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Examination of Charge Alternation in CH₄ and CH₃F from *ab initio* LCAO SCF MO Wavefunctions and Their Localized Bond Orbitals

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The question of whether or not fluorine substitution produces charge alternation is examined for CH₄ and CH₃F. Two sets of *ab initio* LCAO SCF MO wavefunctions (one a 3 G STO based one, the other a double zeta based one) are analyzed *via* charge density, localized CH bond moment, and population analysis calculations. Although both sets of wavefunctions show a slightly more negative H region in CH₃F relative to CH₄, in qualitative agreement with earlier work by Pople *et al.*, the differences are small, and their sources are not clear. For example, in the 3 G calculations the CH localized orbital is the essential source of the increased density in CH₃F, while for the double zeta calculations the increased density is due to the tail of an F lone-pair orbital *trans* to the CH bond. Consideration of details of these studies as well as those from large STO based SCF MO wavefunctions by Arrighini *et al.*, suggests that one will need very accurate wavefunctions to resolve the problem unambiguously.

Key words: Charge density – Atomic charge – Inductive effect – Localized orbitals

Introduction

In an early application of the CNDO semi-empirical self-consistent field molecular orbital (SCF MO) method, Pople and Gordon [1] studied substituent effects and dipole moments in a series of simple organic molecules. They found the rather surprising result that fluorine substitution in a saturated hydrocarbon gives rise to a charge alternation effect, instead of inducing a positive character which diminishes down the chain (as suggested by older concepts of the inductive effect). For example, the hydrogens in CH₃F were predicted to be more negative than those in CH₄. The consequences of this charge alternation were discussed and shown to be consistent with dipole moment data. However, Schwartz, Coulson, and Allen [2] later analyzed the Mulliken population charge distribution from *ab initio* SCF MO wavefunctions (based on atomic SCF orbitals) for the fluorinated methanes and obtained the opposite results – to charge alternation. But later, Hefre and Pople [3] utilized their optimized minimum Slater orbital basis set approach to find *ab initio* SCF MO population analysis results in essential agreement with the earlier CNDO ones. In the present paper we consider this

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problem in a more detailed way, to try answer the question of whether charge alternation does or does not occur.

Let us briefly outline why we believe the previous investigations are inconclusive, and then our own approach to the problem. Firstly, the charge distributions of the preceding work were taken from Mulliken population analyses [4] of the wavefunction, which do not correspond to direct examination of the electronic distributions, and which are sensitive to basis set composition. Secondly, since CNDO is a calibrated semi-empirical theory and the *ab initio* SCF MO results were based on modest basis sets, there are possible ambiguities in the previously considered wavefunctions, irrespective of how they might be analyzed. We eliminate the first of these ambiguities by direct examination of the electronic density. This is done not only for the total density but also, for further elucidation, by a partitioning of the density into contributions from the chemically appealing localized molecular orbitals [5] (LMO's). In this connection we also examine average values of some electronic position operators for the LMO's. The basis set question is considered by examination of two different sets of *ab initio* LCAO SCF MO wavefunctions we have determined – one with a modest basis set, and the other with a more extended, more flexible basis set. In this paper we consider just the two molecules CH_4 and CH_3F , which are the simplest appropriate molecules. Although charge alternation is not as large here as in other molecules [1] it does exist, and, of course, the systems are small enough for careful examination.

Examination of the electronic densities throughout the entire 3-dimensional regions of the molecules is unreasonable, and we employ the simpler approach of investigating densities along the CH internuclear lines. This is clearly sufficient for CH_4 , because the tetrahedral symmetry forces the CH regional density to be concentrated about this line. In CH_3F there is no rigorous *a priori* reason to anticipate this, although chemical intuition suggests it. But as we shall observe later, our analysis will substantiate this approach.

Results and Discussion

For direct comparison with previous work, we have first repeated the 3G optimized STO basis calculations of Hehre and Pople. [3] Figure 1 displays the resultant total electronic densities along the CH lines. It shows that indeed there is more density in the proton region in CH_3F than in CH_4 , in accord with the earlier population analysis results [3] for the same wavefunctions. This more negative character of the CH_3F protons can be further probed with the LMO's. Table 1 shows the total densities in CH_4 and CH_3F as well as the contributions from the appropriate CH bond LMO. After the large density region near the carbon atoms is passed, the total densities are almost entirely due to the CH LMO's. Paralleling the total densities in the CH regions of the molecules, the CH LMO of CH_3F has a greater density than that in CH_4 . The total density differences and CH LMO density differences are not precisely the same, of course, since no orbital is entirely localized, and the "tails" of other orbitals can contribute to the density in the CH region. But for this minimum basis set

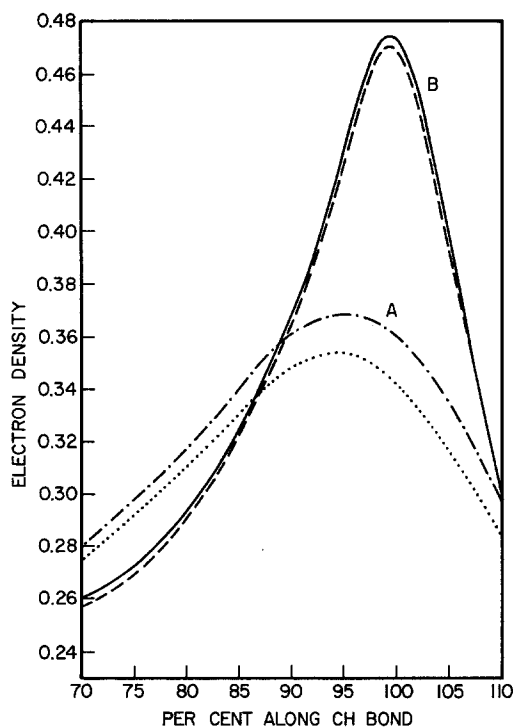


Fig. 1. Total electron densities along the C-H line in CH₄ and CH₃F. Set A presents the 3G STO results; set B, the double zeta results. In both cases the CH₃F density is the upper curve

Table 1. Total and CH LMO density for both CH₃F and CH₄ with minimum basis set

% R(C-H)	CH ₃ F		CH ₄	
	Total density	Density due to CH LMO	Total Density	Density due to CH LMO
24.6	0.58276	0.22194	0.57362	0.21449
58.7	0.26478	0.26455	0.26105	0.26085
77.9	0.30850	0.30546	0.30216	0.30041
87.8	0.35392	0.34690	0.34245	0.33877
97.4	0.36648	0.35626	0.35117	0.34587
100.0	0.36018	0.34963	0.34471	0.33919
107.3	0.31300	0.30278	0.29885	0.29361

calculation the essential source of the more negative proton region in CH₃F is the difference between the CH localized bond orbitals. Further illustration comes from the electronic bond moments of the CH LMO's: $\langle r \rangle = 1.4399$ a.u. in CH₃F and 1.4263 a.u. in CH₄. That is, the average CH electronic positions are nearer the proton in CH₃F. The average CH bond moment in CH₃F does not lie precisely on the CH internuclear line (as it must by symmetry in CH₄), but lies only 17.6' calculation the essential source of the more negative proton region in CH₃F is the

Table 2. Total and CH LMO density for both CH₃F and CH₄ with double zeta basis set

% R · (C-H)	CH ₃ F		CH ₄	
	Total density	Density due to CH LMO	Total density	Density due to CH LMO
50.06	0.27284	0.27097	0.26236	0.25993
80.06	0.29236	0.29059	0.29061	0.29041
90.06	0.36714	0.36292	0.36522	0.36415
97.06	0.45992	0.45296	0.45656	0.45438
100.00	0.47379	0.46605	0.47001	0.46747
110.06	0.29710	0.29129	0.29718	0.29502

by this average CH moment, comparison with CH₄ yields the same conclusion as before – a more negative proton region, due to the CH LMO.

To acquire a more realistic density description we determined a second set of wavefunctions by employing a “double zeta” quality basis set [6] derived from gaussian expansions of atomic SCF orbitals (essentially the same basis set used by Basch, Robin, and Brundle in their recent examination of the fluoromethanes [7]). Experimental molecular geometries were taken from the summary of Gordon and Pople [8]. The resulting data are summarized in Fig. 1 and Table 2. The calculated CH LMO moments were found to be $\langle r \rangle = 1.3910$ in CH₃F and 1.3719 in CH₄, and the average CH moment in CH₃F lies only 18.4° outside the CH internuclear line. The proton region is again calculated to be more negative in CH₃F than in CH₄, but the difference is smaller than for the 3 G STO wavefunctions.

Notice, however (Table 2), that for this more extended basis set the density near the hydrogen due to the CH LMO in CH₄ is greater than in CH₃F: here the CH localized orbital alone does not account for the total density difference in the two molecules. When the density due to the CH LMO plus nearest neighboring LMO's are compared for both molecules, it is found that all of these LMO's collectively cannot account for the more negative character of the protons in CH₃F. The next highest contributing component comes from the fluorine lone pair LMO which is pointing in a *trans* manner away from the proton. (F lone pair LMO's are staggered with respect to CH LMO's). The tail of this orbital is thus directed back at the proton and contributes to its electronic density. Thus, the total density difference might be attributed to the fluorine's contribution, of which the *trans* orientated fluorine lone pair is the principal donor. This donation in part, at least, is due to electronic rearrangement caused by molecular formation and not to a “spilling over” of density from the fluorine atom. This is substantiated by calculations showing that the density contributed by either a fluorine atom or fluorine negative ion (when examined at distances comparable to those in CH₃F) is an order of magnitude smaller than that contributed by the center while in the molecular environment.

Notice by examination of Fig. 1 that the calculated charge density near the protons with the extended basis set is considerably greater than that in the minimum basis set. Calculations of the gross atomic population by use of

Table 3. Summary of population analysis

	Double zeta basis		3G STO basis	
	CH ₃ F	CH ₄	CH ₃ F	CH ₄
Carbon	6.1294	6.7507	5.8316	6.0758
Hydrogen	0.8287	0.8123	1.0044	0.9811
Fluorine	9.3846	—	9.1552	—

Mulliken's analysis for both molecules are summarized in Table 3. In a qualitative way the population analysis seems more closely to coincide with the CH bond moments than it does with the charge density at the hydrogens. Neither bond dipole moment nor population analysis makes apparent the substantial change in charge density at the hydrogen as a function of basis set shown in the figure. Both predict a greater charge density further out along the CH bond in CH₃F, but neither reflects the greater density spike in the extended basis set as compared to the minimum basis set in the region of the proton. Thus it appears that qualitative comparison by use of Mulliken's analysis is limited to similar molecules with comparable basis sets.

Conclusions

Both the minute size of the determined charge alternation as well as its inconclusive source lead us to be wary of establishing a definite view on this problem. Furthermore, interpretation of the work on CH₄ and CH₃F by Arrighini *et al.* [9] with a still more extensive basis set suggests a further diminished charge alternation effect. They found by use of a large STO basis set that the CH LMO [10] moments for CH₃F and CH₄ were nearly equal [$\langle r \rangle = 1.390$ for CH₃F and $\langle r \rangle = 1.386$ for CH₄]. Perhaps such small effects as charge alternation cannot be unambiguously resolved short of essentially solving the problem exactly.

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