A Theoretical Definition of the "Size" of Electron Pairs and Its Stereochemical Implications

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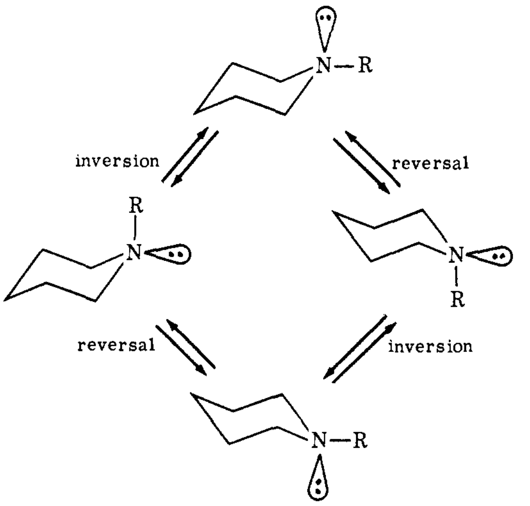
Abstract: The following definition is proposed which relates the semiclassical concept of the "size" of an electron pair (*i.e.*, localized two-electron group) to the expectation values of two quantum mechanical operators corresponding to the first and second moments of the electronic charge distribution of localized molecular orbitals. The "size" of a "localized" electron pair can be represented, for the purposes of chemical interpretation, by the volume of a sphere of radius equal to the root mean square of the distance of an electron associated with the pair from the center of charge (centroid) of the pair. The stereochemistry is given by the geometrical position of the centroid of charge and by the nonspherical components of the second moment calculated with the origin at the centroid. It is illustrated that the above definition is applicable to nonempirical and semiempirical molecular orbital calculations. Some numerical results are given for NH_4^+, NH_3, NH_2^-, NH^{2-}, N^{3-}, and C≡O. The above definition is then extended to give the size of any functional group and the directional properties of its electronic charge distribution. An application to the FCH_2 and OH groups of FCH_2–OH as a function of rotational angle is presented as an example.

In the conformational analysis, developed by Barton[2] and Prelog[3] some 20 years ago, strong emphasis was placed on the structure of cyclohexane derivatives.

(1)

It was generally believed that the ring reversal equilibrium (1) is shifted to the right because of the difference in the magnitude of 1,3,5 (nonbonded) *repulsive interactions.* This has been formulated in a different style by stating that *bulky groups prefer equatorial (e) over axial (a) position.*

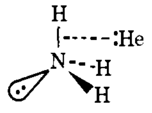
The nitrogen analogs of cyclohexane (*e.g.*, C_1H–R is replaced by N–R) are fundamentally more complicated because inversion at the nitrogen competes with the reversal of the ring.[4a]



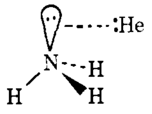
(2)

Nevertheless it seemed reasonable to pose the question: which "group" is larger, *viz.*, the lone pair or the N–H bond (if R = H)? Of course this type of questioning represents a *classical point of view.*

Subsequently the 1,3,5 repulsive interaction was formulated in terms of the concept of *electron pair repulsion* and model studies such as I and II were performed[4b] to provide a quantum chemical description of the problem.



I



II

In recent years, many types of experiments have been conducted to determine whether a certain hydrogen atom bonded to nitrogen is axial or equational (see, for sample, ref 5). This line of research stems from the pioneering work of Fodor and coworkers[6] associated with the phenomenon of selective N-quaternization.[7] Once such determinations are made, conclusions are often made regarding relative size of nitrogen lone pair and N–H bonds.

Allinger and his coworkers were the first[8] to point out how nebulous the concept of the relative size of a lone pair becomes when one is trying to justify experimentally observed phenomena on the basis of empirically derived rules for the relative sizes of lone pairs. There is simply no experiment that requires the size of a lone pair to be considered explicitly.

From a theoretical point of view, the difficulty arises

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(2) D. H. R. Barton, *Quart. Rev., Chem. Soc.*, 10, 44 (1956); *J. Chem. Soc.*, 1027 (1953); *Experientia*, 6, 316 (1950).

(3) V. Prelog, *J. Chem. Soc.*, 420 (1950).

(4) (a) J. B. Lambert, W. L. Oliver, Jr., and B. S. Packard, *J. Amer. Chem. Soc.*, 93, 933 (1971); (b) N. L. Allinger and J. C. Tai, *ibid.*, 87, 1227 (1965).

(5) R. A. Y. Jones, A. R. Katritzky, A. C. Richards, R. J. Wyatt, R. J. Bishop, and L. E. Sutton, *J. Chem. Soc. B*, 127 (1970).

(6) G. Fodor, K. Koczka, and J. Lestyan, *Magy. Kem. Foly.*, 59, 242 (1953); *J. Chem. Soc.*, 1411 (1956).

(7) G. Fodor, N. Mandava, D. Frehel, and M. J. Cooper, "Conformational Analysis," Academic Press, New York, N. Y., 1971, p 73.

(8) N. L. Allinger, J. A. Hirsch, and M. A. Miller, *Tetrahedron Lett.*, 38, 3729 (1967).

because we tend to associate the term size with the spacial extent and directional properties of the electronic charge distribution of electron pairs and then formulate semiclassical electrostatic arguments based on the interaction of these electronic charge distributions (*e.g.*, electron pair repulsion). The classical concept of electrostatic repulsion, *viz.*, that molecules tend to exist preferentially in a structure in which there is a maximum separation between localized groups of electrons, breaks down in this context because there is no way to account for the directional properties of the nuclear repulsion or the "exchange attraction." (For example, one can calculate an electronic bond moment of a lone pair, but there is no precisely defined way to calculate the nuclear contribution to the total bond moment of a lone pair.)

In this paper we propose a definition of the size of an electron pair which can be applied within the framework of almost any non- or semiempirical molecular orbital method. The definition of "size" proposed embodies the notion of spacial extent of the charge distribution and its directional properties. The computed size is then correlated with calculated total energies and other features of the molecules. The important feature of this definition is that it allows a numerical result to be calculated for the size of a given electron pair or functional group for a given molecule. This result can then be compared with numerical results in different molecules or different conformations of the same molecule.

Recent investigations in this laboratory[9,10] using geminal (two-electron) wave functions have shown that the definition of size proposed herein can be correlated with the magnitudes of intra- and inter-pair correlation effects. The present work indicates a much more general applicability.

Theory

In the present paper we shall limit our discussion to the case where the wave function of the molecule can be written as a single antisymmetrized product of doubly occupied molecular orbitals.[11] To be useful the "theoretical" definition of the size of an electron pair should satisfy the following requirements. (1) It should be independent of the choice of atomic orbital (AO) basis in which the molecular orbitals (MO) are expanded. This implies that the definition is *independent* of any assumed *hybridization scheme*. (2) It should be applicable to both semiempirical and nonempirical wave functions. (3) It should be capable of a simple geometric interpretation in terms of the stereochemistry of the molecule under consideration. (4) It should permit calculation of the size to be performed without difficulty.

With these points in mind we propose the following formal definition of the size of an electron pair. For purposes of the interpretation of electronic state wave functions constructed from doubly occupied molecular orbitals, the "size" of an electron pair, which can be *identified* with a doubly occupied localized molecular orbital (LMO), can be represented by a sphere of radius equal to the root mean square of the distance of an electron associated with the pair from the centroid of charge of the pair.

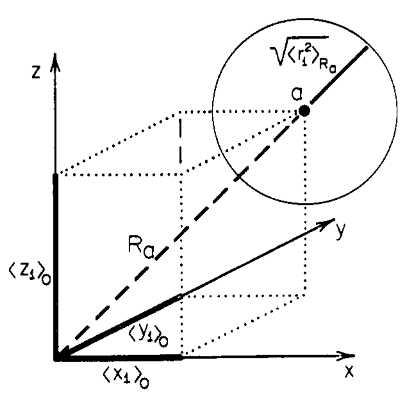

Figure 1. A schematic representation of the centroid of charge (R_a) and the size ($\langle r_1{}^2\rangle_{R_a}$) of an electron pair.

The word "size" implies a rather loose classical concept; however, the centroid of charge is obtained as the expectation value of the dipole length operator $\mathbf{r}_1$ with respect to the LMO, while root mean square of the distance of an electron from the centroid is obtained by taking the square root of the sum of expectation values, with respect to the LMO, of the second moment operator $r_1{}^2$ with the origin taken to be the centroid of charge. Thus the concept of size is related to precisely defined mathematical quantities.

The above definition can be illustrated mathematically in the following way. Let ψ_a be a LMO associated with electron pair a. Let R_a be the centroid of charge (3) of the two electrons associated with the LMO.

$$|R_a| = \sqrt{x_a{}^2 + y_a{}^2 + z_a{}^2} \tag{3}$$

Then the coordinates of R_a may be defined (4) in the following way

$$\begin{aligned} x_a &\equiv \langle x_1\rangle_0 = \langle\psi_a|\mathbf{x}_1|\psi_a\rangle_0 \\ y_a &\equiv \langle y_1\rangle_0 = \langle\psi_a|\mathbf{y}_1|\psi_a\rangle_0 \\ z_a &\equiv \langle z_1\rangle_0 = \langle\psi_a|\mathbf{z}_1|\psi_a\rangle_0 \end{aligned} \tag{4}$$

where the origin for x_1, etc., is arbitrary. The size of the electron pair associated with the LMO a is thus proportional to the expectation value

$$\langle\psi_a|r_1{}^2|\psi_a\rangle_{R_a} \equiv \langle r_1{}^2\rangle_{R_a} \tag{5}$$

where

$$\langle r_1{}^2\rangle_{R_a} = \langle x_1{}^2\rangle_{R_a} + \langle y_1{}^2\rangle_{R_a} + \langle z_1{}^2\rangle_{R_a} \tag{6}$$

The actual calculation can be conveniently carried out by noting the following relation.

$$\langle r_1{}^2\rangle_{R_a} = |\langle\psi_a|r_1{}^2|\psi_a\rangle_0 - R_a{}^2| \tag{7}$$

A graphical representation of some of the above quantities is shown in Figure 1.

We chose to formulate the definition in terms of LMO for the following reasons. (1) LMO's correspond most closely to classical descriptions of molecular structure. (2) For LMO the effect of antisymmetrization is as small as possible. In other words we come as close as possible to the situation where we can *identify* pairs of

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[9] M. A. Robb, Ph.D. Thesis, University of Toronto, 1970.

[10] (a) M. A. Robb and I. G. Csizmadia, *Int. J. Quantum Chem.*, **5**, 605 (1971); (b) *ibid.*, **6**, 367 (1972).

[11] In fact, the definition we propose is applicable to any type of wave function where the first-order density matrix can be written as a direct sum of a density matrix for each pair of electrons.

Table I. Size and Stereochemistry of Electron Pairs in NH_4^+, NH_3, NH_2^-, and NH^{2-} with N^{3-} [a]

Molecule[b]	Distance of centroid from terminal nucleus $\lvert R_a \rvert$ Bonding pair	Lone pair	Angle between lone pairs	Angle between bonding pairs	"Size" of electron pair $\langle \psi_a \lvert r_1^2 \rvert \psi_a \rangle R_a$ Bonding pair	Lone pair
NH_4^+	1.068			109° 28′	1.881	
NH_3	1.164	0.695		107°	2.052	2.505
NH_2^-	1.269	0.816	130°	105°	2.325	3.117
NH^{2-}	1.364	0.976	123°		2.644	3.949
N^{3-}		1.142	109° 28′			4.804

[a] All distances are given in bohr atomic units: 1 bohr = 0.52917 Å. [b] All HNH angles assumed tetrahedral, and all NH bond lengths taken to be 1.918 bohr.

electrons with orbitals.[12,13] (3) The localization process makes each orbital contract as close to its centroid as possible and at the same time maximizes the distances between the centroids.[14]

In the case of nonempirical calculations, LMO can be constructed using the methods of Ruedenberg and Edmiston[12] or Boys.[14] For semiempirical work the method of Boys is still applicable, or one may use the modification of Ruedenberg's method suggested by Sinanoglu.[15]

At this point it is perhaps advisable to comment on the dependence of the results of the proposed analysis on the procedure used to obtain the LMO. While it is unlikely that the results will be very sensitive to whether the Edmiston–Ruedenberg[12] or Boys[12] method is used (provided the basis is fairly complete), in the present context the Edmiston–Ruedenberg method is to be *strongly preferred* on theoretical grounds. Since the interpretation of size given above depends upon identifying a pair of electrons with a particular LMO, the localization method should be chosen so that the effects of antisymmetrizing the wave function are as small as possible. In the Edmiston–Ruedenberg method, the sum of the exchange integrals (which arise in the energy expression because of antisymmetry) is minimized. The LMO's obtained by this method come as close as possible to the situation where the pairs of electrons interact only through their Coulomb repulsion. Boys method,[13] on the other hand, minimizes the sum of the spherical quadratic moments of each LMO with the origin at the centroid of the given LMO. As we shall illustrate, the use of the spherical quadratic moments over the LMO, as proposed by Boys, provides a useful way of *interpreting* the electronic distribution of the LMO. However, it is theoretically more fundamental to *determine* the LMO by minimizing the exchange integrals over the LMO.

The calculation of the size of an electron pair is then easy once the MO from any semiempirical or nonempirical calculation are known. The computation involves only first and second moment integrals which are no more difficult to evaluate than the overlap integrals which are encountered in all but the simplest MO theories. It should be noted that the proposed definition involves only one simple calculation for each MO whereas a definition of the size of electron pairs based on one electron density would involve thousands.

The above definition admits of a simple visual interpretation. One can construct a model of the molecule by regarding the pairs as spheres of radius $[\langle r_1^2 \rangle_{R_a}]^{1/2}$ with the center at R_a. For stereochemical considerations the angle between two electron pairs is simply the angle formed by the centroid with the terminal atom. The *interpenetration* of the pairs is represented by the amount the spheres "overlap."

The proposed definition can be extended to give the size of any functional group A. One simply calculates the centroid of charge, which we shall denote R_A, for all the electron pairs of the group (this can be done by vector addition). Thus the size of the group is given by

$$\langle r_1^2 \rangle_{R_A} = \langle \psi_{a_1} | r_1^2 | \psi_{a_1} \rangle_{R_A} + \langle \psi_{a_2} | r_1^2 | \psi_{a_2} \rangle_{R_A} + \ldots \quad (8)$$

The sum over a_i includes all the pairs associated with the group.

In conclusion, it should be noted that the proposed definition for the size of an electron pair is similar to that which might be extracted directly from the Frost model[16,17] which uses a subminimal basis of floating spherical Gaussians. In Frost's model each electron pair is represented by a single spherical Gaussian (9).

$$\psi_a = (\pi/2\alpha)^{3/4} e^{-\alpha(r_1 - A)^2} \quad (9)$$

The position of the Gaussian A and the exponent α are optimized to give the best total energy. For comparison with the definition proposed in this work, A corresponds to the centroid R_a and α is related to the size of the pair by

$$\langle \psi_a | r_1^2 | \psi_a \rangle_{R_a} = 0.75\alpha^{-1} \quad (10)$$

However, since the ψ_a's in Frost's model are not orthogonal, the two definitions are not exactly comparable. In addition, in his model lone pairs have a tendency to "collapse" into the core of the terminal atom because the core is not well represented.

Results and Discussion

In the following discussion when reference is made to size of an electron pair or functional group, we are referring to $\langle r_1^2 \rangle_{R_a}$, the expectation value of the second moment operator defined in eq 5 or 8. This is the quantity that is tabulated in Tables I–III and V. For purposes of diagrammatic representation, we represent the size by circles of radius $[\langle r_1^2 \rangle_{R_a}]^{1/2}$ as in Figures 2–4.

The results for the size and stereochemistry of electron pairs in NH_4^+, NH_3, NH_2^-, NH^{2-}, N^{3-}, C≡O,

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(12) C. Edmiston and K. Ruedenberg, *Rev. Mod. Phys.*, **35**, 457 (1963).

(13) H. Primas in "Modern Quantum Chemistry," Vol. II, O. Sinanoglu, Ed., Academic Press, New York, N. Y., 1965.

(14) S. F. Boys in "Quantum Theory of Atoms, Molecules and the Solid State," P. O. Löwdin, Ed., Academic Press, New York, N. Y., 1966.

(15) C. Trindle and O. Sinanoglu, *J. Chem. Phys.*, **49**, 65 (1968).

(16) A. A. Frost, *ibid.*, **47**, 3707, 3714 (1967).

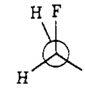
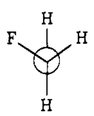
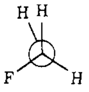
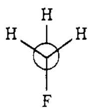
(17) A. A. Frost, *J. Phys. Chem.*, **72**, 1289 (1968).

Table II. Size and Stereochemistry of Electron Pairs in C≡O[a]

Electron pair	Coordinates of centroid of charge[b] x_a	y_a	z_a	$\lvert R_a \rvert$	Size of electron pair $\langle \psi_a \lvert r_1^2 \rvert \psi_a \rangle_{R_a}$
C_{lp}	0.0	0.0	−0.787	0.787	2.688
O_{lp}	0.0	0.0	2.706	2.706	1.539
t_1[c]	0.480	0.0	1.519	1.593	2.163

[a] Computed in a localization scheme that involves three equivalent "bend" bonds (t_1, t_2, t_3). [b] Origin at carbon with oxygen nucleus at (0, 0, 2.132). [c] Parameters for t_2 and t_3 are obtained by rotation through ±120°

Table III. Size of Electron Pairs in FCH_2OH[a] as a Function of Rotation about the C–O Bond

	$\langle r_1^2 \rangle_{R_a}$			
Electron pair	0° 	60° 	120° 	180°[b] 
n_F'	1.047	1.301	1.300	1.331
n_F''	1.312	1.319	1.328	1.310
n_F'''	1.312	1.310	1.324	1.309
n_O'	1.675	1.709	1.728	1.689
n_O''	1.675	1.742	1.826	1.696
C–H′	2.290	2.296	2.291	2.289
C–H″	2.290	2.276	2.277	2.290
O–H	1.827	1.825	1.783	1.826
C–O	2.164	2.135	2.128	2.164
C–F	1.803	1.792	1.816	1.894

[a] Details of the positions of the centroids are too cumbersome to present in this table. They can be found in ref 19. [b] Due to an instability in our method of calculating LMO for this particular conformation, the calculation is not quite converged (*i.e.*, $n_F'' \equiv n_F'''$, etc.); however, this does not effect the qualitative interpretation.

and FCH_2–OH, computed from large Gaussian basis[18] set Hartree–Fock calculations, are presented in Tables I–III. A schematic representation of these results is to be found in Figure 2 of ref 10a, Figure 1 of ref 10b, and Figure 8 of ref 19, respectively.

Detailed plots for both lone electron pairs and bonding electron pairs for the nitrogen hydride series are shown in Figure 2. The solid lines are electron density contours while the broken circles have a radius $[\langle r_1^2 \rangle_{R_a}]^{1/2}$ and represent the size of the electron pairs according to the definition proposed above. This figure shows graphically some of the results presented in Table I, indicating that in a given species the centroid of charge (R_a) for a lone pair is always closer to the nitrogen atom

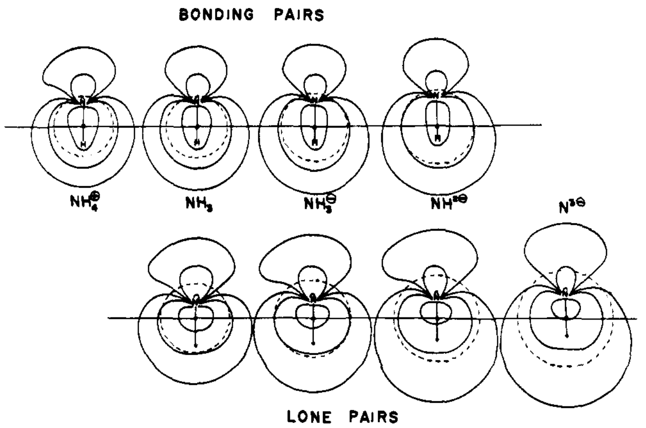


Figure 2. Electron density maps of localized molecular orbitals (LMO), representing both the lone pairs and the bonding pairs for the series of NH_4^+, NH_3, NH_2^-, NH^{2-}, and N^{3-}. The horizontal lines pass through the centroids of charge and the broken circles depict the sizes of the various electron pairs. In each LMO the three contours from the centers outward represent the densities of 0.2, 0.02, and 0.002 e/bohr³. The deviation from cylindrical symmetry in the smaller (upper) lobes is due to the perturbing effect of the adjacent hydrogen nucleus.

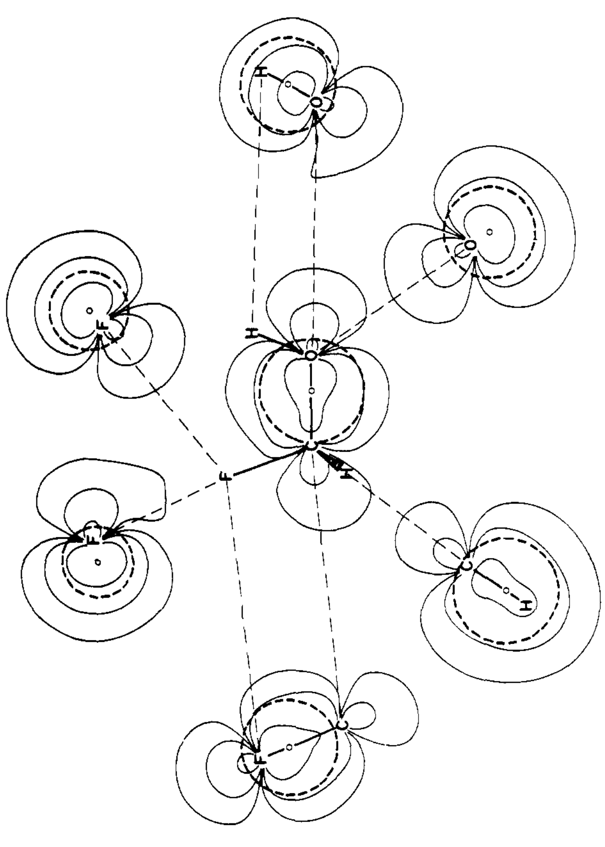


Figure 3. Electron density maps of localized molecular orbitals (LMO) representing the valence electrons in FCH_2–OH. In each LMO the three contours from the centers outward represent the densities of 0.2, 0.02, and 0.002 e/bohr³. The broken circles depict the sizes of the various electron pairs.

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(18) Details of the basis sets can be found in ref 10 and 19. In each case the contracted Gaussian basis sets are of at least "best atom double ζ quality. In addition, for NH_3, calculations have been carried out with and without off-center Gaussian functions to represent the nitrogen lone pair. The value of R_a for the lone pair of NH_3 in Table I is 0.695. This calculation included an off-center set of s- and p-type functions. When these are removed the value of R_a decreases slightly to 0.678. A similar reduction is noted for the bonding pair (*i.e.*, from 1.164 to 1.155). The exchange integrals (used in the localization) for the bond–bond and bond–lone pair interaction in NH_3 were 0.0250 and 0.0353 for the case with off-center Gaussians and 0.0256 and 0.0351 for the case without off-center Gaussians. Thus, as far as the effect we are calculating is concerned, we are confident that the basis is quite complete and thus the results are basis set independent (*i.e.*, the effect of off-center Gaussians is small).

(19) S. Wolfe, L. M. Tel, W. J. Haines, M. A. Robb, and I. G. Csizmadia, unpublished results.

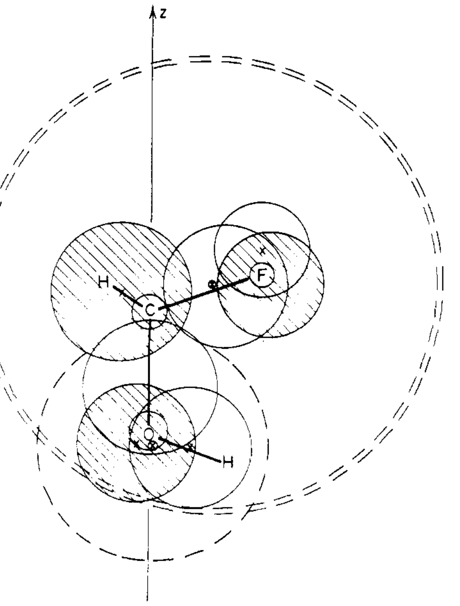

Figure 4. A comparison of LMO sizes and group sizes. The size of the OH group is the lower broken line; the sizes associated with the FCH_2 group are given by the two concentric upper circles (broken lines). The inner circle represents the 0° conformation (as the molecule shown); the outer circle corresponds to the 180° rotation of the OH group.

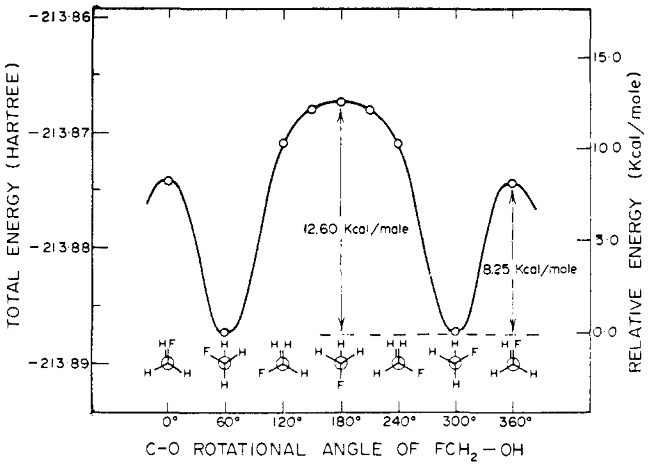

Figure 5. The total energy of FCH_2–OH as a function of rotation about the C–O bond.

Table IV. Correlation between van der Waals' Radii and Size of Electron Pairs[a]

Atom	$D = R_a + [\langle r_1^2\rangle_{R_a}]^{1/2}$	van der Waals' radii (W)[b]
C	1.29[c]	1.8
N	1.20[d]	1.5
O	0.96[c]	1.4
F	0.86[e]	1.35

[a] All values are in ångström units. [b] L. Pauling, "The Nature of Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960, p 260. [c] Calculated from CO lone pairs in "banana" localization. [d] Calculated from nitrogen lone pair in NH_3. [e] Calculated from F lone pairs in FCH_2OH.

than that of a bonding electron pair. However, the size ($\langle r_1^2\rangle_{R_a}$) of a lone electron pair is larger than that of a bonding electron pair. Moreover, both the distance of the centroids (R_a) and the sizes of the electron pairs ($\langle r_1^2\rangle_{R_a}$) are increasing as one goes from NH_4^+ to N^{3-}. It is reassuring to note that the electron density contours convey essentially the same information, in a qualitative sense, as the plots of $[\langle r_1^2\rangle_{R_a}]^{1/2}$.

Figure 3 gives a pictorial summary of the sizes (broken circles) of the bonding and lone electron pairs in FCH_2–OH (*cf.* first column of numbers in Table III) together with the corresponding electron density contours. At this stage it might be appropriate to point out that the individual sizes[20] of the three equivalent bonds in C≡O (2.163 in Table II) are within the range of the size of the C–O σ bond (2.128–2.164 in Table III) as it varies with the internal rotational angle in FCH_2–OH. Also, the size of the oxygen lone pair in :C≡O: was computed to be 1.539 which is within the range of the sizes of the oxygen lone pairs (1.526–1.742) obtained for the different conformations of FCH_2–OH. A recent study[19] which included CH_3OH seems to confirm the "transferability" of electron pairs in the sense that the sizes of corresponding electron pairs (*e.g.*, C–H bonding pair, oxygen lone pair) are practically the same in FCH_2–OH and CH_3–OH.

It is also of interest to see if there is any correlation between the size of the electron pairs on the atoms and the van der Waals' radii (W). We choose the quantity

$$D = R_a + [\langle r_1^2\rangle_{R_a}]^{1/2} \qquad (11)$$

to compare with the van der Waals' radius. The results are tabulated in Table IV. It can be seen that the numbers do indeed suggest some correlation. The systematic discrepancy $D < W$ could be interpreted in two ways. Firstly, the charge distribution is not spherical (*i.e.*, $\langle x^2\rangle \neq \langle y^2\rangle \neq \langle z^2\rangle$) as expected. Secondly, the low electron densities, outside the electron pair spheres, are still of significance in determining the nonbonded potential. However, one would require the results of a large number of calculations to establish a definite corelation.

Another point of interest was the change of size with rotational angle. Because the data presented in Table III revealed no correlation with the rotational potential (*cf.* Figure 5), it seemed desirable to calculate group sizes according to eq 8 utilizing the computed raw data (*cf.* Table V).

The size of the OH group is essentially the same at the 0 and 180° rotational angles and the centroid of the group of electrons falls almost onto the z axis (C–O bond). However, the centroid of the group of electrons calculated for the FCH_2 group did not occur on the rotational z axis (halfway along the C–F bond) and the variation of its size with the rotation about the C–O bond revealed a number of interesting points. First, as might be expected, the size of the FCH_2 group is considerably larger than that of the OH group. More important, however, is the observation that the size of the FCH_2 group varies in a remarkable way with the rotational angle. It is the smallest at 0° rotation and it expands to a somewhat larger volume at 180°. The minima (0 and 360°) and the maximum (180°) are illustrated as two concentric circles (the two largest circles), denoted by broken lines in Figure 4. This periodic function of group size is also shown by the top curve in Figure 6. It is evident that the shape of this

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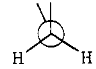
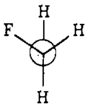
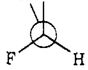
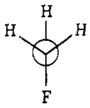
[20] All values are quoted in atomic units, *i.e.*, in units of bohr^2 (1 bohr = 0.52917 Å).

Table V. Sizes of a Group of Electron Pairs in FCH_2OH as a Function of Rotational about the C–O Bond[a]

		Rotational angle			
		0°	60°	120°	180°
Group	Component of $\langle r_1^2 \rangle$				
FCH_2	$\langle x^2 \rangle + \langle y^2 \rangle$	22.543	22.497	22.588	22.715
	$\langle z^2 \rangle$	3.537	3.792	3.728	3.730
	$\langle r^2 \rangle$	26.080	26.289	26.316	26.444
OH	$\langle x^2 \rangle + \langle y^2 \rangle$	4.985	5.019	5.006	5.017
	$\langle z^2 \rangle$	1.655	1.727	1.767	1.677
	$\langle r^2 \rangle$	6.639	6.746	6.773	6.694

[a] Calculated by eq 8. Each term in eq 8 corresponds to the definition given by eq 7.

curve is substantially different from that of the rotational potential (*cf.* Figure 5).

Examination of the various projections (*cf.* second curve from the top in Figure 6) revealed that the fluctuation of the size in the x,y plane (perpendicular to the rotational axis) corresponded most closely to the rotational potential. Its minimum was at 60°, its lowest maximum at 0°, and its highest maximum at 180° (*cf.* Figure 5).

The analysis becomes possible by considering the decomposition of $\langle r^2 \rangle$ for the FCH_2 and OH groups into directions (a) perpendicular to the rotation axis $\langle x^2 \rangle + \langle y^2 \rangle$ and (b) along the rotation axis $\langle z^2 \rangle$. From Figure 6 it can be seen that most of the variation in $\langle r^2 \rangle$ for the OH group results from changes in $\langle z^2 \rangle$ which increases from 0 to 120° and then decreases from 120 to 180°. The variations of the $\langle z^2 \rangle$ and $\langle x^2 \rangle + \langle y^2 \rangle$ components of $\langle r^2 \rangle$ for the FCH_2 group are out of phase. On going from 0 to 60° the size of FCH_2 group shrinks in the x and y directions (perpendicular to the rotation axis) and *increases sharply* in the direction of the rotation axis z. The minimum at 60° in the energy profile (Figure 5), corresponding to the F atom being gauche with respect to the hydroxyl proton, is associated with an increase in $\langle z^2 \rangle$ for both the OH and FCH_2 groups and a small decrease in $\langle x^2 \rangle + \langle y^2 \rangle$ for the FCH_2 groups. From 60 to 180°, $\langle z^2 \rangle$ for the FCH_2 group decreases slightly and the $\langle x^2 \rangle + \langle y^2 \rangle$ increases rapidly to a maximum at 180° corresponding to the least stable conformation. At the same time the $\langle z^2 \rangle$ component for the OH group increases slightly going from 60 to 120° and then decreases from 120 to 80°. Thus, the approach to the energy minimum (60°) is accompanied by an increase of the $\langle z^2 \rangle$ components of both OH and FCH_2 and the approach to energy maxima (0 and 180°) is characterized by a large increase in the $\langle x^2 \rangle + \langle y^2 \rangle$ component of FCH_2 and a decrease of the $\langle z^2 \rangle$ component of the OH group.

In simpler terms, as we approach the energy minimum the size of the groups increases in the direction of the rotation axis. What this means is that in the most stable structure there is a drift of electronic charge from both groups into the C–O bonding region. Conversely, as we approach the energy maxima the charge drifts away from the rotational axis into the plane perpendicular to this axis.

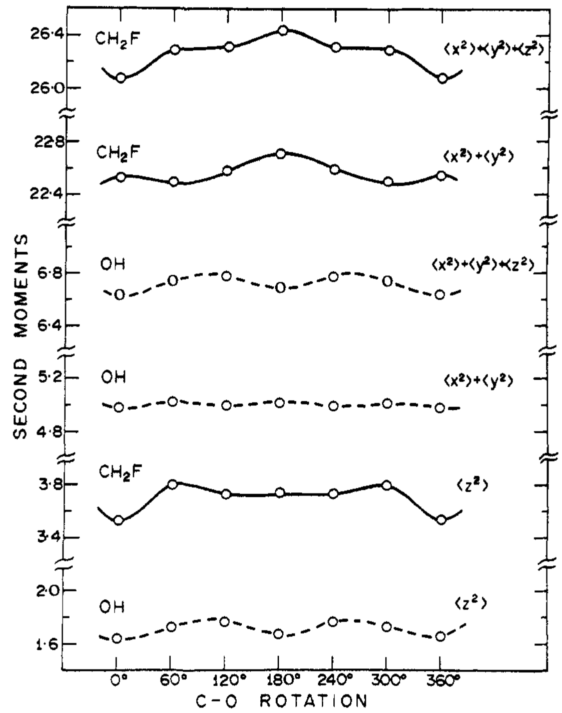


Figure 6. The periodic variation of groups sizes ($\langle x^2 \rangle + \langle y^2 \rangle + \langle z^2 \rangle$) for the FCH_2 and OH groups. The components along the rotational axis ($\langle z^2 \rangle$) as well as in the plane perpendicular to the rotational axis ($\langle x^2 \rangle + \langle y^2 \rangle$) are also shown.

Conclusion

It is important at this point to comment on the chemical significance of these results. In attempting to do so, it must be realized that the analysis of size and directional properties of the *electronic charge distribution* presented in this work must be *correlated* with the calculated *total energy* of the system. Unfortunately there is no method to group *attractive* and *repulsive* effects into an *additive partition* among the localized pairs or functional groups. This is because there is no way to partition the nuclear repulsion energy among the bonding and lone pairs. Thus, we can only establish the correlation of changes in size and shape of pairs of electrons and functional groups with changes in total energy. It is very unsound to attempt to interpret the analysis presented here in terms of electron-pair repulsion arguments because the analysis is based on additive partition of the electronic charge distribution and the effects of nuclear repulsion cannot be unambiguously included.

The most significant feature of the results presented in this work is that they are not necessarily at variance with semiclassical ideas about the electronic charge distribution of electron pairs in molecules, provided one does not fall into the trap outlined in the previous paragraph. For example, the results concerning the increase in the $\langle z^2 \rangle$ components of both FCH_2 and OH are not unexpected; they represent relaxations of the charge distribution which occur because the relaxation of the angle from 0 to 60° allows them to occur with a resultant lowering of the *total* energy (*cf.* Figure 5). The significant fact is that the present analysis allows one to calculate a numerical value for the magnitude of this effect which can be related to similar situations in other molecules and *correlated* with larger or smaller energy lowerings.

The increase in $\langle r_1^2 \rangle$ for the nitrogen lone pairs and bonding pairs on going from NH_4^+ to N^{3-} and the relative magnitudes of $\langle r_1^2 \rangle$ for bonding and lone pairs in these species is completely in accord with semiclassical ideas. However, when we come to a more complicated example[21] like FCH_2OH, one's intuition does not take one quite so far. Nevertheless, the relative magnitude of $\langle r_1^2 \rangle$ for the different pairs is more or less what one would expect and it is reassuring that the value of $\langle r_1^2 \rangle$ for the different pairs does not change too drastically with rotational angle. The change in the electronic charge distribution with rotational angle is a more subtle effect associated with the nonspherical components of $\langle r_1^2 \rangle$ for the functional groups as a whole. Thus the chemical significance of these results lies in the fact that we have been able to correlate a precisely defined mathematical quantity (which can be extracted from both nonempirical and semiempirical wave functions), the expectation values of dipole length and second moment operators, with a loose semiclassical concept.

It is noteworthy that, using the definition proposed in eq 5, it has been possible to transform a rather complicated wave function into a relatively simple picture. We hope therefore that the present results and the conclusions we have reached will stimulate interest in the generation of similar data from semiempirical wave functions as well as nonempirical ones. Provided that LMO's are used, the results from the semiempirical work should be as meaningful as those from nonempirical calculations. Hopefully, after a sufficient number of sufficiently diverse "model" compounds have been studied, it may be possible to derive a new set of empirical rules to correlate the size of electron pairs or the sizes of functional groups with molecular geometry.

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Thermodynamics of Ionization of Diastereoisomeric Forms of 2,3-Dicarboxylic Acids

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Abstract: Thermodynamic parameters for the ionization of the *dl* and meso isomers of 2,3-dimethylsuccinic acid and tartaric acid have been determined from a temperature dependence study of the ionization constants calculated from potentiometric data obtained using cells without liquid junction. The data are significantly different between isomers of the same acid and these differences are discussed in terms of proximity effects between functional groups.

In a recent publication from this laboratory, advantage was taken of the small differences in ionization constants for the *dl* and meso forms of 2,3-disubstituted succinic acids to develop an analytical procedure to determine the composition of mixtures of the two pure forms using data from pH titrations.[2] Subsequent to this, in order to establish the thermodynamic reasons for the subtle differences in $\Delta G°$ of ionization, pK values were determined as a function of temperature to obtain $\Delta H°$ and $\Delta S°$ for the *dl* and meso forms of 2,3-dimethylsuccinic acid (DMSA) and tartaric acid (TA). The results are presented here and contrary to what might have been anticipated, there are significant differences between the $\Delta H°$ terms for the *dl* and meso forms of the same acid. This result could have significant bearing upon our understanding of the specificity of isomeric forms to reaction at the micro-

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