen. This secondary peak, in contrast to the lack of a secondary peak in Figure 9 for methane, can be ascribed to the greater electronegativity of the nitrogen atom than the carbon atom. It should be noted that the nodal line about the nitrogen nucleus passes between the nitrogen nucleus and the proton with a pronounced curvature in the vicinity of the nitrogen nucleus toward the nitrogen nucleus. Qualitatively this node in the region near the nitrogen nucleus is similar to a 2s2p type hybrid orbital. As is the case in methane, the nodal surface passes between the fixed point and the other protons—the sharing to the other protons is again antibonding.

Figure 14 gives the sharing amplitude in H_2O with the fixed point at one of the protons. The plane of the figure contains all three nuclei. The shape of the sharing amplitude has the general characteristics of the amplitudes in CH_4 and NH_3, but with the secondary peak larger relative to the primary peak than found in ammonia. This increase in the height of the secondary peak can again be ascribed to a further increase in the electronegativity of the heavy atom. Again, the nodal line passes

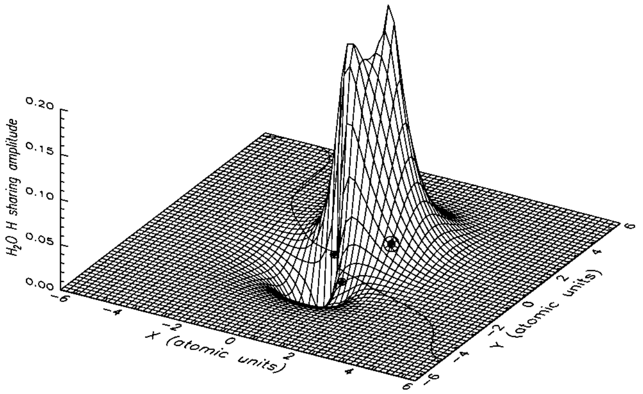

Figure 14. Cut of the sharing amplitude in H_2O with the fixed point on a proton. The plane of the figure contains all three nuclei.

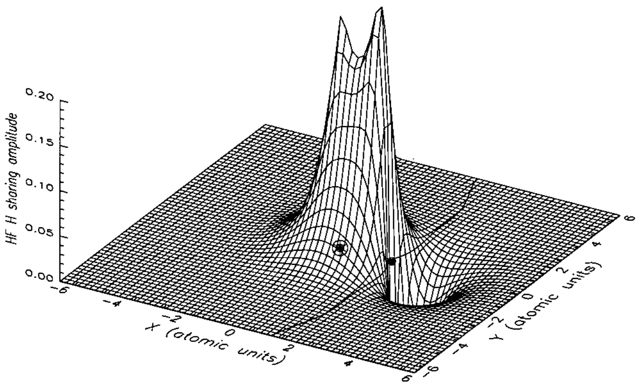

Figure 15. Cut of the sharing amplitude in HF with the fixed point on the proton. The plane of the figure contains both nuclei.

between the fixed point and the nucleus of the heavy atom and has the characteristic curvature near the carbon nucleus of a 2s2p type hybrid orbital. The nodal line also passes between the fixed point and the other proton indicating that the sharing is antibonding to the second proton.

The sharing amplitude in hydrogen fluoride with the fixed point at the proton and both nuclei in the plane of the figure is given in Figure 15. The peak in the sharing amplitude at the fixed point is lower than the peak near the fluorine nucleus—the secondary peak in the hydrides considered above has become the major peak. This shift in relative peak heights is again in accord with the relative electronegativities of the atoms. The nodal plane still passes between the fixed point and the fluorine nucleus as is the case for 2s2p type hybrid orbitals.

The nodal lines for the sharing amplitudes with the fixed point on a proton all have a characteristic shape. Near the heavy nucleus the nodal line curves toward the nucleus, as in a 2s2p hybrid. As the line is traced further from the nucleus, the line curves in the opposite direction, quite unlike a 2s2p hybrid orbital formed from hydrogen-like orbitals having the same effective nuclear charge (in the exponential) for both the s and p components. As alluded to above in the cases of CH_4, NH_3, and H_2O, a part of this behavior can be attributed to the antibonding between the protons. However, a similar type of behavior is apparent in HF, which has but a single proton so there can be no antibonding to other protons. A simple way to explain this behavior in HF is to consider the effective charge for the fluorine 2s orbital to be larger than the effective charge of the 2p orbital, leaving the 2p orbital on fluorine, with its accompanying linear node, as the dominant contribution to this sharing amplitude as the distance from the heavy nucleus increases. This type of contribution is also expected in the other hydrides.

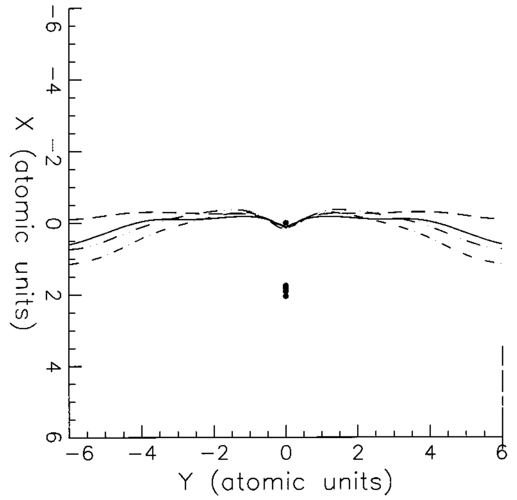

Figure 16. Overlays of the nodes in CH_4, NH_3, H_2O, and HF, all with the fixed points on a proton located along the positive *x*-axis. The heavy nuclei are at the origin. All molecules are oriented such that there is a plane of reflection perpendicular to the cut plane and containing the *x*-axis. The lines cutting across the grid lines are the nodes for CH_4, dash−dot−dot; NH_3, dash−dot; H_2O, dashed; HF, solid line.

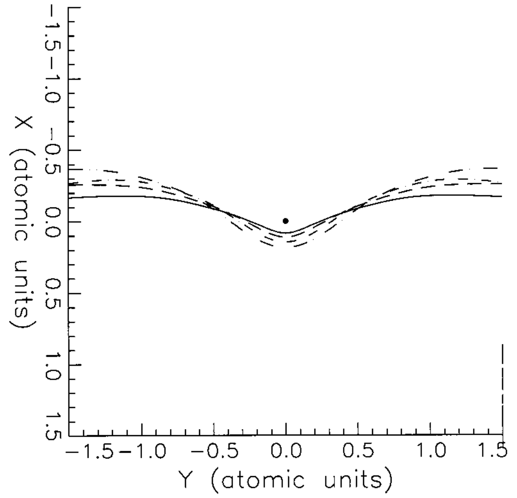

Figure 17. Enlargement of the nodal patterns of Figure 16 to illustrate the changing patterns of the sharing amplitude in the region of the heavy nuclei. The association of the lines with molecules is the same as in Figure 16.

Although the overall shapes of the nodal lines are similar, they are not identical. Figures 16 and 17 give overlays of the nodes in the series of hydrides CH_4, NH_3, H_2O, and HF, all with the fixed point on a proton. The fixed point is located on the positive *x*-axis with the heavy nucleus at the origin of the plot. The sole difference between the two figures is the scale, Figure 17 being an enlargement of the region about the heavy nucleus. (The grid points are at intervals of 0.05 au in Figure 17.) The nodes are identified as follows: CH_4, dash−dot−dot line; NH_3, dash−dot line; H_2O, dashed line; HF, solid line. (The dots do not reproduce well, so read the dots as space indicators.) The positions of the fixed points are indicated by the filled circles at positive values of the *x* -coordinate in Figure 16. The distance between the fixed point and the heavy nucleus decreases in the series from methane to hydrogen fluoride.

The shapes of the nodal lines at the extremes in Figure 16 are dictated in part by the antibonding to the other protons that lie at negative values of *x* and in part by the different effective nuclear charges associated with the 2s and 2p orbitals on the heavy nuclei. The behaviors of the nodes that can more nearly be described by traditional sp hybridization of the heavy atom orbitals occur close to the heavy nucleus. The behaviors of the nodes close to the heavy atom nuclei are shown in Figure 17, which contains a magnified view of the central part of Figure 16. As the charge on the nucleus increases, the distance along the *x*-axis from the heavy nucleus to the node decreases from about 0.2 au for methane to about 0.1 au for hydrogen fluoride. The deviation of the line from a straight line also decreases along this series of molecules. For example, the curvature of the node in HF (solid line) is less than that in H_2O (dashed line). These behaviors are in line with an increasing 2p character of the hybrid orbital which mimics the sharing behavior near the heavy nucleus relative to the 2s character of the orbital and with the increase in the effective nuclear charge on the heavy atom nucleus.

In the simple hydrides in the first row of eight in the periodic table the nodal patterns of the sharing amplitude from a proton are found to run the gamut from a closed, almost pure, 2s-type node in lithium hydride (Figure 6) to a mostly pure 2p-type node in hydrogen fluoride (Figures 15, 16, and 17). In addition, the changes in the shapes of the sharing amplitudes are found to parallel the changes in the traditional electronegativities of the heavy atoms.

VI. Discussion

It is important to recognize that what is called a bond index in the present series of papers is a quantitative measure of how an electron is shared between the distinct volumes of the two basins and is not a measure of the electron density in the region between the nuclei identified with the two basins. Also it is not a measure of the contribution of the orbitals centered on the nuclei in the basins to the electron density between the nuclei. The bond index is a measure of the delocalization of an electron between the distinct volumes. The self-sharing index, which can be interpreted as the number of electrons that are not shared to points outside the basin, is a measure of the localization of an electron within that basin.

It is also important to recognize that although the basins are defined in terms of the criterion given by Bader[2] the fundamental quantities upon which we build the basin−basin indices, the sharing amplitudes, and the associated point−point sharing indices are completely distinct from the definition of what constitutes a basin. For us a Bader basin is a convenient, invariant construct that has a simple geometric origin in the electron density.

The changes in the bond indices associated with the primary bonds in the molecules considered in the present paper follow the differences in the traditional electronegativities of the elements. The bond index in lithium is small; the indices between the heavy atom and a hydrogen increase in the series BeH_2, BH_3, and CH_4 followed by a decrease in the series NH_3, H_2O, and HF. The self-sharing indices also vary in a way that follows the electronegativities when due account is taken of the numbers of core electrons and the numbers of nonbonded valence electrons with the residual self-sharing indices being apportioned among the number of bonded atoms. As expected, the bond index in He_2 is small with the self-sharing indices of each basin being very close to 2, the number of electrons in an isolated atom. H_2 is the prototype for covalent sharing of an electron with an electron approximately equally divided between self-sharing and interbasin sharing.

The delocalization indices of the basins also vary in a systematic fashion along the present series of molecules, with the variations correlated in a general way with the relative electronegativities of the elements and with the number of bonds, with the delocalization index of carbon, on a per proton basis, being a maximum.

The unique heteronuclear molecule in the series is methane in which a proton participates equally with the carbon in the sharing of an electron. Indeed, the value of the bond index of the carbon−hydrogen bond is close to that of the hydrogen−hydrogen bond in H_2. In addition, the values of the self-sharing indices of the hydrogens in CH_4 are close to that part of the per proton self-sharing index that is due to the valence electrons of carbon, and close to the self-sharing index of the hydrogens in H_2. This equality of the carbon and hydrogen atoms in their bonding characteristics is, of course, well-known from the extensive chemistry undergone by the hydrocarbons as compared to compounds based on the other elements, yet it is satisfying to find the equality of carbon and hydrogen on the basis of rigorous calculations, which include effects due to correlation. Incidentally, the equality also extends to carbon−carbon single bonds.[4,11]

In addition to the basin−basin sharing quantities, the relative numbers of electrons in the basins follow the relative electronegativities of the elements forming the primary bonds. That these are consistent with the basin−basin sharing indices, the self-sharing indices, and the numbers of electrons in the basins is, of course, enforced by the sum rules obeyed by the sharing quantities. By basing the basin−basin sharing quantities on the point−point sharing index, the consistency among various levels of description is guaranteed.

The basin−point sharing indices give the next finer detail of the sharing of an electron from a basin to all points in space. In a sense, the basin−point sharing indices give a microscopic description of the valence, or of the delocalization index, of a basin.

The basin−point sharing index of NH_3 with the primary basin including the nitrogen nucleus shows distinct differences from the basin−point sharing index of the carbon basin in CH_4. The prominent difference is in the sharing in the region of the protons. In the methane figure in ref 4, there are three distinct peaks, one in the carbon basin and the other two in the vicinities of the protons in the plane of the figure. On the other hand, in ammonia, the peaks in the vicinity of the protons are nubs. These differences correlate, at least in a qualitative way, with the relative electronegativities of the elements. Similar differences occur in the basin−point sharing indices from the proton basins. As the basin−point sharing indices from a hydrogen basin in the sequence from methane to hydrogen fluoride are followed, the sharing index develops a definite secondary peak on the proton side of the cleft that exists close to the heavy atom nucleus and between the heavy nucleus and the proton. Indeed, in HF the secondary peak is larger than the primary peak.

The most detailed information about the behavior of a single electron in a many electron system is given by the sharing amplitudes. The primary difficulty with these is that they are, in general, functions of eight variables, two spin variables and six spatial variables. In the present paper we have greatly restricted the number of variables by considering only singlet states and by fixing one of the sets of spatial variables. The further restriction in this paper has been to restrict the other set of spatial variables to lie in a plane. In spite of these restrictions, a great deal of information is still encoded in the figures.

The amplitude from a proton in H_2 in its ground electronic state is everywhere positive, with the general features of the amplitude qualitatively being describable in terms of simple constructs such as the superposition of two 1s orbitals, one centered on each proton with the contribution of the orbital at the fixed point making the major contribution. The asymmetry in the amplitude can be ascribed to the inclusion of correlation between the electrons.

The amplitude in LiH with the fixed point on the proton has the characteristics of the two valence electrons being primarily on the proton with a weak covalent bond to the lithium. The nodal structure of the amplitude about the lithium nucleus indicates a main contribution to the sharing amplitude from the 2s orbital on the lithium atom. This node is intrinsic to the lithium atom. The behavior of the sharing amplitude with the fixed point on the lithium nucleus, together with the difference from that when the fixed point is on the proton, is easily explicable in terms of the contribution of the core electrons on the lithium atom.

The sharing amplitude in He_2 with the fixed point on a helium nucleus illustrates the behavior of the amplitude when two closed shell and nonbonding moieties are stabilized by van der Waals' interactions. There is a node, which is not intrinsic to the ground-state helium atom, lying between the fixed point and the second nucleus. We take the existence of such a node to be a signal of either nonbonding or antibonding. The sharing amplitudes in the other molecules considered here vary in a systematic fashion between the molecules. We note that with the fixed point on a proton in CH_4 (and also in NH_3 and H_2O) there is a node that passes between the fixed point and the other protons. When taken with the small secondary hydrogen−hydrogen bond index, the node is an indicator of the nonbonding usually associated with these atoms. The sharing amplitude in the vicinity of the heavy nucleus in these molecules varies in a manner that is simply correlated with the effective charges on the heavy nucleus. The differences in the behavior can be described qualitatively in terms of such classic concepts as sp hybrids of varying contributions of the s and p orbitals to the amplitude.

In general the behaviors of the sharing amplitudes in the various compounds are found to be consistent with the traditional qualitative measures of electronegativities used by chemists. In addition, and in spite of describing the behavior of a single electron in a many electron system by a very different means than is typically done, much of the terminology that has been developed in the past to describe bonding can be meaningfully carried over to the present description. An important point in the present approach to the description of electron behavior is that it is invariant to orbital transformations and to basis sets, provided that the basis sets are sufficiently complete. In addition, the analysis can be carried out for electrons described by correlated wave functions essentially as readily as for uncorrelated wave functions. The limitations are basically those of computational time and computational power.

As a final point, we note that it is also possible to construct many particle sharing indices and sharing amplitudes in a fashion similar to the single particle quantities. In principle the hierarchical procedure mentioned in the introduction can be carried out.

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