similarity in the interactions taking place in the activated complexes.

Finally, the results place some restrictions on the mechanism of the hydroboration reaction in more complex systems. If, in an overall hydroboration reaction, the mechanism involving BH_3 is favored over the direct reaction, then the barrier to reaction is not the reaction of BH_3 with the unsaturated species. For example, if the reaction of B_2H_6 with C_2H_4 proceeds through the intermediate BH_3, the reaction of BH_3 with C_2H_4 is not the slow step of the reaction. The slow step will probably be the production of BH_3. It should be kept in mind that, although an upper limit was placed on the rate constant for the direct reaction of B_2H_6 with C_2H_4, in a conventional thermal system (*e.g.*, ref 5) this upper limit is sufficiently high and the concentration of BH_3 is sufficiently low that it is still possible for the direct reaction to take place.

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Theory of the Rotational Barriers in Ethyl Fluoride and Ethane

Leland Cullen Allen[*1a] **and Harold Basch**[1b]

Contribution from the Department of Chemistry, Princeton University,
Princeton, New Jersey 08540, and the Scientific Laboratory,
Ford Motor Company, Dearborn, Michigan 48121. *Received March 1, 1971*

Abstract: *Ab initio* LCAO–MO–SCF wave functions have been computed with an atomic orbital basis set of double-ζ accuracy for the staggered and eclipsed conformations of ethyl fluoride and ethane. Total energy differences, ΔE_T, yield barriers of 2.59 and 2.58 kcal/mol for ethyl fluoride and ethane, respectively. These calculations are in reasonable agreement with the experimental result that barriers in these two molecules differ by about 10%. Our wave functions also substantiate and extend a previous conclusion that the origin of barriers is contained within the framework of the Hartree–Fock approximation. To obtain a more detailed understanding of the barrier mechanism, the total energy has been separated into its two competing and out-of-phase components: $V_{\text{attractive}} \equiv V_{\text{ne}}$ and $V_{\text{repulsive}} \equiv V_{\text{nn}} + T + V_{\text{ee}}$. Both ethyl fluoride and ethane are repulsive dominant. One result of the repulsive dominance is a small difference in dipole moment between staggered and eclipsed ethyl fluoride. A physical rationalization of the rough equality of these two barriers also follows from their common repulsive dominance. The sum of one-electron molecular orbital energies (Walsh criterion) is investigated as a means of predicting barrier magnitudes. This is shown to be reasonable for ethyl fluoride and ethane but not for some other molecules.

To understand the origin of internal rotation barriers, it has become apparent that it is necessary to generate and analyze *ab initio* wave functions for a considerable variety of molecules. In particular, an explanation of the surprisingly similar barriers displayed by ethyl fluoride and ethane is required if one is to provide a convincing barrier mechanism.

LCAO–MO–SCF *ab initio* wave functions have proved adequate for representing the principal features of barriers in ten other important molecules,[2] and wave functions at this level of approximation are shown here to be capable of producing reasonable magnitudes for the barriers in ethyl fluoride and ethane. This is the first report of an *ab initio* ethyl fluoride wave function, but there exist several ethane solutions of comparable accuracy to the one reported here.[3] Because of the small energy change involved in the barrier, it is absolutely essential to maintain perfectly balanced basis sets and identical computational machinery in generating wave functions for the two molecules.

I. Method and Basis Set

LCAO–MO–SCF wave functions were obtained *via* Roothaan's finite-expansion scheme. An atomic orbital basis set of double-δ quality was constructed from Gaussian functions. The carbon and fluorine s orbitals are made from the Gaussians given by Whitten[4] contracted into two groups, with the Gaussian of smallest exponent treated as one of the basis functions. The p's are a six-term Cartesian Gaussian set contracted to two basis functions, one of which is the Gaussian with smallest exponent, and the hydrogen 1s's are a four-term Gaussian set (contracted to a single function); both are taken from Huzinaga's tabulations.[5a] The H 1s was scaled so that it is equivalent to $\exp(-\sqrt{2}r)$. Atomic coordinates for the two molecules taken from the experimentally observed geometries[6] are listed in Table I.

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(1) (a) Princeton University; (b) Ford Motor Co.; Department of Chemistry, Bar Ilan University, Ramat-Gan, Israel.

(2) Methylamine, methanol, hydrogen peroxide, hydrazine, propane, and butane, L. C. Allen, *Annu. Rev. Phys. Chem.*, **20**, 315 (1969); acetaldehyde, R. B. Davidson and L. C. Allen, *J. Chem. Phys.*, in press; nitrosomethane, P. A. Kollman and L. C. Allen, *Chem. Phys. Lett.*, **5**, 75 (1970); propene and *cis*-fluoropropene, E. Scarzafava and L. C. Allen, *J. Amer. Chem. Soc.*, **93**, 311 (1971).

(3) Summarized in W. H. Fink and L. C. Allen, *J. Chem. Phys.*, **47**, 895 (1967).

(4) J. Whitten, *ibid.*, **44**, 359 (1966).

(5) (a) S. Huzinaga, *ibid.*, **42**, 1293 (1965). (b) It may be that the C_1C_2F angle undergoes a small opening or closing as the barrier is traversed. In ethane, geometrical distortion is known to modify the barrier height by no more than 0.1 kcal, and we have not tested this for ethyl fluoride.

Table I. Coordinates of Atoms

	x	y	z
		C_2H_5F	
		Staggered	
C_1	0.0	0.0	−1.45510849
C_2	0.0	0.0	1.45510849
H_1	1.70741268	−0.98577517	−2.15225127
H_2	−1.70741268	−0.98577517	−2.15225127
H_3	0.0	1.97155033	−2.15225127
H_4	1.70741268	0.98577517	2.15225127
H_5	−1.70741268	0.98577517	2.15225127
F	0.0	−2.44972199	2.32133368
		Eclipsed[a]	
H_4	1.70741268	−0.98577517	2.15225127
H_5	−1.70741268	−0.98577517	2.15225127
F	0.0	2.44972199	2.32133368
		C_2H_6	
		Staggered	
C_1	0.0	0.0	−1.45795000
H_1	1.69855762	−0.98066292	−2.15791169
H_2	−1.69855762	−0.98066292	−2.15791169
H_3	0.0	1.96132584	−2.15791169
C_2	0.0	0.0	1.45795000
H_4	1.69855762	0.98066292	2.15791169
H_5	0.0	−1.96132584	2.15791169
H_6	−1.69855762	0.98066292	2.15791169
		Eclipsed[a]	
H_4	1.69855762	−0.98066292	2.15791169
H_5	−1.69855762	−0.98066292	2.15791169
H_6	0.0	1.96132584	2.15791169

[a] C_1, C_2 and H_1, H_2, and H_3 remain the same as for staggered.

Table II. Energy Components[a]

		E_T	$V_{ne} = V_{att}$	V_{ee}	V_{nn}	T	$V_{rep} = V_{ee} + V_{nn} + T$	$\eta = -V/2T$
C_2H_5F	Staggered	−177.9409504	−579.2712708	144.1566620	78.86429787	178.3093605	401.3303204	0.99896693
	Eclipsed	−177.9368229	−579.3673859	144.2018509	78.89841556	178.3302994	401.4305659	0.99889676
C_2H_6	Staggered	−79.14754963	−267.2514305	67.19479561	41.93097734	78.97811031	188.1038833	1.0010727
	Eclipsed	−79.14343834	−267.2834244	67.20999050	41.93844700	78.99154949	188.1399870	1.0009614

[a] Hartree units.

Table III. Energy Component Differences (Eclipsed − Staggered)

	$\Delta E_T(1)$	$\Delta E_T(\eta)$ (scaled)	$\Delta V_{rep}(1)$	$\Delta V_{rep}(1)$ (scaled)	$\Delta V_{att}(1)$	$\Delta V_{att}(\eta)$ (scaled)
C_2H_5F	0.0041275[a] (2.59)[b]	0.0040770 (2.56)[b]	0.1002455	0.0594791	0.0961151	0.0554021
C_2H_6	0.0041113 (2.58)[b]	0.0041294 (2.59)[b]	0.0361037	0.0064089	0.0319939	0.0022796

[a] Hartree units. [b] Values in parentheses are in kilocalories.

II. Energy Components

Total energies, their components, and η, the virial parameter ($\eta = 1$ if the virial theorem is exactly satisfied), are presented in Table II. The barrier magnitudes obtained for C_2H_5F and C_2H_6 are 0.004127 au (2.59 kcal) and 0.0041113 au (2.58 kcal), respectively.[5b] The experimental barrier values are 3.330 ± 0.050 and 2.928 ± 0.025 kcal/mol for ethyl fluoride and ethane, respectively.[6]

The ethane barrier magnitude which we have obtained is close to that reported for *ab initio* LCAO–MO-SCF calculations carried out at a number of other laboratories.[3] Thus, in the same manner as the previously published work, we again conclude—with even greater assurance—that correct trends, reasonable magnitudes, and the information required for a detailed explanation of barriers may be obtained within the framework of the Hartree–Fock approximation.

To provide a physical and mathematical basis for understanding the barrier origin, we consider the two components[7] $V_{attractive}$ and $V_{repulsive}$, whose sum is the total energy

$$V_{att} \equiv V_{ne} \qquad V_{rep} \equiv V_{ee} + V_{nn} + T$$

Figure 1 displays E_T, V_{att}, and V_{rep} for C_2H_5F and illustrates the fact that the component changes across barrier ΔV_{att} and ΔV_{rep} are generally of comparable or greater magnitude than the barrier itself. It also shows the opposing phase relationship between the two components.[8] The V_{att}, V_{rep} "cross" is the characteristic feature of every barrier in every molecule.

In Figure 2 the components for C_2H_5F and C_2H_6 are superimposed, and we note that there is a large energy difference—approximately 40 kcal—separating the two pairs of components even though the two barriers are practically identical. For both molecules $\Delta V_{rep} > \Delta V_{att}$ and the V_{att}, V_{rep} cross is thus repulsive dominant. Figure 2 was prepared from the energy components of the usual Hartree–Fock Roothaan solution given in Table I, and the results do not perfectly satisfy the virial theorem. When our wave functions are scaled to force satisfaction of the virial theorem (Table III), the relative positions of the V_{att} and V_{rep} components are closely maintained, and the differences between both ΔV_{rep} and ΔV_{att} for ethyl fluoride and ethane are again equal and large—now near to 33 kcal. The well-known constancy of the barrier magnitude ΔE_T under scaling is also demonstrated in our results. As a practical matter, the relative invariance

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[6] High-resolution infrared [G. Sage and W. Klemperer, *J. Chem. Phys.*, **39**, 371 (1963)] and microwave spectroscopy [D. R. Herschbach, *ibid.*, **25**, 358 (1956)] measurements agree for the ethyl fluoride barrier. For ethane, see S. Weiss and G. E. Leroi, *ibid.*, **48**, 962 (1968). Coordinates for ethane given in G. E. Hansen and D. M. Dennison, *ibid.*, **20**, 313 (1952).

[7] L. C. Allen, *Chem. Phys. Lett.*, **2**, 597 (1968). This paper analyzed a wide variety of molecules and quoted the barrier magnitudes for ethane and ethyl fluoride obtained in the present article.

[8] Only the end points, 0° (staggered) and 60° (eclipsed), have been computed, and the curves between these points have been sketched in Figures 1 and 2. However, many intermediate values have been obtained for ethane as well as other molecules (see ref 2), and there is no question as to the correctness of the shape.

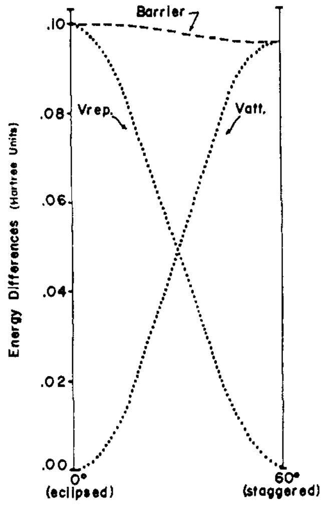

Figure 1. Barrier and V_{att}, V_{rep} energy components for ethyl fluoride. V_{att}, V_{rep} form a repulsive dominant "cross" for this barrier. (In Figures 1 and 2, V_{att} and V_{rep} are plotted on the same side of a reference level so that the relative magnitudes of ΔV_{att} and ΔV_{rep} and the shape of the barrier are readily apparent.)

to scaling displayed by ΔV_{rep} and ΔV_{att} seems to be largely a consequence of ΔE_{T} invariance, but, of course, there is no mathematical or physical relationship that forces this to be true.

Since ethane and ethyl fluoride are very different in the potential energy change seen by an infinitesimal test charge as the barrier is traversed (Figure 2), but the experimentally observed barriers are only 10% different, it is as if a large potential energy term was being added almost equally to V_{att} and V_{rep}. This large term is essentially the difference in the effective potential between fluorine and hydrogen atoms.

Table IV lists the one-electron energies and dipole moments computed from our wave function for the two molecules. The one-electron energies are valuable for several reasons. They represent a good estimate of first ionization potentials for the various molecular shells (Koopmans' theorem), they constitute a test for one important theory of the barrier (see section IV), and they provide an extensive quantitative check with other ethane wave functions.

Table IV. One-Electron Energies and Dipole Moments

	C_2H_5F		C_2H_6	
	Staggered	Eclipsed	Staggered	Eclipsed
	−0.4861[a]	−0.4863	−0.4803	−0.4786
	−0.4902	−0.4873	−0.4803	−0.4786
	−0.5481	−0.5449	−0.4888	−0.4884
	−0.5692	−0.5732	−0.5958	−0.5965
	−0.6237	−0.6216	−0.5958	−0.5965
	−0.6678	−0.6692	−0.8316	−0.8311
	−0.6965	−0.6959	−1.0067	−1.0064
	0.8603	−0.8602	−11.2318	−11.2304
	−1.0320	−1.0315	−11.2322	−11.2309
	−1.5479	−1.5479		
	−11.2659	−11.2640		
	−11.3957	−11.3948		
	−26.1409	−26.1401		
$\sum_{i}^{\text{val}} \epsilon_i$				
	−15.0436	−15.0360	−8.9586	−8.9522
$\Delta\sum(\epsilon)$				
	0.0076 (4.77)[b]		0.0064 (4.02)[b]	
μ				
		2.56 D	2.52 D	
y component		2.30 D	2.26 D	
z component		1.12 D	1.13 D	

[a] Hartree units. [b] Values in parentheses are in kilocalories.

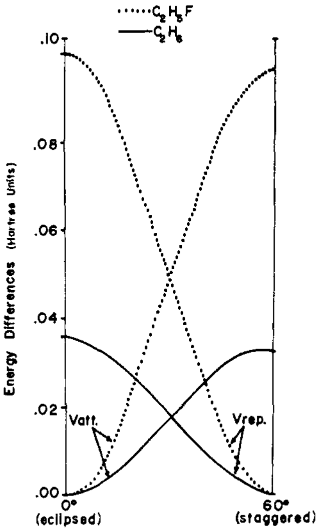

Figure 2. V_{att} and V_{rep} energy components for ethyl fluoride (· · ·) and ethane (——). Both of the "crosses" are repulsive dominant.

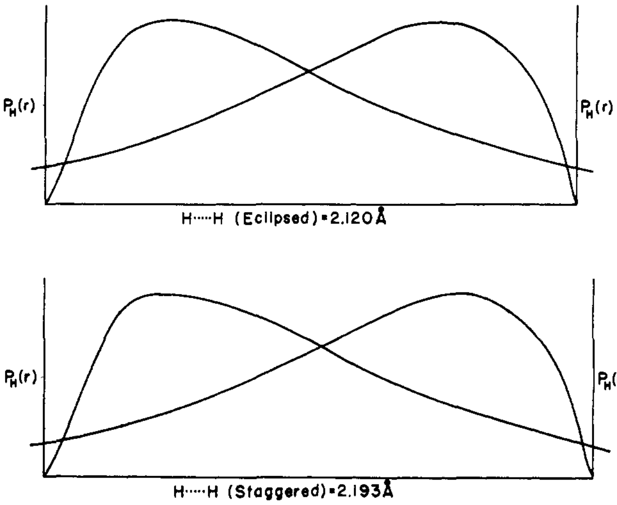

Figure 3. Volume element weighted radial amplitude functions for hydrogen 1s functions on opposite ends of ethane plotted along the H· · ·H internuclear axis: top graph, overlap at eclipsed separation; bottom graph, overlap at staggered separation.

III. Physical Description of Barrier Mechanism

Because barrier magnitudes are very small energies, there is a tendency to believe that there is little orbital overlap between the opposite ends of the molecule. This is far from the case as shown by the hydrogen radial overlap plot of Figure 3. It is also obvious from Figure 3 that the change in overlap under rotation is small, but it seems likely that the changes which characterize the barrier mechanism will be of a distributed rather than localized nature. To find an appropriate measure is thus difficult because many parts of the molecule will be involved, and in addition the measure must be expressed in terms of a difference between staggered and eclipsed conformations if it is to achieve conceptual and practical utility. The V_{att} and V_{rep} energy components which we have previously introduced[7] are one attempt at finding such a measure. Component changes, ΔV_{att} and ΔV_{rep}, characterize a barrier as either attractive dominant or repulsive dominant according to which component realizes the greatest absolute change under rotation. Just as in the ordinary strong-interaction situation, net attraction and net repulsion are both found, but for rotational barriers there is a large preponderance of repulsive-dominant cases. Categorization of barriers by means of energy components has been followed up and substantiated by a detailed analysis of charge density changes for both attractive- and repulsive-dominant examples.[9]

For the present molecules the principal question of interest is the relatively small difference in the ethane and ethyl fluoride barriers, and we find that energy components provide a satisfying physical rationalization of this situation. Since both barriers are repulsive dominant and since the radius of the fluorine atom is close to that of hydrogen, we are simply seeing the effect of lowering the potential well around one of the rotating atoms due to the high charge density of fluorine. As the CH_3 group rotates against the CH_2F group in ethyl fluoride, one of the C–H bond tails passes through a region of much greater potential energy than it did for ethane, and this adds a roughly constant amount to both energy components (the V_{att}, V_{rep} components are subject to the additive energy rather than E_{T} itself, because V_{att} and V_{rep} have opposite signs).

IV. Dipole Moments, Population Analysis, and Hückel Theory

Table IV lists the computed dipole moments of ethyl fluoride in staggered and eclipsed conformations, and these numbers show that there is only a very small change in moment. This observation and examination of charge density contours in ethane[9a] demonstrates that only a very small charge redistribution occurs during traverse of the barrier. This small change can be understood with the aid of the dipole moment components in Table IV and population-analysis-derived atomic charges tabulated in Table V. Vectorial decomposition of the dipole moment shows that all of the change is perpendicular to the rotation axis, therefore along the C–F and C–H bonds, while the atomic charges show that the C–F charge separation (bond dipole) is the same for both staggered and eclipsed conformations and that the fluorine end is strongly negative (in contrast to the hydrogens). The preponderant change from staggered to eclipsed is reduction in the amount of charge on a hydrogen when it eclipses the fluorine. The C_2H_5F barrier is repulsive dominant, V_{rep} is largest in the eclipsed conformation, and the negative fluorine atom therefore repels the charge on its opposing hydrogen atom. It is worth noting that while population analysis is frequently successful in describing simple and specific charge redistribution effects such as our example here, it is too crude a measure for systematizing and analyzing barrier mechanisms.

Table V. Atomic Charges from Population Analysis of C_2H_5F[a]

	Staggered	Eclipsed
C_1[b]	−0.8136	−0.8164
C_2[c]	−0.2850	−0.2848
H_1	0.2910	0.2841
H_2	0.2910	0.2841
H_3	0.2849	0.3017
H_4	0.2911	0.2910
H_5	0.2911	0.2910
F	−0.3505	−0.3507

[a] Net charge on molecule is zero. [b] H_1, H_2, and H_3 are attached to C_1. [c] H_4, H_5, and F are attached to C_2.

Some time ago,[10] the one-electron molecular orbital energies generated by three-dimensional Hückel theory were used to predict the barrier in ethane. The difference in $\Sigma_i^{\mathrm{val}}\epsilon_i$ for staggered and eclipsed conformations was found to yield a number near to the observed barrier magnitude. Since $\Sigma_i^{\mathrm{val}}\epsilon_i$ is the Walsh criterion for assigning molecular shape which has been widely successful in organic and inorganic chemistry, it is important to investigate the validity of this scheme for computing barrier magnitudes. We may test the $\Sigma\epsilon$ barrier predicting potential, independent of any particular set of assumed Hückel parameters, by employing the *ab initio* results in Table IV. They are seen to confirm the original hypothesis for both ethane and ethyl fluoride. Unfortunately, however, when $\Sigma\epsilon$ is computed for the sequence ethane, methylamine, and methanol from wave functions whose total energy differences yield the correct order and reasonable barrier magnitudes,[2] one finds that the order is lost and magnitudes are off by factors as great as 4. Another part of the original study[10] pointed out that the highest occupied orbitals (a degenerate pair in ethane) were responsible for almost all of the barrier energy. Again, our *ab initio* results verify this for ethane, and also for methylamine and methanol. But in ethyl fluoride, hydrogen peroxide, hydrazine, and hydroxylamine, a number of molecular orbitals contribute large and comparable amounts.

A referee has requested that we include a discussion of several recent papers devoted to barrier mechanisms. Lowe[11] has examined the shape and energy of the molecular orbitals in ethane and finds that the two principal sets of orbitals which control the barrier have opposing energy contributions. A planar node bisecting the C–C bond allows the dominating orbitals to be associated with a larger normalization coefficient. Because this explanation depends heavily on a symmetry element not present in most other molecules with barriers, and because the barrier mechanism is ultimately related to the chemically unappealing idea of a normalization coefficient, this scheme does not appear promising. In further work he relates favored conformations to highest occupied molecular orbitals, and we have discussed this scheme in the paragraph above. Epstein and Lipscomb[12] have made various sorts of energy decompositions for two ethane wave functions that employed one STO per AO as a basis set, and they were unable to discern any system in their decomposi-

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(9) (a) W. L. Jorgensen and L. C. Allen, *J. Amer. Chem. Soc.*, **93**, 567 (1971); (b) W. L. Jorgensen and L. C. Allen, *Chem. Phys. Lett.*, 7, 483 (1970).

(10) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).

(11) J. P. Lowe, *J. Amer. Chem. Soc.*, **92**, 3799 (1970).

(12) I. R. Epstein and W. N. Lipscomb, *ibid.*, **92**, 6094 (1970).

tions. This is to be expected, since the total energies of the two wave functions they examined are greatly above the Hartree–Fock limit (by a value of approximately 20 times the barrier height), and energy decompositions for this quality of wave function are generally very erratic. Clementi and von Niessen[13] have decomposed the ethane total energy as a function of rotational angle into one-, two-, three-, and four-center contributions. The three-center term undergoes the greatest change of magnitude, but the sign of its change is opposite to the barrier itself, and no physical or chemical concept emerges. A further decomposition assuming that basis functions mounted on a given center possess an energy solely associated with that center leads to a set of 26 energy *vs.* angle curves that do not reveal any chemically useful pattern. A comprehensive review of methods for analyzing barrier mechanisms has been recently made by Lehn.[14]

V. Summary and Conclusions

In order to understand the origin of rotational barriers, it is necessary to analyze a considerable number and variety of molecules showing different barrier characteristics. Ethyl fluoride and ethane constitute an important pair of molecules in such a list because their barriers are surprisingly similar.

To investigate these two molecules, *ab initio* LCAO–MO–SCF wave functions with total energies reasonably close to the molecular Hartree–Fock solution were computed with an atomic orbital basis set of double-ζ quality. The computed barriers were found to be nearly equal, in agreement with experiment. This result substantiates and extends our previous conclusion that the barrier mechanism is contained within the framework of the Hartree–Fock approximation.

Energy components, V_{att} and V_{rep}, were employed to aid in understanding various aspects of the barrier mechanism. The barriers in ethane and ethyl fluoride are both repulsive dominant and therefore arise predominantly from the action of the Pauli principle.[7,9a,15] That the two barriers are quite similar can be interpreted as arising from the tail of the methyl group passing through the high potential field of the fluorine atom and adding roughly equal energy increments to both V_{att} and V_{rep} over their values for ethane. The small change in dipole moment during rotation in ethyl fluoride can also be accounted for with this type of analysis. Since this barrier is repulsive dominant, the slightly smaller moment in the eclipsed configuration arises from a reduced bond dipole in this conformation produced by the repulsion of the fluorine atom.

The possibility of using one-electron energies to characterize and predict barriers is evaluated. It is found to yield reasonably satisfactory barrier predictions for ethyl fluoride and ethane but not for several other molecules.

Acknowledgment. L. C. A. wishes to thank Robert B. Davidson for several helpful discussions during the development and application of the energy component analysis. The National Science Foundation, Grant No. GP 8907, provided support for this research.

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(13) E. Clementi and W. von Niessen, *J. Chem. Phys.*, **54**, 521 (1971).

(14) J.-M. Lehn in "Conformational Analysis," Academic Press, New York, N. Y., 1971, p 129.

(15) The first published suggestion that the Pauli principle plays the dominant role in the ethane barrier appears to have been made by J. van Dranen, *J. Chem. Phys.*, **20**, 1982 (1952). van Dranen based his hypothesis on a semiempirical estimate of the interaction between He and H_2. E. B. Wilson, Jr., *Advan. Chem. Phys.*, **2**, 367 (1959), discussed this question, and his article focused attention on the lack of adequate explanations for barrier mechanisms at that time. More recently, a significant quantitative attempt to show the central importance of the Pauli principle has been made by comparing a Hartree product of locally orthogonal bond orbitals with the corresponding antisymmetrized product: O. J. Sovers, C. W. Kern, R. M. Pitzer, and M. Karplus, *J. Chem. Phys.*, **49**, 2592 (1968). Although completely *ab initio*, the bond orbital method introduces a mixing parameter between a C–H hybrid orbital and a hydrogen 1s which constricts the wave function and considerably raises its energy over a molecular orbital wave function employing the same basis set and interaction integrals. The complexity of the interpretation in this work is illustrative of the very general difficulty inherent in any attempt to meaningfully decompose a molecular wave function which will clearly bring out the workings of the Pauli principle. Another way of approaching this problem is to make a quantitative potential energy curve analogy to the well-understood He–He case (see ref 7).

Molecular Orbital Theory of the Electronic Structure of Organic Compounds. X. A Systematic Study of Geometries and Energies of AH_n Molecules and Cations

W. A. Lathan, W. J. Hehre, L. A. Curtiss, and J. A. Pople*

Contribution from the Department of Chemistry, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213.

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Abstract: An *ab initio* molecular orbital study of the geometries and energies of neutral systems AH_n and their singly charged cations AH_n^+ (A = C, N, O, or F) is presented. Two previously reported basis sets are employed: the minimal, STO-3G, basis and the extended, 4-31G, basis in which valence shells are split into inner and outer parts. Comparisons are made between experimental and theoretically predicted properties.

Self-consistent molecular orbital theory with a well-defined set of basis functions centered at nuclear positions provides a complete theoretical model for molecular structure. Deficiencies of such models due to partial neglect of electron correlation are widely appreciated, but it nevertheless appears that quite simple molecular orbital treatments give successful accounts of molecular geometries,[1] rotational po-