separation between the average lone pair orbital IP and the σ orbital IP's for trioxane is less than in trithiane. For example, the separation between the lone pairs and the first σ ionization is 1.2 eV in trioxane and 2.2 eV in trithiane. On this basis one expects the trioxane lone pair orbitals to be mixed in with the σ network to a greater extent, *i.e.*, be more bonding and so, other things being equal, be more susceptible to Jahn–Teller forces.

Finally, we observe that the first σ orbital bands in trioxane and trithiane are split. From group theory and overlap arguments one expects the first σ level to be degenerate (e) and hence susceptible to Jahn–Teller forces. This may be the origin of the σ level splitting. The first σ band (Figure 5) is split by 0.40 eV in trioxane and 0.2 eV in trithiane. By the above arguments one indeed would expect a greater splitting in the trioxane σ level if Jahn–Teller forces operate.

It is of interest to note that the arguments presented above for oxygen and sulfur heterocycles cannot be applied to the analogous nitrogen systems. This is due to the different symmetry properties of the nitrogen lone pair orbitals, as is discussed above. For example, the lone pair splitting in piperazine[20] and *N*,*N*-dimethylpiperazine[21] is very small while, as seen above, it is substantial in the oxygen and sulfur systems.

In conclusion we emphasize that lone pair splitting in the heterocycles studied here is greater in sulfur when through space and greater in oxygen when through bond.

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Ab Initio Studies of Hyperfine Coupling in Free Radicals. II. Methyl and Fluoromethyl Radicals, and α-Fluorine Spin Coupling Parameters[1]

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Abstract: By using an *ab initio* LCAO-SCF-MO-CI method with Slater sis basets, the isotropic H, ^{19}F, and ^{13}C coupling constants of planar CH_3 and planar and nonplanar CH_2F are calculated. The basis set DZS proposed in I improves the calculated ^{13}C and ^{19}F coupling drastically. Angular dependency of the ^{19}F coupling is very small as a result of cancellation between an increase of the spin delocalization contribution and a decrease of the spin polarization contribution. Based on models in which the half-occupied π^* orbital of CH_2F is artificially modified, new sets of values of spin coupling parameters Q which are very different from existing ones are proposed. An important feature of the new values suggests that the $a(^{19}F)$ is mainly due to the net π spin population on the C–F bond that polarizes the fluorine s spin.

Isotropic and anisotropic hyperfine coupling constants by electron spin resonance (esr) and nuclear magnetic resonance (nmr) spectroscopy provide an important insight to the electron distribution in polyatomic free radicals. Interpretation of coupling constants has been carried out mostly by semiempirical molecular orbital (MO) and valence bond methods. Semiempirical methods can often explain experimental results, but always leave an ambiguity in their conclusions due to the arbitrary parametrization.

The recent development of programs and faster computers has made it possible to carry out reliable *ab initio* calculations of electronic structures for polyatomic molecules. Nevertheless hyperfine coupling calculations by *ab initio* methods have been limited to simple hydrides such as CH, OH, NH_2, and CH_3.[3-5] One of the reasons for this is that the minimal basis set, the double ζ basis set and the double ζ set with additional p and d polarization orbitals, which predict the geometry, energy, and other expectation values reasonably well, often give coupling constants in poor agreement with experiments. More extended basis sets are often prohibitive for calculations of larger molecules.

In the preceding paper,[1] we proposed two new basis sets of Slater-type orbitals, called MZS and DZS sets, for some of the first-row atoms. They are the minimal and double ζ Slater-type basis sets, respectively, augmented by an extra 2s orbital with a large exponent. These basis sets are proposed upon our belief that the minimal or double ζ basis sets predict correctly most electronic properties of molecules and that the only main reason why they failed to predict spin densities is their inadequacy near the nucleus. The extra 2s orbital drastically improves the behavior of the spin density

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near the nucleus. The exponent of the orbital was determined to fit the experimental spin density at the nucleus of the ground-state atoms with the spin density calculated by the self-consistent field (SCF) molecular orbital (MO) configuration interaction (CI) method. These new basis sets, small enough for molecular calculations, are anticipated to give a spin density for a molecule in good agreement with experiments.

It appears that there exist a number of problems of hyperfine coupling which requires examination or reexamination by *ab initio* theories. In this series of papers we intend to study a few of these problems by using the SCF–MO–CI method with the above-mentioned basis sets.

In this paper we plan to study the isotropic hyperfine interaction of the α-fluorine, the fluorine atom attached directly to a conjugated carbon atom. Interpretation of coupling mechanisms has been exclusively carried out empirically or by semiempirical quantum mechanical methods.[6–21] The following three types of equations have been used to relate the isotropic ^{19}F coupling constant $a(^{19}\text{F})$ to spin densities.

$$a(^{19}\text{F}) = Q_{\text{eff}}\rho^{\pi}{}_{\text{C}} \tag{1}$$

$$a(^{19}\text{F}) = Q^{\text{F}}{}_{\text{C}}\rho^{\pi}{}_{\text{C}} + Q^{\text{F}}{}_{\text{F}}\rho^{\pi}{}_{\text{F}} \tag{2}$$

$$a(^{19}\text{F}) = Q^{\text{F}}{}_{\text{C}}\rho^{\pi}{}_{\text{C}} + Q^{\text{F}}{}_{\text{CF}}\rho^{\pi}{}_{\text{CF}} + Q^{\text{F}}{}_{\text{F}}\rho^{\pi}{}_{\text{F}} \tag{3}$$

$\rho^{\pi}{}_{\text{F}}$ and $\rho^{\pi}{}_{\text{C}}$ are the π spin density at the fluorine atom and the adjacent carbon atom, respectively, and $\rho^{\pi}{}_{\text{CF}}$ is the π spin density on the C–F bonds.

The simplest expression, eq 1, has been used by many workers[6–13] with a value of Q_{eff} between +40 and +60 G. Since $\rho^{\pi}{}_{\text{F}}$ is approximately proportional to $\rho^{\pi}{}_{\text{C}}$ in a series of free radicals, eq 1 can account for the effective spin polarization quite well. On the other hand, more sophisticated expressions, eq 2 and 3, attempt to describe the spin polarization mechanisms, one mechanism in which the fluorine π spin density $\rho^{\pi}{}_{\text{F}}$ polarizes the fluorine 1s and 2s electrons and one in which the carbon π spin density $\rho^{\pi}{}_{\text{C}}$ polarizes the fluorine s electrons and, in eq 3, one in which the off-diagonal π spin density $\rho^{\pi}{}_{\text{CF}}$ polarizes the fluorine s electrons. Experimentally or semiempirically determined values of Q's are scattered over a wide range: $Q^{\text{F}}{}_{\text{F}}$ from +146 to +1043 G and $Q^{\text{F}}{}_{\text{C}}$ from −147 to +48 G in eq 2[11,14–19] and $Q^{\text{F}}{}_{\text{F}}$ from −150 to +3100 G, $Q^{\text{F}}{}_{\text{C}}$ from −620 to +90 G, and $Q^{\text{F}}{}_{\text{CF}}$ from −70 to +600 G in eq 3.[11,20,21]

Recently Icli and Kreilick[13] examined eq 1 and 2 for fluorinated phenoxy radicals and concluded that, because of the approximate proportionality between $\rho^{\pi}{}_{\text{C}}$ and $\rho^{\pi}{}_{\text{F}}$ for most free radicals so far studied, one could not experimentally determine individual Q values but only Q_{eff}.

With all the scattering of determined Q values it appears that a careful *ab initio* theoretical study might be able to make an independent and significant contribution to the problem. In the present paper we carry out *ab initio* SCF–MO–CI calculations for $\cdot\text{CH}_2\text{F}$ as a model of the α-fluorine containing free radicals. First we confirmed that the DZS set in fact gives a reliable result for molecular free radicals by performing calculations for the well-established methyl radical. Then we examine the angular dependency of ^{19}F, ^{13}C, and ^{1}H isotropic coupling constants in CH_2F. Finally, we obtain and discuss the Q values for the three types of ^{19}F and ^{13}C hyperfine coupling expressions.

Method

We adopt the restricted SCF–CI method over a simpler unrestricted SCF method, because in the latter the mixing of higher multiplets and the problem of projection or nonprojection to the spin eigenstate after the SCF calculation obscures the theoretical significance of the result and also because the former method is more suitable for analyzing various coupling mechanisms and deducing Q values.

The SCF calculation was performed on Slater-type basis sets with Nesbet's symmetry-adopted approximate SCF method[22] by using the POLYCAL program package.[23] The CI calculation, carried out by our general purpose CI program,[24] included only the ground and singly excited configurations. According to Chang, *et al.*'s, result[3] of the methyl radical, our results for F atom (^{2}P),[1] and our preliminary calculations for CH_2F, the singly excited configurations account for about 90% of the isotropic coupling constants.

The isotropic hyperfine coupling constant was calculated by the ONEXP program.[24] The program calculates from CI wave functions the one-electron MO density matrices for α and β electrons $\rho_{ij}{}^{\alpha}$ and $\rho_{ij}{}^{\beta}$, and then the basis function (BO) density matrices, $\rho_{rs}{}^{\alpha}$ and $\rho_{rs}{}^{\beta}$. The BO total electron density p_{rs} and spin density ρ_{rs} are then given by

$$\begin{aligned} \rho_{rs} &= \rho_{rs}{}^{\alpha} - \rho_{rs}{}^{\beta} \\ p_{rs} &= \rho_{rs}{}^{\alpha} + \rho_{rs}{}^{\beta} \end{aligned} \tag{4}$$

It is noted that we do not neglect the overlap integrals; the spin density in a free radical is normalized to unity by including the off-diagonal ($r \neq s$) contributions

$$1 = \sum_{r} \rho_{rr} + 2\sum_{r<s} \rho_{rs}S_{rs} \tag{5}$$

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Table I. Calculated Proton and Carbon-13 Hyperfine Coupling and Total Energy for Planar CH_3

Basis set	Ref	Total energy, hartrees SCF	SCF–CI[a]	a(H),[a] G	$a(^{13}C)$,[a] G	$(\text{Cusp})_{\gamma,H}$	$(\text{Cusp})_{\gamma,C}$
MZ (Slater rule)	CDV	−39.4148	−39.4240	−29.2	+133.6	1.042	1.050
MZ (optimized)	CDV	−39.4873	−39.4941	−38.9	+132.3	1.217	1.060
MZS	This work	−39.4186	−39.4279	−29.6	+62.3	1.043	0.969
DZ	CDV	−39.5471	−39.5543	−36.1	+23.0	1.151	0.528
DZS	This work	−39.5491	−39.5565	−27.6	+35.6	1.083	1.022
Experimental[b]				(−)23.0	(+)38.3		

[a] All the CDV values referred are based on SCF–CI(S) calculation to be consistent with the present work. [b] Reference 26. Experimental values are averages over the vibrational motion. The coupling constants, a(H) and $a(^{13}C)$, for a planar CH_3 are anticipated to be a little smaller in magnitude than the vibrationally averaged values.

Table II. Exponents for Slater-Type Orbitals for Various Basis Sets

Basis set	Atomic orbitals H	1sC	2sC	2pC	1sF	2sF	2pF
MZ (Slater rule)	1.00	5.70	1.625	1.625	8.70	2.60	2.60
MZS[a]			3.08			4.61	
DZ	1.00	5.231	1.168	1.256	7.918	1.947	1.845
	1.26	7.969	1.820	2.726	11.011	3.096	4.171
DZS[b]	3.00		4.00			7.95	

[a] In addition to the MZ set. [b] In addition to the DZ set.

where S_{rs} is the overlap integral between BO's r and s. The isotropic hyperfine coupling constant of a nucleus N is given by

$$a(N) = C_N\sum_{r,s} \rho_{rs}\langle\chi_r|\delta(R_N)|\chi_s\rangle = C_N\rho(N,N) \quad (6)$$

where $C_N = (8\pi/3)g\beta\hbar\gamma_N$ is 1592 G for a proton, 400.3 G for ^{13}C, and 1498 G for ^{19}F. $\langle\chi_r|\delta(R_N)|\chi_s\rangle$ is the product of the values of BO's, χ_r and χ_s, evaluated at the nucleus N. The summation $\Sigma_{r,s}$ covers all the BO's including BO's on the nucleus N and BO's on other nuclei. $\rho(N,N)$ is the one-electron spin-density matrix evaluated at the nucleus N.[3]

The spin-density cusp at the nucleus N is calculated as follows[3]

$$(\text{cusp})_{\gamma.N} = -[Z_N\rho(N,N)]^{-1}[(\partial/\partial r_{i\beta})\hat{\rho}(r_{i\beta},N)|_{r_{i\beta}=r_{iN}} \quad (7)$$

where Z_N is the charge of the nucleus N, $\rho(N,N)$ is the spin density at the nucleus N, r_{iN} is the distance between N and the electron i, and $\hat{\rho}(r_{iN},N)$ denotes the spherical average of $\rho(r_{iN},N)$ about point N which is an element of the spin-density matrix. For the exact wave function of the system, this quantity should be unity at every nucleus. For an approximate wave function this would serve as a measure of its accuracy in the region close to a nucleus. In the LCAO approximation of Slater-type orbitals of $n \leq 2$, the cusp is actually calculated as follows[3]

$$(\text{cusp})_{\gamma.N} = [Z_N\rho(N,N)\sqrt{\pi}]^{-1} \times \left\{\sum_k \zeta_{1sNk}{}^{5/2}\sum_j \rho_{1sNk.j}\chi_j(N) - 3^{-1/2}\sum_k \zeta_{2sNk}{}^{5/2} \times \sum_j \rho_{2sNk.j}\chi_j(N)\right\} \quad (8)$$

where ζ_{1sNk} and ζ_{2sNk} are exponents of the kth 1s and 2s Slater orbitals on the nucleus N and $\rho_{1sNk.j}$ (and $\rho_{2sNk.j}$) is BO spin density matrix (eq 4) between 1sNk (and 2sNk) and j. $\chi_j(N)$ is the value of BO χ_j evaluated at the nucleus N.

Methyl Radical. *Ab initio* studies of isotropic hyperfine coupling of methyl radical have been carried out by several investigators.[3-5] Here we refer mainly to the SCF–CI calculation using Slater-type orbitals by Chang, Davidson, and Vincow (CDV).[3] They used a double ζ (DZ) basis set[5] as well as two minimal (MZ) basis sets, one with exponents by Slater's rule and another with exponents which minimized the SCF energy. As summarized in Table I, both MZ sets give a ^{13}C coupling constant $a(^{13}C)$ much larger than experiment.[26,27] The DZ set gives a better (but too small) coupling constant, but the cusp at ^{13}C is very bad, indicating that the spin density near the nucleus is poorly represented in this molecule as in the atom.[1] As for a(H), the unoptimized MZ set shows a closer agreement with experiment than the optimized MZ or DZ. Again the DZ set gives a poor cusp value. According to Poling, Davidson, and Vincow,[28] who introduced the cusp constraint procedures with several basis sets including the one more extended than the DZ set, the cusp constrained wave function does not necessarily lead to a stable value of $a(^{13}C)$ for the radical CH.

We want to use the DZS and MZS sets proposed in our previous paper and shown in Table II. An argument based on the atomic hyperfine coupling should give a hydrogen basis set consisting of a single 1s orbital of an exponent 1.0. CDV gives the best DZ functions for hydrogen with the exponents $\zeta_1 = 1.0$ and $\zeta_2 = 1.26$. An effort to decrease the calculated a(H) to fit with experiment by changing ζ_2 increased the energy remarkably and worsened the cusp. So the third 1s orbital was added, and a much improved a(H) and cusp was obtained with $\zeta_3 = 3.0$. Thus the DZS set for hydrogen includes three 1s orbitals, as shown in Table II. The addition of a condensed s orbital is consistent with what was done with the DZS set in other atoms in ref 1. For the MZS set, for which a less accurate result is anticipated, there are two possible

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Table III. First-Order Contribution of the Excited Configurations to $a(^{13}C)$ and $a(H)$ for CH_3

Excitation[a] From	To	$a(^{13}C)$, G MZ	MZS	DZ	DZS	$a(H)$,[b] G MZ	MZS	DZ	DZS
$1a_1$	$3a_1$	−15.5	−12.1	−6.4	−4.3	0.0	0.0	0.0	0.0
	$4a_1$		−38.7	+0.5	+0.8		0.0	0.0	0.0
	$5a_1$			−12.4	−13.1			0.0	0.0
	$6a_1$			−32.7	−13.4			0.0	0.0
	$7a_1$				−0.9				0.0
	$8a_1$				−8.1				0.0
$2a_1$	$3a_1$	+140.1	+111.9	+55.5	+37.8	−12.6	−13.0	+0.9	−3.4
	$4a_1$		−5.8	−14.7	−14.1		−0.1	−11.4	−6.2
	$5a_1$			+32.1	+50.0			−8.7	−3.5
	$6a_1$			−3.1	−2.4			−0.0	−0.4
	$7a_1$				−0.2				+0.4
	$8a_1$				−0.5				0.0
$1e_y$	$2e_y$					−18.3	−18.4	+2.5	−2.7
	$3e_y$							−20.1	−7.5
	$4e_y$							−1.3	−0.9
	$5e_y$								−4.7
Sum ($1a_1 \to i$)		−15.5	−50.8	−51.1	−39.0	0.0	0.0	0.0	0.0
Sum ($2a_1 \to i$)		+140.1	+106.1	+69.9	+70.5	−12.6	−13.1	−19.2	−13.1
Sum ($1e \to i$)						−18.3	−18.4	−18.9	−15.8
Sum (first order)		+124.6	+55.3	+18.8	+31.5	−30.9	−31.4	−38.0	−28.9
Total		+133.6	+62.3	+23.0	+35.6	−29.6	−29.6	−36.1	−27.6

[a] The excited configurations corresponding to the excitation of an electron from an MO, say $1a_1$, to another MO, say $3a_1$. [b] The hydrogen atom is assumed to be on the y axis with the carbon atom at the origin.

choices for the hydrogen atom, one using two 1s orbitals with the exponents $\zeta_1 = 1.0$ and $\zeta_2 = 1.26$ and another using 1s orbital with $\zeta_1 = 1.0$. Since they were found to give almost identical results, the latter was adopted in this paper (Table II).

In Table I, the DZS and MZS results are compared with existing calculations. The DZS set improves not only both of the coupling constants, $a(H)$ and $a(^{13}C)$, but also the spin-density cusp drastically over the DZ results. The improved cusp condition is an indication of the correct spin-density behavior near the nuclei as anticipated from the atomic hyperfine calculations.[1] Thus the DZS set is shown to be reliable for discussing the spin density of a molecule at the nucleus and will be used mainly for the calculation of CH_2F in the following sections.

The MZS set improves the ^{13}C coupling constant significantly over the MZ set, but not so much as to agree quantitatively with experiment.

It is often illustrative to examine contributions of various excited configurations to the coupling constant. The CI wave function can be regarded as the sum of the ground configuration (zero order) and various singly excited configurations (first order). The zero-order coupling constant in the restricted SCF method is zero because the odd electron is in a π MO. The first-order contribution to the spin density from the configuration corresponding to a single electron excitation from MO i to MO p is given by

$$(32\pi/3)g\beta\hbar\gamma_N\sum_{\gamma} C_0C^{\gamma}_{i\to p}\langle\Phi_0 \times \left|\sum_j \delta(r_j - r_N)s_{jz}\right|\Phi^{\gamma}_{i\to p}\rangle \quad (9)$$

where Σ_γ denotes the summation over all the spin eigenstates belonging to the configuration, and C_0 and $C^{\gamma}_{i\to p}$ are the coefficients of the ground and the excited configuration functions, Φ_0 and $\Phi^{\gamma}_{i\to p}$, respectively, in the ground state CI wave function.

Table III summarizes the first-order contribution to $a(^{13}C)$ and $a(H)$ for various basis sets. The $1a_1$ MO is essentially the carbon 1s orbital, and $2a_1$ and $1e_y$ are C–H bonding MO's. For any basis set the inner shell ($1a_1$) polarization, *i.e.*, the sum of ($1a_1 \to i$) over i, gives a negative contribution to $a(^{13}C)$, while the valence shell ($2a_1$) polarization makes a large positive contribution, but their magnitude depends very much on the basis set. As for the valence shell polarization contribution to $a(^{13}C)$, the DZ value is almost identical with the DZS value. But the inner shell polarization contribution of the DZ is about 11 G larger in magnitude than the DZS value. This again reflects the deficiency of the DZ set in describing the atomic polarization correctly, as was already pointed out.[1]

Fluoromethyl Radical. Angular Dependency. The angular dependency of proton, ^{13}C, and ^{19}F coupling constants in fluorinated methyl radicals has been a problem of experimental and theoretical interest.[29–31] We carried out restricted SCF–CI calculations on the CH_2F radical for several nonplanar conformations with the DZS basis set as well as for the planar conformation with DZS, DZ, MZS, and MZ basis sets of Table II. A C–H distance of 1.08 Å, C–F distance of 1.35 Å, and an HCH angle of 120° were used. The C–F axis was assumed to be on the bisector plane of the HCH angle. The nonplanarity angle θ was defined as the angle between the C–F and the HCH plane. The exponents for the DZS set were not reoptimized for the θ variation, because in the DZ or larger basis sets the necessary readjustment of orbitals is anticipated to take place automatically through varied weights of individual basis functions.

The energy and hyperfine coupling results are shown in Table IV. The DZS angular dependency of the energy suggests a minimum around θ = 25–30° with an inversion barrier 0.3–0.4 kcal/mol in the SCF–CI

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Table IV. ^1H, ^{13}C, and ^{19}F Hyperfine Coupling Constants (Gauss) and Energy (kcal/mol) in CI and SCF Calculations for CH_2F as Functions of Nonplanarity θ

Basis set, θ		MZ, 0°	MZS, 0°	DZ, 0°	DZS				Expt
					0°	10°	20°	40°	
^1H	CI	−27.26	−27.84	−38.63	−28.92	−27.49	−23.51	−10.23	(−)21.1
	SCF				0	+0.99	+3.77	+12.60	
	Δ[a]				−28.92	−28.48	−27.28	−22.83	
^{13}C	CI	+113.43	+62.28	+34.47	+47.49	+52.11	+64.85	+103.43	(+)54.8
	SCF				0	+3.80	+14.19	+44.80	
	Δ				+47.49	+48.31	+50.66	+58.63	
^{19}F	CI	+148.68	+140.45	+72.81	+100.82	+101.44	+102.70	+102.48	(+)64.3
	SCF				0	+1.04	+3.58	+7.85	
	Δ				+100.82	+100.36	+99.12	+94.63	
Energy[b]	CI				0	−0.09	−0.28	+0.86	
	SCF				0	−0.21	−0.65	+0.02	

[a] The difference between the SCF–CI result and the SCF result. [b] The energy in kcal/mol measured from $\theta = 0°$. Since the CI includes only singly excited configurations, only a small portion of the correlation energy is taken into account in the CI result. The DZS energies at 0° are −138.39909 (SCF–CI) and −138.38738 hartrees (SCF).

and 0.7–0.8 kcal/mol in the SCF calculations. The results are qualitatively in agreement with previous INDO calculation ($\theta \sim 36°$)[31] and *ab initio* calculation with a small Gaussian basis set ($\theta \sim 8°$ with a C_{3v} symmetry assumed, inversion barrier 0.6 kcal/mol).[30] A large zero-point vibration is expected because of the small inversion barrier.

The DZS angular dependency of coupling constants is shown in Figure 1. As θ increases, $a(^{13}C)$ increases drastically and $a(H)$ decreases in magnitude slowly. These angular dependencies are similar to the CDV results on $\cdot CH_3$. The calculated fluorine coupling $a(^{19}F)$ is positive as experimentally shown for the α-fluorine in various free radicals.[6–21] It changes little as θ increases from 0 to 40°. One might have expected that as the nonplanarity of the system increases, the odd electron originally localized in the $2p\pi$ orbitals will have more chance to delocalize directly to the fluorine 1s and 2s orbitals, leading to an increase (more positive or less negative) in the coupling constant. This is the case for $a(^{13}C)$ and $a(H)$ but not for $a(^{19}F)$. The situation becomes clearer if we compare the two contributions to the coupling: the spin delocalization contribution a_{SCF} (the coupling constant obtained in the restricted SCF calculation) and the spin polarization contribution a_Δ (the difference between the SCF–CI and SCF coupling constants). Figure 1 shows that for H both a_{SCF} and a_Δ increase as θ increases, resulting in a net increase (a decrease in magnitude) in the total $a(H)$. On the other hand, for F, a_{SCF} increases while a_Δ decreases, giving a net cancellation of the angular dependency. Thus it appears that the increase of the experimental $a(^{19}F)$ from CH_2F (64.3 G) to CHF_2 (84.2 G) to CF_3 (142.2 G)[27] is not simply related to the increase in the nonplanarity but also can be attributed to the electronic structure change due to fluorine substitution.

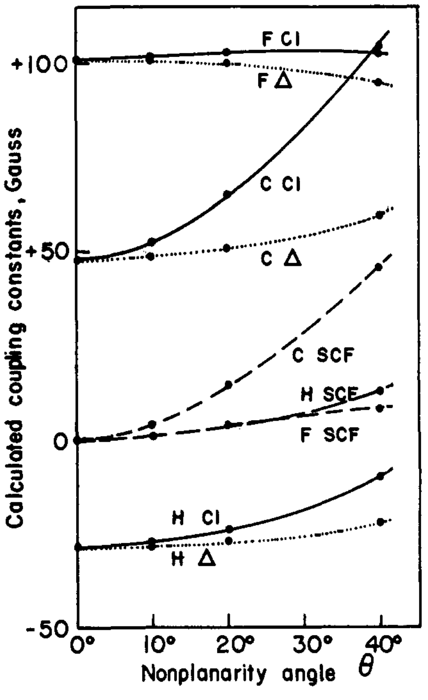

Figure 1. Angular dependency of $a(H)$, $a(^{19}F)$, $a(^{13}C)$, and their delocalization and polarization contributions for CH_2F in SCF–CI calculations with the DZS basis set. The label CI refers to the complete result, SCF to the SCF result, *i.e.*, the delocalization contribution, and Δ to the difference between CI and SCF, the polarization contribution.

Following the scheme mentioned in the previous section, we calculated contributions of various excited electronic configurations to the coupling constants for the planar CH_2F. The ground configuration of the molecule is $(1a_1\sigma)^2(2a_1\sigma)^2(3a_1\sigma)^2(4a_1\sigma)^2(1b_1\sigma)^2(5a_1\sigma)^2(1b_2\pi)^2(2b_1\sigma)^2(2b_2\pi)$. The first-order contributions come only from $a_1\sigma \rightarrow a_1\sigma^*$ excited configurations, because $b_1\sigma$ and $b_2\pi$ orbitals have a node on the F atom. Table V shows some of the results. For $a(^{13}C)$ and $a(H)$ the contribution scheme was found to be very similar to that in CH_3 and was not listed in the table. For ^{19}F, the inner shell contribution, the sum of all the $1a_1 \rightarrow \sigma^*$ contributions is negative as in ^{13}C and the atomic ^{19}F.[1] The major valence shell contributions in the DZS calculation come from $3a_1 \rightarrow 7a_1$, $10a_1$, $11a_1$ and $4a_1 \rightarrow 6a_1$, $7a_1$, $11a_1$ resulting in a large positive value.

It should be noted that even with the DZS set the quantitative agreement of $a(^{19}F)$ between theory and experiment was not accomplished. In the range not too close to the nucleus the spin-density and electron-density behavior of the double ζ set are very similar to those of the Hartree–Fock set. Therefore we tend to attribute the discrepancy mainly to the fact that the wave function very close to the nucleus is not still completely adequate. Such an error would not affect the angular dependency or the spin polarization mechanisms which

Table V. Gross Population of Occupied MO's and First-Order Contribution of the Excited Configurations to $a(^{19}F)$ for CH_2F in Gauss

Basis set		Excitation from MO				
		$1a_1$	$2a_1$	$3a_1$	$4a_1$	$5a_1$
DZS						
Gross population	Fs	1.0000	0	0.9095	0.0518	0.0249
	Fpx	0	0	0.0219	0.1826	0.5608
	Cs	0	1.0000	0.0223	0.5147	0.0748
	Cpx	0	0	0.0335	0.0190	0.2564
	Hs	0	0	0.0064	0.1160	0.0415
Excitation to MO	$6a_1$	0	0	−9	+21	−4
	$7a_1$	−3	0	−44	+98	+9
	$8a_1$	0	0	−1	−7	+6
	$9a_1$	0	0	0	0	0
	$10a_1$	−4	0	+35	−3	−4
	$11a_1$	−9	0	+54	−28	+13
	$12a_1$	−1	0	+14	−10	+2
	$13a_1$	0	0	0	+6	0
	$14a_1$	0	0	0	0	0
	$15a_1$	−22	0	+6	+9	−1
	$16a_1$	0	0	0	0	0
	$17a_1$	−8	0	−3	−2	0
	Sum	−48	0	+51	+85	+22
MZS						
Excitation to MO	$6a_1$	−1	0	−31	+73	−7
	$7a_1$	−3	0	−20	+36	+54
	$8a_1$	−2	0	+11	−1	−1
	$9a_1$	−75	0	+131	−32	+4
	Sum	−80	0	+91	+77	+49

are determined by the wave function in the interaction region.

So far we have discussed results of our best basis set, DZS. Table IV gives the results with other basis sets at $\theta = 0°$. The DZ results for $a(^{13}C)$ and $a(H)$ are consistent with those in the CH_3 radical: a smaller $a(^{13}C)$ and a larger $|a(H)|$ than DZS. The DZ $a(^{19}F)$ agrees better with experiment than the DZS result. This better agreement is fortuitous; because of the defect near the fluorine nucleus,[1] the DZ set gives a much smaller inner shell contribution (−73.2 G) than the improved DZS set (−47.7 G) which cancels with a too large valence shell contribution in either set. The $a(^{19}F)$ by the MZS set is even larger than the DZS result, due to an excessive contribution of the valence shell polarization (Table V).

Estimate of Q Values. By using the planar $\cdot CH_2F$ as a model for the α-fluorine containing radicals, we now want to obtain the Q values in eq 1–3.

As mentioned previously, eq 1 describes only the overall ^{19}F coupling, while eq 2 and 3 distinguish two or three mechanisms contributing to the α-fluorine spin coupling. For instance, eq 2 could be interpreted to mean that $a(^{19}F)$ would be $Q^F{}_F$ if $\rho^\pi{}_C = 1$ and $\rho^\pi{}_F = 0$ and would be $Q^F{}_C$ if $\rho^\pi{}_F = 1$ and $\rho^\pi{}_C = 0$. But such an extreme as $\rho^\pi{}_F = 1$ and $\rho^\pi{}_C = 0$ actually never occurs and electronic structures of radicals at the extreme would be completely different from reality. In real free radicals the values of $\rho^\pi{}_F$ and $\rho^\pi{}_C$ may vary widely, but the ratio of the two, $\rho^\pi{}_F/\rho^\pi{}_C$, is relatively constant.[13] Therefore, it appears that for an $a(^{19}F)$ *vs.* ρ relationship, such as is shown in eq 2, to be meaningful, the Q values should be interpreted to mean a rate of change of $a(^{19}F)$ due to a change in ρ near the fixed value of $\rho^\pi{}_F/\rho^\pi{}_C$

$$Q^F{}_F = (\partial a(^{19}F)/\partial \rho^\pi{}_F)_0$$
$$Q^F{}_C = (\partial a(^{19}F)/\partial \rho^\pi{}_C)_0 \qquad (10)$$

where the subscript 0 means that the value is to be evaluated near realistic values of the ratio $\rho^\pi{}_F/\rho^\pi{}_C$.

A few comments could be made here on the π spin-density coupling relationships, eq 2 and 3. In any calculation in which more than one basis function is used to describe one atomic orbital as in the DZS calculation, the spin density matrix as defined by eq 4 is not a convenient quantity to use. More convenient is *the net spin population d* on an atom or on a bond, defined as follows

$$d_X = \sum_r^X \sum_s^X \rho_{rs} S_{rs}$$
$$d_{XY} = 2\sum_r^X \sum_s^Y \rho_{rs} S_{rs} \; (X \neq Y) \qquad (11)$$

where ρ_{rs} and S_{rs} are the basis function (BO) spin density and the overlap integral, respectively, and the summation covers all the BO's on the specified atom. These represent the spin density on each atom and bond, and the sum of them over all the atoms and the bonds gives a unit spin

$$1 = \sum_X d_X + \sum_{(XY)} d_{XY} \qquad (12)$$

The net π spin populations $d^\pi{}_C$, $d^\pi{}_F$, and $d^\pi{}_{CF}$ are most logically used in the three-term expression eq 3. If one wants to adopt the two-term eq 2, the most reasonable quantity to use as ρ is the *gross spin population D* on F and C atom, generally defined as

$$D_X = d_X + 1/2\sum_Y d_{XY} \qquad (13)$$

Here the net bond population d_{XY} is partitioned equally into the atom X and Y. Therefore the sum of D_X gives unit spin

$$1 = \sum_X D_X \qquad (14)$$

The spin-density coupling relationships are often used in conjunction with such MO methods as INDO

Table VI. Hyperfine Coupling Constants and Population Analysis for Models Used in Q Estimation for CH_2F

Model		Standard	I	II	III	IV	V
MO coefficients							
MO 2b	$BO\pi_C1$	0.8741	0.8692	0.8853	0.8741	0.8610	0.8465
	$BO\pi_C2$	0.1780	0.1770	0.1802	0.1780	0.1753	0.1723
	$BO\pi_F1$	−0.3358	0.0	−0.2764	−0.3358	−0.3828	−0.4227
	$BO\pi_F2$	−0.1168	0.0	−0.0961	−0.1168	−0.1332	−0.1471
MO 1b	$BO\pi_C1$	0.1655	−0.1679	0.1042	0.1655	0.2148	0.2574
	$BO\pi_C2$	0.0630	−0.0639	0.0396	0.0630	0.0817	0.0979
	$BO\pi_F1$	0.6884	0.7512	0.7099	0.6884	0.6676	0.6471
	$BO\pi_F2$	0.3226	0.3521	0.3328	0.3226	0.3129	0.3033
SCF spin population	$d^{\pi}{}_{C}$	1.0113	1.0	1.0374	1.0113	0.9812	0.9485
	$d^{\pi}{}_{F}$	0.1788	0.0	0.1211	0.1788	0.2323	0.2833
	$d^{\pi}{}_{CF}$	−0.1901	0.0	−0.1585	−0.1901	−0.2134	−0.2318
	$D^{\pi}{}_{C}$	0.9163	1.0	0.9582	0.9163	0.8744	0.8326
	$D^{\pi}{}_{F}$	0.0837	0.0	0.0418	0.0837	0.1256	0.1674
CI energy gain, hartree		−0.0117	−0.0099	−0.0075	−0.0065	−0.0065	−0.0074
a(H), G		−28.92	−28.61	−29.10	−28.57	−27.90	−27.12
$a(^{13}C)$, G		+47.49	+46.95	+46.52	+44.91	+43.18	+41.37
$a(^{19}F)$, G		+100.82	−5.04	+77.62	+95.95	+109.98	+121.27

and the McLachlan procedure, in which one basis function is used for one AO and the overlap integrals are completely neglected. In such a case, the sum of the spin-density diagonal element ρ_{rr} gives a unit spin

$$1 = \sum_r \rho_{rr} \tag{15}$$

$\rho^{\pi}{}_{FF}$ and $\rho^{\pi}{}_{CC}$ can be conveniently used with eq 2 and the results would be expected to be comparable with those obtained with $D^{\pi}{}_{F}$ and $D^{\pi}{}_{C}$. It should be noted that the off-diagonal element ρ_{rs} loses its physical meaning, in the sense that it does not contribute to the total unit spin of the molecule (compare eq 12 and 15). Therefore, the use of eq 3 is not justified in the methods where overlap integrals are neglected. But if one just tries to "fit" experimental data, the additional flexibility of eq 3 might result in greater success, and this has been actually done. If one would like to simulate this situation in our *ab initio* DZS calculation, one would use $D^{\pi}{}_{C}$ and $D^{\pi}{}_{F}$ for the diagonal $\rho^{\pi}{}_{CC}$ and $\rho^{\pi}{}_{FF}$ because both D and ρ satisfy the same normalization condition, eq 14 and 15. For the off-diagonal element $\rho^{\pi}{}_{CF}$, some arbitrary choice has to be made. One possibility is to assume

$$D^{\pi}{}_{CF} = -(D^{\pi}{}_{C}D^{\pi}{}_{F})^{1/2} \tag{16}$$

This is based on a simple consideration that if the half-occupied π MO is given as

$$\Phi = C_F\chi_F + C_C\chi_C \quad C_CC_F < 0$$

then $\rho^{\pi}{}_{FF} = (C_F)^2$, $\rho^{\pi}{}_{CC} = (C_C)^2$, and $\rho^{\pi}{}_{CF} = C_CC_F$ and therefore $\rho^{\pi}{}_{CF}$ satisfies

$$\rho^{\pi}{}_{CF} = -(\rho^{\pi}{}_{FF}\rho^{\pi}{}_{CC})^{1/2} \tag{17}$$

Now let us proceed to establish models for estimating Q values. For an actual calculation of Q, the explicit differentiation of eq 10 is hard to carry out. Therefore, to accomplish this in effect we used models in which spin populations are changed around a realistic F/C ratio. The DZS CI calculation in the previous section was taken as the starting point, and is called the "standard" calculation. The half-occupied π MO ($2b_2$) in this calculation is found to be

$$\phi(2b_2) = 0.8741\chi_{C2p\pi1} + 0.1780\chi_{C2p\pi2} - 0.3358\chi_{F2p\pi1} - 0.1168\chi_{F2p\pi2} \tag{18}$$

where χ's are basis functions; *e.g.*, $\chi_{C2p\pi1}$ is the first (exponent $\zeta = 1.256$) $2p\pi$ orbital on the carbon atom. The populations of the SCF wave function are thus calculated to be $d^{\pi}{}_{C} = 1.0113$, $d^{\pi}{}_{F} = 0.1788$, and $d^{\pi}{}_{CF} = -0.1901$, $D^{\pi}{}_{C} = 0.9163$, and $D^{\pi}{}_{F} = 0.0837$. The calculation called model III uses $\phi(2b_2)$ of eq 18 as the half-occupied MO but excludes in the CI all the configurations involving any excitation of π electrons (into π^* MO's). This is to be consistent with the following models. The results are shown in Table VI. The changes between "standard" and model III are small.

In model I, we artificially modified the half-occupied π MO to

$$\phi(2b_2,\mathrm{I}) = 0.8692\chi_{C2p\pi1} + 0.1770\chi_{C2p\pi2} \tag{19}$$

which gives d and D shown in Table VI. In this and the following models, the ratio of the MO coefficient of the two basis functions belonging to the same atom was assumed to be unchanged from the standard value (*i.e.*, $C_{C2p\pi2}/C_{C2p\pi1} = 0.2036$ and $C_{F2p\pi2}/C_{F2p\pi1} = 0.3479$). The other occupied π MO, $\phi(1b_2)$, was changed so as to be orthogonalized to $\phi(2b_2,\mathrm{I})$, again assuming the coefficient ratio in this MO is unchanged from the standard value. All other SCF-MO's were unchanged. Then using these new MO's, the CI calculation was carried out excluding π excitations. The exclusion is necessary here because the inclusion would bring the new π spin populations back close to those of the standard calculation and would make these models meaningless. Models I–V were chosen so that the gross spin populations, $D^{\pi}{}_{C}$ and $D^{\pi}{}_{F}$, are equally spaced between I and II, II and III, III and IV, and IV and V (Table VI).

Now we will estimate Q values. For eq 1, by using the gross spin population $D^{\pi}{}_{C} = 0.9163$ and $a(^{19}F) = +100.82$ G in the standard calculation, $Q^{F}{}_{eff} = +110$ G is obtained. If $D^{\pi}{}_{C} = 1$ is used by implying that

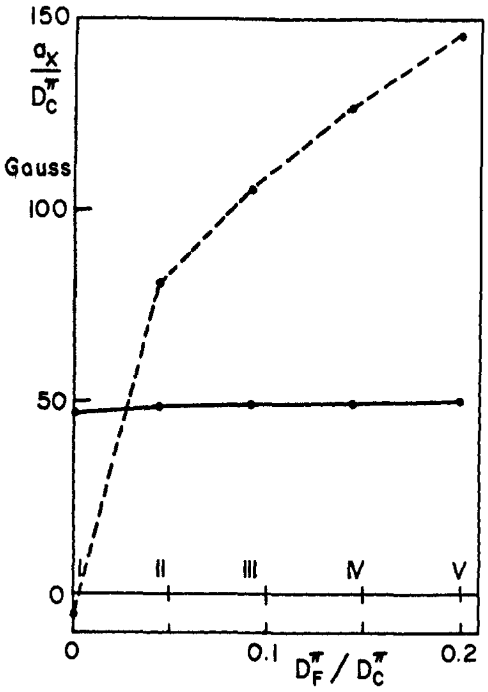

Figure 2. The plot of $a(^{19}F)/D^{\pi}_C$ and $a(^{13}C)/D^{\pi}_C$ against D^{π}_F/D^{π}_C for five models (I–V) of the α-fluorine coupling calculation: the broken line for $a(^{19}F)$ and the solid line for $a(^{13}C)$.

CH_2F has no conjugated system into which π electrons can delocalize, $Q^F_{eff} = +100$ G. Experimental values are around +40 to +60 G. A scale factor of approximately 2 seems to be needed to make the calculated Q agree quantitatively with experiments.

For eq 2 it is most logical to use the gross spin population D^{π}_C and D^{π}_F. The plot of a_F/D^{π}_C against D^{π}_F/D^{π}_C for five models is shown in Figure 2. Model I deviates extremely from a straight line, but others are reasonably straight. Taking the middle three points, II, III, and IV, we obtain a fit to a straight line with $Q^F_F = +450$ G and $Q^F_C = +63$ G. A poor fit for model I suggests that the extreme $D^{\pi}_F = 0$ cannot be handled with eq 2. The same technique can be used to evaluate Q values for the ^{13}C coupling.

$$a(^{13}C) = Q^C_C D^{\pi}_C + Q^C_F D^{\pi}_F \qquad (20)$$

The Q values calculated from II, III, and IV are (see also Figure 2) $Q^C_C = +48$ G and $Q^C_F = +8$ G. Also it is noted that the fit is quite straight for all the models.

Now we will examine eq 3 using the net spin populations d^{π}_C, d^{π}_F, and d^{π}_{CF}. A good least-squares fit was obtained for three Q's from five models. The fitted values are $Q^F_F = +46$ G, $Q^F_C = -5$ G, and $Q^F_{CF} = -488$ G. The general appearance of the fit is insensitive to the exclusion of a specific model. For instance, the exclusion of model I results in $Q^F_F = +29$ G, $Q^F_C = -8$ G, and $Q^F_{CF} = -522$ G. These values suggest that the bond spin population, the spin distribution in the overlap region between the F and C orbitals, plays an essential role in the F hyperfine coupling. This is illustrated in Figure 3, where CI calculated $a(^{19}F)$ is plotted against d^{π}_F and d^{π}_{CF}. The coupling constant is almost completely linear with respect to d^{π}_{CF} but nonlinear with respect to d^{π}_F.

The same technique for $a(^{13}C)$ yields a three-parameter fit

$$a(^{13}C) = Q^C_C d^{\pi}_C + Q^C_F d^{\pi}_F + Q^C_{CF} d^{\pi}_{CF} \qquad (21)$$

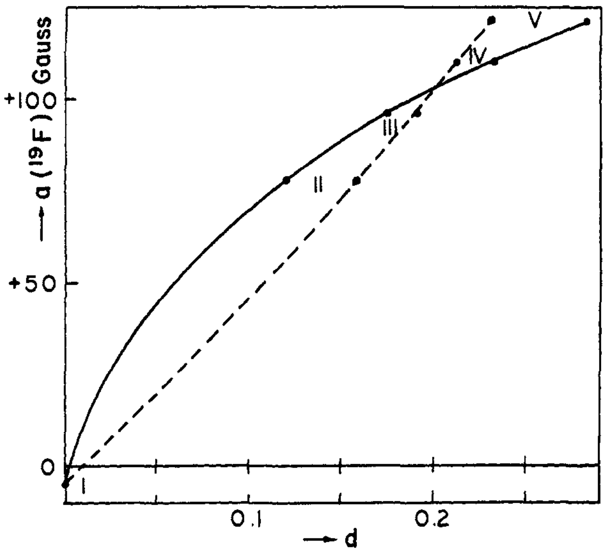

Figure 3. The plot of $a(^{19}F)$ against the net fluorine atom π spin density d^{π}_F and the C–F bond π spin density d^{π}_{CF} for five models (I–V) of the α-fluorine coupling calculation: the broken line for ρ^{π}_{CF} and the solid line for $^{\pi}\rho_F$.

where $Q^C_C = +47$ G, $Q^C_F = 0$ G, and $Q^C_{CF} = +14$ G.

Next D^{π}_C, D^{π}_F, and D^{π}_{CF} of eq 16 are used for eq 2 to simulate the results of calculations neglecting overlap integrals. A least-squares fit for five models yielded the following Q values: $Q^F_F = -285$ G, $Q^F_C = -5$ G, and $Q^F_{CF} = -457$ G. The condition of the fit is very poor, and a large simultaneous change in Q^F_F and Q^F_{CF} (up to 70 G) causes little change in the calculated $a(^{19}F)$.

Discussion

The spin-density fluorine hyperfine coupling relationships we examined in the preceding section have been extensively studied by others.[6–19] Some of the Q values previously proposed are shown in Table VII. Q values were usually estimated by the least-squares fit of $a(^{19}F)$, ρ^{π}_C, and ρ^{π}_F obtained as shown below for a series of free radicals of similar structure. $a(^{19}F)$ was always determined directly from esr and nmr experiments. ρ^{π}_C was usually determined from the observed a(H) and well-established Q^H_C of the proton analog of the free radical. ρ^{π}_F was determined in an exceptional case from the line width of fluorine nmr absorption.[14] In most cases, ρ^{π}_F was calculated by varieties of semiempirical molecular orbital methods, *e.g.*, the Hückel method, the McLachlan procedure of the Hückel method, the INDO or CNDO unrestricted self-consistent field (SCF) method (with or without spin annihilation to a pure doublet state), and the Pariser–Parr–Pople (PPP) unrestricted SCF method. Various values of coulomb, resonance, and electron repulsion integral parameters were used in these calculations. Considering the diversity of compounds and MO methods used, a small scattering of Q values would not be surprising, but Table VII shows that the scattering is extremely large. We will examine the physical significance of existing Q values in comparison with our *ab initio* results.

Our result for the one-parameter eq 1 gives $Q^F_{eff} = +110$ G. The positive sign of Q agrees with the nmr determined fact that the α-fluorine coupling constant

Table VII. α-Fluorine Hyperfine Coupling Parameters Q^{F}_{F}, Q^{F}_{C}, and Q^{F}_{CF} in Gauss from Various Sources

Q^{F}_{F}[a]	Q^{F}_{C}[a]	Q^{F}_{CF}[a]	Ref
	±40		6
	±47.5		7
	+50		8
	+62		9
	+57		10
	+54.5		11
	+54		12
	+64		13
+848	−147		15
+580	−83		16
+1393	−147		17
+371	−37.5		18
+1043	−85		19
+146	+48.1		11
+497	+6.2		14
−143 to +3086	+8 to −620	+56 to +595	20a
+264	+4	−64	20b,c
+200	−11	−57	21
+931	+86.6	+345	11
	(+55)		This work
+225	+32		
+23	−2	−244[b]	
(−143)	(−2)	(−229)[c]	

[a] When Q^{F}_{C} only is given, eq 1 is used. When both Q^{F}_{F} and Q^{F}_{C} are supplied, eq 2 is to be used. When all three are supplied, eq 3 should be used. [b] When the net spin population, d^{π}_{C}, d^{π}_{F}, and d^{π}_{CF} are used. [c] When the gross spin population is used or the spin density in the neglect-overlap approximation is used.

has the same sign as the carbon π spin-density ρ^{π}_{C}. This sign is in accord with most existing Q^{F}_{eff}. The proposal by Kulkarni and Trapp that $a(^{19}F)$ and ρ^{π}_{C} have different signs[19] seems to be unjustified. The absolute values of our Q^{F}_{eff} are about twice as large as the Q^{F}_{eff}'s in Table VII. A scale factor of about 2 is needed to make the calculated coupling constant agree with the experiment. In examining eq 2 and 3, we also adopt a scale factor of 2 to make the equations more quantitative. This is probably justified because we are mainly interested in the relative magnitude of the Q values in understanding the coupling mechanism. Our Q values after scaling are also added in Table VII.

Our scaled two-parameter equation

$$a(^{19}F) = +225D^{\pi}_{F} + 32D^{F}_{C}\ G \qquad (22)$$

is not equal to any existing one. This is not unexpected because of the difficulty of obtaining Q values[13] by methods other than ours. The equation happens to be close to the one by Fischer and Colpa[11] and by Espersen and Kreilick[14] in the sense both Q^{F}_{F} and Q^{F}_{C} are positive. However, in eq 22 the carbon and fluorine gross spin population contributions, $Q^{F}_{C}D^{\pi}_{C}$ and $Q^{F}_{F}D^{\pi}_{F}$, are nearly identical, while in Fischer and Colpa's work $\rho^{\pi}_{C}Q^{F}_{C}$ predominates, and in Espersen and Kreilick's, $\rho^{\pi}_{F}Q^{F}_{F}$ is predominant. We give two sets of three-parameter equations. One is

$$a(^{19}F) = +23d^{\pi}_{F} - 2d^{\pi}_{C} - 244d^{\pi}_{CF}\ G \qquad (23)$$

which is to be used with the net spin populations d which satisfy the normalization condition eq 12. Another is

$$a(^{19}F) = -143D^{\pi}_{F} - 2D^{\pi}_{C} - 229D^{\pi}_{CF}\ G \quad (24)$$

which is to be used with the gross spin population and D^{π}_{CF} of eq 16, or with the spin-density calculated in the neglect-of-overlap approximation as in INDO, Hückel, or PPP methods. The most significant feature of these equations is that the bond spin population makes the predominant contribution to the total hyperfine coupling. With 20–30% error, we can use eq 25 rather than eq 23.

$$a(^{19}F) \sim -244d^{\pi}_{CF}\ G \qquad (25)$$

Since d^{π}_{CF} and d^{π}_{F} have opposite signs, $-244d^{\pi}_{CF}$ gives a coupling constant with the same sign as d^{π}_{F}. Equation 25 suggests the α-fluorine coupling is mainly due to the spin polarization of fluorine s electrons by the bond spin population. A rather small Q^{F}_{F} value could be related to a small hyperfine coupling +36 G in the atomic fluorine (^2P)[32] where the spin density is 1 on its 2pπ orbital.

We might estimate the hybridization of the fluorine σ orbital and the ionicity of the C–Fσ bond using an oversimplified method. Let the hybridization of the Fσ orbital be sp^n.

$$\chi_{sp^n} = [s + \sqrt{n}p]/\sqrt{1 + n}$$

Then the F lone-pair orbital has to be s^{n}p.

$$\chi_{\text{lone pair}} = [\sqrt{n}s - p]/\sqrt{1 + n}$$

The number of electrons on the $\chi_{\text{lone pair}}$ is assumed to be two. If the occupancy on the Fσ orbital is λ (λ = 1 corresponding to a homopolar C–F bond, λ > 1 to an ionic bond C$^+$F$^-$), then density on the Fs orbital should be

$$2 \times \frac{n}{1 + n} + \lambda \times \frac{1}{1 + n} = \frac{2n + \lambda}{1 + n}$$

and the density on the Fpσ orbital should be

$$\lambda \times \frac{n}{1 + n} + 2 \times \frac{1}{1 + n} = \frac{2 + \lambda n}{1 + n}$$

If one uses 1.9824 and 1.5273, the gross populations on F2s and F2pσ obtained by our *ab initio* CI calculation, one obtains λ = 1.5 and n = 27. This means that the Fσ orbital is almost pure p, and the bond is polar C$^{+0.5}$–F$^{-0.5}$.

A rather small Q^{F}_{C} value is surprising in comparison with $Q^{H}_{C} = -23$ G for a C–H proton coupling. This difference could be explained by the polarity of the C–F bond (therefore small exchange between ρ^{π}_{C} and σ electrons) and by the small s character of the Fσ orbital.

The above results also suggest that even though the two-parameter eq 24 may be used to fit experimental data, it does not really describe the "mechanism" of spin polarization because of its apparent lack of d^{π}_{CF} contribution. The use of the three-parameter equation of type 23 is strongly encouraged if one wants to elaborate on the spin polarization mechanisms.

Equations 23 and 24 resemble none of the existing relationships. To demonstrate that a wide range of Q values can reproduce experimental results quite well, in Table VIII we used eq 23 and 24 to calculate the fluorine coupling of fluorobenzyl radicals and compared our results with experiments and three-parameter fits[33] based on Schastnev, Zhidomirov, and Chuvylkin[20b,c] and Hincliffe and Murrell[21] (see Table

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Table VIII. Experimental Value and Prediction of $a(^{19}F)$ Based on Equation 3 with Various Values of Q^{F}_{F}, Q^{F}_{C}, and Q^{F}_{CF}[a]

Radical	Eq 23	Eq 24	SZC[b]	HM[b]	Expt[b]
2-Fluorobenzyl	+12.8	+12.4	+11.1	+5.9	8.17
3-Fluorobenzyl	−5.6	−6.0	−5.1	−2.7	(−)4.87
4-Fluorobenzyl	+13.1	+13.9	+12.4	+6.7	14.53

[a] The spin density obtained after spin annihilation by the INDO unrestricted SCF calculation was used as d or D in the equations. [b] Taken from ref 33.

VII for their Q values). All of them agree with experiments almost to the same extent. As Icli and Kreilick pointed out,[13] the near proportionality between ρ^{π}_{F} and ρ^{π}_{C} (and also ρ^{π}_{CF}) in actual free radicals makes it almost impossible to determine reliable individual Q values by fitting experimental $a(^{19}F)$ against spin densities. On the other hand, our results are based on physical models that would retain the significance of individual Q values. Therefore it is not surprising that existing values which are already well scattered did not agree with our values.

A few words of caution may be added to our results. First, even though our DZS set is anticipated to give a reliable overall picture, the individual Q values could be more sensitive to the choice of basis set. Also, our model of analysis using an artificially modified half-occupied π^* orbital is certainly a good way of obtaining Q values, but it is not necessarily the only way of doing so. Different models may result in somewhat different results. Also there is the lack of the quantitative agreement of experiment $a(^{19}F)$ with the theory for the CH_2F molecule. As the result an an arbitrary scaling factor of 2 had to be introduced. A better wave function may alter the interpretation somewhat, but the qualitative conclusion would not be affected.

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Calculation of Ground and Excited State Potential Surfaces of Conjugated Molecules.[1] I. Formulation and Parametrization

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Abstract: A formulation is developed for the consistent calculation of ground and excited state potential surfaces of conjugated molecules. The method is based on the formal separation of σ and π electrons, the former being represented by an empirical potential function and the latter by a semiempirical model of the Pariser–Parr–Pople type corrected for nearest-neighbor orbital overlap. A single parameter set is used to represent all of the molecular properties considered; these include atomization energies, electronic excitation energies, ionization potentials, and the equilibrium geometries and vibrational frequencies of the ground and excited electronic states, and take account of all bond length and bond angle variations. To permit rapid determination of the potential surfaces, the σ potential function and SCF–MO–CI energy of the π electrons are expressed as analytic functions of the molecular coordinates from which the first and second derivatives can be obtained. Illustrative applications to 1,3-butadiene, 1,3,5-hexatriene, α,ω-diphenyloctatetraene, and 1,3-cyclohexadiene are given.

A detailed interpretation of electronic transitions and concomitant photochemical processes in conjugated molecules requires a knowledge of the ground and excited state potential surfaces. The determination of such surfaces has long been a goal of theoretical chemistry. Difficulties in a reliable *a priori* approach to the problem for a system as simple as ethylene[2] are such that calculations for more complicated molecules are prohibitive at present. Consequently, a variety of methods that utilize experimental data have been introduced. Completely empirical treatments, in which the energy surface is expressed as a function of potential parameters fitted to the available information (equilibrium geometry, vibrational frequencies, etc.), have had considerable success in applications to molecules for which a localized electron description is applicable.[3] The great advantage of this type of approach, which leaves open questions of reliability when extended from one class of molecules to another, is the ease and speed of the calculations; this had made possible applications to systems as large as certain nucleic acids and globular proteins.[4] For conjugated molecules, however, the importance of delocalization introduces difficulties into such an empirical treatment.[5]

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