JOURNAL

OF THE AMERICAN CHEMICAL SOCIETY

Registered in U.S. Patent Office. © *Copyright, 1975, by the American Chemical Society*

VOLUME 97, NUMBER 26 DECEMBER 24, 1975

Spatial Localization of the Electronic Pair and Number Distributions in Molecules

R. F. W. Bader* and M. E. Stephens

Contribution from the Department of Chemistry, McMaster University, Hamilton, Ontario, Canada L8S 4M1. *Received April 4, 1975*

Abstract: It is shown that the quantum mechanical requirement for the spatial localization of an electron in a many-electron system is that the Fermi correlation hole for the electron be totally contained within the same spatial region. Correspondingly, the extent to which this requirement is not met provides a quantitative measure of its delocalization over the remaining space of the system. The localizability of the Fermi hole is a property of the pair density and the total localization of some number of electrons $\bar{N}(\Omega)$ in a region (Ω) of real space is obtained only when the exclusion principle acts so as to reduce the average pair population of (Ω) to its limiting value of $\bar{N}(\Omega)(\bar{N}(\Omega) - 1)$. It is shown that the partitioning of a system which most closely approaches the limit of spatially localized subsets of electrons may be determined by demanding that the fluctuation in the average population of each of the spatial regions be a minimum. The extent to which the (Hartree-Fock) charge distributions of LiH, BeH_2, BH_3, BH_4^-, CH_4, NH_3, OH_2, FH, Ne, N_2, and F_2 may be regarded as arising from the localization of individual α,β pairs of electrons in distinct spatial regions is determined. The model of spatially localized pairs is appropriate for LiH, BeH_2, BH_3, and BH_4^-, it is borderline for CH_4, but in the remaining systems, the motions of the valence electrons are so strongly inter-correlated, the localized pair model ceases to afford a suitable description. For example, the properties of the charge and pair densities of H_2O provide no physical basis for the view that there are two separately localized pairs of nonbonded electrons in this system. The same analysis indicates that a wave function constructed from $N/2$ intra-correlated pair functions would fail to recover the major fraction of the correlation energy in this latter set of molecules.

In this paper we investigate the extent to which the electronic charge distribution of a molecular system may be regarded as arising from the localization of individual pairs of electrons in well-defined and nonoverlapping regions of space. We do this in the following way. We determine the average number of pairs in a given region of space by integration of the quantum mechanical expression for the pair density over that region. We next show that this average number of pairs is dependent upon the correlative interactions between the electrons and in particular, that the decomposition of a total system which most closely approaches the limit of spatially localized pairs of electrons is attained by maximizing the extent to which the integrated Fermi correlation hole of each electron in a given pair is localized within the same spatial domain. Finally, we show that this latter condition is attained by demanding that the fluctuation in the average population of each of the spatial regions be a minimum.

Daudel and co-workers[1,2] have reasoned that there should be some "best" decomposition of the physical space of a system into a number of mutually exclusive spaces called loges. The "best" loges were to represent the most probable division of the physical space of a system into localized groups of electrons. The best loges were ultimately defined as being those which minimized the missing information function $I(P_n,\Omega)$,[3]

$$I(P_n,\Omega) = -\sum_n P_n(\Omega) \ln P_n(\Omega)$$

where $P_n(\Omega)$ is the probability that n electrons occupy the restricted region of space (or loge) Ω, when the other $(N - n)$ are confined to the remainder of the system. Within the framework of information theory, minimization of $I(P_n,\Omega)$ corresponds to a situation in which one has the maximum information about the state of the region (Ω). Using this definition for the "best" loges, Daudel et al.[4] have obtained a loge decomposition of a number of simple molecules. In each case, the most probable partitioning found localizes an average of two electrons in those regions of space which are generally associated with core, bonded, and nonbonded electrons.

The work described herein may be considered as providing an alternative definition of the "best" loges in the sense implied by Daudel. We show that the extent to which some number of electrons meet the quantum mechanical definition of localization in real space is determined solely by the properties of the pair density, and does not require the knowledge of the full (spinless) N-particle density matrix as is demanded by the calculation of $I(P_n,\Omega)$.

It is well-established that the molecular correlation energy may be approximated by a sum of pair correlation energies.[5,6] Associated with this result is the assumption that in some systems, a large fraction of the correlation energy may be described in terms of just $N/2$ strongly intra-correlated pair functions, functions which are considered to be spatially localized and as a result transferrable between systems. This assumption is embodied in the method of "separated electron pairs" [7,8] and in the use of "strongly orthogonal geminals".[9,10] The independent electron pair approximation, as recently reviewed by Kutzelnigg,[11] is another such approach, but one which may be generalized to include all $N(N-1)/2$ pair interactions. The present work is related to these approaches in a useful way since it details the definition of regions of space which possess pure pair properties and in addition, yields values of the extent of intra- and inter-pair correlation over and between well-defined spatial regions. The method itself provides a simple test, which can be applied to the Hartree-Fock starting wave function, to determine whether or not an intra-pair biased approach will be successful in recovering a major fraction of the correlation energy in a particular molecule.

Ludeña and Amzel[12] and Aslangul et al.[13] have derived methods for the calculation of correlated wave functions using directly the information of the "best loge" boundaries. The present results substantiate their expectations that such regions should exhibit maximum intracorrelated behavior.

There is hardly a need to stress the central role played by the concept of the "electron pair" in chemistry. The results of this paper provide a quantitative test of the localized pair concept in molecular systems, or of the validity of Lewis structures. The assumption of preferred spatial arrangements for fixed numbers of electron pairs about some central nucleus is a concept common to most theories of molecular geometry. In a forth-coming paper we will illustrate that the most stable geometry of an AH_n system is the one whose distribution of charge most nearly approaches the limit of spatially localized pairs of electrons.

The Pair and Number Densities

The quantum-mechanical definition of the pair density is

$$D_2(\mathbf{r}_1,\mathbf{r}_2) = N(N-1)\int d\mathbf{s}_1 \int d\mathbf{s}_2 \int d\mathbf{x}_3 \ldots \int d\mathbf{x}_N \psi^*(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_N)\psi(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_N) \quad (1)$$

where $\mathbf{x}_i = \mathbf{r}_i\mathbf{s}_i$ denotes a product of space and spin coordinates of the ith electron. The integration of $D_2(\mathbf{r}_1,\mathbf{r}_2)$ over all space for both electrons yields $N(N-1)$, the total number of (nondistinct) pairs in a system of N electrons. Integration of the coordinates $\mathbf{r}_1$ and $\mathbf{r}_2$ over a restricted region of space (Ω) yields the average number of pairs of electrons in that region, $D_2(\Omega,\Omega)$

$$D_2(\Omega,\Omega) = \int_\Omega d\mathbf{r}_1 \int_\Omega d\mathbf{r}_2 D_2(\mathbf{r}_1,\mathbf{r}_2) = \text{average number of pairs in } (\Omega) \quad (2)$$

To determine the relationship between the average pair density and the usual number (or charge) density and to obtain the criterion for defining spatial regions with pure pair properties, we introduce the concept of correlation as usually defined.[14] That is, we write $D_2(\mathbf{r}_1,\mathbf{r}_2)$ as[15]

$$D_2(\mathbf{r}_1,\mathbf{r}_2) = D_1(\mathbf{r}_1)D_1(\mathbf{r}_2)[1 + f(\mathbf{r}_1,\mathbf{r}_2)] \quad (3)$$

where $D_1(\mathbf{r}_1)$ is the number density

$$D_1(\mathbf{r}_1) = N\int d\mathbf{s}_1 \int d\mathbf{x}_2 \ldots \int d\mathbf{x}_N \psi^*(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_N)\psi(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_N)$$

The correlation factor $D_1(\mathbf{r}_1)D_1(\mathbf{r}_2)f(\mathbf{r}_1,\mathbf{r}_2)$ is a measure of the extent by which the pair density deviates from that predicted by the simple product of number densities $D_1(\mathbf{r}_1)D_1(\mathbf{r}_2)$. Because of the differing normalizations ascribed to D_2 and D_1, certain limiting values may be assigned to the correlation correction. That is, a pair density can never be equal to a product of number densities as the product $D_1(\mathbf{r}_1)D_1(\mathbf{r}_2)$ includes the self-pairing of the electrons and hence, when integrated over all space, yields N^2 pairs, or N pairs in excess of the total number of actual pairs, $N(N-1)$. Because of this, integration of eq 3 over the coordinates of just one of the electrons yields

$$\int d\mathbf{r}_2 D_1(\mathbf{r}_2)f(\mathbf{r}_1,\mathbf{r}_2) = -1, \quad (4)$$

for any fixed value of $\mathbf{r}_1$ and the total effect of the correlation over all space is simply to remove the N self-pairs,

$$\int d r_1 \int d r_2 D_1(\mathbf{r}_1)D_1(\mathbf{r}_2)f(\mathbf{r}_1,\mathbf{r}_2) = -N \quad (5)$$

Since the net effect of $D_1(\mathbf{r}_2)f(\mathbf{r}_1,\mathbf{r}_2)$ must be to decrease the density of other electrons in the vicinity of the one fixed at $\mathbf{r}_1$, its general effect is to create a hole, a correlation hole, in the pair distribution function $D_2(\mathbf{r}_1,\mathbf{r}_2)$.

In this work we are particularly concerned with the spatial extent of the effects of the self-pairing correlation on the motions of the electrons, and whether or not the net effect of this correlation for any one particle, the correlation hole, may be largely localized to one particular region of space.

In an electronic system it is useful to distinguish between the correlation of electrons with identical spin, Fermi correlation, from that of electrons with opposite spins, Coulomb correlation. The correlation term $f(\mathbf{r}_1,\mathbf{r}_2)$ as defined in eq 3 will measure both types of correlation. However, the limiting value of the correlation hole as expressed in eq 4 arises only from the correlation between electrons of the same spin, the Fermi hole. That part of $f(\mathbf{r}_1,\mathbf{r}_2)$ which refers to the correlation between electrons of opposite spin contributes zero when integrated over all space.[15] In a system which is in a definite spin state, the numbers of α and β electrons, N_α and N_β, respectively, are separately conserved. If the coordinates of an α-spin electron are held fixed during the integration over all space in eq 4, then only the removal of α-spin density contributes to the limiting value of -1. Mathematically, this result is obtained during the integration over the spin functions. Conceptually, it arises because the α and β electrons form two distinct sets and self-pairing can occur only within a set of identical particles. (The total number of pairs which can be formed between five α electrons and five β electrons is 50, or $(5 \times 5) \times 2$. However, the number of pairs which can be formed from the five electrons of either set is 20 or $5(5-1)$.)

Any properly antisymmetrized wave function will correct for the self-pairing of the α and β electrons. One can view the net result of the Pauli principle and its associated Fermi correlation as correcting for the self-pairing of the α and the β electrons in a nontrivial way. What we now show is that the extent to which sets of electrons may be localized in real space within some total system is determined solely by the spatial properties of the Fermi or self-pairing correlation.

Consider a molecular system which contains N electrons. The probability of the event that n electrons will be found in a particular fragment (Ω) of the total space of the system when the remaining $(N-n)$ are confined to the disjoint region (Ω') is[4]

$$P_n(\Omega) = \frac{N!}{n!(N-n)!}\int_\Omega d\mathbf{r}_1 \ldots \int_\Omega d\mathbf{r}_n \times \int_{\Omega'} d\mathbf{r}_{n+1} \ldots \int_{\Omega'} d\mathbf{r}_N \Gamma^{(N)}(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)$$

In terms of these event probabilities, the average number of pairs in a region (Ω) is

$$D_2(\Omega,\Omega) = \sum_n P_n(\Omega)n(n-1) = \overline{N(\Omega)^2} - \bar{N}(\Omega) \quad (6)$$

where $\bar{N}(\Omega) = D_1(\Omega)$ is the average number of electrons in (Ω).

Now consider the properties of the region (Ω) in the limiting situation when $P_n(\Omega)$, the probability of one particular event, equals unity, and the probabilities of all other events are thus zero. In this situation $\bar{N}(\Omega)$, the average number of electrons in (Ω), equals n. The number of pairs which can be formed is $n(n-1) = \bar{N}(\Omega)(\bar{N}(\Omega)-1)$, the number of pairs which can be formed from an isolated and distinct set of n objects. When the pair population of a region or loge (Ω) is expressible as $\bar{N}(\Omega)(\bar{N}(\Omega)-1)$ we refer to it as being a "*pure pair*" population. A set of electrons with such properties would be perfectly localized in the region (Ω); i.e., they would behave as a separate and distinguishable subset of electrons and since the self-pairing is totally accounted for within the region, the wave function for the total system could be expressed as a simple product of separately antisymmetrized wave functions for the n electrons in (Ω) and the $(N-n)$ in (Ω'). This is the limiting case of localization in an electronic system and we show that it occurs when the total Fermi hole for each of the n electrons in (Ω) is itself confined totally to the region (Ω).

Using eq 3, the expression for the average number of pairs in a region (Ω) may be expressed so as to incorporate the correlation term to yield

$$D_2(\Omega,\Omega) = \int_\Omega d\mathbf{r}_1 \int_\Omega d\mathbf{r}_2 D_2(\mathbf{r}_1,\mathbf{r}_2) = \bar{N}(\Omega)^2 + F(\Omega,\Omega) \quad (7)$$

where

$$F(\Omega,\Omega) = \int_\Omega d\mathbf{r}_1 \int_\Omega d\mathbf{r}_2 D_1(\mathbf{r}_1)D_1(\mathbf{r}_2)f(\mathbf{r}_1,\mathbf{r}_2) \quad (8)$$

$F(\Omega,\Omega)$ is a measure of the total correlation which is contained within the region (Ω), i.e., a measure of the intraloge correlation. For a Hartree–Fock wave function, which inclues only Fermi correlation, the magnitude of $F(\Omega,\Omega)$ is a measure of the total (integrated) Fermi hole of the $\bar{N}(\Omega)$ particles that lies within the region (Ω). From eq 4 and 8 and as demonstrated below, the limiting value of the intraloge correlation is seen to be $-\bar{N}(\Omega)$. Thus, only if the total correlation hole of the $\bar{N}(\Omega)$ particles in (Ω) is totally contained in this region will $D_2(\Omega,\Omega)$ correspond to the exact number of pairs which can be formed from a distinct set of $\bar{N}(\Omega)$ particles. That is, in this limiting situation the $\bar{N}(\Omega)$ electrons (where $\bar{N}(\Omega)$ is necessarily a whole number) generate a pure pair population, with

$$D_2(\Omega,\Omega) = \bar{N}(\Omega)(\bar{N}(\Omega)-1) \quad (9)$$

Otherwise, $\bar{N}(\Omega) < [\overline{N(\Omega)^2}]^{1/2}$ and, from eq 6, $D_2(\Omega,\Omega) > \bar{N}(\Omega)(\bar{N}(\Omega)-1)$. Only when the relationship as expressed in eq 9 applies is the number of pairs in a region determined by (or in any way related to) the average number of particles within this same region. In this limit both $\bar{N}(\Omega)$ and $D_2(\Omega,\Omega)$ yield pure populations as their values are determined by a single event.

The fluctuation in the population of a region (Ω) is defined as

$$\Lambda(\Omega) = \sum_{n=0}^{N} P_n(\Omega)(n-\bar{N}(\Omega))^2 = \overline{N(\Omega)^2} - \bar{N}(\Omega)^2 \quad (10)$$

It provides a direct measure of the spread in events which contribute to the average population of a region of space. Furthermore, the fluctuation in a population is determined solely by the average pair and the number densities and a knowledge of the individual event probabilities $P_n(\Omega)$ is not required for its calculation.[16] Thus, one finds

$$\Lambda(\Omega) = D_2(\Omega,\Omega) + \bar{N}(\Omega) - \bar{N}(\Omega)^2 \quad (11)$$

Substitution of eq 7 for $D_2(\Omega,\Omega)$ into eq 11 yields

$$\Lambda(\Omega) = \bar{N}(\Omega) + F(\Omega,\Omega) \quad (12)$$

The fluctuation attains its minimum value of zero under the same condition that $D_2(\Omega,\Omega)$ is reduced to a pure pair population, that is, when one particular event has a probability of unity. From eq 12 the limiting value of $F(\Omega,\Omega)$ is thus equal to $-\bar{N}(\Omega)$, a value, which as stated previously, implies that the total Fermi correlation hole for each electron in (Ω) is totally contained within the region (Ω). Thus, the surface defining a loge for which $\Lambda(\Omega)$ has been minimized is one enclosing a volume of space within which the magnitude of the correlation per particle is a maximum.[16] Minimization of $\Lambda(\Omega)$ also ensures that the extent to which $\bar{N}(\Omega)$ and $D_2(\Omega,\Omega)$ approach their limiting values for pure populations, obeying the relationship expressed in eq 9, is maximized.

In general, for a system described by a fully correlated wave function, $F(\Omega,\Omega)$ will measure the magnitude of the Fermi and the Coulomb correlations over a region (Ω). However, since the limiting case of $F(\Omega,\Omega) = -\bar{N}(\Omega)$ yields a pure pair population for (Ω), this value must be a measure of only the self-pairing or Fermi correlation. Thus, *one must conclude that in this limiting situation of total localization, the Coulomb correlation integrates to zero over the region* (Ω), *as it does over the total system.* While the Coulomb correlation acts only within each localized set of electrons in this limiting situation, there are residual correlative interactions between electrons of like spin in the different loges. The Fermi hole integrates to minus N (or $-\bar{N}(\Omega)$ for a region) thereby correcting for the statistical counting of pairs. However, it does so in a particular way, such that correlation over and above the statistical correlation (we may call it a "pure correlation") is introduced into the wave function for motions of electrons with parallel spins.[16] Thus, the total localization of one or more electrons of say α spin in some region (Ω) is obtained as a result of the pair *probability*[16] for α pairs in (Ω) being decreased from that predicted by the uncorrelated result, while the probability of forming α pairs between the α electrons in (Ω) and those outside of (Ω) is increased. Hence the localization of the Fermi hole into distinct spatial regions is obtained as a result of a pure correlation between electrons of identical spin which is negative within each loge and positive when the two electrons are in different loges. It integrates to zero only over all space. In the same limit, the Coulomb correlation is zero over each loge separately, implying that the density of α,β pairs is both increased and decreased over the uncorrelated result by equal amounts within each loge.

One can obtain a measure of the extent of the correlative interactions between the electrons in two different loges (Ω) and (Ω') by determining the fluctuation in the population of the combined loge $(\Omega + \Omega') = (\Omega'')$. One finds,

$$\Lambda(\Omega'') = \Lambda(\Omega) + \Lambda(\Omega') + 2F(\Omega,\Omega') \quad (13)$$

where

$$F(\Omega,\Omega') = \int_\Omega d\mathbf{r}_1 \int_{\Omega'} d\mathbf{r}_2 D_1(\mathbf{r}_1)D_1(\mathbf{r}_2)f(\mathbf{r}_1,\mathbf{r}_2) \quad (14)$$

In a system described by a Hartree–Fock wave function the magnitude of the inter-loge correlation $F(\Omega,\Omega')$ is a measure of that part of the total correlation hole for the electrons in (Ω) which is present in (Ω') and vice versa. Just as $-F(\Omega,\Omega)/\bar{N}(\Omega)$ provides a measure of the extent of localization of the electrons in (Ω) by measuring the fraction of the total Fermi hole contained in (Ω), so $-F(\Omega,\Omega')/\bar{N}(\Omega)$ is a measure of the extent to which electrons in (Ω) are delocalized over (Ω').

The number of pairs which can be formed between the electrons in (Ω) and those in (Ω') is also related to $F(\Omega,\Omega')$,

$$D_2(\Omega,\Omega') = \int_{\Omega} d\mathbf{r}_1 \int_{\Omega'} d\mathbf{r}_2 D_2(\mathbf{r}_1,\mathbf{r}_2) = \bar{N}(\Omega)\bar{N}(\Omega') + F(\Omega,\Omega') = D_2(\Omega',\Omega) \quad (15)$$

Consider a two-loge partitioning of a total system, in which case $\Lambda(\Omega'') = 0$ (since (Ω'') now refers to all space) and eq 13 yields

$$\Lambda(\Omega) + \Lambda(\Omega') = -2F(\Omega,\Omega') = 2\Lambda(\Omega) \quad (16)$$

and where in addition one has

$$F(\Omega,\Omega) + F(\Omega',\Omega') + 2F(\Omega,\Omega') = -N \quad (17)$$

By minimizing the sum of the loge fluctuations in eq 16, one minimizes the magnitude of the inter-loge correlation, which from eq 17 is equivalent to maximizing the magnitude of the intra-loge correlations. In the limit of perfect localization of the electrons into two subsets, one in (Ω) and one in (Ω'), the inter-loge correlation vanishes, and from eq 15, the number of pairs formed between the two loges reduces to $2\bar{N}(\Omega)\bar{N}(\Omega')$, i.e., the number of pairs which can be formed between two sets of objects, the objects in each set being distinct from those in the other. When $F(\Omega,\Omega')$ is not zero, this number of pairs is decreased from its limiting value and $2F(\Omega,\Omega')$ may be interpreted as a measure of the extent to which the identities of the electrons in (Ω) and (Ω') are spread over both loges.

These results are easily extended to the partitioning of a system into an arbitrary number of loges, ν. The operational expression for determining the most localized description of the electronic charge distribution in a molecular system into ν spatially defined subsets is given by

$$\sum_{\Omega}^{\nu} \Lambda(\Omega) = -2 \sum_{\Omega<\Omega'}^{\nu} F(\Omega,\Omega') \quad (18)$$

The minimization of the sum of the loge fluctuations minimizes the total extent of inter-loge correlation, and from eq 19

$$\sum_{\Omega} F(\Omega,\Omega) + 2 \sum_{\Omega<\Omega'} F(\Omega,\Omega') = -N \quad (19)$$

it maximizes the extent of intra-loge correlation.

In real systems, the perfect localization of the charge distribution of a system into two or more subsets of electrons can be approached but never attained. Thus, in general $\bar{N}(\Omega)$ is the average of a number of events. It should be stressed that the knowledge of the average population of a region does not in general yield any information about the number of pairs in that region. Thus, for example, a spatial region of a molecular system with an average population of two will not in general contain two pairs (i.e., one α,β pair) of electrons. Instead, the average number of pairs for a region and the extent to which the electrons are localized in the region are both determined by the pair density. Only certain special spatial regions possess properties which approach the relationship between $\bar{N}(\Omega)$ and $D_2(\Omega,\Omega)$ expressed in eq 9.

In summary, in a many-electron system, any one electron has an identity in a restricted region of space only if its correlation hole is totally confined to the same region of space. One cannot spatially localize an electron without at the same time localizing its Fermi hole.

Correlation in Hartree–Fock Charge Distributions

As is well-known, a Hartree–Fock wave function includes only Fermi correlation. Slater[17] has pointed out that the exchange terms obtained through the introduction of antisymmetrization into a simple product of one-electron wave functions has the effect of correcting the energy expression for the self-repulsion of the electrons. This is the energetic analogue of correcting for self-pairing. Maslen[18] has shown that the average exchange charge density, the quantity defined by Slater to account for the removal of charge density of an amount equivalent to one electronic charge for each electron in the system, is identical with the integrand in eq 4, the Fermi hole. Thus, $F(\Omega,\Omega)$ is a measure of the total exchange charge for the electrons in (Ω) which is contained within (Ω). For a Hartree–Fock wave function, the expression for $F(\Omega,\Omega)$ assumes a particularly simple form, namely,

$$F(\Omega,\Omega) = -\sum_{i,j}^{N} S_{ij}^2(\Omega) \quad (20)$$

where $S_{ij}(\Omega)$ is the overlap of the spin orbitals ϕ_i and ϕ_j over the region (Ω). Because of the orthogonality of the spin functions, $F(\Omega,\Omega)$ may be expressed in terms of separate contributions from the α and β electrons as

$$F(\Omega,\Omega) = -\sum_{i,j}^{N_\alpha} S_{ij}^2(\Omega) - \sum_{i,j}^{N_\beta} S_{ij}^2(\Omega) = F^{\alpha}(\Omega,\Omega) + F^{\beta}(\Omega,\Omega) \quad (21)$$

a result which shows that the Fermi or self-pairing correlation operates separately within the α- and β-spin distributions. It is clear from eq 21 that for a closed-shell system the total Fermi correlation contained within a region (Ω) may be divided into equal contributions from the α and β electrons.

Any evidence for pairing which is found for a system when it is described by a Hartree–Fock wave function must be the result of Fermi correlation. Consider a region of space with an average population of two in a closed-shell system for which $F(\Omega,\Omega)$ attains its limiting value. In this instance $F^{\alpha}(\Omega,\Omega) = F^{\beta}(\Omega,\Omega) = -1$ and one α and one β electron are confined to the region (Ω) *with the total exclusion of all* other electrons of α and β spin. Thus, Fermi correlation does not act directly to "pair up" electrons. Rather, since there is no Fermi correlation between electrons of opposite spin, an α,β pair is obtained as a result of all other electrons of α and all other electrons of β spin being excluded from a given region of space. In this manner, some number of α,β pairs of electrons may be spatially localized, the number being determined by the depth of the nuclear potential in that region.

In view of the manner in which the Fermi correlation operates, one can argue that a Hartree–Fock wave function should over-emphasize the extent to which the pair density is spatially localized. That is, the introduction of a repulsive Coulomb correlation between the electrons of opposite spin within a localized set would tend to reduce the extent of localization. A similar view has been expressed by Sinanoğlu;[19] "Shell structure in atoms and molecules is due to nuclear wells and the exclusion principle. Long-range Coulomb repulsions between electrons have a disrupting influence on this structure".

The results reported in the following section, which were obtained from Hartree–Fock wave functions, should, if the above argument is correct, represent an upper limit of the

Table I. Properties of Core Loges

Molecule	r, au	$\bar{N}(\Omega)$	$D_2(\Omega,\Omega)$	$F(\Omega,\Omega)$	$\lvert F(\Omega,\Omega)/\bar{N}(\Omega)\rvert \times 100$ percentage localization
LiH	1.42	1.999	2.088	−1.908	95.5
BeH_2	0.95	2.012	2.173	−1.875	93.2
BH_3	0.70	2.023	2.256	−1.836	90.8
BH_4^-	0.70	2.026	2.291	−1.814	89.5
CH_4	0.53	2.005	2.254	−1.766	88.1
NH_3	0.43	2.002	2.282	−1.726	86.2
OH_2	0.36	2.001	2.314	−1.691	84.5
FH	0.30	1.966	2.244	−1.621	82.5
N_2	0.43	2.001	2.271	−1.733	86.6
F_2	0.31	2.008	2.367	−1.667	83.0
Ne	0.26	1.963	2.348	−1.506	76.7
Ar	0.12	1.856	2.090	−1.355	73.0

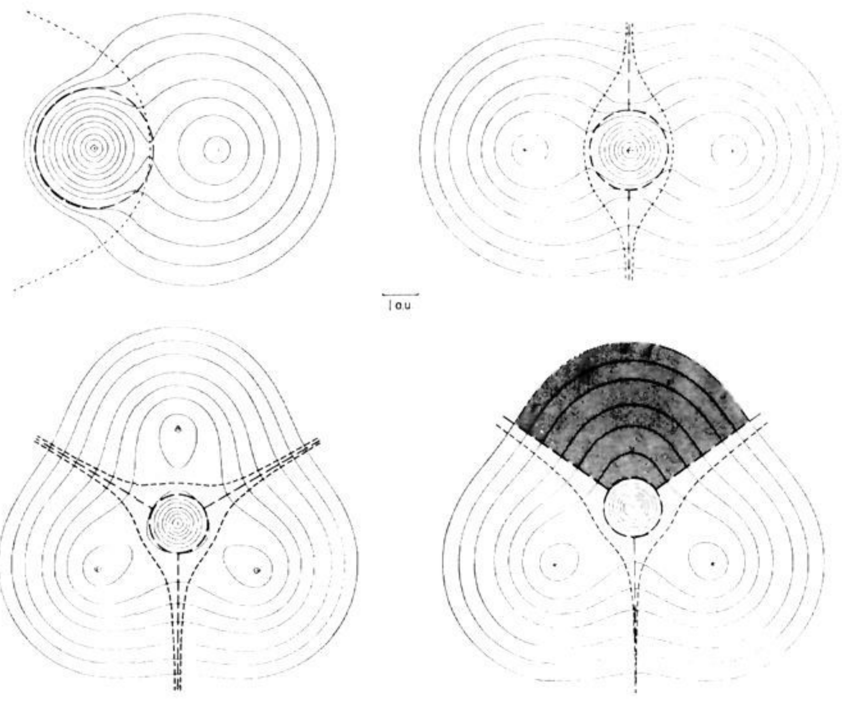


Figure 1. Contour maps of the molecular charge distributions (from left to right) of $LiH(X^1\Sigma^+)$, $BeH_2(X^1\Sigma^+)$, and $BH_3(X^1A')$, $BH_4^-(X^1A_1)$. The loge boundaries are indicated by long dashed lines, the zero-flux surfaces, which indicate "paths of minimum density" by short dashed lines. The shaded area indicates that portion of the plane which forms a common boundary for two loges. The contours in this and the following figures are in au and increase in value from the outermost contour inward in steps of 2×10^n, 4×10^n, and 8×10^n. The smallest contour value is 0.002 au with n increasing in steps of unity.

extent to which the pair density and hence the charge density in a given molecular system may be spatially localized.

Localization in Hartree–Fock Charge Distributions

The real space of a number of molecular systems is searched for regions which yield a minimum in the fluctuation of their populations to determine the nature of the spatial localization of their Hartree–Fock number and pair densities. The systems studied are LiH, BeH_2, BH_3, BH_4^-, CH_4, NH_3, OH_2, FH, Ne, Ar, N_2, and F_2, all at their equilibrium geometries. We first search for those individual regions of space in which localization occurs.

Localization of Core Density. Loges of arbitrary shape, located in arbitrary regions of space, do not exhibit a minimum in their fluctuations as their boundaries are varied, other than when their volumes tend to either zero or all space. However, a spherical loge centered on any of the nuclei in the above systems, save the protons, yields a region of space, a core loge, with a minimum in its fluctuation for some value of the radius r. The parameters and properties of the core loges are listed in Table I. In every case the optimum core loge is found to have an average number and pair population in the neighborhood of two. In general, no other single partitioning of the systems is found to yield a more localizable description than that obtained by the division of the system into one core loge for each heavy nucleus, and a single valence loge. For the elements Li through to Ne, the percent localization (as measured by $|F(\Omega,\Omega)/\bar{N}(\Omega)|$) ranges from 95 to 77%. Clearly, for these elements, the concept of distinguishing between a pair of core electrons and some number of valence pairs has some justification.

As anticipated, the radius of the core loge decreases with increasing nuclear charge. Of all systems so far studied, the charge distribution of LiH (and of LiH^+)[16] approaches most closely the idealized localization into separated pairs (or into one core pair and one valence electron in the ion). This property is reflected in the very localized nature of the charge distribution for these systems, Figure 1.

The decrease in both the intra-loge correlation and the percentage localization with increasing nuclear charge parallels the increase in the compactness of the core density. In general, one finds the extent of localization to decrease as a charge distribution becomes more contracted. Note that while the argon core has a pair population close to two, the average number population is significantly less than two. This situation is characteristic of a loge for which $P_2(\Omega)$ is dominant, but for which $P_1(\Omega)$ exceeds $P_3(\Omega)$ by a significant amount, thereby decreasing the average number population.

Aside from the zeroes in the fluctuation at $r = 0$ and $r = \infty$, the Ne atom was found to exhibit only the one minimum in $\Lambda(\Omega)$ as the radius of the core loge was varied from zero to infinity. Thus, the Ne atom yields a core and a valence loge, or K and L shells of density, and the inter-shell correlations, the value of $2F(K,L)$, amounts to only 9.1% of the total possible Fermi correlation.

The Ar atom exhibited two minima in $\Lambda(\Omega)$ as r was varied, indicating the presence of three localizable shells of density. The middle shell was bounded by spheres of radii $r_1 = 0.12$ au and $r_2 = 0.75$ au, yielding average populations of 1.86, 8.28, and 7.86 electrons for the three shells. (The minima in the radial distribution plot for Ar occur at 0.14 and 0.80 au.) The sum of the fluctuations for these three shells of density is also a minimum for simultaneous variation in r_1 and r_2. Thus, from eq 18, any change in the values of r_1 or r_2 quoted above increases the inter-shell correlation and decreases the localization of charge in each shell. The percentage localization within each of the three shells is 73, 87, and 87% for the K, L, and M shells, respectively. The values of the inter-shell Fermi correlations are, $2F(K,L) = -0.972$, $2F(K,M) = -0.031$, and $2F(L,M) = -1.133$, which sum to 12% of the total Fermi correlation.

Localization of Valence Density. Having defined a valence region as the total space minus a localized core on each heavy atom, we now search for a loge in the space of the valence density which yields a minimum in its fluctuation. Such a search is successful only in the systems BeH_2, BH_3, and BH_4^- (and of course in the two-loge system, LiH). In these three AH_n systems, the loge which yields a minimum in its fluctuation corresponds to $1/n$ of the valence region with boundaries symmetrically located with respect to the enclosed proton (see Figure 1). Any variation in the boundaries of one of these bond loges increases its fluctuation and decreases the magnitude of the intra-loge correlation $F(\Omega,\Omega)$. The sum of the fluctuations for the core and n valence loges is also minimized for these bond loges. From eq 18, any change in the boundaries of any of the loges in these three systems increases the magnitude of the interloge correlations and decreases the extent of intra-loge correlations. The spatial regions thus obtained represent the most

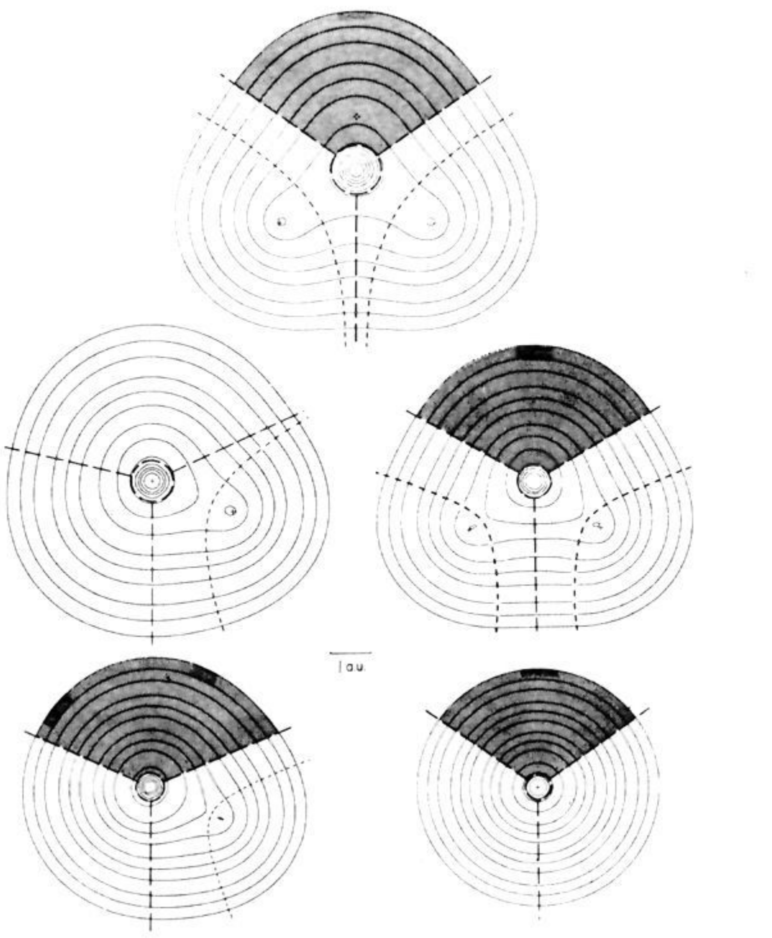


Figure 2. Contour maps of the molecular charge distributions of $CH_4(X^1A_1)$ in an HCH plane, of $NH_3(X^1A_1)$ in an NH plane, of $H_2O(X^1A_1)$ in the HOH plane, of $HF(X^1\Sigma^+)$, and of $Ne(X^1S_0)$. The long dashed lines denote boundaries of loges which have average populations of 2.0 electrons.

localized possible partitioning of the system, in the traditional sense, into core and bond loges. While the average population of the bond loges is close to two (see Table II) in BeH_2, BH_3, and BH_4^-, the average number of pairs contained in these regions deviates significantly from the value two obtained from one pure α,β pair of electrons. What makes these systems unique among the molecules studied here with the exception of F_2 is that a partitioning of the valence region which yields a set of maximally intra-correlated spatial regions is possible. It was for the diatomic hydrides of the same elements, Li, Be, and B, and BeH_2 that Daudel et al.[4] were able to find localized pairs of electrons using the minimization of the information function for defining the "best" loges.[20] Methane is borderline in its behavior, but the motions of the valence electrons in the remaining molecules are so strongly inter-correlated that no best partitioning is found and the localized pair concept loses its meaning. For example, a bond loge in HF which has a number population of two is occupied on the average by three pairs.

In methane a bond loge was defined as a three-sided pyramidal region with its apex at the carbon nucleus and centered about a carbon-hydrogen internuclear axis, but excluding the region cut off by the core. A set of four such loges with variable apex angles fulfills the necessary requirement of exhausting the space occupied by the valence density. The fluctuation of a single bond loge, while not possessing a minimum, does exhibit a plateau in its values in the immediate region of $\bar{N}(\Omega) = 2$ as the apex angle is varied to change the volume and population of the loge. However, in this molecule the *sum* of the loge fluctuations is minimized for a core and four identical bond loges (all with $\bar{N}(\Omega) = 2.0$) with respect to any variation in the core radius or apex angles defining the bond loges. The fluctuation of the population contained in one-quarter of the valence region reaches a maximum value when the loge is located so that the three edges of the loge lie along three of the carbon-hydrogen internuclear axes.

Table II. Properties of Bonded Loges

Molecule	$\bar{N}(\Omega)$	$D_2(\Omega,\Omega)$	$F(\Omega,\Omega)$	$\lvert F(\Omega,\Omega)/\bar{N}(\Omega)\rvert \times 100$ percentage localization
LiH	2.001	2.094	−1.910	95.5
BeH_2	1.994	2.126	−1.850	92.8
BH_3	1.992	2.341	−1.623	81.8
BH_4^-	1.994	2.454	−1.522	76.3
CH_4	1.999	2.619	−1.377	68.9
NH_3	1.997	2.762	−1.226	61.4
OH_2	1.987	2.833	−1.117	56.2
FH	2.037	3.067	−1.081	53.1
$N_2(\sigma)$	1.995	3.420	−0.560	28.1
$N_2(\pi)$	1.966	3.296	−0.569	28.9
F_2	2.034	3.785	−0.353	17.4

In methane, only 69% of Fermi correlation required for the self-pairing correction for one α,β pair of electrons is contained in each of the bond loges, and on the average they are occupied by 2.6 pairs of electrons. From all the systems considered here, it appears that the fluctuation of a single loge may be minimized with respect to a variation in its boundaries only if the intra-loge Fermi correlation attains at least 70% of its limiting value.

The same pyramidal-type loges were used in the partitioning of the valence regions in NH_3, H_2O, HF, and Ne. In NH_3, a nonbonded loge with variable apex angle is centered about the C_{3v} axis above the nitrogen nucleus (Figure 2), and the remaining space is divided equally into three bond loges. In H_2O such partitioning yields two equivalent bond loges and two equivalent nonbonded loges (the latter sharing a common face in the plane containing the nuclei). In HF, it yields three equivalent nonbonded loges and one bond loge and in Ne, four nonbonded loges.

No single region of the space of the valence density can be found which exhibits a minimum in its fluctuation for these systems. In Ne, for example, as loges of various shapes (pyramids, cones, and wedges) are varied in size, the fluctuation increases from zero to some maximum value and then decreases, as the loge is further increased, to approach the value of the core loge fluctuation in the limit of the loge encompassing all of the valence space. Similar results are obtained for loges in the valence region of NH_3. These same variations in loge boundaries yield values of $|F(\Omega,\Omega)/\bar{N}(\Omega)|$, the percentage localization, which increase monotonically to the limiting value obtained for the total valence region. Thus, in NH_3, H_2O, HF, and Ne, the Fermi hole for some number of electrons less than the total number of valence electrons cannot be well-localized in a region of space separate from that of the remaining electrons. The motions of the valence electrons are so strongly inter-correlated that no spatial localization into some number of subsets is possible.

What we do report in Table II (for the bond loges) and Table III (for the nonbonded loges) are the results obtained when these systems are partitioned, in the manner described above, so as to yield the required number of equivalent bond and nonbonded loges with average populations of two.

The molecules BH_4^-, CH_4, NH_3, OH_2, HF, and Ne form a ten-electron series. From Figures 1 and 2, the overall distribution of charge in these systems undergoes a steady contraction as the nuclear charge of the heavy atom is increased. Correspondingly, the electronic charge distribution becomes increasingly less localized. Table IV lists the sum of the loge fluctuations for a five loge partitioning in this series of molecules. From eq 18, this sum equals the magnitude of the total inter-loge Fermi correlation. The total Fermi correlation equals −10 for these molecules and the

Table III. Properties of Nonbonded Loges

Molecule	$\bar{N}(\Omega)$	$D_2(\Omega,\Omega)$	$F(\Omega,\Omega)$	$\lvert F(\Omega,\Omega)/\bar{N}(\Omega)\rvert \times 100$ percentage localization
NH_3	2.005	2.914	−1.106	55.2
OH_2	2.005	2.981	−1.037	51.7
FH	1.999	3.010	−0.988	49.4
Ne	2.009	3.070	−0.967	48.1
N_2	2.035	2.943	−1.199	58.9

Table IV. Extent of Localization into Five Pairs for Some Ten-Electron Systems

Molecule	$\Sigma\Lambda(\Omega,\Omega)$ magnitude of total inter-loge correlation	$\lvert \Sigma F(\Omega,\Omega)/N\rvert \times 100$ percentage of total intra-loge correlation required for localized pairs
BH_4^-	2.101	79
CH_4	2.725	73
NH_3	3.489	65
OH_2	3.987	60
FH	4.336	57
Ne	4.549	55

results in Table IV indicate that the interloge correlation accounts for an increasingly larger fraction of the total correlation through the series, 21% in BH_4^- to 43 and 45% respectively in FH and Ne. The column labeled total percentage localization is simply the percentage of the total Fermi correlation contributed by the intra-loge correlations, $\Sigma_\Omega F(\Omega,\Omega)$. For example, H_2O possesses only 60% of the self-pairing correction required to yield five separate and spatially identifiable α,β pairs of electrons.

The values of the inter-loge Fermi correlations $F(\Omega,\Omega')$ are given in Table V. Their magnitude is seen to decrease in the order nonbonded–nonbonded, nonbonded–bonded, bonded–bonded, nonbonded–core, and bonded–core. This order is in accord with the order of increasing localization found for the various loges themselves, i.e., nonbonded < bonded < core.

The values of $F(\Omega,\Omega')$ provide a measure of the extent of delocalization of the electrons in (Ω) into (Ω'), and (since $F(\Omega,\Omega') = F(\Omega',\Omega)$) of the delocalization of those in (Ω') into (Ω). Consider H_2O as an example. On the average, two electrons occupy the core loge. The extent to which this average number does not represent a single event ($P_2(c) = 1.00$) is determined by the extent to which the Fermi hole for the electrons in the core is spread over other loges. From Table V, the fraction of the Fermi hole of the core electrons which resides in the two bond loges is $2F(c,b)/\bar{N}(c) = -0.069$ or 6.9%. Similarly, one finds that 8.6% of the Fermi hole for the core population is contained in the nonbonded loges. An α,β pair of electrons in a bond loge of H_2O is distributed so that 56% of the charge is in the bond loge, 3% in the core, ~12% in the other bonded loge, and ~14% in each of the nonbonded loges. Finally, only 52% of a nonbonded α,β pair in H_2O is found within the loge, the remaining density being distributed ~4% in the core, 13% in each of the bonded loges and 18% in the second nonbonded loge.

The delocalized nature of the pairs in these systems is also reflected in the average values of $D_2(\Omega,\Omega')$, the number of pairs formed between the electrons in (Ω) and (Ω'). These values are easily calculated from the data in the tables, using eq 15. For example, the value of $D_2(n,n')$ in H_2O is reduced to 3.68 as compared to the value 4.00 obtained for two separately localized, or distinct, α,β pairs of electrons.

Table V. Interloge Correlations[a]

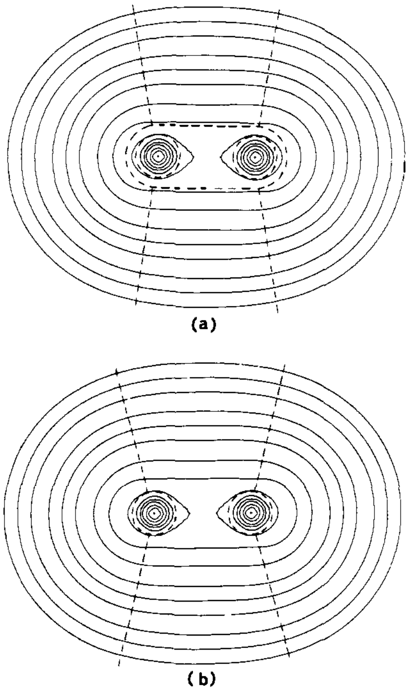
Molecule	$2F(c,b)$	$2F(c,n)$	$2F(b,b')$	$2F(b,n)$	$2F(n,n')$
LiH	−0.182				
BeH_2	−0.136		−0.153		
BH_3	−0.124		−0.304		
BH_4^-	−0.106		−0.279		
CH_4	−0.119		−0.374		
NH_3	−0.129	−0.164	−0.445	−0.544	
OH_2	−0.138	−0.171	−0.480	−0.558	−0.688
FH	−0.152	−0.179		−0.586	−0.629
Ne		−0.189			−0.632

[a] The loges are labeled (c) ≡ core loge, (b) ≡ bonded loge, (n) ≡ nonbonded loge.

In those cases where the extent of intra-loge correlations can be maximized, LiH through to BH_4^-, each loge boundary approaches the surface defined by those paths of steepest descent through the charge distribution which originate at the internuclear saddle point in the charge desity, the zero-flux surfaces of the virial (atomic) fragments.[21,22] Clearly, the extent of localization of the Fermi correlation is reflected in the spatial localization of the charge density. The zero-flux surfaces become less pronounced and the charge density contours increasingly less localized on the protons through the series LiH → HF. The contraction of and the increase in sphericity of the charge contours with Ne at the limit reflect the increasing dominance of the field of the heavy nucleus on the form of the charge distribution. Loges separated by boundaries which cut circular or near circular lines of constant density, such as the valence loges in Ne or the nonbonded loges in H_2O and HF, always exhibit a considerable degree of inter-loge correlation. Thus when the distribution of charge does not exhibit any evidence of localization, reference to localization of any number of electrons in real or pair space has no physical significance. For example, the contours of constant charge density for the water molecule in a plane perpendicular to the nuclear plane are nearly circular, particularly in the nonbonded region where the form of the charge distribution resembles that shown for neon. Any reference as to this region containing two separately localized α,β pairs of nonbonded electrons requires that these near circular contours of charge density be cut by a planar surface. This seems arbitrary, and in view of the large inter-loge correlations thus obtained, to be without physical basis in terms of the properties exhibited by the charge and number densities in this system.

The *localized* bond loges referred to in the above examples do not coincide with the binuclear form usually associated with a bonding molecular orbital. Instead they encompass only the proton[23] and the partitionings can be regarded as yielding atomic-like fragments rather than bond loges. This observation is not restricted to hydrogen fragments. Attempts to localize a pair of electrons in a loge defined along the lines of a σ-bonding molecular orbital fail completely in both N_2 and F_2. Figure 3a illustrates an attempted loge partitioning of N_2 into two core loges, two nonbonded loges, and a cylindrical σ-bond and two π-bond loges. The boundaries of the core loges (as reported in Table I) are such as to maximize their intra-loge correlation. No variations of the boundaries of the valence loges shown in Figure 3a are found which yield minima in the loge fluctuations. Instead, the boundaries of the σ-bond loge and the nonbonded loges were varied to obtain average populations of approximately two for each loge.

The nonbonded regions, with localizations of 59% (Table III), are the most localized of the valence loges in the parti-


(a)

(b)

Figure 3. Contour maps of the charge distribution of $N_2(X^1\Sigma_g^+)$ showing two attempted loge partitionings. In (a) there are two core loges, two conical nonbonded loges, a cylindrical σ-bond loge and the remaining torus of density is divided by a σ_v plane into two π-bond loges. All the loges have an average population of approximately two. In (b) the nonbonded loges border directly on the core loges and the central bond loge has an average population of six.

tioning of N_2. The σ-bond loge contains only 28% of the intra-loge correlation required to localize a single α,β pair of electrons (Table II). A similar σ-bond loge in F_2 contains only 17% of the same required Fermi correlation. The electrons of the π-bond loges in N_2 are also poorly localized and there is considerable inter-loge correlation between the three-bond loges. For example, the value of $F(\sigma,\pi)$ indicates that the σ electrons are 37% delocalized over the π loges. There is no physical basis for σ–π pair separability in N_2, and less so in F_2.

The strongly inter-correlated nature of the electrons in the three-bond loges of N_2 is further demonstrated by noting the large increase in the percentage localization obtained if they are grouped into a single loge. A partitioning of N_2 into two cores, two conical nonbonded loges, bordering directly on the cores, and a single intervening bond loge with an average population of six electrons (see Figure 3b) yields a localization of 72% for the bonded population and 60% for the nonbonded. Of course, in cases such as these, where no minimum in the fluctuation is obtained other than at the limit of $\bar{N}(\Omega)$ equaling zero or the total number of valence electrons, the larger the population of the loge, the larger the fraction of the intra-loge correlation it contains. Still this latter description as illustrated in Figure 3b is probably the most reasonable quantum analogue of the Lewis structure for N_2. Such a structure predicts three α,β pairs which, if totally localized in the bonded region, would yield precisely a pair population of 30, compared to the average number of 31.2 actually found.

It is interesting to compare these localizations, obtained for partitioning along traditional lines, with those obtained by a partitioning into atomic fragments. That is, we inquire as to the extent to which each atom retains its own identity in a molecule.

Of all the first-row homonuclear diatomic molecules, the charge distribution of N_2 appears to be the most delocalized.[24] That of F_2 is at the other extreme, being atomic-like in nature, with the charge density contours exhibiting a distinct pinched effect at the position of the σ_h symmetry plane. A partitioning of N_2 by the σ_h symmetry plane yields two nitrogen fragments each of which contains 78% of its original atomic Fermi correlation. Thus, in this example, which one expects to be typical of a highly delocalized system, the charge density of either atom is delocalized into the region of the other to the extent of 22% on bond formation. This percentage delocalization increases, of course, if one considers only the valence density. In N_2 the valence density of one (N) fragment is 67% localized, being delocalized to the extent of 28% over the second valence region and 1% over the external core.

In F_2, one finds that a surface coincident with the σ_h symmetry plane, the zero-flux surface, minimizes the fluctuation of each fluorine fragment and the degree of internal Fermi correlation is maximized. In the Hartree–Fock approximation, each (F) fragment retains 93% of its original Fermi correlation. The valence density of such a (F) fragment is also localizable as the fluctuation of the fragment with the core loge excluded is still minimized by the zero-flux surface. The valence density of a (F) fragment in F_2 is 86% localized, being delocalized to the extent of 9% over the other valence region and ~0.2% over the external core.

As is well known, the Hartree–Fock model for F_2 fails to predict binding relative to the atoms,[25] and this is probably the result of the intra-atomic Fermi correlation being over-emphasized in the absence of the Coulomb correlation. This over-emphasis is probably most pronounced for fluorine because of the very strong potential field exerted on its valence charge density. The Hartree–Fock charge distribution of a (F) fragment is always very localized in nature and, except in the case of F_2, possesses a population approaching ten electrons.[21] While the over-emphasis of the internal correlation is greater in F_2 than in N_2 at the Hartree–Fock level, the charge density of (F) is in reality doubtlessly more localized than is that of (N).

The strong potential field exerted on the valence electrons by the fluorine nucleus and core, while providing the major source of binding in fluorides via a charge transfer to the (F) fragment,[26] also causes the weak binding found in F_2. In the absence of a net transfer of charge between fragments as in A_2 systems, binding results from the accumulation of charge in the region between the nuclei via the formation of new α,β pairs. The formation of new pairs within each fragment is, of course, determined by the extent of delocalization. From the values of $F(\Omega,\Omega)$ for the atom (where it equals $-N/2$) and for the fragment in the molecule, one finds the average number of pairs in each (N) fragment to increase by 1.52 on bond formation, while in F_2, the corresponding increase for a (F) fragment is only 0.65. Therefore, the difficulty in disrupting the very pronounced intraatomic correlation in (F) and the resulting small degree of delocalization of the charge density provides an explanation for the weak binding found in F_2 as compared to N_2.

Conclusions

The theory and results given here determine and illustrate the effect of the Pauli exclusion principle on the distribution of electronic charge in real space. It has been demonstrated that the localization of charge in real space is determined by the localization of the Fermi correlation in pair space and that the extent of pairing and localization proceed hand in hand.

It should be pointed out that while the presence of potential wells determines where localization occurs, the localization referred to here is entirely the result of Fermi correlation. Thus there is no preferred spatial localization of the charge or pair densities in a system of particles whose motions are uncorrelated, i.e., in a system where the pair *probability* is equal to the product of the single particle *probabilities*.[16] It is, of course, still necessary to statistically correct the product of number densities if one is to obtain the correct pair density in eq 3. In this case, however, $f(r_1,r_2)$ has a constant value of $-1/N$ and the degree of localization and the average number of pairs for a region are determined by $\bar{N}(\Omega)$ itself; $|F(\Omega,\Omega)/\bar{N}(\Omega)| = \bar{N}(\Omega)/N$ and $D_2(\Omega,\Omega) = \bar{N}(\Omega)(\bar{N}(\Omega) - \bar{N}(\Omega)/N)$. In an uncorrelated system all spatial regions with the same average population possess the same degree of localization. The localization simply increases as the volume of (Ω) is increased so that $\bar{N}(\Omega)$ approaches N in value. Correspondingly, one finds that the fluctuation $\Lambda(\Omega)$ in such a system cannot be minimized for any value of $\bar{N}(\Omega)$ between zero and N. This behavior is to be contrasted with that found here for systems with Fermi correlation. For example, in Ar one can define a particular region, the core loge, whose fluctuation is minimized when $\bar{N}(\Omega) = 1.9$. The electrons in this region are found to be 73% localized. In an uncorrelated 18-electron system, the percentage localization of *any* region which on the average contained 1.9 particles would equal (1.9/18)100 = 11%.

If one restricts the use of the word "localized" to the description of spatial regions for which the extent of internal Fermi correlation is maximized, then in general, a molecular charge distribution is localized into core and valence distributions. The valence density is further localized into subsets only in those cases where the charge density itself exhibits a considerable degree of spatial localization. This observation leads one to the conclusion that when such localized groupings are found they will correspond to atomic-like fragments, for only such fragments are topographically defined by the valence charge distribution.

Whether or not one wishes to so restrict the meaning of the term "localized", the degree of localization and the extent of pairing in any spatial region may be quantitatively defined and the role they play in determining molecular properties critically examined. For example, is the most stable geometry of a system related to the extent of pairing imposed on it by the Pauli exclusion principle?

The relative magnitudes of the intra- and inter-loge Fermi correlations as determined here parallel the relative importance of the intrapair and interpair correlation energies as determined by the various "correlated pair" theories referred to in the introductory section. Thus Ebbing and Henderson[28] found that a wave function constructed from strongly orthogonal geminals was able to account for a large fraction of the total correlation energy in LiH, a system which we find to be over 90% localized into two distinct pairs. Sinanoğlu and Skutnik,[29] on the other hand, have argued that such an approach would be inadequate for CH_4 or Ne as they predicted that the correlations between neighboring tetrahedral orbitals in these systems should contribute about twice as much to the valence shell correlation energy as do the four intrabond pairs. Kutzelnigg[11] has recently reviewed the results obtained by the IEPA method for a number of small molecules and from his results one finds the ratio of the intrapair correlation energy to the total pair correlation energy for the bond pairs in BeH_2, BH_3, and CH_4 to be 86, 77, and 56%, respectively. Similarly, we find the Hartree–Fock wave functions for the same three systems to yield intra-loge correlations for the bond loges which account for 93, 82, and 69% of their total Fermi correlation, respectively. It will be recalled that CH_4 is borderline in that it is not possible to maximize the intra-loge Fermi correlation for a single bond loge in this system. It would appear from the comparison with the energetic results given above that if the Hartree–Fock wave function, which in general over-estimates the extent of pairing, fails to yield a localization of the Fermi pairs in excess of 70% for spatial regions with average populations of two, then the interpair correlation energies will equal or exceed the corresponding intrapair contributions.

Acknowledgment. We wish to thank Dr. M. Levy for helpful criticisms and comments.

References and Notes

(1) R. Daudel, *C. R. Hebd. Seances Acad. Sci.*, **237**, 601 (1953); "The Fundamentals of Theoretical Chemistry", Pergamon Press, Oxford, 1968.

(2) R. Daudel, H. Brion, and S. Odiot, *J. Chem. Phys.*, **23**, 2080 (1955).

(3) C. Aslangul, *C. R. Hebd. Seances Acad. Sci., Ser. B*, **272**, 1 (1971); C. Aslangul, R. Constanciel, R. Daudel and P. Kottis, *Adv. Quantum Chem.*, **6**, 93 (1972).

(4) R. Daudel, R. F. W. Bader, M. E. Stephens, and D. S. Borrett, *Can. J. Chem.*, **52**, 1310 (1974); **52**, 3077 (1974).

(5) O. Sinanoglu and K. A. Bruechner, "Three Approaches in Electron Correlation in Atoms", Yale University Press, New Haven, Conn., 1970.

(6) R. K. Nesbet, *Int. J. Quantum Chem.*, **4** 117 (1971).

(7) M. A. Robb and I. G. Csizmadia, *J. Chem. Phys.*, **54**, 3646 (1971).

(8) D. M. Silver, E. L. Mehler, and K. Ruedenberg, *J. Chem. Phys.*, **52**, 1174, 1181, 1206 (1970).

(9) M. Levy, W. J. Stevens, H. Shull, and S. Hagstrom, *J. Chem. Phys.*, **61**, 1844 (1974).

(10) M. Levy, *J. Chem. Phys.*, **61**, 1857 (1974). This reference provides an up to date documentation of the literature of pair correlation.

(11) W. Kutzelnigg, *Fortshr. Chem. Forsch.*, **41**, 31 (1973).

(12) E. Ludena and V. Amzel, *J. Chem. Phys.*, **52**, 5923 (1970).

(13) C. Aslangul, R. Constanciel, R. Daudel, L. Esnault, and E. V. Ludeña, *Int. J. Quantum Chem.*, **8**, 499 (1974).

(14) E. P. Wigner and F. Seitz, *Phys. Rev.*, **43**, 804 (1933); **46**, 509 (1934).

(15) R. McWeeny, *Rev. Mod. Phys.*, **32**, 335 (1960).

(16) R. F. W. Bader and M. E. Stephens, *Chem. Phys. Lett.*, **26**, 445 (1974).

(17) J. C. Slater, *Phys. Rev.*, **81**, 385 (1951); "Quantum Theory of Atomic Structure", Vol. 11, McGraw-Hill, New York, N.Y., 1960, pp 8–15.

(18) C. W. Maslen, *Proc. Phys. Soc., London, Sect. A*, **69**, 734 (1956).

(19) O. Sinanoglu, *J. Chem. Phys.*, **36**, 706 (1962).

(20) Both $I(P_n,\Omega)$ and $\Lambda(\Omega)$ are minimized when one event, $P_2(\Omega)$ in these examples, is dominant, and minimization of either function yields the same boundaries for the "best" loges.[4,16] The calculation of $I(P_n,\Omega)$, however, requires a knowledge of the diagonal elements of the full N-electron density matrix, and the calculation of this quantity for the ten-electron systems discussed here is beyond the available computational facilities (CDC 6400). Thus the conclusions regarding the localizability of electron pairs in the specific systems studied in ref 4 are in full agreement with the present results but the conclusion given there regarding the "reality of the electron pair in chemical systems" is not a general one. Rather as shown here, it is restricted to systems in which the charge density exhibits pronounced spatial localizations, as is found in the ionic hydrides, LiH, BeH_2, and BH_3, for example.

(21) R. F. W. Bader, *Acc. Chem. Res.*, **8**, 34 (1975).

(22) In LiH^+ the virial fragments (Li) and (H), as defined by the zero-flux surface $\nabla\rho(r)\cdot n = 0$ for all r in the surface, minimize the fluctuation, yielding percentage localizations of 98 and 95%, respectively. The virial fragments in LiH are only slightly less localized than the above core and bond loges, the (Li) fragment having a percentage localization of 95.3% compared to the 95.5% for the core loge.

(23) Contours of low density, 0.004 au and less, do encompass the Li core in LiH, but see footnote 22 regarding the virial partitioning of this system.

(24) R. F. W. Bader, W. H. Henneker, and P. E. Cade, *J. Chem. Phys.*, **46**, 3341 (1967).

(25) A. C. Wahl, *J. Chem. Phys.*, 41, 2600 (1964).

(26) For example, the decrease in the energy of a (F) fragment per electron transferred to the fragment in the formation of BF or BF_3 is ~430 kcal/mol.[27]

(27) G. Runtz and R. F. W. Bader, *Mol. Phys.*, **30**, 129 (1975).

(28) D. D. Ebbing and R. C. Henderson, *J. Chem. Phys.*, **42**, 2225 (1965).

(29) O. Sinanoglu and B. Skutnik, *Chem. Phys. Lett.*, **1**, 699 (1968).