The Lewis Model and Beyond

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The electron pair density, in conjunction with the definition of an atom in a molecule, enables one to determine the average number of electron pairs that are localized to each atom and the number that are formed between any given pair of atoms. Thus, it is through the pair density that the Lewis model of electronic structure finds physical expression. The pairing of electrons is a consequence of the Pauli principle whose effect is made manifest through the creation of the Fermi hole. The density describing the spatial distribution of the Fermi hole for an electron of given spin determines how the density of that electron is spread out in space, excluding an equivalent amount of same-spin density. The averaging of the Fermi density over single atoms or pairs of atoms determines the corresponding contributions to the total Fermi correlation. It is these terms that yield the localization and delocalization indices that determine the intra- and interatomic distribution of electron pairs that enables one to compare the pairing predicted by theory with that of a Lewis structure. The agreement is best at the Hartree−Fock level, where the Fermi hole is the sole source of correlation between the electrons. The introduction of the remaining correlation, the Coulomb correlation, disrupts the sharing of electron pairs between the atoms, and its effect is therefore, most pronounced for shared interactions. For example, Coulomb correlation reduces the number of shared pairs in N_2 from the Hartree−Fock value of three to just above two. In ionic systems, the electrons are strongly localized within each atomic basin and the effect of Coulomb correlation on the atomic pairing is minimal, approaching zero over each of the atomic basins, as it does for the total molecule.

The Physical Expression of the Lewis Model

The Lewis model describes the electronic structure of a molecule in terms of electron pairs: bonding, nonbonding, and core. Thus, its relation to physics must be through the pair density. The formation of localized α,β pairs is a consequence of the pair density being antisymmetric with respect to the exchange of the space and spin coordinates of every pair of electrons, as required by the Pauli exclusion principle. The "exclusion" is a result of the Fermi hole[1,2] that is created in the pair density by the antisymmetrization requirement. The Fermi hole, as discussed below, has a simple physical interpretation: it may be viewed as a description of how the density of an electron of given spin, the reference electron e*, is spread out in space, thereby excluding the presence of an identical amount of same-spin density.[3] As recently emphasized,[4] all physical measures of the localization or delocalization of an electron are determined by the corresponding localization or delocalization of its Fermi hole.[3] Since this behavior is obtained separately for an α and a β electron in a closed-shell system, the density of the Fermi hole determines the spatial pairing of the electrons. It is this property of the electron distribution that enables one to determine the number of electron pairs that are localized to a given atom and the number that are shared between pairs of atoms, the very information needed to assign a Lewis structure.

The determination of the atomic contributions to the total Fermi correlation requires, as does the quantum mechanical definition of any physical property, that the atoms be defined as bounded regions of real space, thereby precluding the use of any orbitally based definitions. This condition is met by atoms defined as proper open systems, a region of space bounded by a surface of zero flux in the gradient vector field of the electron density $\rho(\mathbf{r})$.[5−7]

Unsurprisingly, the Lewis model finds its most direct expression at the Hartree−Fock level of theory where the state function is described by a single determinant, an antisymmetrized sum of products of $N/2$ occupied orbitals for an N-electron closed-shell molecule. At this level of theory, the only correlation is between the motions of same-spin electrons resulting from the antisymmetry requirement, as described by the Fermi correlation. In this model, each electron moves in the self-consistently determined average field of the remaining electrons. The extension of the description of the state function from the one- to the many-determinant form through the use of a configuration interaction (CI) calculation goes beyond the average field approximation by describing the specific Coulombic interactions between both opposite and same-spin electrons, thereby introducing the so-called Coulomb correlation. This paper first relates the agreement found between the pairing of electrons predicted by the Lewis model and the nature of the pairs defined by the Fermi correlation at the Hartree−Fock level of theory and then describes how these predictions are affected by the introduction of Coulomb correlation. The latter study is of interest not only as it applies to the Lewis model, but for its resulting chemical interpretation of the effect that Coulomb correlation has on electronic structure.

Ponec and Strnad[8] have previously defined population indices based on the pair density to obtain a link between the quantum mechanical and classical pictures of chemical structures. This involves the definition and use of effective pair populations

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determined by an "effective pair density" that is proportional to the Hartree−Fock exchange density.[9] They[8] show that the use of the Mulliken approximation to define atomic indices from the charge-density−bond-order matrix, which is used in their expression for the pair density, causes their indices to reduce to those of Wiberg,[10] which are in turn closely related to the effective-pair populations obtained from spin-coupled state functions.[11]

The pair density is receiving increased attention in the areas of structure and bonding. In addition to the work of Cooper et al,[11] Nalewajski, Koster, and Jug[12] have analyzed the contributions to the two-particle density matrix in an orthogonal atomic orbital basis to obtain atomic and diatomic valence indices at the Hartree−Fock level.

Properties of the Fermi Hole and Definition of Electron Pair Indices

The density distribution of the Fermi hole is a function of the position of the coordinate $\mathbf{r}_1$ assigned to the so-called reference electron e*. However, e* is not localized to $\mathbf{r}_1$. Instead the Fermi hole describes how the density of e* is spread out from this point into the space of another same-spin electron described by the coordinate $\mathbf{r}_2$, excluding an equivalent amount of density at $\mathbf{r}_2$. The value of the Fermi hole is equal to the negative of the same-spin density when $\mathbf{r}_2 = \mathbf{r}_1$, thereby totally excluding all other same-spin electrons from the reference point.[1] If this total exclusion of same-spin density persists as $\mathbf{r}_2$ is displaced from $\mathbf{r}_1$, then the hole will describe a region of space from which all other same-spin electrons are excluded. In this situation, the Fermi hole is maximally localized and its density excludes the density of all other same-spin electrons from the vicinity of e*. In a closed-shell molecule, the same behavior will be obtained for an electron of opposite spin and the result will be a region of space occupied by the density of an α,β pair of electrons. If this total degree of exclusion is maintained for motion of the pair of reference electrons over the region of exclusion, the result is a spatially localized electron pair.[3] Thus, the requirement for the localization of an electron of either spin to a given region of space, and hence for the formation of a localized pair, is that the density of their Fermi holes be completely contained within the region, thereby excluding all other electrons of either spin.

While this degree of localization of the Fermi-hole density, hereafter referred to as the Fermi density, can be approached, it is usually found only for core electrons. For valence electrons, the hole is, in general, delocalized and the magnitude of its density is less than the same-spin density for positions other than the coordinate of e*. Thus, the exclusion is less than complete, the density from other same-spin electrons is found within the Fermi hole of e*, and it in turn is delocalized into the Fermi holes of the other same-spin electrons. Clearly, the extent of localization or delocalization of the density of an electron is determined by the corresponding localization or delocalization of its Fermi hole.[3]

The Fermi density integrates to −1, corresponding to the removal of the density of one electron.[1] The total Fermi correlation, which is defined as the integral of the Fermi density for each of the electrons over all space thus equals $-N$, the total number of α and β electrons. It is the total Fermi correlation that provides the link between physics and the Lewis model. Its value for a given atom A, denoted by $F(\mathrm{A,A})$, may be defined in terms of the expression for the average number of electron pairs in atom A that is obtained by the double integration of the pair density $\rho_2(\mathbf{r}_1,\mathbf{r}_2)$, eq 1,[3,5] where $N(\mathrm{A})$ is the population of atom A. This expression demonstrates that the net effect of

$$D_2(\mathrm{A,A}) = \int_{\mathrm{A}} \mathrm{d}\mathbf{r_1} \int_{\mathrm{A}} \mathrm{d}\mathbf{r_2} \rho(\mathbf{r_1},\mathbf{r_2}) = [N(\mathrm{A})^2 + F(\mathrm{A,A})]/2 \quad (1)$$

the Fermi correlation is to ensure that the pair density integrates to the correct number of pairs formed between a set of identical spin electrons by correcting for the self-pairing of the electrons. When A equals all space, $F(\mathrm{A,A}) = -N$, thereby reducing the number of pairs from $^1/_2N^2$, which includes self-pairing, by $N/2$, to $^1/_2N(N - 1)$. Similarly, if $F(\mathrm{A,A})$ attains its limiting value of $-N(\mathrm{A})$ for atom A in a molecule, the self-pairing correction would be complete within the atom and the $N(\mathrm{A})$ electrons would form a distinct set, separate from the remainder of the molecule—they would be totally localized to atom A. In general, $|F(\mathrm{A,A})| < N(\mathrm{A})$, indicating that the Fermi density for electrons referenced to A extends into other atomic basins and the electrons are not completely localized to A. The magnitude of $F(\mathrm{A,A})$ is termed *the atomic localization index and is denoted by the symbol* $\lambda(A)$.

The delocalization of the electrons referenced to A into another atom B is determined by $F(\mathrm{A,B})$, a quantity that measures the extent to which the Fermi density of e* in atom A is spread into the basin of atom B. It is defined in the expression for the average number of pairs formed between the electrons on atoms A and B that is obtained by integrating the coordinates of one electron of the pair density over atom A, the coordinates of the other over atom B, as in eq 2.[3] The same

$$D_2(\mathrm{A,B}) = \int_{\mathrm{A}} \mathrm{d}\mathbf{r_1} \int_{\mathrm{B}} \mathrm{d}\mathbf{r_2} \rho(\mathbf{r_1},\mathbf{r_2}) = [N(\mathrm{A})N(\mathrm{B}) + F(\mathrm{A,B})]/2 \quad (2)$$

expression holds for $D_2(\mathrm{B,A})$, and one necessarily has $F(\mathrm{A,B}) = F(\mathrm{B,A})$. The total number of pairs formed between A and B is given by the sum of the two pair populations. Integration of the coordinates of one electron of the pair density over A and of the second over A + B yields an expression for the sum $D_2(\mathrm{A,A}) + D_2(\mathrm{A,B})$, the number of pairs in atom A plus the number of pairs shared between A and B. Combining this result with the definitions of $D_2(\mathrm{A,A})$ and $D_2(\mathrm{A,B})$ yields an expression for the total Fermi correlation obtained from reference electrons situated within the atomic basin of A

$$F(\mathrm{A,A}) + \sum_{\mathrm{B}} F(\mathrm{A,B}) = -N(\mathrm{A}) \quad (3)$$

where, in the general case, the sum runs over all the atoms in the molecule other than A. This result shows that the Fermi density of $N(\mathrm{A})$ electrons referenced within the basin of atom A is spread out over the remaining atoms in the molecule, the amount delocalized onto any atom B being given by $F(\mathrm{A,B})$. As pointed out in the original paper on the role of Fermi correlation in electron localization, $F(\mathrm{A,B})$ is a measure of the extent to which the electrons in A are delocalized into atom B and *vice versa*.[3] The sum of the magnitudes of $F(\mathrm{A,B})$ and $F(\mathrm{B,A})$ is termed *the delocalization index* and is denoted by $\delta(\mathrm{A,B})$. It provides a quantitative measure of the sharing of electrons between A and B.

The atomic localization and delocalization indices have simple physical interpretations at the Hartree−Fock level: they are obtained from the double integration, over the atom or atoms in question, of the exchange density, the contribution to the pair density that describes the exchange of same-spin electrons between the spin orbitals $\phi_i(\mathbf{r})$. Denoting the overlap of a pair of spin orbitals over an atom A by $S_{ij}(\mathrm{A})$, the relevant expressions are[3]

$$F(\mathrm{A,A}) = -\sum_i \sum_j S_{ij}(\mathrm{A})^2 \tag{4}$$

for the atomic localization and for the delocalization

$$F(\mathrm{A,B}) = F(\mathrm{B,A}) = -\sum_i \sum_j S_{ij}(\mathrm{A}) S_{ij}(\mathrm{B}) \tag{5}$$

Calculations

The atomic values of the localization and delocalization indices are readily determined at the Hartree−Fock level using eqs 4 and 5. The program for the implementation of the theory of atoms in molecules[13] determines the atomic overlap matrix consisting of the terms $S_{ij}(\mathrm{A})$ required for the evaluation of the atomic and shared contributions to the Fermi correlation. The program GAMESS[14] includes in its output the second-order density matrix obtained in a CI calculation expressed in terms of products of basis functions used in the expansion of the molecular orbitals multiplied by the appropriate coefficients. This enables one to determine the contribution to the pair density in terms of the atomic overlap integrals from a CI state function. The CI expression for the pairs formed between atoms A and B is

$$D_2(\mathrm{A,B}) = \sum_{\mu\nu\lambda\sigma} C_{\mu\nu\lambda\sigma} S_{\mu\nu}(\mathrm{A}) S_{\lambda\sigma}(\mathrm{B}) \tag{6}$$

with a corresponding expression for $D_2(\mathrm{A,A})$. This expression is employed in the analysis of the singles and doubles CI (CISD) output from GAMESS. The values of $F(\mathrm{A,A})$ and $F(\mathrm{A,B})$ are determined from eqs 1 and 2 using the appropriate value for the average number of pairs. The accuracy of the calculated results are verified by ensuring that the atomic integrations of the pair and number densities sum to their appropriate values, as indicated in the Tables.

Hartree−Fock Expression of the Lewis Model

Now we are in the position to transcribe a Lewis electron-pair structure into a set of atomic localization and delocalization values. An electron of either spin totally localized within the basin of a single atom A, a core electron for example, will contribute −1 to $F(\mathrm{A,A})$ since its Fermi correlation is totally contained within the atom. For a localized pair of electrons, the contribution to the atomic localization index $\lambda(\mathrm{A})$ will be 2. An electron shared between two atomic basins A and B will make both localized and delocalized contributions. Consider H_2 as an example of an equally shared electron. (The Fermi correlation in this molecule simply corrects for the self-pairing of each electron.) The overlap of the single σ_g orbital over each atomic basin equals one-half, and thus the contribution to each atomic localization index from a single equally shared electron is $^1/_2 \times {}^1/_2 = {}^1/_4$. Similarly, the delocalization contribution is $^1/_4$. For a pair of electrons equally shared between two atoms, $\lambda(\mathrm{H})$ is $^1/_2$ for each atom and the total delocalization contribution $\delta(\mathrm{H,H'})$, which is given by $|F(\mathrm{H,H'}) + F(\mathrm{H',H})|$, is unity. *Thus, the delocalization index is unity for an equally shared pair of electrons.*

These rules are applied first to the Lewis structure (:N:::N:) for the N_2 molecule. The atomic contributions will consist of the following; 2 from the $1s^2$ core, 2 from the lone pair, and $^3/_2$ for the three shared pairs yielding $|F(\mathrm{N,N})| = \lambda(\mathrm{N}) = 5.5$. The bonded pairs are equally shared and will yield $|F(\mathrm{N,N'})| = |F(\mathrm{N',N})| = {}^3/_2$ and $\delta(\mathrm{N,N'}) = 3$, corresponding to the presence of three equally shared pairs of electrons. The sum of these contributions equals 14, the number of electrons. The Hartree−Fock results for N_2 are remarkably close to these values, equalling them to two-figure accuracy, Table 1. That $\delta(\mathrm{A,B}) > 3$ indicates that the nonbonded pairs are slightly delocalized.

Consider next the ionic system LiF where the net charges on the atoms are ±0.94e. Lewis stressed that in his model the two extremes of bonding "corresponding to the polar and very nonpolar compounds" differed not in kind but only in degree, corresponding to the unequal or equal sharing of the electron pair between the two atomic "kernels".[15] In the ionic limit, the bonding electron pair is localized on the anion, and in the Lewis model of LiF, two electrons are localized on Li and 10 on F, yielding $\lambda(\mathrm{Li}) = 2$, $\lambda(\mathrm{F}) = 10$, and $\delta(\mathrm{Li,F}) = 0$, values that agree closely with the respective Hartree−Fock values in Table 1.

In the interpretation of the delocalization index in the presence of charge transfer, it is necessary to distinguish between a Lewis-bonded pair and the particular case wherein a bonded pair is equally shared. The Lewis model for LiF predicts a single bonded pair but one that is very unequally shared, as reflected in the delocalization index of 0.18 and atomic localization values that approach the ionic limit. The value of $\delta(\mathrm{Li,F})$ does *not* imply a Lewis bond formed from 0.18 pairs of electrons. Only in a nonpolar interaction, as in H_2 or N_2 can one equate $\delta(\mathrm{A,B})$ to the actual number of Lewis-bonded pairs linking A to B. This is made clear by appealing to the individual molecular orbital contributions to the pair indices in LiF, Table 1b. The electrons in each of the π orbitals in a linear molecule form a distinct set, since they are prevented by symmetry from exchanging with each other or with the σ electrons and there are three distinct sets of indices in LiF, the two π contributions being equivalent. With $\lambda_\pi(\mathrm{Li}) = 0$ and a vanishingly small delocalization index, the indices indicate that the π electrons are essentially localized on F. The principal contribution to $\delta(\mathrm{Li,F})$ comes from the pair of electrons in the top σ orbital with the remainder of the pair localized on F, the 1s core on Li accounting for $\lambda(\mathrm{Li}) = 2.0$. Thus, the orbital contributions to the pair indices in LiF approximate a picture in which the bonding results from a single σ-bonded pair of electrons that is unequally shared between the two atomic basins.

It is instructive to view the formation of the same two molecules from the point of view of changes in the pair density. For each of the separated nitrogen atoms, $D_2(\mathrm{N,N}) = 7 \times 6/2 = 21$ while $2D_2(\mathrm{N,N'}) = 7 \times 7 = 49$, the number of pairs formed between two *distinct* sets of electrons. Comparison with the corresponding values in Table 1a shows that the formation of the molecule reduces the number of pairs of electrons formed between the two atoms while increasing the pair formation within each atomic basin. The reduction in $D_2(\mathrm{N,N'})$ is the result of the formation of *shared* pairs between the two atoms. The two sets of electrons are no longer distinct because of the delocalization of the density of each atom into the basin of the other, and there is a nonzero contribution from $F(\mathrm{N,N'}) < 0$ in eq 2. The reduction in the number of pairs formed between two atoms is 1/2 for each equally shared pair, equalling 1/2 for H_2 and 3/2 for N_2. A reduction in the number of pairs formed between two atoms is thus a necessary consequence of the interaction between them. For the separated Li and F atoms, one has $D_2(\mathrm{Li,Li}) = 3$, $D_2(\mathrm{F,F}) = 36$, and $2D_2(\mathrm{Li,F}) = 27$. In this case, the formation of the molecule causes a relatively large reduction in the number of pairs formed between the two atoms despite the small magnitude of $F(\mathrm{Li,F})$, a consequence of the transfer of nearly one electronic charge from Li to F. At the ionic limit,

TABLE 1: Localization and Delocalization Indices of Diatomic Molecules[a]

(a) Hartree−Fock results[b]

molecule	atom	N(A)	D_2(A,A)	λ(A)	$2D_2$(A,B)	δ(A,B)	$\sum_A N$(A)	$\sum_{A,B} D_2$(A,B)	$\sum_{A,B} F$(A,B)
H_2	H	1.000	0.250	0.500	0.500	1.000	2.000	1.000	−2.000
N_2	N	7.000	21.761	5.479	47.479	3.042	14.000	91.000	−14.000
F_2	F	9.000	36.321	8.358	80.358	1.283	18.000	153.000	−18.000
LiF	Li	2.060	1.136	1.971	20.387	0.178	12.000	66.001	−12.000
	F	9.940	44.447	9.851					
CO	C	4.647	8.865	3.860	42.677	1.574	14.000	91.006	−14.000
	O	9.354	39.463	8.567					
CN^-	C	5.227	11.598	4.121	44.748	2.210	14.000	90.995	−13.999
	N	8.773	34.649	7.668					
NO^+	N	5.525	13.102	4.323	45.622	2.405	14.000	91.000	−14.000
	O	8.475	32.276	7.273					

(b) σ and π orbital contributions to Hartree−Fock localization and delocalization indices

molecule	atoms (A, B)	symmetry	λ(A)	λ(B)	δ(A,B)
N_2	N, N′	σ	4.479	4.479	1.042
		π	0.500	0.500	1.000
LiF	Li, F	σ	1.970	5.903	0.126
		π	0.000	1.974	0.026
CO	C, O	σ	3.788	5.566	0.646
		π	0.036	1.500	0.464
CN^-	C, N	σ	3.883	5.383	0.734
		π	0.119	1.143	0.738
NO^+	N, O	σ	4.019	5.172	0.808
		π	0.152	1.050	0.798

(c) correlated results[c]

molecule	atom	N(A)	D_2(A,A)	λ(A)	$2D_2$(A,B)	δ(A,B)	$\sum_A N$(A)	$\sum_{A,B} D_2$(A,B)	$\sum_{A,B} F$(A,B)
H_2	H	1.000	0.212	0.575	0.573	0.849	2.000	1.000	−2.000
N_2	N	7.000	21.555	5.891	47.890	2.219	14.000	91.000	−14.001
F_2	F	9.000	36.251	8.498	80.497	1.005	18.000		
LiF	Li	2.067	1.151	1.973	20.440	0.193	12.000	65.999	−12.005
	F	9.932	44.409	9.838					
CO	C	4.794	9.454	4.072	43.410	1.443	14.000	90.997	−14.001
	O	9.206	38.133	8.484					
CN^-	C	5.434	12.519	4.490	45.601	1.888	14.000	90.995	−14.000
	N	8.566	32.874	7.621					
NO^+	N	5.803	14.421	4.837	46.605	1.934	14.000	91.008	−14.001
	O	8.197	29.982	7.231					
He_2[d]	He	2.000	1.001	1.998	3.998	0.004	4.000	6.000	−4.000
Ar_2[d]	Ar	18.000	153.003	17.993	323.994	0.013	36.000	630.000	−36.000

[a] The summations over N(A), D_2(A,B), and F(A,B), which should equal N, $N(N - 1)/2$, and $-N$, are given to demonstrate the numerical accuracy of the results. [b] HF 6-311++G(2d,2p)//6-311++G(2d,2p). [c] CISD 6-311++G(2d,2p)//6-311++G(2d,2p). [d] CISD 6-311G(2d,2p)//6-311G(2d,2p).

the pair populations have the values $D_2(\text{Li,Li}) = 1$, $D_2(\text{F,F}) = 45$, and $2D_2(\text{Li,F}) = 20$, values close to those in Table 1a. Unlike the case of equally shared pairs, there is no direct relationship between the reduction in the value of $2D_2$(A,B) and the number of Lewis-bonded pairs that are unequally shared in the presence of charge transfer. This is further illustrated for the polar molecules NO^+, CN^-, and CO, isoelectronic with N_2, with degrees of charge-transfer intermediate between the perfect sharing in N_2 and the ionic case of LiF.

Counting Lewis-Bonded Pairs in Polar Interactions

The delocalization index δ(A,B) is a measure of the number of electrons that are shared or exchanged between A and B independent of the nature of the interaction, but it determines the corresponding number of contributing bonded pairs only when the pairs are equally shared. The counting of Lewis-bonded pairs in the presence of charge transfer is not determined solely by the pair density but is instead a model-dependent concept, one that requires the introduction of the orbital contributions to the atomic indices, as done in Table 1b. These contributions indicate that the two π electron pairs and one σ pair contribute substantially to δ(A,B) in all three molecules, NO^+, CN^-, and CO, corresponding to the triply bonded Lewis model for N_2. Thus the value of 2.4 for δ(N,O) in NO^+, for example, does not imply the sharing of 2.4 bonded electron pairs. Instead, the sharing of each of the three pairs is unequal, with the degree of sharing decreasing with the increasing polar nature of the interaction, NO^+ to CN^- to CO. In CO, the three bonded pairs make only negligible contributions to the electrons localized on C, the value of ∼4.0 for λ(C) being accounted for by the 1s core and the nonbonded pair.

The formal atomic charges associated with a Lewis structure, such as C^-O^+, are assigned on the basis that each bonded pair of electrons is equally shared between the two atoms, a step that in general is not consistent with the statement of Lewis that a bonded pair can exhibit any degree of sharing between the two possible extremes. Instead the charges that are consistent with the indices in Tables 1a and b are those determined by the distribution of charge present in the molecule. The atomic populations in Table 1a indicate that the direction and degree of charge transfer from A to B parallels the disparity in the λ(A) and λ(B) values for the bonding pairs of electrons. Note

TABLE 2: Delocalization Indices for N_2, CO, and LiF Using Different Basis Sets

basis set	molecule	δ(A,B) (HF)	δ(A,B) (CISD)
6-31G	N_2	3.042	2.097
	LiF	0.208	0.247
	CO	1.780	1.539
6-31G*	N_2	3.037	2.179
	LiF	0.180	0.184
	CO	1.508	1.394
6-311G(2d)	N_2	3.040	2.215
	LiF	0.183	0.195
	CO	1.572	1.441
6-311+G(2d)	N_2	3.042	2.219
	LiF	0.178	0.193
	CO	1.574	1.443

that the vanishingly small dipole of CO with C negative is not at variance with the substantial positive charge of 1.4e on C but only with the spherical atom model of the charge density.[5]

Basis-Set Dependence of Pair Indices

All of the above results are calculated using the relatively large basis set 6-311+G(2d).[16] Table 2 reports the delocalization indices for N_2, CO, and LiF calculated for basis sets of increasing size, for both the Hartree–Fock and correlated results. The effect of increasing the size of the basis set is relatively small in all three cases at the Hartree–Fock level, being largest for CO. The inclusion of one polarization function appears to ensure that the change is restricted to the second place after the decimal or less. The CI results are more sensitive to basis-set size and composition. Even here, however, the variation appears in the second decimal place for sets that include at least a single polarization function. No serious errors are incurred if one employs the 6-31G* basis in a qualitative discussion of electron pairing. All of the results for the diatomic molecules, the second-row hydrides (AH_n), and benzene are obtained using the 6-311++G(2d,2p) basis set with the 6-31G** set being used for the other polyatomic molecules.

Delocalization Index and Bond Order

The delocalization index is not identified with a bond order because, as demonstrated above, while determining the *number* of electrons that are shared between two atoms, it does not, with the exception of equally shared pairs, determine the number of contributing Lewis electron *pairs*. It is the number of Lewis-bonded pairs that determines the bond order, and this information is obtained only by using the orbital model in the single determinant level in conjunction with the pair density to identify the orbitals that contribute to the delocalization index. In addition, atoms are bonded to one another only if linked by a bond path, as defined in terms of the equilibrium electron density distribution.[5,17] The same-spin pair density, however, is delocalized between every pair of atoms in a molecule, and a delocalization index exists for each pair. Defining an order for bonds assumed to exist between every pair of atoms in a molecule is neither useful nor physically meaningful. The information provided by the delocalization index is independent of any association with bonding between the atoms involved.

It has been previously proposed that the definition of electron delocalization determined by the properties of the Fermi density be used to provide a common quantitative basis for the concept of delocalization throughout chemistry.[18] Thus, the atomic patterns of delocalization recover the classical resonance structures of valence-bond theory and the effect of heteroatoms and substituents on the delocalization of the π electrons of benzene is quantified. The delocalization of Fermi density between non-neighboring atoms does not necessarily exhibit a simple falloff with distance but can instead reflect particular correlative effects. The delocalization of same-spin density is the mechanism by which distant atoms "talk" to one another, by transmitting, for example, the perturbation caused by the presence of a nuclear magnetic moment. Thus, the delocalization of the Fermi density between vicinal hydrogens was shown to correlate with their nuclear spin–spin coupling as a function of torsion angle.[18]

Ponec and Uhlik have also proposed, but not implemented, the use of the terms F(A,A) and F(A,B) in the description of the pairing in a Lewis structure.[19] They base their proposal on expressions obtained by Bader and Stephens[3] that relate the fluctuations in electron populations of single or pairs of regions to F(A,A) and F(A,B), respectively, but do so without identifying these quantities with the Fermi correlation. Indeed, both F(A,A) and F(A,B) are left unexplained as is the physics underlying the localization of an electron. The physical condition required to minimize the fluctuation in an electron population is that its contained Fermi correlation be maximized, the fluctuation vanishing when $|F(A,A)|$ attains its maximum value N(A) corresponding to complete localization of the electrons to A.[3] This illustrates the intimate dependence of the fluctuation on the Fermi correlation, but this effect cannot be said to be the cause of the localization. Ponec and Uhlik incorrectly state that Bader and Stephens discounted the Lewis model when in fact the model was not considered in their paper. What they did demonstrate[3] is that the distribution of the valence electron density does not, in general, exhibit bounded regions of space which maximize the contained Fermi correlation, thereby giving rise to spatially localized pairs of electrons, as envisioned in Daudel's loge theory[20] or in models derived from localized molecular orbitals. These conclusions remain valid, as they are determined by the pair density.

The notion of a spatially localized electron pair that is in some manner interspaced between two "atoms" is to be sharply distinguished from the concept of the delocalization index which provides a measure of the extent of delocalization of the electrons from one atomic basin into another. The adoption of the theory of atoms in molecules requires the replacement of the model of structure that imparts an existence to a *bond* separate from the atoms it links—the ball-and-stick model or its orbital equivalents—with the concept of *bonding* between atoms; two atoms are bonded if they share an interatomic surface and are consequently linked by a bond path.[17] In a sense, the interatomic surface replaces the bond in the theory of atoms in molecules, since it is through the exchange of electrons and the fluxes in properties across this surface, described by the physics of a proper open system, that atoms adjust to the presence of their bonded neighbors.[6,17]

Ponec and Uhlik[19] use the Mulliken approach to partition the pair density into "atomic" contributions rather than using the atomic overlap contributions, as in eqs 4 and 5. Thus, their expressions degenerate into those they previously obtained using the "effective pair density"[8] wherein the two-center contributions are identified with bond orders for both homopolar and heteropolar interactions. To this end, they propose that one ignore the nonvanishing delocalizations found between atoms that are not formally bonded to one another when these contributions are found to be "small". When the correct expressions, eqs 4 and 5, are used, these contributions are generally not "small" and one cannot ignore them without incurring significant error in the electron count. For example,

TABLE 3: Localization and Delocalization Indices for Second- and Third-Row Hydrides

molecule	atom	N(A)	D_2(A,A)	λ(A)	Pair	$2D_2$(A,B)	δ(A,B)	$\sum_A N$(A)	$\sum_{A,B} D_2$(A,B)	$\sum_{A,B} F$(A,B)
				(a) Hartree−Fock Results[a]						
LiH	Li	2.088	1.186	1.990	Li, H	3.893	0.197	4.000	5.999	−3.999
	H	1.911	0.920	1.812						
BeH_2	Be	2.275	1.587	2.003	Be, H	4.101	0.272	6.000	14.999	−6.000
	H	1.862	0.893	1.681	H, H′	3.422	0.090			
BH_3	B	2.886	3.099	2.131	B, H	4.666	0.503	7.998	27.988	−7.996
	H	1.704	0.799	1.306	H, H′	2.831	0.145			
CH_4	C	5.825	15.033	3.861	C, H	5.589	0.982	10.000	45.000	−10.000
	H	1.048	0.301	0.486	H, H′	1.067	0.044			
NH_3	N	8.048	29.029	6.706	N, H	4.790	0.894	10.000	45.000	−10.000
	H	0.414	0.019	0.185	H, H′	0.414	0.018			
H_2O	O	9.254	38.504	8.638	O, H	3.141	0.616	10.000	45.000	−10.000
	H	0.372	0.039	0.061	H, H′	0.136	0.007			
HF	F	9.779	43.027	9.580	F, H	1.960	0.398	10.000	45.000	−10.000
	H	0.221	0.013	0.022						
NaH	Na	10.187	46.886	9.997	Na, H	18.275	0.380	11.999	65.993	−11.999
	H	1.813	0.832	1.622						
MgH_2	Mg	10.386	48.935	10.008	Mg, H	18.576	0.378	13.999	90.999	−14.000
	H	1.807	0.832	1.600	H, H′	3.246	0.036			
AlH_3	Al	10.639	51.569	10.047	Al, H	18.814	0.393	16.000	119.996	−15.998
	H	1.787	0.845	1.503	H, H′	3.150	0.087			
SiH_4	Si	11.088	56.405	10.142	Si, H	18.922	0.472	18.000	152.995	−17.996
	H	1.728	0.828	1.329	H, H′	2.931	0.108			
PH_3	P	13.288	82.278	12.028	P, H	20.446	0.839	17.999	152.987	−17.997
	H	1.570	0.720	1.026	H, H′	2.403	0.124			
H_2S	S	15.697	115.925	14.555	S, H	17.502	1.142	18.000	153.000	−17.999
	H	1.151	0.387	0.552	H, H′	1.297	0.057			
HCl	Cl	17.224	139.989	16.702	Cl, H	12.836	1.045	18.000	153.000	−18.000
	H	0.776	0.174	0.253						
				(b) Correlated Results[b]						
LiH	Li	2.097	1.202	1.993	Li, H	3.885	0.208	3.999	5.997	−3.999
	H	1.902	0.910	1.798						
BeH_2	Be	2.299	1.633	2.021	Be, H	4.115	0.279	6.000	15.000	−6.002
	H	1.850	0.880	1.664	H, H′	3.377	0.093			
BH_3	B	3.027	3.455	2.256	B, H	4.760	0.515	7.999	27.991	−8.005
	H	1.657	0.737	1.272	H, H′	2.682	0.128			
CH_4	C	5.955	15.578	4.310	C, H	5.610	0.823	10.000	45.000	−10.000
	H	1.011	0.252	0.519	H, H′	0.995	0.054			
NH_3	N	7.995	28.549	6.819	N, H	4.952	0.784	10.000	44.999	−10.001
	H	0.668	0.102	0.243	H, H′	0.430	0.034			
H_2O	O	9.156	37.648	8.543	O, H	3.556	0.613	10.000	45.000	−10.000
	H	0.422	0.036	0.106	H, H′	0.168	0.019			
HF	F	9.738	42.658	9.521	F, H	2.330	0.435	10.000	45.000	−10.001
	H	0.262	0.0102	0.044						
NaH	Na	10.214	47.158	10.014	Na, H	18.038	0.402	12.000	65.998	−12.002
	H	1.786	0.801	1.586						
MgH_2	Mg	10.421	49.281	10.039	Mg, H	18.457	0.382	14.000	91.000	−14.000
	H	1.789	0.811	1.579	H, H′	3.183	0.038			
AlH_3	Al	10.698	52.176	10.106	Al, H	18.708	0.395	16.000	120.000	−16.000
	H	1.767	0.819	1.485	H, H′	3.081	0.084			
SiH_4	Si	11.209	57.686	10.266	Si, H	18.793	0.471	18.000	152.992	−17.999
	H	1.698	0.784	1.313	H, H′	2.833	0.099			
PH_3	P	13.483	84.737	12.324	P, H	19.911	0.774	18.000	152.993	−17.999
	H	1.505	0.628	1.009	H, H′	2.212	0.109			
H_2S	S	15.782	117.132	14.802	S, H	17.013	0.980	18.000	153.000	−18.000
	H	1.109	0.321	0.589	H, H′	1.199	0.061			
HCl	Cl	17.203	139.608	16.739	Cl, H	13.235	0.938	18.000	152.996	−18.007
	H	0.797	0.152	0.330						

[a] HF 6-311++G(2d,2p)//6-311++G(2d,2p). [b] CISD 6-311++G(2d,2p)//6-311++G(2d,2p).

the delocalization between the nonbonded atoms in ethane contributes 10% to the total while in SO_2 and SO_3 δ(O,O) $\approx$ 0.3, Tables 3 and 4. More importantly, ignoring the nonbonded contributions to the delocalization ignores important chemical consequences of the Fermi delocalization, as previously demonstrated[18]and *vide infra*.

Angyan, Loos, and Mayer[21] and Fulton[22] define bond orders in terms of products of overlap integrals defined over atomic basins which, at the Hartree−Fock level of theory, are equivalent to one another and to the delocalization index δ(A,B) defined here. Angyan et al. base their definition on the atomic partitioning of the exchange portion of the second-order Hartree−Fock density matrix, an expression whose form they choose to preserve and use even at correlated levels of theory to obtain what they call the “formal exchange component”. Fulton describes a sharing index using products of terms in the first-order density matrix to describe the probability that one electron be found at two different points in space. The expression he develops from this idea, when applied to atomic basins, is identical to the product of spin−orbital overlap integrals appearing in the Hartree−Fock exchange term but with the products multiplied by the square roots of the orbital occupation

TABLE 4: Localization and Delocalization Indices for Polyatomic Molecules

molecule	atom	N(A)	D_2(A,A)	λ(A)	pair	$2D_2$(A,B)	δ(A,B)	$\sum_A N$(A)	$\sum_{A,B} D_2$(A,B)	$\sum_{A,B} F$(A,B)
(a) Hartree−Fock Results[a]										
CO_2	C	3.243	4.165	2.187	C, O	29.887	1.056	22.000	231.000	−22.000
	O	9.378	39.648	8.660	O, O	87.765	0.380			
SO_2	S	13.212	81.302	11.947	S, O	123.479	1.265	32.000	495.994	−31.999
	O	9.394	39.831	8.585	O, O	88.072	0.352			
SO_3	S	11.745	63.821	10.299	S, O	110.127	0.963	39.998	779.913	−39.995
	O	9.418	40.016	8.660	O, O	88.555	0.275			
C_2H_4[b]	C	5.920	15.557	3.927	C, C	34.097	1.889	16.000	120.008	−16.001
	H	1.040	0.298	0.486	C, H	6.125	0.066			
					C, H′	5.667	0.981			
					H, H	1.062	0.040			
					H, H′ (c)	1.076	0.013			
					H, H′ (t)	1.078	0.008			
C_2H_6[b]	C	5.763	14.729.	3.755	C, C	32.719	0.988	18.000	153.006	−18.000
	H	1.079	0.323	0.518	C, H	5.736	0.966			
					C, H′	6.197	0.044			
					H, H	1.141	0.046			
					H, H′ (g)	1.158	0.012			
					H, H′ (a)	1.162	0.004			
B_2H_6[c]	B	2.881	3.099	2.103	B, B′	8.276	0.047	15.995	119.927	−15.990
	H	1.699	0.815	1.257	B, H	4.658	0.473			
	H′	1.719	0.925	1.103	B, H′	4.820	0.264			
					B, H″	4.886	0.017			
					H, H	2.819	0.134			
					H′, H′	2.836	0.237			
					H, H′	2.862	0.116			
					H, H″ (c)	2.881	0.011			
					H, H″ (t)	2.879	0.015			
C_6H_6[d]	C	5.977	15.904	3.916	C, C (o)	35.030	1.389	42.001	861.024	−42.001
	H	1.023	0.289	0.468	C, C (m)	35.687	0.074			
					C, C (p)	35.675	0.100			
					C, H	5.627	0.975			
					C, H (o)	6.090	0.049			
					C, H (m)	6.110	0.008			
					C, H (p)	6.112	0.006			
					H, H (o)	1.044	0.006			
					H, H (m)	1.046	0.001			
					H, H (p)	1.046	0.000			
(b) Correlated Results[e]										
CO_2	C	3.518	4.967	2.443	C, O	31.974	1.075	22.000	231.000	−22.002
	O	9.241	38.423	8.547	O, O	85.237	0.313			
SO_2	S	13.448	84.294	12.251	S, O	124.144	1.196	32.000	495.999	−32.000
	O	9.276	38.757	8.533	O, O	85.902	0.290			
SO_3	S	12.052	67.322	10.610	S, O	111.795	0.961	40.000	779.990	−40.000
	O	9.316	39.095	8.595	O, O	86.665	0.240			
C_2H_4[b]	C	5.969	15.637	4.356	C, C	34.920	1.422	16.001	120.006	−16.008
	H	1.016	0.256	0.519	C, H	6.032	0.061			
					C, H′	5.641	0.843			
					H, H	1.005	0.053			
					H, H′ (c)	1.021	0.021			
					H, H′ (t)	1.022	0.018			
C_2H_6[b]	C	5.847	15.154	3.892	C, C	33.717	0.825	18.000	152.998	−18.000
	H	1.051	0.306	0.492	C, H	5.689	0.913			
					C, H′	6.108	0.075			
					H, H	1.083	0.043			
					H, H′ (g)	1.101	0.008			
					H, H′ (a)	1.093	0.022			
B_2H_6[c]	B	2.993	3.375	2.207	B, B′	8.940	0.033	15.996	119.948	−15.993
	H	1.660	0.761	1.235	B, H	4.730	0.477			
	H′	1.685	0.870	1.100	B, H′	4.901	0.282			
					B, H″	4.964	0.009			
					H, H	2.696	0.120			
					H′, H′	2.742	0.194			
					H, H′	2.746	0.103			
					H, H″ (c)	2.746	0.021			
					H, H″ (t)	2.748	0.017			

[a] HF 6-31G*//6-31G*. [b] (C, H) and (C, H′) refer to the pairs formed by a carbon and its bonded hydrogen and a carbon and the hydrogen bonded to the other carbon, respectively. (H, H) refers to a pair formed by two hydrogens bonded to the same carbon and (H, H′) to pairs formed by hydrogens bonded to different carbons. For C_2H_4, c and t refer to the pair of hydrogens being in cis or trans position, and for C_2H_6, g and a refer to the pair of hydrogens being in gauche or anti position. [c] (B, H), (B, H′), and (B, H″) refer to the pairs formed by a boron atom with one of its terminal hydrogens, with one of the bridge hydrogens, and with a terminal hydrogen bonded to the other boron atom, respectively; (H, H), and (H′, H′) refer to the pairs formed by two terminal hydrogens bonded to the same boron and by the two bridging hydrogens, respectively; (H, H′) and (H, H″) refer to the pairs formed by a terminal hydrogen and a bridging hydrogen and by two terminal hydrogens bonded to different boron atoms, respectively. c and t stand for cis and trans pairs. [d] HF 6-311++G(2d,2p)//6-311++G(2d,2p). o, m, and p refer to pairs of atoms in ortho, meta, or para positions, respectively. (C, H) refers to a C and its neighboring H. [e] CISD 6-31G*//6-31G*.

numbers. This latter step is taken to ensure that the sum of the bond indices, both "self-sharing" and between basins, equals N at all levels of theory, a property not shared by the definition of Angyan et al. At the Hartree−Fock level, for which all occupation numbers are unity, the two expressions for bond order and the one for the delocalization index are identical, while for a correlated function, all three are different. Cioslowski and Mixon also define a bond order[23] using products of overlap integrals defined over atomic basins, but their procedure uses a particular transformed set of "population-localized" orbitals which, as emphasized by Angyan et al. and by Fulton, results in a definition that is not invariant to a unitary transformation of the orbitals.

The definition of the delocalization index proposed here is nonarbitrary, being determined by the second-order density matrix at all levels of theory. While the definitions of a bond order given by Angyan et al. and by Fulton have proved useful, they are not defined in terms of the pair density but fortuitously reduce to the correct expression at the Hartree−Fock level. Hence, they will not, in general, reflect the spatial properties of the Fermi correlation, the physical feature of the pair density that is solely responsible for defining the extent of localization and the spatial pairing of electrons.

Effect of Coulomb Correlation on the Localization and Delocalization Indices

The definitions of the atomic localization and delocalization indices in eqs 1 and 2 remain unaltered with the inclusion of Coulomb correlation. In this case, however, the atomic and interatomic correlation terms $F(\mathrm{A,A})$ and $F(\mathrm{A,B})$ include Coulomb as well as Fermi correlation. The limiting value of the correlation, when summed over all the atoms in the molecule, still equals $-N$, the correction for the self-pairing of the electrons. Thus, the integral of the Coulomb correlation over all space vanishes, the increased probability of pairing in some regions being balanced by decreases in other regions.[3] The Coulomb correlation vanishes for the same reason over an atom when the Fermi correlation attains its limiting value of $-N(\mathrm{A})$. Thus, in closed-shell or ionic systems, where the density is strongly localized within the basin of each atom and $\lambda(\mathrm{A}) \approx N(\mathrm{A})$, the net effect of Coulomb correlation on the pairing of electrons within each atomic basin will be minimal. This is borne out by the CI results for LiF where the atomic localizations change by 0.01 or less and the delocalization contribution remains small.

The effect of Coulomb correlation on the atomic contributions to the pair density is most pronounced for shared interactions, as it disrupts the pairing of electrons between the atoms. It is well-documented that the Hartree−Fock density overestimates the amount of density accumulated in the internuclear region,[24] a result reflected in the decrease in ρ_b, the value of the density at the bond critical point, with correlation as illustrated for the CISD level in the Appendix. The effect is most pronounced for homopolar bonding, as found in N_2, F_2, and H_2, for example, where the delocalization index decreases from 3.0 to 2.2 for N_2, from 1.3 to 1.0 for F_2, and from 1.0 to 0.85 in H_2. In polar molecules, the effect of Coulomb correlation on the extent of interatomic pairing and on ρ_b is reduced, as exemplified by the results for CO, where the delocalization index changes from 1.6 to 1.4 and the decrease of 0.025 au in ρ_b is one-half that for isoelectronic N_2. These examples, together with the other molecules listed in the tables, enable one to make the following generalizations regarding the effect of Coulomb correlation on the atomic contributions to the electronic structure of a molecule:

(a) In shared, homopolar bonding, H_2, N_2, and F_2, Coulomb correlation causes electron density to be removed from the vicinity of the interatomic surface and concentrated in each atomic basin. The pair density reflects these changes in the number density, with a decrease in the number of electron pairs formed between the two atoms and an increase in the pairing within each atomic basin. Thus, Coulomb correlation causes the attraction of the H, N, or F nucleus for the density within its own basin to increase with correlation, but because of the accompanying increase in bond length, its attractive interaction with the density of the neighboring basin is lessened. Thus overall, the attractive potential energy becomes less negative and the decrease in energy caused by Coulomb correlation in the homopolar systems arises from a decrease in the repulsive contributions to the potential energy.

(b) In shared polar interactions, the transfer of density from the region of the bond critical point to the nuclear regions is decreased from that found in an isoelectronic homopolar molecule. The effect of Coulomb correlation is always to reduce the extent of charge transfer in both polar and ionic molecules, and the population of the least electronegative atom increases compared to its Hartree−Fock value. The decrease in the delocalization index is smaller than that for the homopolar molecules, and as a consequence of the reduction in charge transfer, the resulting increase in the atomic localization index is greatest for the least electronegative atom. In CO, Coulomb correlation causes the potential energy of interaction of the carbon nucleus with its own density and with the density in the oxygen basin to decrease, but this is offset by a larger increase in the corresponding energies for the oxygen nucleus.

(c) In closed-shell ionic molecules, the reduction in charge transfer is less than in the polar molecules. In systems that approach the interaction of two closed-shell ions, the delocalization index exhibits a small increase, one that comes primarily as a result of a decrease in the atomic localization on the anion. One should bear in mind that the effect of Coulomb correlation on electron pairing appears minimal in an ionic molecule because it effectively vanishes separately over each atomic basin, a result of the high degree of atomic localization in the ionic molecules.

Electron Pairing and the Lewis Model

The effects of Coulomb correlation are well-illustrated by the second-row hydrides AH_n which span the range of possible bonding types, Table 3. The bonding in LiH approaches the closed-shell ionic limit, followed by a decreasing extent of charge transfer from A to H in BeH_2 and BH_3 and essentially vanishing in the shared interaction in CH_4. The polar interactions in NH_3, H_2O, and HF exhibit an increasing degree of charge transfer from H to A. The transfer of charge decreases with Coulomb correlation, the population of H decreasing from LiH to CH_4 and that of A decreasing in the remainder. The delocalization index increases slightly for the ionic members, undergoes a declining decrease for CH_4, NH_3, and H_2O, and finally undergoes a small increase in the very polar HF. The atomic localization increases for the atom whose population is increased, the index for the donor decreasing by a smaller amount.

Because of the pronounced charge transfer in the molecules other than methane, only this molecule exhibits a delocalization index approaching unity at the Hartree−Fock level, one that decreases to 0.82 with correlation. For the remaining molecules, there is significant transfer of charge between the atoms and $\delta(\mathrm{A,H})$ does not determine the number of Lewis bonded pairs but rather provides a measure of the degree of sharing of the bonded pairs. In the Hartree−Fock description of the hydrides however, Table 3a, it is reasonable to associate the equivalent Lewis-bonded pairs with a corresponding number of canonical molecular orbitals which can be combined into a set of equivalent orbitals.[25] LiH is similar to LiF with indices characteristic of a single bonded pair close to the ionic limit. This is true to a lesser extent for BeH_2, but for BH_3, $\delta(B,H)$ indicates a significantly greater degree of sharing of the bonded pair. There is a steady decline in $\delta(A,H)$ for the molecules following methane, with a corresponding increase in the extent of localization of the density on A. The delocalization of density between nonbonded hydrogens is most pronounced for the ionic molecules where hydrogen possesses a negative charge, $\delta(H,H')$ equalling one-quarter of $\delta(B,H)$ in BH_3.

There is significant charge transfer from A to H in the third-row hydrides from A = Na to Si, with $q(H) \approx -0.8$. Charge is transferred to A only in HCl. The CI values for $\delta(A,H) \approx 0.4$ for A = Na, Mg, and Al do not differ qualitatively from the Hartree−Fock results and indicate a greater degree of sharing of the bonded pairs of electrons for Na and Mg than found in the second-row congeners. Because of the considerable polarity of the Si−H interaction, $\delta(Si,H)$ is approximately equal to 0.5 compared to $\delta(C-H) \approx 0.8$ in methane. At the Hartree−Fock level, the bonded pairs approach equal sharing between A and H for PH_3, H_2S, and HCl, values that decrease somewhat with correlation. Of course, with the inclusion of electron correlation, many orbitals contribute to the description of every bonded pair of electrons but its effect on the pair indices is least for the polar interactions. Thus, the Hartree−Fock description of the Lewis model is still recognizable in the correlated pair indices obtained for the polar hydrides.

The $\delta(C,O)$ and $\delta(S,O)$ values found for CO_2, SO_2, and SO_3, Table 4a, are all close to unity. Nonetheless, the orbital contributions for CO_2 are consistent with the presence of four bonded Lewis pairs, in agreement with the Lewis model, although it is not possible to separate the contributions from the four valence orbitals of σ symmetry. The primary contributions to the delocalization index $\delta(C,O)$ are from the bonding π_u, σ_g, and σ_u orbitals, with 0.26 from each π_u component and the σ orbitals accounting for the remaining 0.51. The nonbonding π_g and σ valence orbitals describe the pairs that are primarily localized on the oxygens and contribute to $\lambda(O)$ and $\delta(O,O)$. The delocalization of the density between the nonbonded oxygen atoms makes a significant contribution to the shared density in these molecules, $\delta(O,O')$ being of the order of 0.3 and arising primarily from the π_g orbital in CO_2. It becomes increasingly difficult to assign orbital contributions to the delocalization index as the number of orbitals of a given symmetry increases. In SO_2, one can distinguish between orbitals that are symmetric "s" and antisymmetric "a" with respect to the plane of the nuclei and between the core and valence contributions to the indices. The "s" and "a" core contributions to $\lambda(S)$ are 8 and 2, as anticipated, and 2 for each oxygen. The two "a" orbitals contribute 0.46 to $\delta(S,O)$, the remaining 0.79 from the "s" orbitals. The polarity of the "a" orbitals is reflected in their differing contributions to $\lambda(S) = 0.16$ and to $\lambda(O) = 1.4$, the corresponding contributions from the "s" orbitals being 1.8 and 5.2. Both the "a" and "s" sets contribute to $\delta(O,O)$. The results are consistent with four orbitals contributing to $\delta(S,O)$, two "a" and two "s" giving the Lewis structure for SO_2 with two bonds to each oxygen, but the counting of the contributing σ pairs is imprecise. The information provided by the delocalization index is, of course, independent of any model, and it indicates that the extent of sharing of the electrons between C or S with oxygen decreases in the order SO_2, SO_3, and CO_2.

The Hartree−Fock description of the electron pairing in the hydrocarbons C_2H_6, C_2H_4, and C_6H_6 is, like that of methane, close to that anticipated for the corresponding Lewis structures, with $\delta(C,C0)$ equalling approximately 1 for ethane, 1.4 for benzene, and 2 for ethene, with $\delta(C,H)$ being close to unity for all three molecules, the value increasing slightly with the slight decrease in charge transfer from C to H in the order ethane, benzene, and ethene, Table 4. The delocalization values are significantly decreased with the introduction of Coulomb correlation, the value of $\delta(C,C')$ decreasing from 1.9 to 1.4 in ethene. There are significant contributions to the sharing from nonbonded atoms, equalling approximately 10% in ethane. The nonbonded delocalization indices are of particular interest in benzene,[18] where the delocalization of the density is greater between *para*-related carbons, $\delta(C,C') = 0.10$, than between *meta*-related atoms, $\delta(C,C') = 0.07$.

The delocalization index between nonbonded atoms is of particular interest in B_2H_6 with respect to the possible presence of so-called three-center bonding. Ponec and Uhlik[19] claim evidence for three-center B−H−B bonds in terms of a $\delta(B,B)$ value of 0.255, one which exceeds their value for $\delta(B-H_b)$, where H_b denotes a bridging H bonded to B. These values are, however, an artifact of their use of the Mulliken definition of the atomic contributions to the pair indices, a procedure that in some instances, including B_2H_6, yields physically impossible positive Fermi correlations. When the atoms are defined as proper open systems,[6] there is a transfer of ~0.7e from B to each H, Table 4, a degree of charge transfer that a Mulliken partitioning is incapable of describing. The molecular graph obtained for diborane agrees with the accepted structure, with each boron linked by bond paths to two terminal hydrogens and to two bridging hydrogens, the latter set forming a four-membered ring. The characteristic feature of the electron density in these electron-deficient molecules is the delocalization of the electron density over the surfaces of the three- and four-membered rings formed by the bonds of formal reduced order.[26] Because of the charge of +2.1e on each boron, the delocalization of electrons between them is slight, with $\delta(B,B') = 0.05$. It is the diffuse density of the two negatively charged bridging hydrogens that is delocalized over the ring, and one finds $\delta(H_b,H_b') = 0.24$, a value twice that for the delocalization of the density between two terminal hydrogens and considerably greater than the value of $\delta(H,H')$ in BH_3. Thus, there is no evidence in the nonbonded delocalization indices of $B-H_b-B$ three-center bonding. Instead, the data indicates incipient bonding between the two bridging hydrogen atoms, as occurs when the ring is distorted by a small decrease in their separation, a distortion that causes the ring critical point to bifurcate into a bond critical point, whose associated bond path links the two hydrogens, and two new ring critical points. No such structural change occurs when the B−B separation is moderately decreased. The atomic populations and pair indices defined by the theory of atoms in molecules will always recover both the static and dynamic properties of the electron density.

All atomic interactions involve some degree of pairing of the electrons on the two atoms, even so-called nonbonded interactions.[17] The description of the van der Waals interaction that leads to the binding in rare-gas diatomics and condensed phases requires a correlated wave function. Thus, $\delta(A,A')$ for He_2 and Ar_2 while equalling zero at the Hartree−Fock level exhibits small values that increase with the size and polarizability of the atoms involved, Table 1.

Conclusions

The localization and delocalization indices, defined by the intra- and interatomic contributions to the Fermi correlation, enable one to compare the number of localized and bonded electron pairs present in a molecule with a pairing structure predicted by the Lewis model. The comparison is most faithful at the Hartree–Fock level for the pair densities obtained for homopolar molecules, such as H_2 and N_2, or shared interactions with low polarities, as found in the hydrocarbons, both saturated and unsaturated or in H_2S and HCl. In the presence of charge transfer, one must augment the information obtained from the pair density with the orbital contributions to the delocalization index to determine the number of contributing Lewis-bonded pairs, a procedure that becomes imprecise in systems with many orbitals of similar symmetry. One may of course, forego the Lewis-pair model and simply use the model-independent information regarding the localization and sharing of electrons that is provided by the pair indices.

In general, the introduction of Coulomb correlation takes one beyond the Lewis model. It reduces the delocalization index for shared interactions, and fewer electron pairs are shared in homopolar interactions than predicted by the Lewis model at the correlated level. The effect of Coulomb correlation on the pairing indices is minimal for ionic molecules because of the high degree of localization of the density within each atomic basin. As a general conclusion, the Lewis electron-pair model is most recognizable in the pairing obtained from theory at the Hartree–Fock level. However, the model is recognizable even at the correlated level, a reflection of the importance of the Pauli principle in determining electronic structure.

Ponec and Uhlik[19] claim a greater correspondence of the Hartree–Fock pair density with the Lewis model. However, this is a result of their use of the Mulliken population analysis for the definition of the atomic contributions. This method generally overestimates the values of the delocalization indices in polar molecules, since it underestimates the extent of charge transfer. In addition, they identify the delocalization index with the Lewis bond order in all cases, a correspondence that fails if they were to consider ionic molecules or polar molecules with multiple bonding.

The Lewis model is also evident in the local maxima or charge concentrations (CCs) displayed by $L(\mathbf{r}) = -\nabla^2\rho(\mathbf{r})$. The CCs have been shown to yield a faithful mapping of the localized electron domains that are assumed to be present in the valence shell of a central atom in the VSEPR model of molecular geometry, there being agreement not only in the number of maxima but also in their angular orientation and relative sizes.[7,28] Recently, a one-to-one correspondence has been shown to exist between the maxima in $L(\mathbf{r})$ with the maxima displayed in the conditional pair probability for same-spin electrons.[29] These latter maxima result from corresponding localizations of the Fermi density, and the correspondence demonstrates that the CCs do indeed determine the spatial regions where increased electron pairing occurs, as determined by a corresponding localization of the Fermi density.

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Appendix

Interatomic Distances (*R*, in Å) and Densities at the b.c.p. (ρ_b, in au) for All the Molecules Reported in the Paper

molecule	pair	HF		CISD	
		R	ρ_b	R	ρ_b
H_2[a]	H, H′	0.734	0.275	0.742	0.268
N_2[a]	N, N′	1.066	0.765	1.087	0.714
F_2[a]	F, F′	1.329	0.367	1.377	0.268
LiF[a]	Li, F	1.563	0.076	1.571	0.007
CO[a]	C, O	1.103	0.533	1.121	0.508
CN^-[a]	C, N	1.152	0.503	1.168	0.482
NO^+[a]	N, O	1.026	0.827	1.071	0.772
He_2[b]	He, He′			2.985	0.001
Ar_2[b]	Ar, Ar′			4.174	0.001
LiH[a]	Li, H	1.607	0.040	1.598	0.040
BeH_2[a]	Be, H	1.331	0.098	1.327	0.098
BH_3[a]	B, H	1.187	0.186	1.187	0.187
CH_4[a]	C, H	1.082	0.289	1.083	0.283
NH_3[a]	N, H	0.998	0.360	1.006	0.347
H_2O[a]	O, H	0.940	0.396	0.952	0.380
HF[a]	F, H	0.897	0.404	0.911	0.388
NaH[a]	Na, H	1.917	0.032	1.896	0.030
MgH_2[a]	Mg, H	1.707	0.054	1.701	0.055
AlH_3[a]	Al, H	1.577	0.084	1.573	0.084
SiH_4[a]	Si, H	1.474	0.122	1.471	0.122
PH_3[a]	P, H	1.404	0.165	1.408	0.162
H_2S[a]	S, H	1.326	0.221	1.330	0.214
HCl[a]	Cl, H	1.265	0.257	1.269	0.250
CO_2[c]	C,O	1.143	0.476	1.161	0.453
SO_2[c]	S,O	1.414	0.301	1.441	0.286
SO_3[c]	S,O	1.405	0.317	1.427	0.302
C_2H_4[c]	C, C	1.316	0.364	1.328	0.350
	C, H	2.093	0.295	2.104	0.289
C_2H_6[c]	C, C	1.527	0.253	1.523	0.249
	C, H	2.170	0.287	2.166	0.283
C_6H_6[a]	C, C′	1.381	0.313		
	C, H	1.072	0.302		
B_2H_6[c]	B, H′	1.184	0.184	1.181	0.185
	B, H	1.317	0.120	1.304	0.125

[a] 6-311++G(2d,2p)//6-311++G(2d,2p). [b] 6-311G(2d,2p)//6-311G(2d,2p). [c] 6-31G**//6-31G**.

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