The Gauche Effect. A Study of Localized Molecular Orbitals and Excited-State Geometries in FCH_2OH

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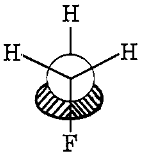
Abstract: Near Hartree–Fock molecular wave functions have been computed for several conformations of fluoromethanol using a contracted Gaussian basis set. The computed potential energy curve for the ground state shows a single minimum which corresponds to the conformation in which the polar CF and OH bonds are gauche. The conformation in which these bonds are *anticoplanar* is the energy maximum. However, in the lowest lying singlet excited state the anticoplanar conformation is an energy minimum and is *more stable* than the gauche. The canonical molecular orbitals (CMO) have been localized by the method of Edmiston and Ruedenberg. The group sizes derived from the localized molecular orbitals (LMO) have been correlated with the potential curve associated with rotation along the C–O bond. Analysis of these latter data has provided additional theoretical support for the notion that, in a system containing geminal lone pairs, these jointly behave in a nondirectional manner.

In the course of our theoretical studies of the gauche effect,[3] we have already presented[4] the results of a series of near molecular Hartree–Fock calculations on fluoromethanol (FCH_2OH). On the basis of several types of criteria, it was concluded that the gauche effect exhibited by this compound is best understood in terms of the interactions of the polar C–F and O–H bonds with each other. Support for this conclusion, and for its formalization into rule 3 of the gauche effect, was obtained subsequently from a study of rotation–inversion in ethylene dicarbanion.[5]

The somewhat provocative physical description that seems to be emerging from these studies is that electron pairs adjacent to each other or to polar bonds behave as though they have no directional character. Structure **1**, for example, which corresponds to the energy maximum of FCH_2OH,[6] represents an attempt to convey this idea.



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It seemed important to subject this (intuitively deduced) concept to more rigorous analysis, beginning with an examination of the localized molecular orbitals (LMO)[7] and the derivation of theoretical descriptions for the size of an electron pair or group of electron pairs.[8] These criteria have already been applied in an illustrative manner[8,9] to our fluoromethanol wave functions, and the purpose of the present paper is to provide a detailed account of the results and their possible significance. In the course of these further studies, we have also determined a number of additional properties of FCH_2OH. These have led, among others, to the finding that the gauche effect *is a ground-state property only.*

Method

An extensive contracted Gaussian basis set was used in which the primitive Gaussian-type functions (GTF) were contracted to a set of double ζ basis functions (BF). The basis set consisted of 13^s7^p primitive GTF on C, O, and F, and 4^s primitive GTF on H, yielding a total of 114 primitive GTF. The contraction to 36 BF, corresponding to a double ζ basis, was achieved by the following scheme: [4, 4, 3, 2; 4, 3] on C, O, and F, and [3, 1] on H. The orbital exponents and contraction coefficients are summarized in Table I.[10,11] The nonempirical SCF–MO computations were performed on an IBM 7094-II computer using a modified version of the IBMOL-II program system.[12a] The nuclear-electron potential (V_{ne}) was computed by the one-electron properties package of the POLYATOM-2 program system.[12b] The algorithm required for the localization program has been discussed elsewhere.[12c] Standard bond lengths and bond angles[4] were used for the study of internal rotation along the C–O bond. The corresponding atomic coordinates are summarized in Table II.

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[3] S. Wolfe, *Accounts Chem. Res.*, **5**, 102 (1972).

[4] S. Wolfe, A. Rauk, L. M. Tel, and I. G. Csizmadia, *J. Chem. Soc. B*, 136 (1971).

[5] S. Wolfe, L. M. Tel, J. H. Liang, and I. G. Csizmadia, *J. Amer. Chem. Soc.*, **94**, 1361 (1972).

[6] This corresponds to structure **52** of ref 4.

[7] W. England, L. S. Salmon, and K. Ruedenberg, *Top. Curr. Chem.*, **23**, 31 (1971).

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[9] R. F. W. Bader in "The Chemistry of the Hydroxyl Group," S. Patai, Ed., Wiley, New York, N. Y., 1971, Chapter 1.

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[11] S. Huzinaga, *ibid.*, **50**, 1371 (1969).

[12] (a) E. Clementi and D. R. Davis, *J. Comput. Phys.*, **1**, 223 (1966); Quantum Chemistry Program Exchange, No. 92, Indiana University, Bloomington, Ind., 1967; (b) I. G. Csizmadia, M. C. Harrison, J. W. Moskowitz, and B. T. Sutcliffe, *Theor. Chim. Acta*, **6**, 191 (1966); **7**, 156 (1967); Quantum Chemistry Program Exchange, No. 47, Indiana University, Bloomington, Ind., 1966; (c) M. A. Robb, Ph.D. Thesis, University of Toronto, 1970; microfilmed copies of this thesis may be obtained by writing to the National Library of Canada, Ottawa, Canada.

Table I. Orbital Exponents and Contraction Coefficients

AO	H		C		O		F	
	α	c	α	c	α	c	α	c
1s	0.65341	0.817238	16,067.118	0.00488113	30,518.035	0.00596971	26,923.4	0.00420568
	2.89915	0.231208	2,365.8824	0.03666171	4,547.8916	0.03377690	3,428.22	0.03781164
	19.24060	0.032828	542.29752	0.19235652	1,044.4654	0.21239072	745.107	0.19785567
			148.23131	0.83226855	284.96896	0.81642901	203.344	0.82782317
1s′	0.17758	1.000000	46.007872	0.14054240	91.606655	0.12837000	63.5067	0.23514007
			15.853338	0.33170913	30.986724	0.31878733	22.4373	0.43711627
			5.8801611	0.44811123	11.579711	0.44575201	8.63279	0.36917806
			2.2821385	0.20070592	4.4835041	0.22882639	3.22857	0.06485356
2s			4.1833454	−0.11120774	8.7266833	−0.10592444	10.473688	−0.10205764
			0.61690053	0.45737488	1.1646190	0.48187350	1.6207397	0.44611175
			0.27424365	0.61628652	0.50640464	0.58931175	0.70588463	0.62641995
2s′			0.13395691	0.88103498	0.24817481	0.85204459	0.33187308	0.85900674
			0.06156188	0.13097420	0.12280187	0.15971827	0.15353852	0.15458379
2p			42.0201	0.00972229	78.6030	0.01164590	101.240	0.01107586
			8.90332	0.07475669	17.5167	0.08317463	24.4512	0.07521217
			2.57917	0.30378031	5.54421	0.30401735	7.76131	0.29432156
			0.894870	0.72648088	2.05152	0.71187222	2.77672	0.72856355
2p′			0.338303	0.59375648	0.794239	0.52044716	1.03703	0.52821036
			0.137610	0.40757742	0.305583	0.45886016	0.385520	0.45678189
			0.055645	0.08518435	0.112384	0.13213193	0.136844	0.13348833

Table II. Atomic Coordinates (in Atomic Units)[a]

Atom	x	y	z
C	0	0	−1.34928030
O	0	0	1.34928030
F	2.4498022	0	−2.2154051
H_1[b]	−0.97190328	−1.6833860	−2.0365109
H_2[b]	−0.97190328	1.6833860	−2.0365109
H_3[c] (0°)[d]	1.7104074	0	1.9539929
H_3 (60°)	0.8552037	1.4812562	1.9539929
H_3 (120°)	−0.8552037	1.4812562	1.9539929
H_3 (150°)	−1.4812563	0.85520357	1.9539929
H_3 (180°)	−1.7104074	0	1.9539929

[a] Bond lengths are C–F, 1.375 Å; C–H, 1.091 A; C–O, 1.428 Å; O–H, 0.96 Å. All angles between bonds attached to the same atom are tetrahedral. [b] Methylene protons. [c] O–H proton. [d] Fluorine eclipsed with H_3.

The total energy of a molecular system is given as

$$E = \mathrm{tr}(2\rho\mathbf{H}) + \mathrm{tr}(\rho\mathbf{G}) \qquad (1)$$

and the symmetry-adapted canonical molecular orbitals (CMO) are obtained, in the SCF procedure, from the Fock matrix.

$$\mathbf{F} = \mathbf{H} + \mathbf{G} \qquad (2)$$

In these expressions, ρ is the density matrix, **H** is the matrix representative of the total one-electron operator, and **G** is the matrix representative of the two-electron operator. Since this latter term represents electron–electron repulsion, the last term in eq 1 is often labeled V_{ee}. The V_{ee} term, in turn, is frequently expressed as a combination of Coulombic (V_{ee}^{Coul}) and exchange (V_{ee}^{Exch}) terms.

$$V_{ee} = V_{ee}^{\mathrm{Coul}} - V_{ee}^{\mathrm{Exch}} \qquad (3)$$

These are formed by the summation of Coulomb (J_{ij}) and exchange (K_{ij}) integrals, respectively. Although the J and K integrals may be expressed over any orbital basis, the expressions become simpler if they are transformed to the MO basis.

Because the diagonal elements (J_{ii} and K_{ii}) are identical, there is no unique way to carry out the summation of J_{ij} and K_{ij} and, in principle, they might be included in the Coulombic term, in the exchange term, or in both. Thus, one way to separate the integrals (method A) involves the inclusion of the diagonal elements in both the Coulombic and exchange terms.

$$V_{ee}^{\mathrm{Coul}} = 2\sum_i\sum_j J_{ij} \qquad (4a)$$

$$V_{ee}^{\mathrm{Exch}} = \sum_i\sum_j K_{ij} \qquad (4b)$$

A second separation (method B) involves the inclusion of the diagonal elements in the Coulombic term only, and implies that "self-exchange" has no physical meaning.

$$V_{ee}^{\mathrm{Coul}} = \sum_i J_{ii} + 2\sum_i \sum_{j(\neq i)} J_{ij} \qquad (5a)$$

$$V_{ee}^{\mathrm{Exch}} = \sum_i \sum_{j(\neq i)} K_{ij} \qquad (5b)$$

It is important to note that, in method A, both terms are invariant under any unitary transformation of the MO basis (*i.e.*, their numerical values are identical for both delocalized and any localized MO). However, in method B, neither of the terms is invariant. In fact, it is this characteristic property which is utilized as the localization criterion in the method of Edmiston and Ruedenberg.[13]

The most objective localization procedure that could be employed would involve the construction of orbitals which are separated from each other as much as possible, without having to stipulate in advance the location of these orbitals in space. Such a localization would require only that the definition of "separation" be decided upon *ab initio*. The Edmiston–Ruedenberg separation of orbitals involves maximization of the total self-repulsion, *i.e.*, of the first term on the right-hand side of eq 5a. This term is referred to as the localization sum.

$$J_0 = \sum_i J_{ii} \qquad (6)$$

The larger the J_0, the more localized the orbitals. Because V_{ee}, as defined in eq 3, remains invariant, the

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(13) C. Edmiston and K. Ruedenberg, *Rev. Mod. Phys.*, 35, 457 (1963); *J. Chem. Phys.*, 43, 597 (1965).

maximization of J_0 automatically implies a minimization of the remaining terms of eq 5a and 5b.

Following the suggested nomenclature of Edmiston and Ruedenberg,[13] these "energy localized" orbitals are referred to as "localized molecular orbitals" (LMO). Although in their original method the unitary matrix (U), which transforms the HF-type CMO basis (ϕ) to the LMO basis (ψ), is obtained by a series of Jacobi

$$\psi = \phi \mathbf{U} \tag{7}$$

type 2 × 2 rotations, in the present work localization was achieved by the method of steepest ascent, as suggested by Taylor.[14,15]

Results and Discussion

Estimation of the Hartree–Fock Limit. Comparison of a calculated energy with that estimated for the Hartree–Fock Limit (HFL) is always an important criterion for the accuracy of a computed wave function. To estimate the HFL one needs the experimental energy (E_{exp}) which is the sum of the atomic energies (E_{atom}), the experimental dissociation (*i.e.*, atomization) energy (E_{diss}), and the zero point vibrational energy $(E)_{\text{ZPV}}$.

$$E_{\text{exp}} = E_{\text{atom}} + E_{\text{diss}} + E_{\text{ZPV}} \tag{8}$$

We define

$$E_{\text{exp}} = E_{\text{tot}} \tag{9}$$

where E_{tot}, the total energy of the molecule, is the sum of the following theoretical quantities: E_{HFL}, the correlation energy (E_{corr}), and the relativistic correction (E_{rel}).

$$E_{\text{tot}} = E_{\text{HFL}} + E_{\text{corr}} + E_{\text{rel}} \tag{10}$$

From eq 8–10 we have

$$E_{\text{HFL}} = E_{\text{tot}} - (E_{\text{corr}} + E_{\text{rel}}) \tag{11}$$

The estimation of E_{corr} and E_{rel} is explained in the footnotes to Table III. It should be noted that the components E_{diss} and E_{ZPV} of E_{exp} are not available so that the HFL calculation summarized in Table III should therefore be considered as a preliminary estimate only. A schematic comparison, for the gauche structure, of the energy values reported by Pople[16] and the present values with the estimated molecular energetics is given in Figure 1.

Conformational Analysis. The orbital energies and the total energy values are summarized in Tables IV and V, respectively. Figure 2 shows these latter data as a function of the rotational angle about the C–O bond, together with the computed rotational potential function obtained for methanol.[17] Intuitively, one might have expected from such a comparison that an energy minimum should have been observed for fluoromethanol at the 180° (anticoplanar) conforma-

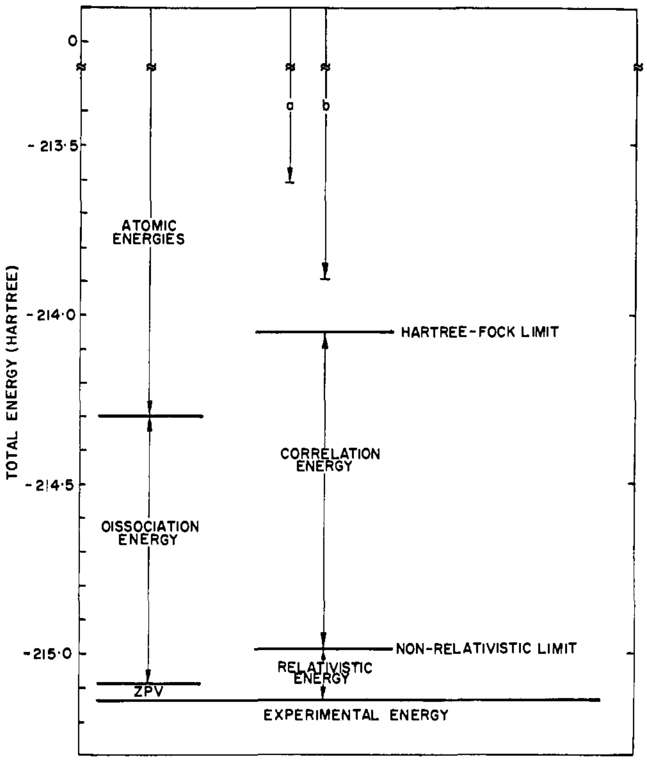

Figure 1. The estimated molecular energetics of fluoromethanol: (a) ref 16; (b) present work.

Table III. Data Employed to Estimate the Hartree–Fock (HF) Limit for Fluoromethanol

A. Data for the Constituent Atoms of FCH_2OH

Atom	E_{HF}[a]	E_{corr}[b]	E_{rel}[c]	Total atomic energy
C	−37.6886	−0.1581	−0.0138	−37.8605
O	−74.8093	−0.2575	−0.0494	−75.1162
F	−99.4093	−0.3236	−0.0829	−99.8158
H	−0.5000			−0.5000
Sum for FCH_2OH	−213.4072	−0.7392	−0.1461	−214.2925

B. Data for FCH_2–OH

Exptl component	E (hartrees)	Theoretical component	E (hartrees)
Total atomic energy	−214.293[d]	Hartree–Fock energy[g]	−214.053
Dissociation energy	−0.799[e]	Correlation energy[h]	−0.937
Zero-point energy	−0.044[f]	Relativistic energy[i]	−0.146
Experimental energy	−215.136	Total energy	−215.136

[a] From E. Clementi, *J. Chem. Phys.*, **38**, 1007 (1963). [b] From E. Clementi, *ibid.*, **39**, 175 (1963). [c] From E. Clementi and A. D. McLean, *Phys. Rev. A*, **133**, 419 (1964). [d] Given as the final sum in Table IIIA. [e] Calculated from the heats of formation; R. C. Weast, S. M. Selby, and C. D. Hodgman in "Handbook of Physics and Chemistry," 46th ed, The Chemical Rubber Co., Cleveland, Ohio, 1965–1966, pp D51 and F126. [f] Fluorine substitution on small molecules causes a lowering of the zero-point vibrational energy by about 3 kcal/mol. This correction was also employed for the ZPV energy of methanol (31.13 kcal/mol) reported elsewhere (ref 17). [g] Assumed to be equal to that of the atomic relativistic energy (E_{rel}) of Table IIIA. [h] The molecular correlation energy of FCH_2OH was calculated as the following sum: $E_{\text{corr}}(CH_2{=}O) + E_{\text{corr}}(F{-}H) + \Delta E_{\text{corr}}(\text{bond}) = -0.495 - 0.377 - 0.065 = -0.937$ hartree. [i] The Hartree–Fock limit (HFL) was estimated as $E_{\text{HF}} = E_{\text{exp}} - (E_{\text{corr}} + E_{\text{rel}})$.

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(14) W. J. Taylor, *J. Chem. Phys.*, 48, 2285 (1968).

(15) The latter method seems to be computationally the more practical of the two because it ensures that systems which contain equivalent bonds will yield equivalent LMO, and because the overall localization procedure requires a smaller number of computational operations.

(16) L. Radom, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, 93, 289 (1971); 94, 2371 (1972).

(17) L. M. Tel, S. Wolfe, and I. G. Csizmadia, *J. Chem. Phys.*, in press.

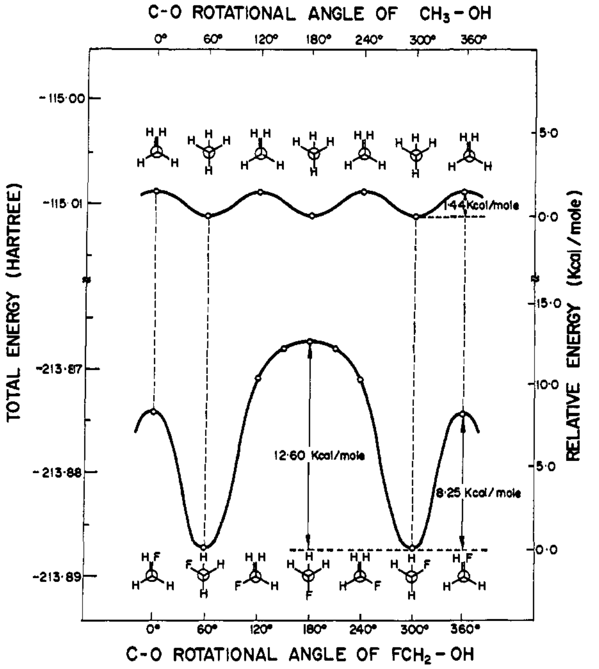

Figure 2. The total energies of methanol (upper curve) and fluoromethanol (lower curve) as a function of rotation about the C–O bond.

Table IV. Orbital Energies

MO	Rotational angle, deg: 0	60	120	190
1	−26.287978	−26.2771	−26.2710	−26.2794
2	−20.564552	−20.5717	−20.5731	−20.5690
3	−11.391178	−11.3925	−11.3936	−11.3942
4	−1.6276301	−1.6156	−1.6075	−1.6114
5	−1.3824973	−1.3865	−1.3902	−1.3893
6	−0.95809519	−0.9556	−0.9546	−0.9540
7	−0.74402599	−0.7526	−0.7576	−0.7534
8	−0.73151696	−0.7204	−0.7261	−0.7379
9	−0.71532833	−0.7098	−0.6901	−0.6858
10	−0.61677372	−0.6262	−0.6248	−0.6162
11	−0.59736755	−0.5764	−0.5744	−0.5937
12	−0.54422608	−0.5313	−0.5268	−0.5371
13	−0.47455719	−0.4942	−0.4953	−0.4775
14	0.26555217	0.2568	0.2356	0.2452
15	0.33400591	0.3351	0.3357	0.3309
16	0.35627595	0.3530	0.3505	0.3512
17	0.35804546	0.3640	0.3606	0.3531

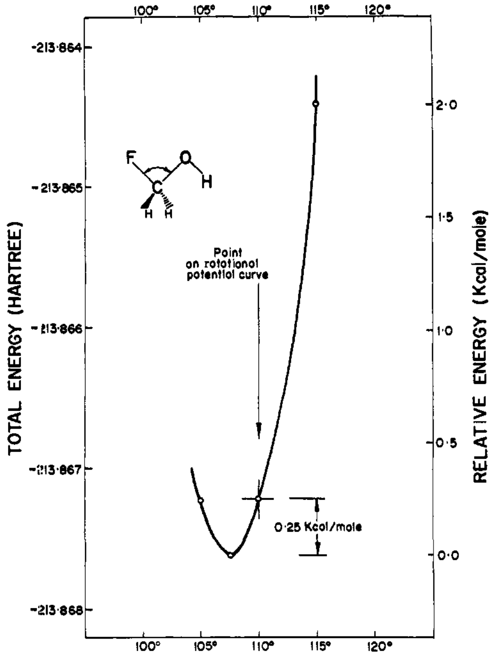

Figure 3. The total energy of fluoromethanol as a function of the FCO angle.

Table V. Calculated Energies in Hartrees[a] for Fluoromethanol as a Function of Rotation about the C–O Bond

Energy term	Rotational angle, deg: 0[b]	60	120	150	180
V_{ne}[c]	−666.0476	−665.7188	−665.2122	−450.9019[d]	−664.9927
T	214.1976	214.1746	214.1511		214.1507
V_{nn}	78.68682	78.49479	78.24488	78.17508	78.15205
V_{ee}	159.28900	159.16214	158.94526	158.85800	158.82276
E_{Total}	−213.87420	−213.88729	−213.87096	−213.86803	−213.86722
$-2T/V$[e]	1.000755	1.000671	1.000655		1.000662

[a] 1 hartree = 627.7 kcal/mol. [b] C–F and O–H bonds eclipsed. [c] The one-electron potential energy (V_{ne}) is calculated from the potentials at the nuclei (F_i) which, in turn, were obtained from the calculation of one-electron properties: $V_{ne} = \Sigma_i Z_i F_i$. The kinetic energy ($T$) was then calculated from the one-electron energy (E_1) listed in the IBMOL output ($T = E_1 - V_{ne}$). The numbers for T and V_{ne} are quoted to four decimal places only because the accuracies of the two-program systems are comparable only to this extent. [d] One-electron energy ($E_1 = T + V_{ne}$) computed by IBMOL. [e] $V = V_{nn} + V_{ne} + V_{ee}$.

tion. An additional SCF computation was, therefore, performed for the 150° rotational angle, but, as seen in Figure 2, this gave no indication of a second minimum.

In order to establish with greater certainty that the anticoplanar conformation represents an energy maximum it would have been necessary to perform a complete geometry optimization. However, this was not practical because each point required close to 12 hr of computer time. Therefore, only the FCO angle was varied since this seemed likely to be the most important internal coordinate. The results of this variation are summarized in Table VI and plotted in Figure 3. There is indeed some energy lowering associated with the *closing* of the FCO angle (from 110 to 107.5°), but this is not more than 0.25 kcal/mol. Such a change is hardly noticeable on the rotational potential. Consequently, we expect that the computed rotational curve shown at the bottom of Figure 2 would not differ substantially from the experimental result of spectroscopic examination of this compound.[18]

The form of this curve has already been discussed[4] in terms of the relationship of the conformation of FCH_2OH to the Edward–Lemieux effect and to the gauche effect. One point of interest in this discussion

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[18] A synthesis of protonated fluoromethanol has been reported recently by G. A. Olah and G. D. Mateescu, *J. Amer. Chem. Soc.*, **93**, 781 (1971). The parent compound has not yet been described.

Table VI. Calculated Energies for Fluoromethanol as a Function of the FCO Angle[a]

	FCO angle			
	105°	107.5°	110°	115°
V_{nn}	78.65647	78.39504	78.15205	77.71820
$T + V_{ne}$	−451.89138	−451.34827	−450.84203	−449.93567
V_{ee}	159.36814	159.08560	158.82276	158.35306
E_{Total}	−213.86723	−213.86762	−213.86722	−213.86441
ΔE, kcal/mol	0.245	0	0.251	2.015

[a] Rotational angle 180°.

was the possible interpretation of the results in terms of "Coulombic repulsion." To assess, in the quantum mechanical sense, the nature of the contribution of Coulombic repulsion (V_{ee}^{Coul}) to the total energy curve, the V_{ee} term was separated into its Coulomb and exchange terms, expressed over the LMO basis, using method B (see Method). However, this method is not invariant under a unitary transformation of the orbital basis used. Therefore an additional partition was performed according to method A, for which the CMO and LMO bases give the same numerical results. The two sets of results are summarized in Table VII and plotted in Figure 4. Because, in eq 3, the V_{ee}^{Exch} term enters with a negative sign, it is possible to consider that this term represents the "attractive" part of the total two-electron potential term and, for this reason, it has been plotted in Figure 4 as a negative quantity (*i.e.*, V_{ee} is the sum of the two curves in each case). It is evident that both separation methods yield curves which are qualitatively similar although numerically different, and that by neither method is there any obvious relationship between V_{ee}^{Coul} and the total energy curve (Figure 2). In both cases the $-V_{ee}^{\text{Exch}}$ term has the maximum at 180° which is also observed in the total energy curve. Although this maximum is more pronounced in the curve obtained from method B, it does not follow that the latter represents the more suitable separation technique, and more work will be needed to establish this point.

Table VII. Partitioning of V_{ee} into Its Coulombic and Exchange[a] Terms

Rotational angle, deg	Method A		Method B	
	Coulomb	Exchange	Coulomb	Exchange
0	183.87910	24.59010	164.81350	5.52450
60	183.74558	24.58344	164.67106	5.50892
120	183.52129	24.57603	164.39502	5.44976
180	183.39551	24.57275	164.24161	5.41885

[a] The negative sign of eq 3 is not included in these data.

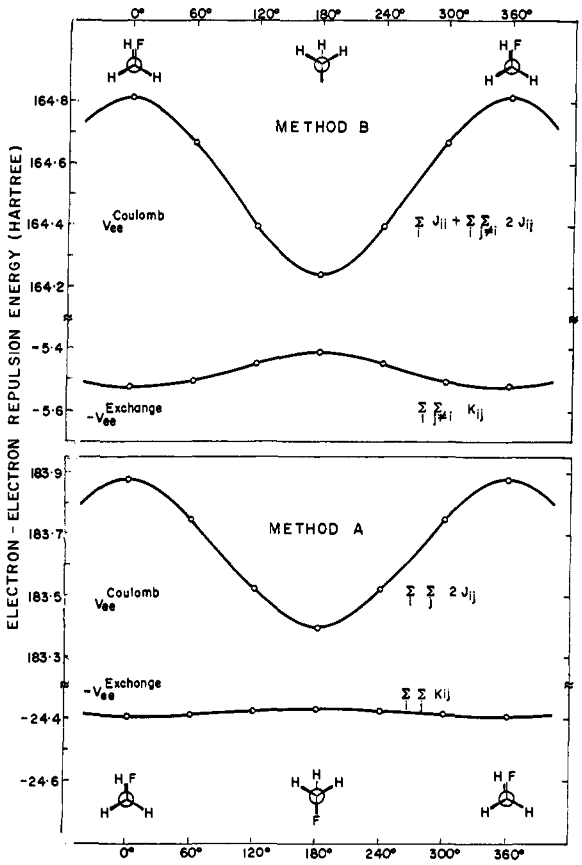

Figure 4. Partitioning of the electron–electron repulsion term of fluoromethanol into its Coulombic and exchange components, as a function of rotation about the C–O bond: upper curves, partition according to method B; lower curves, partition according to method A.

Excited Electronic Configurations. A. Electronic Excitations. The orbital energies have been presented in Table IV. Only the four highest filled (No. 10–13) and the four lowest vacant (No. 14–17) MO were used for the calculation of excited configurations shown in Table VIII. The singlet and triplet excitation energies were computed by the virtual orbital technique,[19] as described elsewhere for CH_3OH.[17] It was of particular interest to compare these excitation patterns with those of CH_3OH because the ground state conformational properties of the two compounds are so different (Figure 2). The comparison is given in Figure 5 for the first five excited configurations. The first transition energy is lower for fluoromethanol by about 10 kcal/mol (0.014 hartree). This does not agree with the trends observed experimentally (and analyzed by RCNDO calculations) for various nongeminally substituted fluorinated alcohols.[20]

Although our calculation is not completely definitive because no configuration interaction was employed, and Rydberg-type orbitals were not included in the basis set, it should, nevertheless, be anticipated that the excitation patterns associated with the attachment of two heteroatoms to the same carbon should differ from those for two heteroatoms attached to different carbon atoms. Further work is needed to check this conclusion.

B. Excited State Conformations. It is well estab-

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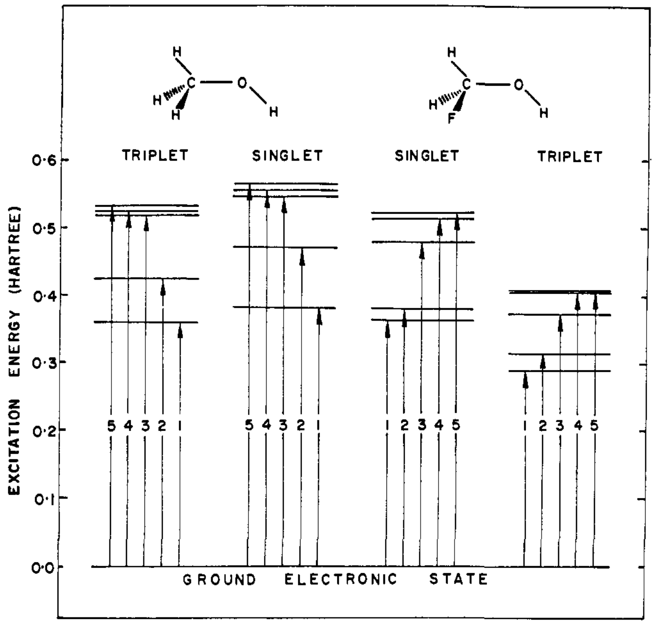

Figure 5. A comparison of electronic excitations of methanol and fluoromethanol.

lished[21] that excited and ground electronic states have different geometries, because of their different electronic distributions. In general, however, because of the experimental difficulties associated with the vibrational analysis of uv spectra, which is necessary to determine the conformations of excited states, data are available only for very simple compounds (NH_3)[22] or simple multiply bonded systems (C_2H_2, C_2H_4, CH_2O).[21] Thus, to our knowledge, no discussion has appeared which considers the possible changes in geometry associated with the excitation of singly bonded organic compounds. It is entirely conceivable that such compounds could undergo geometry changes sufficiently large to reverse the positions of ground-state energies, as in the case of NH_3, or even the phase of the ground state conformational curve. Therefore, the rotational curves associated with the low-lying excited states of FCH_2OH were of some interest. The results are summarized in Table VIII, and the first three excited configurations are shown in Figure 6.[23]

The difference between the curves of the excited configurations (S_1, S_2, and S_3) and the ground state rotational curve (S_0) is very striking. Each of the excited configurations possesses a *minimum* at 180° and, for two of the configurations (S_1 and S_3), *the anticoplanar conformation (180°) is more stable than the gauche conformation (60°)*. The second excited configuration (S_2) has a potential curve which almost shows a threefold symmetry. On the basis of these results it can be predicted that *the gauche effect exhibited by FCH_2OH is a ground-state phenomenon.* Although this conclusion applies at present only to FCH_2OH, because of the broad applicability of the gauche effect,[3] we strongly suspect this to be a general property of molecules which exhibit the effect and that it will have important implications for structural and synthetic work.[24]

Table VIII. Calculation of Electronic Excitations

Rotational angle	MO indices $k \leftarrow l$		J_{kl}	K_{kl}	Excitation energy (hartree)	
	k	l			Singlet	Triplet
0°	14	10	0.39780	0.07853	0.642	0.485
	14	11	0.41332	0.02078	0.491	0.450
	14	12	0.43700	0.06910	0.510	0.378
	14	13	0.44216	0.13091	0.560	0.298
	15	10	0.39042	0.03416	0.628	0.560
	15	11	0.46087	0.18157	0.834	0.471
	15	12	0.45251	0.01995	0.466	0.426
	15	13	0.44564	0.01599	0.395	0.366
	16	10	0.36449	0.02671	0.662	0.609
	16	11	0.34938	0.00791	0.620	0.604
	16	12	0.41650	0.08444	0.656	0.484
	16	13	0.42297	0.08022	0.568	0.408
	17	10	0.38223	0.04139	0.675	0.596
	17	11	0.33942	0.06389	0.744	0.616
	17	12	0.35612	0.01070	0.568	0.546
	17	13	0.36700	0.01171	0.489	0.465
60°	14	10	0.37619	0.03708	0.581	0.507
	14	11	0.42722	0.13288	0.672	0.406
	14	12	0.47364	0.03235	0.379	0.314
	14	13	0.45974	0.03667	0.365	0.291
	15	10	0.40128	0.05797	0.675	0.560
	15	11	0.40750	0.03961	0.583	0.504
	15	12	0.45740	0.05225	0.514	0.409
	15	13	0.45594	0.13670	0.647	0.373
	16	10	0.36751	0.02909	0.670	0.612
	16	11	0.38469	0.02963	0.604	0.545
	16	12	0.37557	0.09745	0.704	0.509
	16	13	0.40094	0.01716	0.481	0.446
	17	10	0.38069	0.04159	0.696	0.610
	17	11	0.38545	0.06058	0.676	0.555
	17	12	0.33692	0.02388	0.606	0.558
	17	13	0.37455	0.01665	0.517	0.484
120°	14	10	0.27234	0.01872	0.626	0.588
	14	11	0.26912	0.00684	0.555	0.540
	14	12	0.34026	0.01843	0.459	0.422
	14	13	0.33317	0.01264	0.423	0.398
	15	10	0.26380	0.00458	0.701	0.692
	15	11	0.29988	0.01017	0.630	0.610
	15	12	0.31319	0.02625	0.602	0.549
	15	13	0.31754	0.01522	0.544	0.513
	16	10	0.29682	0.00491	0.688	0.678
	16	11	0.33643	0.02798	0.644	0.588
	16	12	0.29221	0.01282	0.611	0.585
	16	13	0.31720	0.02102	0.571	0.529
	17	10	0.36659	0.01341	0.646	0.619
	17	11	0.37314	0.01479	0.591	0.562
	17	12	0.32601	0.02221	0.606	0.561
	17	13	0.32058	0.02152	0.578	0.535
180°	14	10	0.36842	0.02169	0.536	0.498
	14	11	0.44151	0.17881	0.755	0.397
	14	12	0.43108	0.01367	0.378	0.350
	14	13	0.50470	0.02660	0.271	0.218
	15	10	0.38635	0.03117	0.623	0.561
	15	11	0.40488	0.01455	0.549	0.520
	15	12	0.45408	0.17575	0.765	0.414
	15	13	0.47847	0.02153	0.373	0.330
	16	10	0.37656	0.05277	0.686	0.590
	16	11	0.41470	0.03904	0.608	0.530
	16	12	0.33815	0.01227	0.574	0.549
	16	13	0.36783	0.06517	0.591	0.461
	17	10	0.38225	0.04328	0.674	0.587
	17	11	0.40205	0.01807	0.581	0.545
	17	12	0.34959	0.07142	0.683	0.542
	17	13	0.34132	0.00993	0.509	0.489

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(23) It should be noted that the points joined to form these potential curves do not always involve the same MO in the excitation.

(24) Although this result is not quantitative because configuration interaction was not employed in the calculations, the magnitude of the

Table IX. Size and Stereochemistry of Electron Pairs in Fluoromethanol as a Function of Rotation about the C–O Bond

Rotational angle	Electron pair	Coordinates of centroids of charge $\langle x_a \rangle$	$\langle y_a \rangle$	$\langle z_a \rangle$	Size of electron pair $\langle r_1^2 \rangle^{R_a}$
0°	$1s_F$	2.450	0	−2.215	0.058
	$1s_O$	0	0	1.264	0.180
	$1s_C$	0	0	−1.349	0.125
	n_F	2.638	0.433	−2.002	1.312
	n_F	2.638	−0.433	−2.002	1.312
	n_F	2.435	0	−2.775	1.047
	n_O	−0.265	0.516	1.509	1.675
	n_O	−0.265	−0.516	1.509	1.675
	C–H	−0.633	1.132	−1.808	2.290
	C–H	−0.633	−1.132	−1.808	2.290
	C–O	0.055	0	0.310	2.164
	C–F	1.627	0	−1.957	1.803
	O–H	0.911	0	1.612	1.827
60°	$1s_F$	2.450	0.000	−2.212	0.075
	$1s_O$	0.000	0.000	1.349	0.073
	$1s_C$	0.000	0.000	−1.349	0.124
	n_F	2.408	0.105	−2.718	1.310
	n_F	2.665	0.381	−1.935	1.320
	n_F	2.623	−0.476	−2.106	1.301
	n_O	0.233	−0.514	1.554	1.709
	n_O	−0.576	0.019	1.428	1.742
	C–H	−0.629	−1.123	−1.799	2.296
	C–H	−0.628	1.151	−1.814	2.276
	C–O	0.085	0.016	0.321	2.135
	C–F	1.634	−0.005	−1.930	1.792
	O–H	0.486	0.775	1.636	1.825
120°	$1s_F$	2.450	0.000	−2.215	0.058
	$1s_O$	0.000	0.000	1.349	0.073
	$1s_C$	0.000	0.000	−1.349	0.124
	n_F	2.620	0.468	−2.067	1.300
	n_F	2.414	−0.068	−2.723	1.328
	n_F	2.655	−0.392	−1.955	1.324
	n_O	−0.406	−0.412	1.415	1.727
	n_O	0.531	−0.108	1.555	1.826
	C–H	−0.641	1.147	−1.811	2.291
	C–H	−0.629	−1.133	−1.809	2.277
	C–O	0.061	0.074	0.322	2.128
	C–F	1.620	−0.005	−1.943	1.816
	O–H	−0.398	0.825	1.645	1.783
180°	$1s_F$	2.450	0.000	−2.215	0.057
	$1s_O$	0.000	0.000	1.349	0.073
	$1s_C$	0.000	0.000	−1.349	0.124
	n_F	2.385	−0.046	2.723	1.331
	n_F	2.659	−0.414	−1.990	1.310
	n_F	2.638	0.451	−2.060	1.309
	n_O	0.254	0.524	1.499	1.692
	n_O	0.270	−0.513	1.508	1.692
	C–H	−0.644	1.140	−1.814	2.290
	C–H	−0.644	−1.140	−1.814	2.290
	C–O	−0.041	−0.004	0.305	2.164
	C–F	1.602	−0.002	−1.909	1.894
	O–H	−0.922	−0.006	1.628	1.826

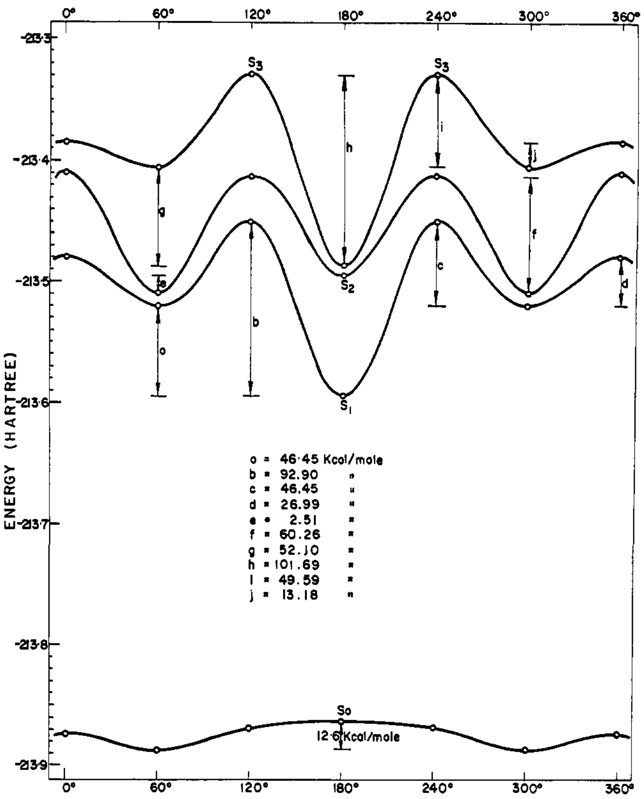

Figure 6. A comparison of the ground-state rotational potential of fluoromethanol (lower curve) with the rotational potentials of the three lowest lying singlet excited states.

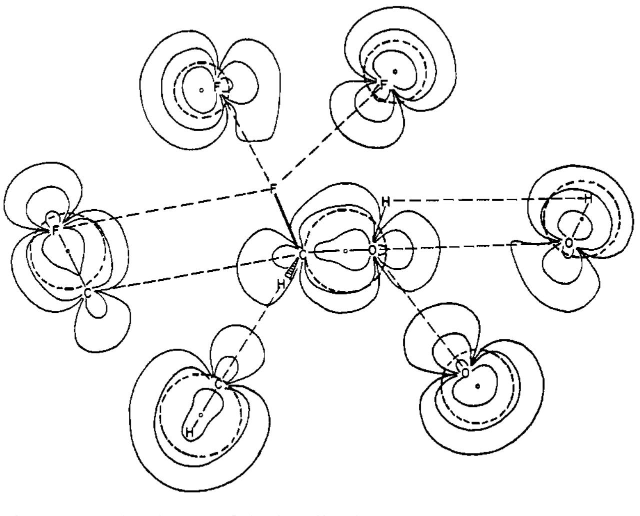

Figure 7. The shapes of the localized molecular orbitals associated with the valence electrons of fluoromethanol in its 0° ground-state conformation.

The Localized Molecular Orbitals. The shapes of the LMO for the valence electrons, computed from the 0° ground electronic state wave function, are presented in Figure 7. The centroids of charge, as well as the "sizes" of these localized electron pairs,[8] defined in terms of the first and second moments over the LMO basis, are also shown as the small circles and the large broken circles of Figure 7, respectively. A simplified picture of the LMO sizes is shown in Figure 8. The coordinates of the centroids of charge and the sizes of the electron pairs are summarized in Table IX.

One point of interest is to compare the "sizes" of the electron pairs (*i.e.*, the LMO) for CH_3OH (calculated from the wave function reported in ref 17) and for FCH_2OH. This comparison is presented in Table X. It is evident that replacement of H by F leads to a significant contraction in the sizes of the geminally attached C–H bonds. However, fluorination does not affect the size of the O–H bonding electron pair. In-

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energy difference (>35 kcal/mol) between the gauche and trans structures in the S_1 and S_3 excited states is much too large to be fortuitous. Furthermore, to convert the energy minimum at 180° into an energy maximum in the various excited states, as in the ground state, would require an energy change in excess of 100 kcal/mol, and inclusion of configuration interaction in the calculation is not expected to cause such a large change in the energies.

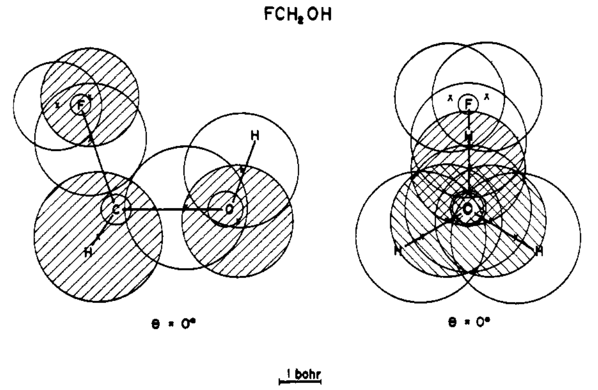

Figure 8. Sizes of the bonding and nonbonding electron pairs of fluoromethanol in its 0° ground-state conformation. For the structure on the left, open circles represent the sizes of electron pairs and shaded circles represent the sizes of the projection of two equivalent electron pairs. The structure on the right is a view along the C–O bond from carbon to oxygen; open circles represent electron pairs associated with the CH$_2$F moiety at the front, and shaded circles represent electron pairs associated with the OH moiety at the rear.

Table X. A Comparison of the Sizes of Electron Pairs in Methanol and Fluoromethanol as a Function of Rotation about the C–O Bond

Electron pair	CH$_3$OH Eclipsed	CH$_3$OH Staggered	FCH$_2$OH 0°	FCH$_2$OH 60°	FCH$_2$OH 180°
C–H	2.488	2.482			
C–H	2.481	2.483	2.290	2.296	2.290
C–H	2.481	2.483	2.290	2.276	2.290
C–O	2.244	2.247	2.164	2.135	2.164
O–H	1.815	1.833	1.827	1.825	1.826
n_O	1.678	1.672	1.675	1.709	1.692
n_O	1.678	1.672	1.675	1.742	1.692

terestingly, there is an effect upon the oxygen lone pairs which is manifested at the energy minimum (60°), an increase in the sizes of these orbitals in the direction of the O–H bond (the $\langle z^2 \rangle$ component) being observed. Table XI shows the group sizes. The size of the OH group (*i.e.*, of its four electron pairs) is virtually the same in CH$_3$OH and FCH$_2$OH. The sizes of the CH$_3$ and FCH$_2$ groups are, of course, different because they contain different numbers of electron pairs.

There is no anomaly in the individual densities associated with the oxygen lone pairs (*cf.* Figure 8). However, it was pointed out previously[4] that the interaction of the C–F bonding electron pair with the two oxygen lone pairs appears to be constant in the 120° sector between 120 and 240°, and this result led to the structural representation shown in **1**. To test the validity of this picture, the sum of the densities of the two oxygen lone pairs shown in Figure 9a (corresponding to the 180° conformation) was plotted, with the result shown in Figure 9b. Clearly, the sum of the densities (for 4 electrons) agrees well with the earlier qualitative interpretation, and may be taken as support for the view that the two lone pairs together behave as though they have no directional character.

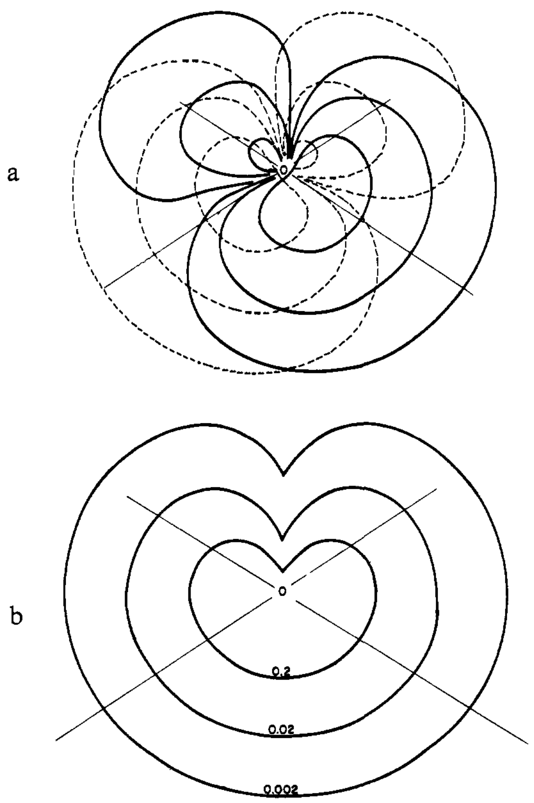

Figure 9. (a) The two oxygen lone pairs of fluoromethanol in the 180° ground-state conformation. (b) The sum of the densities associated with the two oxygen lone pairs of Figure 9a.

Table XI. A Comparison of Group Sizes in Methanol and Fluoromethanol as a Function of Rotation about the C–O Bond

Group	Component of $\langle r_i \rangle^2$	X = H (CH$_3$OH) Eclipsed	X = H (CH$_3$OH) Staggered	X = F (FCH$_2$OH) 0°	X = F (FCH$_2$OH) 60°	X = F (FCH$_2$OH) 180°
XCH$_2$–[a]	$\langle x^2 \rangle + \langle y^2 \rangle$	10.426	10.420	22.543	22.497	22.715
	$\langle z^2 \rangle$	2.107	2.118	3.537	3.792	3.730
	$\langle r^2 \rangle$	12.533	12.538	26.080	26.289	26.444
-OH[b]	$\langle x^2 \rangle + \langle y^2 \rangle$	5.018	5.024	4.985	5.019	5.017
	$\langle z^2 \rangle$	1.655	1.656	1.655	1.727	1.677
	$\langle r^2 \rangle$	6.673	6.680	6.639	6.746	6.694

[a] The number of electrons in CH$_3$ is 8 and in FCH$_2$ is 16. [b] The number of electrons in OH is 8.

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