J. Am. Chem. Soc. 1988, 110, 7329-7336

A Physical Basis for the VSEPR Model of Molecular Geometry

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Abstract: The Laplacian of the electronic charge distribution demonstrates the presence of local concentrations of charge in the valence shell of an atom in a molecule. These local maxima faithfully duplicate in number, location, and size the spatially localized electron pairs of the VSEPR model. Thus the Laplacian of the charge density provides a physical basis for the Lewis and VSEPR models. This paper shows that the arrangement of the local charge concentrations within the valence shell of an atom is a consequence of the partial condensation of the valence electrons into pairs. This condensation is caused by a corresponding spatial localization of the Fermi hole. Such localization arises from the ligand field operating in concert with the Pauli exclusion principle. The VSEPR model is now reduced to a single postulate, namely, that the most stable molecular geometry of a molecule AX_n corresponds to maximizing the separations between the local maxima in the valence shell of charge concentration of the atom A as defined by the Laplacian of the charge density.

1. Introduction

The valence-shell electron pair repulsion (VSEPR) model,[1] which is a natural extension of the electron pair model of Lewis,[2] has become the most successful and widely used model for the prediction of geometries of closed-shell molecules. The VSEPR model has two basic assumptions: (1) the valence charge density is spatially localized into pairs of electrons, and (2) The geometrical arrangement of the ligands about an atom is that which maximizes the interpair separation, for both the bonded and nonbonded pairs. The Laplacian of the electronic charge density, the quantity $\nabla^2\rho$, exhibits extrema which indicate the presence of localized concentrations of electronic charge in the valence shell of an atom in a molecule. These local charge concentrations duplicate in number, location, and size the spatially localized electron pairs of the VSEPR model.[3] So faithful is the mapping of the number and properties of the localized electron pairs assumed in the VSEPR model onto the number and properties of the local maxima found in the valence-shell charge concentration (VSCC) of the central atom,[3] that one can conclude that the Laplacian of the charge density provides the physical basis for the Lewis and VSEPR models. One cannot, however, equate the existence of the local charge concentrations in the Laplacian distribution with the actual existence of the localized electron pairs assumed in the model, particularly since it has been previously demonstrated that the valence electrons in a molecule are, in general, not spatially localized into pairs.[4]

This paper is concerned with the origin of the local charge concentrations in the valence shell of the central atom. It is shown that they are a consequence of the partial condensation of the valence electrons into pairs as a result of the spatial localization of the Fermi hole. This localization results from the ligand field operating in concert with the Pauli exclusion principle. Hence the properties of the Laplacian of the charge density serve as a bridge linking the electron pairing effect of the Pauli exclusion principle with the corresponding assumption of the VSEPR model.

2. The VSEPR Model and the Properties of the VSCC

The Valence-Shell Charge Concentration. The Laplacian of a scalar field, such as the electronic charge density, has the important property of determining where the field is locally concentrated[5] (where $\nabla^2\rho < 0$) and where it is locally depleted (where $\nabla^2\rho > 0$). We review here very briefly the properties of the Laplacian of the electronic charge density in order to define the valence-shell charge concentration (VSCC) and illustrate its relation to the Lewis model of electron pairs. The structure of the Laplacian distribution in an atom reflects its shell structure, there being a shell of charge concentration and one of charge depletion associated with each quantum shell with the innermost region being a spike-like maximum in charge concentration.[6-8] Since electronic charge is concentrated where $\nabla^2\rho < 0$, it is more convenient to work with the function $-\nabla^2\rho$, a maximum in this function being a maximum in charge concentration. It is important to recall that the charge density itself does not exhibit a shell structure, as ρ decays monotonically in all directions away from a nucleus. The radial distribution function for an atom, obtained through an integration of ρ over its two angular coordinates, is a one-dimensional function giving the probability of finding electronic charge in the volume of the infinitesimal shell lying between two concentric spheres of radii r and $r + \mathrm{d}r$. The maxima observed in such a distribution determine values of r at which one is most likely to find electronic charge averaged over all spatial angles, but the actual distribution of charge in three-dimensional space does not exhibit a maximum at the corresponding value of r. The Laplacian distribution, on the other hand, exhibits shell structure in real space not only for an isolated atom, but also for an atom in a molecule.

The portion of the outer quantum shell over which $-\nabla^2\rho > 0$ is called the valence-shell charge concentration or VSCC. Within this shell is a sphere over whose surface electronic charge is maximally and uniformly concentrated. In general, this surface persists when the atom is in chemical combination, but the sphere is distorted and is no longer of uniform concentration because of the formation of local maxima, minima, and saddles on its surface.[9] It has been amply demonstrated,[3,10-13] and new examples are given

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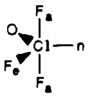
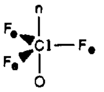
[8] Sagar, R. P.; Ku, A. C. T.; Smith, V. H.; Simas, A. M. *J. Chem. Phys.* **1988**, *88*, 4367. The number of shells defined in this manner by the Laplacian of the charge density or in terms of the number of maxima in the radial distribution function can be less than the principal quantum number for elements with $Z > 40$.

[9] An extremum in $-\nabla^2\rho$, a point where $\nabla(-\nabla^2\rho) = 0$, is called a critical point. If all three principal curvatures of $(-\nabla^2\rho)$ are negative at such a point, $-\nabla^2\rho$ is a maximum there and the point is labeled as (3, −3). The radial curvature at a critical point on the surface of the sphere of charge concentration is negative. If one of the remaining curvatures is negative and the other positive, the point is labeled as (3, −1), while if both remaining curvatures are positive, it is labeled as (3, +1). A two-dimensional display of a (3, −1) critical point in a plane containing the two negative curvatures has the appearance of a maximum. A two-dimensional display of a (3, −1) or a (3, +1) critical point in a plane containing one positive and one negative curvature has the appearance of a saddle. A two-dimensional display of a (3, +1) critical point in a plane containing two positive curvatures has the appearance of a minimum.

0002-7863/88/1510-7329$01.50/0

Table I. Bonded and Nonbonded Charge Concentrations on Cl in ClF_3O

geometry[a]	net atomic charges,[b] e	type	properties of charge concentrations in VSCC of Cl[c]			
			r_{Cl}, Å	$\nabla^2\rho(r_c)$	size, Å^2	intermaxima angles, deg
 C_s	Cl, +2.859	n	0.600	1.832	1.48	$nClb_O$ = 138.6, $nClb_a$ = 89.5
	O, −1.118	b_O	0.648	1.060	1.33	$nClb_e$ = 116.5, b_OClb_a = 97.0
	F_e, −0.547	b_e	0.668	0.646	0.70	b_OClb_e = 104.9, b_eClb_a = 81.2
	F_a, −0.597	b_a	0.682	0.414	0.41	
 C_{3v}	Cl, +2.790	n	0.602	1.633	1.59	$nClb_e$ = 80.9, b_eClb_e = 117.5
	O, −1.134	b_O	0.655	1.066	1.46	b_OClb_e = 99.1, $nClb_O$ = 180.0
	F_e, −0.552	b_e	0.650	0.420	0.50	

[a] C_s geometry: $R(Cl–O)$ = 1.4184, $R(Cl–F_a)$ = 1.6372, $R(Cl–F_e)$ = 1.5591, $\angle(OClF_e)$ = 110.13, $\angle(OClF_a)$ = 95.15, $\angle(F_eClF_a)$ = 84.72, all in Å and degrees, $E(HF)$ = −831.774983 hartrees. C_{3v} geometry: $R(Cl–O)$ = 1.4024, $R(Cl–F_e)$ = 1.6604, $\angle(F_eClO)$ = 93.78, all in Å and degrees, $E(HF)$ = −831.698421 hartrees. [b] The population of atom Ω in a molecule, $N(\Omega)$, is obtained by integration of ρ over the basin of the atom. The corresponding net charge is $q(\Omega) = Z_\Omega - N(\Omega)$, where Z_Ω is the nuclear charge. [c] The first column gives the radial distance of the maximum of charge concentration from the Cl nucleus. The next column gives the value of $-\nabla^2\rho$ (in au) at this maximum, or (3, −3) critical point.

here, that the local maxima that are created within the VSCC of a bonded atom provide a mapping of the bonding and nonbonding electron pairs of the Lewis and VSEPR models.

The Laplacian of the charge density plays a central role in the theory of atoms in molecules,[7,14] where it appears as an energy density, that is, as the quantity $(-\hbar^2/4m)\nabla^2\rho(\mathbf{r})$. It appears in this form in the local expression for the virial theorem, and, as a consequence, one can show that in regions of space where the Laplacian is negative and electronic charge is concentrated, the potential energy dominates both the local total energy and the local virial relationship. In general, the more negative the value of the Laplacian over some region of space, the greater is the contribution of the electronic charge in that region to the total energy of the system.

A Physical Basis for the VSEPR Model. It has been shown that the assumptions made in the VSEPR model of the presence of spatially localized pairs of electrons, in particular geometrical arrangements in the valence shell of the central atom, and of the properties ascribed to these bonding and nonbonding pairs, are recovered in the properties of the local maxima in the VSCC of the central atom.[3] The spherical surface on which the electron pairs are assumed to be localized in the VSEPR model is identified with the sphere of maximum charge concentration in the VSCC of the central atom, and the localized pairs of electrons are identified with the local maxima on this sphere of maximum charge concentration. The relative positions of these local maxima are determined by the coordinates of the corresponding (3, −3) critical points in $-\nabla^2\rho$. A bonded charge maximum is distinguished from a nonbonded one by virtue of its occurrence on a bond path linking neighboring nuclei.

The VSCC of the central atom in each of the molecules CH_4, NH_3, and OH_2 possesses four local maxima.[3] A nonbonded charge concentration is of larger magnitude and occupies a larger fraction of the surface of charge concentration than does a bonded charge concentration. Consequently, the angle subtended by two nonbonded charge concentrations is larger than that subtended by two bonded concentrations in an equilibrium geometry.[3] These results confirm that the maxima in the VSCC of the central atom recover the most important of the subsidiary postulates of the VSEPR model, namely, that nonbonding or lone pairs have larger domains than bonding pairs in the same valence shell. Another subsidiary postulate of the VSEPR model, previously illustrated, is that the domain of a bonded pair in the valence shell of the central atom decreases (increases) in size as the ligand becomes more (less) electronegative. The size of a local maximum in $-\nabla^2\rho$ is determined by the area it covers on the surface of the sphere of charge concentration.[3] The final subsidiary postulate of the VSEPR model is that double- and triple-bond domains which are composed of two and three electron pairs, respectively, are larger than single-bond electron pair domains. This postulate can be illustrated using the sizes of the C–C bonded maxima in ethane, ethylene, and acetylene which, expressed in terms of surface areas, are 0.62, 1.24, and 1.97 Å^2, respectively. By including the size of a nonbonded charge concentration in the VSCC of carbon in singlet methylene which is 0.94 Å^2, one establishes that for carbon, a double bond charge concentration occupies a larger fraction of the VSCC than does a nonbonded one. The same is true for sulfur in SO_2 where the size of the nonbonded charge maximum is 1.56 Å^2 while the size of the double bond charge maximum is 1.82 Å^2.

Examples of systems in which the VSCC of the central atom contains five maxima[3] (ClF_3, SF_4 and SF_4O), six maxima[3] (ClF_5), and seven maxima[15] (ClF_6^-) have also been reported in detail. It was also shown using these examples that forcing a system into a nonequilibrium geometry resulted in smaller angles between nonbonded charge concentrations, or between a bonded and a nonbonded charge concentration as predicted by the VSEPR model. The properties of the VSCC of the Cl atom in the ClF_3O system are reported here to further illustrate these same features of the VSEPR model and relate them to the new developments regarding the partial condensation of the valence electrons. This molecule allows for a comparison of the charge concentrations associated with singly bonded, doubly bonded, and nonbonded pairs of electrons.

The Laplacian Distribution of ClF_3O. Single determinant SCF calculations using the 6-21G* basis set have been carried out for the ClF_3O system.[16] The optimized geometry, of C_s symmetry, is derived from that of a distorted trigonal bipyramid (see Table I). This geometry is as predicted by the VSEPR model. The largest of the electron pair domains (the lone pair on Cl and the doubly bonded pairs to O) occupy the less crowded equatorial sites while the smallest (bonded pair to F) occupy the more crowded axial sites. The energy, geometrical parameters, and atomic charges are given in Table I. The axial and equatorial fluorines are denoted by F_a and F_e, respectively. As predicted by the VSEPR model, the Cl–F_a bonds are longer than the Cl–F_e bond as a consequence of the more crowded nature of the axial positions. The F_eClO angle is less than 120° which, according to the model, implies that the domain of the nonbonded pair on Cl is larger than

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(16) Calculations performed using Gaussian 82: Binkley, J. J.; Frisch, M. J.; DeFrees, D. J.; Ragavachari, K.; Whiteside, R. A.; Schlegel, H. B.; Fluder, E. M.; Pople, J. A. Gaussian 82, Carnegie-Mellon University Publication Unit, Pittsburgh, PA, 1983. The 6-21G* basis set contained in this program has *d* functions on all atoms other than hydrogen. The previously reported calculations[3] using the 6-21G* set were obtained using Gaussian 80. In this program *d* functions are placed only on the third-row atoms.

that for the two pairs in the double bond to oxygen. The F_aClF_a angle is 170° and these fluorines are bent away from the oxygen atom and displaced slightly toward the equatorial fluorine, the F_aClO and F_aClF_e angles equaling 91.7 and 84.7°, respectively. The C_{3v} geometry, which results when all three fluorines are equivalent and occupy the equatorial plane and the larger domains associated with the oxygen double bond and the Cl nonbonded pair occupy the axial positions, should, according to the VSEPR model, be of higher energy (see Table I). An SCF calculation constrained to yield this symmetry gives the geometrical parameters listed in Table I. It predicts the energy of the C_{3v} geometry to be 48.0 kcal/mol greater than that of the optimized geometry. The plane of the fluorine atoms is displaced below the Cl nucleus to give an FClO angle of 93.8°. In the equilibrium geometry the axial fluorines, in addition to having a slightly longer bond length than the equatorial fluorine, also possess a greater negative charge. These charges are in accord with the VSEPR prediction that the ligands in the axial positions, which are the most crowded positions, should have the largest negative charges. The charges on the fluorine atoms in the higher energy geometry are intermediate in value, being slightly greater than that for the equatorial fluorine in the C_s geometry. The chlorine and oxygen atoms bear substantial positive and negative charges respectively in both geometries.

The properties of the maxima, both bonded and nonbonded, derived from the VSCC of the Cl atom are listed in Table I, and the Laplacian distributions for the two geometries are illustrated in Figure 1.[17] The VSCC of the Cl atom in the equilibrium geometry exhibits the anticipated five maxima: a bonded charge concentration for each of the axial fluorines, a slightly larger bonded charge concentration for the less electronegative equatorial fluorine, a still larger one for the doubly bonded oxygen, and a nonbonded charge concentration which is largest of all. This ordering according to size refers to both the magnitude of the Laplacian at the maxima and the areas they cover on the surface of charge concentration. The relief map for the equatorial plane illustrates the relative sizes of the local charge concentrations corresponding to the nonbonded, doubly bonded, and singly bonded electron pairs. The critical points for the bonded maxima for the oxygen and the equatorial and axial fluorines are referred to as b_o, b_e, and b_a, respectively, and the nonbonded maximum as n. As anticipated on the basis of the relative sizes of the n and b_o maxima, the $nClb_e$ angle is greater than the b_oClb_e angle, a result, which according to the VSEPR model, accounts for the fact that the $OClF_e$ bond angle is less than 120°. The relative values of the angles are also reflected in the result that the angle b_oClb_a is greater than the angle $nClb_a$. The dominant size of the nonbonded pair determines the bond angle in the equatorial plane, but is not the deciding factor in determining the relative displacement of the axial fluorines away from the oxygen. This final element of geometry, and the corresponding observation that the equatorial fluorines are displaced away from the oxygen in the C_{3v} geometry, can be rationalized by assigning stereochemical activity to the nonbonded electrons on the ligands. The VSCC of the oxygen atom in the C_s geometry does indeed possess two nonbonded charge concentrations which lie on either side of the equatorial plane. In the C_{3v} geometry the VSCC of oxygen has three nonbonded maxima which are staggered with respect to the bonded maxima to the three equatorial fluorines.

The magnitude of the nonbonded maximum on Cl in the C_{3v} geometry is decreased from its value in the equilibrium geometry while the magnitude of the oxygen bonded maximum remains nearly unchanged. However, the sizes of both these maxima increase over their values in the equilibrium geometry. The maxima of the three equivalent fluorines and their sizes are decreased considerably in value from those found for the single equatorial F in the C_s geometry, a result of their increased crowding from the maxima associated with the lone pair and the oxygen atom. Figure 1 illustrates that this crowding is particularly severe with the lone pair maximum which nearly envelopes the equatorial bonded maxima. The postulates of the VSEPR model are quantitatively satisfied if one identifies the localized electron pairs of the model with the bonded and nonbonded charge concentrations of the Laplacian and predicts the most stable geometry to be that which maximizes the separations between these local charge concentrations. The angles formed by the bonded maxima of the three fluorines with the nonbonded charge concentration decrease from 90, 90, and 117° in the equilibrium geometry to a value of 86° for all three in the less stable C_{3v} geometry. Similarly, the angles these same bonded maxima make with the double bond maxima decrease from 95, 95, and 105° to a common value of 94° in the C_{3v} geometry.

The many examples that have been so far reported demonstrate a remarkable mapping of the number and properties of the localized electron pairs assumed in the VSEPR model of molecular geometry onto the number and properties of the local maxima found in the VSCC of an atom as determined by the Laplacian of the electronic charge distribution. The question to be answered next is why the Laplacian exhibits local concentrations of electronic charge where the VSEPR model assumes electron pairs to be?

3. Electron Localization and Local Maxima in the VSCC

Are Electrons Localized in Pairs? The concept of the localized electron pair has been a central theme in the development of bonding theories since Lewis[2] first postulated that a chemical bond was a consequence of a shared electron pair. However, the total electron density distribution in a molecule shows no indication of discrete bonding or nonbonding electron pairs. The principal topological property of the charge density of a many-electron system is that, in general, it exhibits local maxima only at the positions of nuclei.[18,19] When one sums the individual orbital densities in the determination of the total charge density, all suggestions of spatially localized patterns of charge and the associated nodes disappear to yield the relatively simple topology exhibited by the *total* charge density ρ. While this topology provides a faithful mapping of the concepts of atoms, bonds, and structure,[18,20] it does not provide any indication of the maxima in a charge distribution which would correspond to the spatially localized pairs of bonded and nonbonded electrons as anticipated on the basis of the VSEPR model.

The concept of a localized electron pair implies that there exists a region of real space in which there is a high probability of finding two electrons of opposite spin and for which there is a correspondingly small probability of exchange of these electrons with the electrons in other regions. Such physical localization of charge is a direct result of the operation of the Pauli exclusion principle as it affects the pair distribution function for electrons.[4] The charge density $\rho(r_1)$, the density of electrons at r_1, is given by N times the probability of finding one electron at r_1. Its integral over the coordinates of one electron gives N, the total number of electrons. Similarly, the pair density $\rho(r_1,r_2)$, the density of pairs of electrons with coordinates r_1 and r_2, is given by $N(N-1)/2$

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(17) There is no direct constraint on the topology of the Laplacian within the atomic basin of a bound atom or even a requirement that the VSCC must persist on bonding, or remain within the atomic surface of the given atom. Thus, an atom which loses most of its valence charge density on bonding, as Li does in many of its compounds, does not possess a VSCC in its bonded form.[10] In the present example, the VSCC initially associated with a free Cl atom is shared with its more electronegative bonded neighbors. For a bond between identical atoms and for polar bonds between dissimilar atoms, there are, in general, two bonded maxima, one associated with each atom. Thus a single bonded pair of the Lewis model is represented by two bonded maxima, one in each VSCC. An example of a polar bond with two bonded maxima is provided by the Cl–O bond in the C_s geometry (Figure 1). In situations of more extreme charge transfer, only a single bonded maximum may be found in the VSCC of the more electronegative atom. It appears that fluorine is unique in its behavior. The charge density of a fluorine atom is tightly bound and very localized in all of its compounds[4] with the result that its VSCC exhibits only a torus of nonbonded charge encircling the bond axis and no bonded charge concentration, not even in F_2.[7] Only in HF has the VSCC of fluorine been found to exhibit a bonded maximum.

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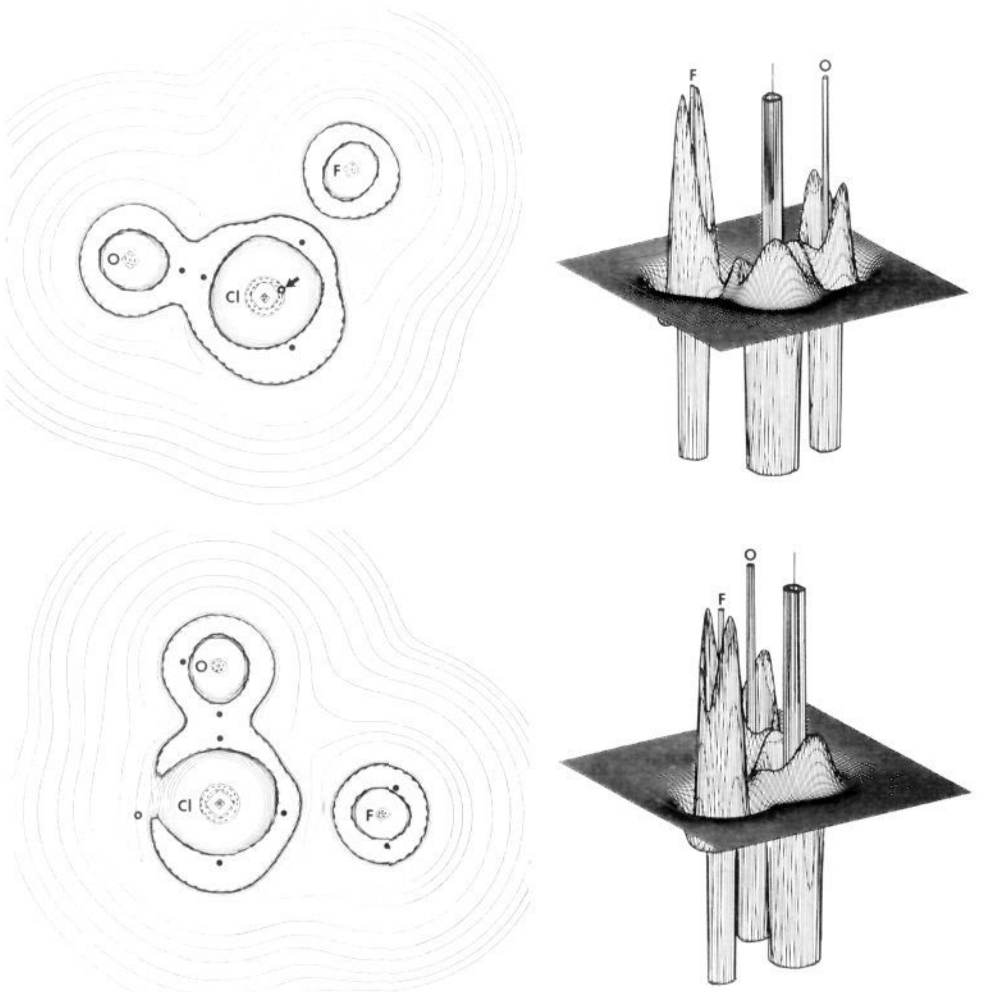

Figure 1. Contour and relief maps of the Laplacian distribution for ClF_3O. The relief maps are a display of $-\nabla^2\rho$ and negative contours are denoted by dashed lines. Maxima in $-\nabla^2\rho$ are denoted by dots and their values are given in Table I. The Laplacian exhibits three quantum shells for Cl and two for F and for O. The upper diagram is for a plane containing the nuclei of the O, Cl, and F_e atoms in the equilibrium geometry. The VSCC of Cl exhibits three maxima of decreasing size and magnitude, nonbonded, bonded to O, and bonded to F_e. The lower diagram is for a plane showing the axial oxygen and nonbonded maximum and one of the three equivalent equatorial F atoms in the C_{3v} geometry. The bonded maximum of an equatorial F is severely crowded by the nonbonded maximum in this geometry.

times the probability that one electron is at r_1 when the other is at r_2. Its integral over the coordinates of both electrons gives $N(N-1)/2$, the total number of distinct pairs of electrons. The antisymmetry requirement of the Pauli principle is imposed on the pair density through the introduction of the so-called Fermi hole. The theoretical development of the effect which the resulting Fermi correlation has on the pair distribution function has been previously given.[4] We give here a qualitative discussion of how the operation of the Pauli exclusion principle can lead to the localization of pairs of electrons just as is assumed in the VSEPR model, but follow this with a demonstration that the requirements for achieving localization are, in general, not met.

As an electron moves through space, it carries with it a doppelgänger, its Fermi hole. The Fermi hole is a distribution function defined relative to an uncorrelated pair density which determines the *decrease* in the probability of finding an electron with the same spin as some reference electron, relative to a given position of the reference electron. The orbital expression for the Fermi hole is given in the Appendix. Its magnitude at the position of an α (or β) reference electron equals the total density of α (or β) electrons at that point, thereby ensuring that there is a zero probability of finding another α (or β) electron at the position *of the reference electron. The Fermi hole, when integrated over* all space for a fixed position of the reference electron, corresponds to the removal of one electronic charge of identical spin. One may equally interpret the Fermi hole as a distribution function whose magnitude describes the spatial delocalization of the charge of the reference electron. An electron can go only where its hole goes, and if the Fermi hole is localized, then so is the electron.

Consider an electron of α spin in the proximity of a nucleus. Because the electron is tightly bound in a deep potential well, its Fermi hole is strongly localized in the immediate vicinity of the nucleus. If the Fermi hole is localized so as to equal $-\rho^{\alpha}$, the negative of the total density of α electrons, at every point over this region of space, then all other electrons of α spin are excluded from the potential well. The same result will be obtained for an electron of β spin, and, as a consequence, a pair of electrons is confined to a region of space from which all other electrons of both α and β spin are excluded. 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 both α and β spin being excluded from a given region of space in which they are both bound by some attractive force. Repulsions between the electrons act in opposition to this effect, and one finds that the long-range nature of the Coulomb force disrupts and limits the localization of charge.

The perfect localization of a pair of electrons to some domain *Ω as described above requires the total removal of one electronic* charge within Ω (that is, the Fermi hole is totally contained within Ω) for every position of the reference electron within the region. The total Fermi correlation contained in a domain Ω, a quantity denoted by $F(\Omega,\Omega)$, is obtained by a double integration of the Fermi hole weighted by ρ^{α}; one integrates the hole density over the domain for a given position of the reference electron and then repeats this for every position of the reference electron in the same domain. For perfect localization of a pair of electrons to a region Ω, $F(\Omega,\Omega)$ integrates to -2, corresponding to the removal of one α and one β electron. Thus, the ratio $|F(\Omega,\Omega)|/N(\Omega)$ is a measure of the fraction of the Fermi correlation required for complete localization of the $N(\Omega)$ electrons to the domain Ω. Complete localization of a pair of electrons is possible only in the limit of their complete isolation. However, one finds 1s core regions of atoms which approach this limiting situation. In these cases it is possible to find a spherical boundary such that the contained Fermi correlation is found to be maximized for an average population of two, with values ranging from to 96% in Li to 73% in Ar of that required for complete localization of the pair. As shown previously, maximizing the Fermi correlation is equivalent to minimizing the fluctuation in the average population of the contained charge. In these cases where the domain of localization is defined by *extremization* of the pertinent physical parameters, it is meaningful to refer to the electrons as being physically localized.[4] Correspondingly, the Laplacian of the charge density attains its most negative values for this region of space in an atom and thus contributes maximally to the lowering of the potential energy.

Such physically localized pairs of electrons are found in a few simple hydrides such as LiH, BeH_2, and BH_3 in which there are, in addition to the pair of core electrons, one, two, and three pairs of electrons 96, 93, and 82% localized on the protons, respectively. These are the same systems which possess localized electron pairs according to Daudel's loge theory.[21] In the remaining second-row hydrides CH_4 to HF, however, where the bonding density is evenly shared between A and H, or strongly polarized toward A, bounded regions which maximize the contained Fermi correlation do not exist and the electrons are not physically localized into pairs.[4,22]

As previously demonstrated,[4] the orbital requirement for physical localization of electron pairs is not that a set of orbitals be localized, but that each orbital be localized to its own separate region of space. Such separate localization is apparent even in the canonical set of orbitals for the same hydride molecules, LiH, BeH_2, and BH_3, which as noted above exhibit localization of electron pairs. Localized orbitals are in general, however, not that localized and they are not localized to separate regions of space.[23]

A physically localized pair of electrons is maximally isolated from the remainder of the system in that their exchange and all of their correlative interactions with the remainder of the system are minimized. Hence the degree of physical localization as determined by the properties of the Fermi correlation parallels the relative importance of the intra- and interpair correlation energies as determined by various "correlated pair" theories. In LiH, BeH_2, and BH_3,[24,25] for example, intrapair correlation accounts respectively, for over 90, 86, and 77% of the total correlation energy, for which the corresponding Fermi localizations are 96, 93 and 82%. As pointed out by Davidson,[26] Sinanoğlu and Skutnik,[27] and Kutzelnigg,[25] this is not the general result, and in molecules such as CH_4 and NH, the intrapair correlation contribution to the total correlation energy drops to 56 and 20%, respectively. The study of the localizability of the Fermi correlation and the related fluctuation in the average electron population, of the relative importance of the intra- and interpair contributions to the total correlation energy, and of the degree of the separate localizability of orbitals, all provide similar information and all indicate that, in general, the physics of a many-electron system is not dominated by the behavior and properties of individual electron pairs. There is, however, partial localization of the pair density, and it is this partial localization acting in concert with the ligand field that is responsible for the appearance of local charge concentrations in the valence shell of the central atom.

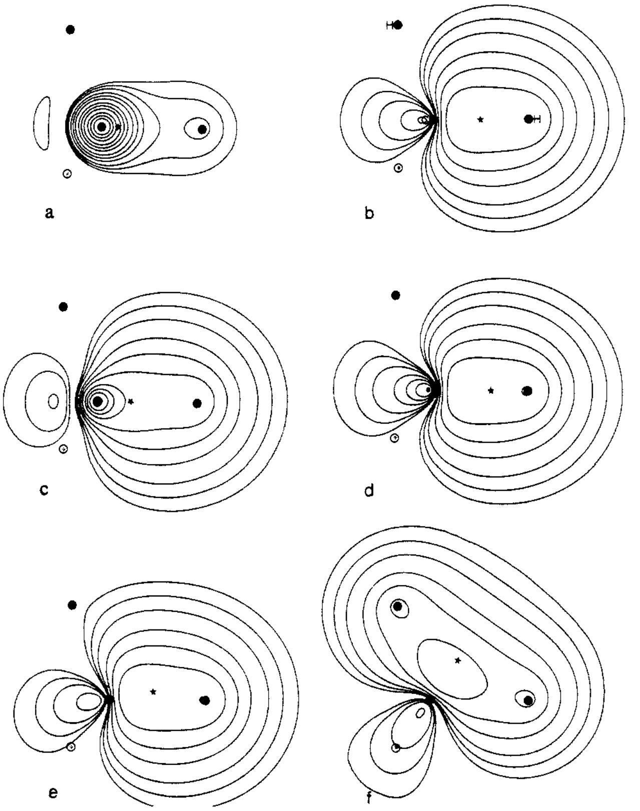

Figure 2. Contour maps of the Fermi hole density in methane for various positions of the reference electron, as indicated by a star. Each map is for a plane containing the carbon and two hydrogen nuclei as labeled in map b. The contours used in this and the following figures are in atomic units and decrease in value from the outermost contour inward in steps of -2×10^n, -4×10^n, and -8×10^n with n beginning at -3 and increasing in steps of unity. (a) Reference electron, 0.35 au from C nucleus, is within the localized core of radius 0.53 au. (b) Reference electron is at position of bonded maximum in VSCC of carbon, 1.02 au from nucleus. (c) Reference electron is 0.69 au from nucleus. The Fermi density is a maximum at the C nucleus and is less localized in the valence region of the C–H bond than in map b. (d) Reference electron is 1.28 au from C nucleus. The area within the inner (0.08 au) C–H "bond" contour is decreased relative to map b and more density is placed within the core and nonbonded regions. (e) Reference electron is moved off bonded maximum toward second proton. It is 0.99 au from nucleus and still within neighborhood of bonded maximum. Map e is essentially unchanged from map b. (f) Reference electron, at same distance from nucleus as in map e, is moved further, to a point on boundary of two bonded regions. This map represents the maximum possible delocalization of the Fermi hole for this distance of the reference electron from the C nucleus.

Local Charge Concentrations and Localization of the Fermi Hole. It is demonstrated through a study of the Fermi hole density that the local decrease in the potential resulting from the approach of each ligand to the central atom results in a corresponding partial condensation of the pair density to yield patterns of localization as anticipated by the VSEPR model. This results in corresponding patterns of charge concentrations and accompanying decreases in the local potential energy for both the bonded and nonbonded charge concentrations.

The properties of the Fermi hole for a physically localized pair of electrons is illustrated by the core electrons in methane. In this molecule, a sphere of radius 0.53 au centered on the carbon

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(21) Daudel, R.; Bader, R. F. W.; Stephens, M. E. *Can. J. Chem.* **1974**, *52*, 1310.

(22) While the valence charge distribution of an atom is, in general, not localized into separate pairs, the *total* charge distribution of an atom can exhibit significant localization. The percentage localization of some average number of electron pairs within the zero flux atomic surface[20] ranges from 65% for C, to 75% for N, to 88% for O, and to 95% for F.

(23) Daudel, R.; Stephens, M. E.; Kapuy, E.; Kozmutza, C. *Chem. Phys. Lett.* **1976**, *40*, 194.

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

(25) Kutzelnigg, W. *Fortschr. Chem. Forsch.* **1973**, *41*, 31.

(26) Davidson, E. R. *Rev. Mod. Phys.* **1972**, *44*, 451.

(27) Sinanoğlu, O.; Skutnik, B. *Chem. Phys. Lett.* **1968**, *1*, 699.

nucleus defines a region of space which maximizes the contained Fermi correlation to yield a pair of electrons which are 88% localized.[4] The localized nature of the Fermi hole is illustrated in Figure 2. In spite of the unsymmetrical position of the reference electron, the hole is nearly symmetrical with respect to the nucleus, and it corresponds closely to a plot of the α density distribution in the region of the core. With the exception of the contours of very low value extending out to the proton, this plot remains essentially unchanged for any position of the reference electron within this localized core region. Thus the core region is maximally isolated from the remainder of the system. The fluctuation in its average population of two is minimized, as is the exchange of its electrons with those in the remainder of the system.

While there is localization into shells in a free atom as is reflected in the Laplacian distribution as well, there is no possibility of defining localized pairs within the L or M shells, as the Fermi hole for each electron is spread over its respective shell. It has already been noted that the uniformity of the outer shell of charge concentration is disrupted with the approach of ligands to the central atom with the resultant formation of local concentrations of charge. The formation of bonded charge maxima in the VSCC of the central atom is understandable in view of a decrease in the electron-nuclear potential in each of the resulting internuclear regions of the molecule. However, the decrease in potential is, in general, not sufficient to condense the Fermi hole of a single electron to a degree sufficient to localize a pair of electrons from the remainder of the system as is found for the core region of an atom. This situation is also illustrated for the methane molecule. While it is not possible to define a valence region which maximizes the contained Fermi correlation in this molecule, the division of space excluding the core into four equivalent bonded domains does represent the best partitioning of its valence space in that it minimizes the *sum* of the fluctuations in the populations of the individual regions.[4] The pair of electrons in each such bonded region is 69% localized. It appears from many examples that it is not possible to maximize the contained Fermi correlation for a region of space containing on the average a pair of electrons when the total Fermi correlation falls below 70%. The diffuse nature of the Fermi hole in the valence region of this molecule which prevents the physical localization of a pair of electrons is illustrated in Figure 2 for a reference electron located at the bonded maximum in the VSCC of carbon. This hole is much less localized than that for the core electrons, extending into the nonbonding region as well. Its shape remains insensitive to the position of the reference electron only for motion of the reference electron within the neighborhood of the bonded maximum. As the reference electron is removed from this region, the hole becomes more delocalized and its overlap with the core and neighboring bonded regions increases. For this reason one cannot maximize the contained Fermi correlation nor, equivalently, minimize the fluctuation in its population; any variation in the boundary of a valence domain causes the average electron population to increase faster than the contained Fermi correlation.[4]

While the valence density is not physically localized into isolated pairs of electrons as is the core density, there is partial localization of the pair density as reflected in the value of 0.69 for the fraction of the total possible Fermi correlation for an average population of two electrons. Rather than a single electron pair, each bonded domain in methane contains an average of 1.3 distinct pairs of electrons as opposed to the 1.75 pairs which would be obtained if the electrons were fully delocalized over the entire valence region.[28] Of equal importance is the observation that the Fermi hole for a reference electron at, or in the neighborhood of a bonded maxima in the VSCC of the carbon atom, attains its minimum values along the axes of the other C–H bonds. Recalling that the Fermi hole is a display of the spread or delocalization of the density of the reference electron, one sees that this density is concentrated along a tetrahedral or threefold axis to maximally avoid the three other corresponding bonded regions.

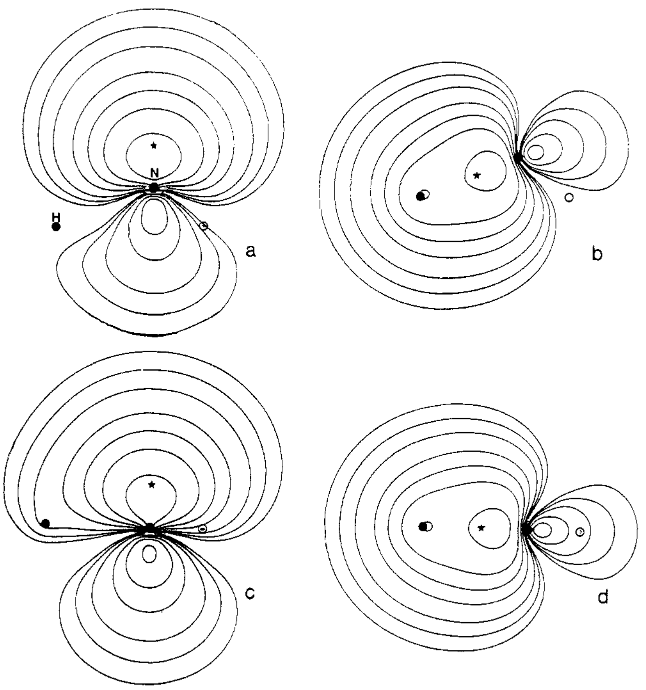

Figure 3. Contour maps of the Fermi hole density for pyramidal (a, b) and planar (c, d) ammonia. In maps a and b the reference electron is positioned at the nonbonded and bonded maxima, respectively, in the VSCC of the nitrogen atom. Note that the Fermi density is more contracted toward the core in NH_3 than it is in CH_4, as are the maxima in its VSCC. Maps c and d are corresponding plots for planar ammonia. The density of the nonbonded Fermi hole, map c, is more delocalized than that for the pyramidal geometry, map a. In the planar geometry, contours of the nonbonded Fermi hole density encompass the N–H internuclear axis. Clearly maps c and d overlap one another to a greater extent than do maps a and b; the electron pairs are more localized in pyramidal than in planar ammonia.

The Fermi hole for the reference electron at a bonded maxima in the VSCC of the carbon atom has the appearance of the density of a directed sp^3 hybrid orbital of valence bond theory or of the density of a localized bonding orbital of molecular orbital theory. Luken[29] has also discussed and illustrated the properties of the Fermi hole. He has noted its insensitivity to the position of the reference electron when in regions of space where it has previously been shown that an electron pair is physically or partially localized.[4] He has also noted the similarity in appearance of the density of a Fermi hole with that for a corresponding localized molecular orbital and has suggested that the form of the Fermi hole be used as a basis for the definition of a localized set of molecular orbitals. We emphasize here again that localized orbitals like the Fermi holes shown above for valence electrons are, in general, not sufficiently localized to separate regions of space to correspond to physically localized or distinct electron pairs. The fact that the Fermi hole resembles localized orbitals in systems where physical localization of pairs is not found further illustrates this point.

It should be borne in mind that the resemblance of a Fermi hole density to that of a localized valence orbital is obtained only when the reference electron is placed in the neighborhood of a local maximum in the VSCC. The Fermi hole and hence the density of the reference electron are much more delocalized for general positions throughout the valence region (see Figures 2f and 6)). Localized molecular orbitals thus overemphasize electron

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[28] The number of distinct pairs formed from eight valence electrons is $(8 \times 7)/2 = 28$. The chance of two electrons being in one-quarter of the total region is $(1/4)(1/4)$ and the average number of pairs is $28\ (1/16) = 1.75$. The same result is obtained from the expression for the average number of pairs in a region Ω; it is $(N(\Omega)^2 + F(\Omega,\Omega))/2$ where $F(\Omega,\Omega)$ is the contained Fermi correlation. For one α,β pair, $F(\Omega,\Omega) = -1/4 - 1/4 = -1/2$ since the total Fermi correlation of -1 for each electron is spread equally over all four regions. Hence the number of pairs equals $(4 - 1/2)/2 = 1.75$.

[29] Luken, W. L. *Croat. Chem. Acta* **1984**, *57*, 1283. Luken, W. L.; Beratan, D. N. *Theor. Chim. Acta* **1982**, *61*, 265.

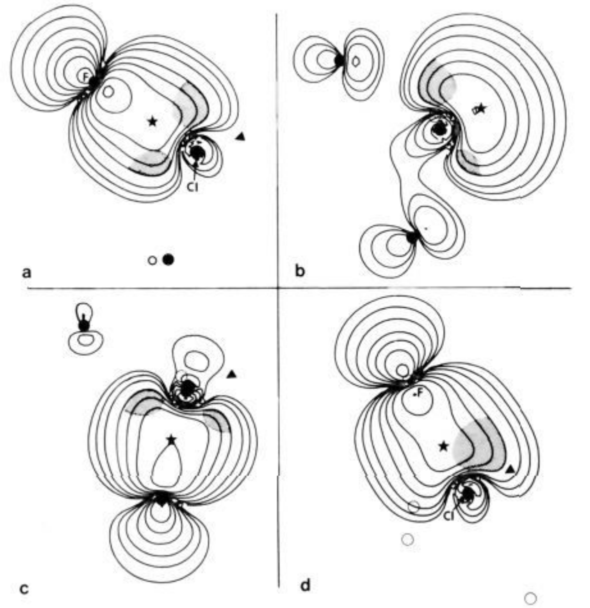

Figure 4. Contour plots of the Fermi hole density for the equilibrium geometry of ClF$_3$O. In-plane nuclei are denoted by solid circles, projected positions of out-of-plane nuclei by open circles. The reference electron is at the bonded maximum to F$_e$ in a, at the nonbonded maximum in b, at the bonded maximum to O in c, and at the bonded maximum to F$_a$ in d. The solid triangle denotes the position of the nonbonded maximum in plots a, c, and d. Plots a, b, and c are for the equatorial plane, and d is for the plane containing the Cl nucleus, the bonded maximum to F$_a$, and the nonbonded maximum. The nucleus of F$_a$ lies slightly out of this plane. The shaded areas indicate the regions of overlap of neighboring Fermi holes bonded by the −0.02-au contour. The shaded area in plot d is the overlap of the hole for the axial bonded maximum with the hole of the nonbonded maximum. This same overlap is slightly larger than the overlap of the nonbonded hole with the hole for a bonded maximum on F$_e$.

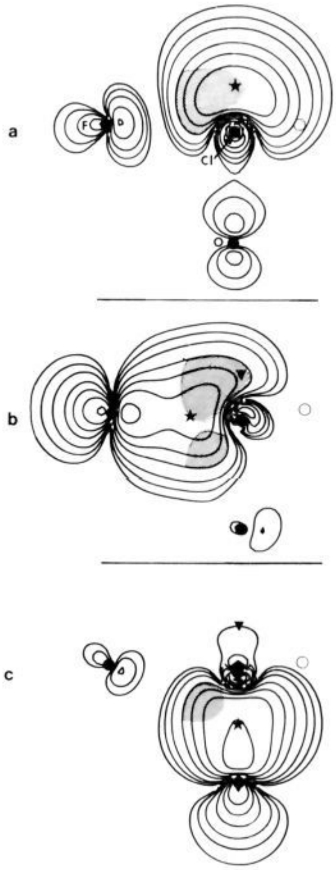

Figure 5. Contour plots of the Fermi hole density for the C_{3v} geometry of ClF$_3$O in a symmetry plane: (a) reference electron at maximum of axial nonbonded maximu, (b) reference electron at bonded maximum of F, and (c) reference electron at bonded maximum of axial oxygen. The shaded areas indicate the overlap of the F bonded hole with the nonbonded hole and with the bonded hole for O, as bounded by the −0.02-au contour. These areas are greater than the corresponding areas in Figure 4 for the equilibrium geometry. This is true, in particular, for the overlap of the holes for the nonbonded pair and the bonded pair on each of the fluorines, which extend up to the positions of the reference electrons.

localizability and they do not provide true representations of the extent to which electrons are spatially localized.

There is partial localization of the valence density in methane. The condensation into four partially localized pairs of electrons arranged along four tetrahedral axes is a result of the combined effects of the ligand field and the Pauli exclusion principle as described above. Most important is that this partial localization of the pair density is reflected in the properties of the VSCC of the carbon atom which undergoes a corresponding condensation into four local concentrations of electronic charge. These properties of the pair density are not just the result of the tetrahedral symmetry of the ligand field in methane because, as we will now see, the Fermi hole exhibits the same behavior in the ammonia molecule.

The Fermi holes obtained for a reference electron at the positions of a bonded and the nonbonded maxima in the VSCC of the nitrogen atom in ammonia are illustrated in Figure 3. This figure shows that there is a partial condensation of the pair density in ammonia to yield four partially localized pairs of electrons arranged along four axes which are approximately tetrahedrally directed. The pair density is less localized than in methane with the bonded and nonbonded domains containing respectively 61 and 55% of the total possible Fermi correlation for average electron populations of two. There are, on the average, 1.38 distinct pairs of electrons in a bonded domain and 1.45 in a nonbonded domain of ammonia, and the pair density is further removed from the limit of localized pairs than it is in methane.[4] As in methane, the pattern of delocalization of the density of a bonded or of the nonbonded reference electron is such as to maximally avoid the three other axes of pair localization. Thus in agreement with the postulated behavior of the electron pairs in the VSEPR model, the most probable arrangement of the partially localized pairs of electrons in ammonia is approximately tetrahedral, even though the ligand field is only threefold. Also in accord with the VSEPR model, the Fermi hole for the nonbonded reference electron is laterally more diffuse than is that for a bonded reference electron, a property also reflected in the properties of the corresponding maxima in the VSCC of the nitrogen atom.

Of equal importance to the VSEPR model is the observation that for geometries which, on the basis of the VSEPR model, do not maximize the distance between the electron pairs, the Fermi holes are less localized and exhibit greater overlap with the holes for neighboring domains. As an example, the Fermi hole for a reference electron on the threefold axis in planar ammonia, situated at one of the two symmetrically related nonbonded charge concentrations, is strongly delocalized over both sides of the plane of the nuclei (Figure 3). The density of the nonbonded reference electron clearly overlaps the holes for reference electrons placed at the bonded maxima more in this geometry than in the most stable pyramidal geometry. *The Fermi holes for reference electrons placed at the corresponding bonded and nonbonded maxima in the VSCC of the central atom are most localized and least mutually overlapping for those geometries which in the VSEPR model maximize the interpair separations or, equivalently, maximize the separations between the local maxima in the VSCC of the central atom.*

It is important to emphasize that the correlation which exists between the properties of the Fermi hole and the VSEPR model are made most evident through the use of the properties of the Laplacian of the charge density. The correspondence is greatest when the position of the reference electron coincides with a local maximum in the VSCC of the central atom. The Fermi holes

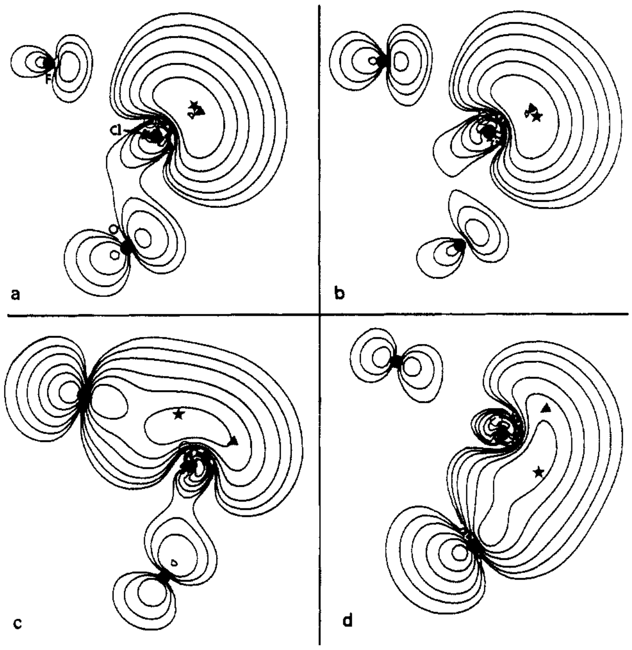

Figure 6. Diagram a is a display of the Fermi hole density for the reference electron moved 0.2 au away from the critical point of the nonbonded maximum toward F_e. Aside from a slight increase in delocalization onto the oxygen, the distribution is essentially unchanged from that shown in Figure 4. For diagram c the reference electron is moved to the critical point on the boundary between the nonbonded and F_e bonded maxima. The distribution is now nearly equally delocalized over the F and Cl atoms. Diagrams b and d show corresponding behavior when the reference electron is displaced slightly off the critical point toward oxygen, and then to the critical point on the boundary between the nonbonded and the oxygen bonded maxima. The pair density is most localized when the reference electron is placed at the position of a charge concentration in the Laplacian distribution.

are individually most localized for such a coincidence in position, and they are least overlapping for that geometry which maximizes the distances between the local maxima in the VSCC of the central atom.

Representations of the Fermi hole in the two geometries of ClF_3O are given in Figures 4 to 6 to demonstrate the generality of these observations. As in the previous plots, the most localized Fermi hole density is obtained when the reference electron is placed at the position of the corresponding maximum in charge concentration. In particular, this is once again true for the nonbonded charge concentration. As in the ammonia molecule, "lone pairs" as well as "bonded pairs" result from the partial condensation of the pair density. These most localized densities are arranged so as to maximize the mutual avoidance of the electron pairs they represent. Figure 6 demonstrates, for the nonbonded electron, that the Fermi hole and hence the density of the reference electron become very delocalized when the reference electron is moved away from the position of its local maximum in the VSCC. Only for the nonbonded position of the reference electron is the Fermi hole localized on Cl and has the appearance of a Cl centered orbital. For the bonded maxima associated with the oxygen and fluorine atoms, the patterns of delocalization of the reference electron are centered primarily on the nuclei of these associated atoms. This behavior is consistent with the finding that only the nonbonded maximum lies totally within the VSCC of the Cl atom.

The density of the reference electron is, in general, more delocalized in the C_{3v} geometry than in the equilibrium geometry. In the equilibrium geometry the only significant overlap of these most localized Fermi distributions, which are meant to model the charge distributions of the bonded and nonbonded electron pairs, is between the holes associated with the nonbonded maximum and those associated with the bonded maxima of the fluorine atoms, particularly that for F_e (Figure 4). In the less stable C_{3v} geometry there is a much greater degree of overlap of all of the Fermi holes, particularly between those for the nonbonded electron and the bonded of the fluorine atoms (Figure 5). This latter observation reflects the behavior of the Laplacian distribution where it was noted that in this geometry the bonded maxima on the fluorines are particularly crowded by the nonbonded charge concentration.

4. Conclusions

This paper has shown that the number and relative positions of the local maxima in the VSCC of the A atom in a molecule AX_n are a consequence of the partial localization of electron pairs in its valence region which results from the ligand field operating in concert with the Pauli principle. Clearly all of the postulates of the VSEPR model, including the effect of the Pauli principle on the most likely arrangement of electron pairs, are recovered in the properties of the VSCC of the central atom. A knowledge of these properties may be used to predict molecular geometries in a modified VSEPR model that requires only a single postulate, namely, that the most stable geometry of a molecule is that which maximizes the separations between the local maxima in the VSCC of the central atom. All other aspects of the VSEPR model are now firmly linked to theory and to the physical properties of the charge and pair densities of a molecular system.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

Appendix

The expression for the density of the Fermi hole obtained from a single determinantal function composed of orthogonal spin orbitals ϕ_i for a reference electron of α spin at r_1 is

$$h^{\alpha}(r_1,r_2) = -\sum_i\sum_j \phi_i(r_1)\phi_j^*(r_1)\phi_i^*(r_2)\phi_j(r_2)/\sum_i \phi_i^*(r_1)\phi_i(r_1) \qquad \text{(A-1)}$$

where the sums run over the α spin orbitals only. The sum in the denominator of eq A-1 is the density of α electrons at r_1, the quantity $\rho^{\alpha}(r_1)$ of the text. It follows from eq A-1 that $h^{\alpha}(r_1,r_2) = -\rho^{\alpha}(r_1)$ when $r_1 = r_2$, corresponding to the removal of all density of α spin, and that the integral of $h^{\alpha}(r_1,r_2)$ over r_2 with r_1 fixed equals -1, corresponding to the removal of one electronic charge of α spin.