Semi-empirical Unrestricted SCF-MO Treatment for Valence Electron Systems. II. The Angular Dependence of the Methyl Group *hfs* Constants

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Since the spin-polarization contribution to the methyl-group *hfs* constant of the ethyl radical has been recognized to be important, the angular dependence of the β-proton *hfs* constants is re-examined for various radicals. Thus, the observed relation, $Q(\theta) = B_0 + B_1 \cos^2 \theta$, is interpreted as being the sum of the following two equations.

$$Q_{SD}(\theta) = (B_1)_{SD} \cos^2 \theta$$
$$Q_{SP}(\theta) = (B_0)_{SP} + (B_1)_{SP} \cos^2 \theta,$$

where SD and SP denote the spin delocalization and spin polarization contributions respectively. θ is the rotational angle about C–C single bond. A molecular orbital description of the above angular dependences is also given.

The methyl-group proton *hfs* constants of aliphatic and aromatic hydrocarbon radicals have been extensively studied from both experimental[1] and theoretical[2] points of view. The theoretical studies of the methyl proton spin densities have been carried out mainly by two different methods, namely by the valence bond (VB) and molecular orbital (MO) methods,[3] and an interesting view of the spin-appearing mechanisms was presented by Lazdins and Karplus.[2g] They stated that the methyl-group proton spin density in the ethyl radical is due to nearly 60% "exchange polarization" and nearly 40% "electron transfer" contributions. In a previous MO study[4b] it was shown that the methyl-

proton spin density is due to 74% "spin delocalization (SD)" and 26% "spin polarization (SP)" contributions.[5]

The angular dependence of the β-proton *hfs* constant on the rotation about the C_α–C_β single bond has been well established experimentally and is explained by the relation[1]:

$$a_\beta^H = Q(\theta)\rho_C^\pi, \qquad (1)$$

where ρ_C^π is the spin density in the $2p_{C\alpha}$ atomic orbital o¹ the contiguous π-carbon atom, and where $Q(\theta)$ is expressed as:

$$Q(\theta) = B_0 + B_1 \cos^2\theta, \qquad (2)$$

where θ is the angle between the axis of the $2p_{C\alpha}$ orbital and the C_β–H bond, both projected on a plane perpendicular to the C_α–C_β bond. Aono and Higuchi[2c] studied the angular dependence of the β-proton *hfs* constant theoretically by considering only the spin delocalization (spin-hyperconjugation) mechanism; they successfully derived the $Q(\theta) = B_1 \cos^2\theta$ relation, where B_1 is a constant. However, since the β-proton spin density is in large part due to the SP mechanism, it seems necessary to examine the angular dependence of the SP contribution in order to interpret the observed relation (2).

In the present study, the methyl-proton *hfs* constants of the various doublet radicals (ethyl, *n*-propyl, methyl-substituted allyl radicals, and toluene ion-radicals) are calculated by the un-restricted Hartree-Fock (UHF) method reported

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1) a) C. Heller and H. M. McConnell, *J. Chem. Phys.*, **32**, 1535 (1960). b) A. Horsfield, J. R. Morton and D. H. Whiffen, *Mol. Phys.*, **4**, 425 (1961). c) J. R. Bolton, A. Carrington and A. D. McLachlan, *ibid.*, **5**, 31 (1962). d) J. R. Bolton, A. Carrington, A. Forman and L. E. Orgel, *ibid.*, **5**, 43 (1962). e) A. Horsfield, J. R. Morton and D. H. Whiffen, *ibid.*, **5**, 115 (1962).

2) a) A. D. McLachlan, *ibid.*, **1**, 233 (1958). b) P. G. Lykos, *J. Chem. Phys.*, **32**, 625 (1960). c) S. Aono and J. Higuchi, *Progr. Theor. Phys.* (Kyoto), **28**, 589 (1962). d) E. W. Stone and A. H. Maki, *J. Chem. Phys.*, **37**, 1326 (1962). e) K. Morokuma and K. Fukui, This Bulletin, **36**, 534 (1963). f) J. P. Colpa and E. de Boer, *Mol. Phys.*, **7**, 333 (1964). g) D. Lazdins and M. Karplus, *J. Chem. Phys.*, **44**, 1600 (1966). h) Z. Luz, *ibid.*, **48**, 4186 (1968).

3) T. H. Brown and M. Karplus, *ibid.*, **46**, 870 (1967).

4) a) T. Yonezawa, H. Nakatsuji, T. Kawamura and H. Kato, *Chem. Phys., Letters*, **2**, 454 (1968). b) T. Yonezawa, H. Nakatsuji, T. Kawamura and H. Kato, *J. Chem. Phys.*, **51**, 669 (1969).

5) J. P. Colpa, E. de Boer, D. Lazdins and M. Karplus, *J. Chem. Phys.*, **47**, 3098 (1967).

Table 1. The methyl proton spin density in the ethyl radical

Angle θ	UHF spin density						AA ρ_{aa}
	ρ_{uhf}	From Eq. (2)	$(\rho)_{SP}$	From Eq. (3)	$(\rho)_{SD}$	From Eq. (4)	
0	0.072	(0.072)	0.020	(0.020)	0.053	(0.053)	0.059
15	0.067	0.067	0.018	0.018	0.050	0.049	0.055
30	0.054	0.053	0.014	0.014	0.039	0.039	0.044
45	0.035	0.035	0.009	0.009	0.026	0.026	0.029
60	0.017	0.017	0.003	0.003	0.013	0.013	0.014
75	0.003	0.003	0.000	0.000	0.004	0.004	0.003
90	−0.002	(−0.002)	−0.002	(−0.002)	0.000	0.000	−0.001

in a previous study of this series,[6] and the mechanistic contributions to the hfs constants are diveded by means of the method previously proposed by the present authors.[7,4] The conclusions are that the SP contribution to the methyl-proton hfs constant has the angular dependence expressed by:

$$Q_{SP}(\theta) = (B_0)_{SP} + (B_1)_{SP} \cos^2\theta \qquad (3)$$

and that the observed relation (2) is to be understood as the sum of the angular dependence of the SD contribution.

$$Q_{SD}(\theta) = (B_1)_{SD} \cos^2\theta \qquad (4)$$

and that of the SP contribution (Eq. (3)). Thus, the constants, B's, in Eq. (2) are expressed as:

$$B_0 = (B_0)_{SP}$$

and:

$$B_1 = (B_1)_{SP} + (B_1)_{SD}. \qquad (5)$$

Moreover, for the isotropic γ-carbon hfs constants, one may expect the same dependences as those for the methyl-proton hfs constants. This is certainly true for the $2s$ AO spin density of the γ-carbon atom of the n-propyl radical.

In the last section, a molecular orbital description of the above angular dependences is given. It is shown that the intrinsic restriction of the UHF method, compared with the configuration interaction method, does not much affect the above conclusions.

Results and Discussion

Angular Dependence. In Table 1 the methyl-proton spin densities in the ethyl radical are given for the various angles, and then they are illustrated in Fig. 1. For the total spin density, ρ_{uhf}, the relation (2) holds fairly satisfactorily, while for the SP and SD contributions Eqs. (3) and (4) excellently represent their angular dependences. The curves obtained from Eqs. (2), (3), and (4) almost overlap with the corresponding curves shown in Fig. 1.

6)   T. Yonezawa, H. Nakatsuji, T. Kawamura and H. Kato, This Bulletin, **42**, 2437 (1969).

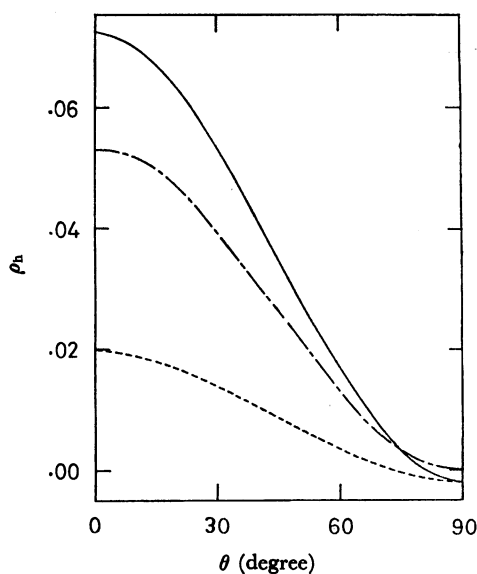7)   H. Nakatsuji, H. Kato and T. Yonezawa, *J. Chem. Phys.*, **51**, 3175 (1969).

Fig. 1. Angular dependence of the methyl proton spin density in the ethyl radical.
——, ρ_{uhf}; ·—, $(\rho_{uhf})_{SD}$; -----, $(\rho_{uhf})_{SP}$

The coefficients, B, calculated from the results shown in Table 1, are given in Table 2.

For the n-propyl radical, the situation is very similar to that of the ethyl radical. For the β-proton spin density, the dependences of ρ_{uhf}, $(\rho_{uhf})_{SP}$, and $(\rho_{uhf})_{SD}$ on the rotational angle, θ, is illustrated in Fig. 2. The relation (2) deviates only slightly from the calculated dependence; this deviation is mainly due to the SD contribution. The constants, B, in Eqs. (2), (3), and (4) were obtained by fitting the calculated curves; they are given in Table 2.

For the isotropic γ-carbon hfs constants of the n-propyl radical, one may expect the same dependences as those for the methyl proton hfs constants in the ethyl radical. This is certainly true for the $2s$ AO spin density of the γ-carbon atom. The angular dependences of the $2s$ AO spin density and of the mechanistic contributions are illustrated in Fig. 3. The curves of this figure are very well represented by $\rho_{uhf} = -0.001 + 0.018 \cos^2\theta$, $(\rho_{uhf})_{SD} =$
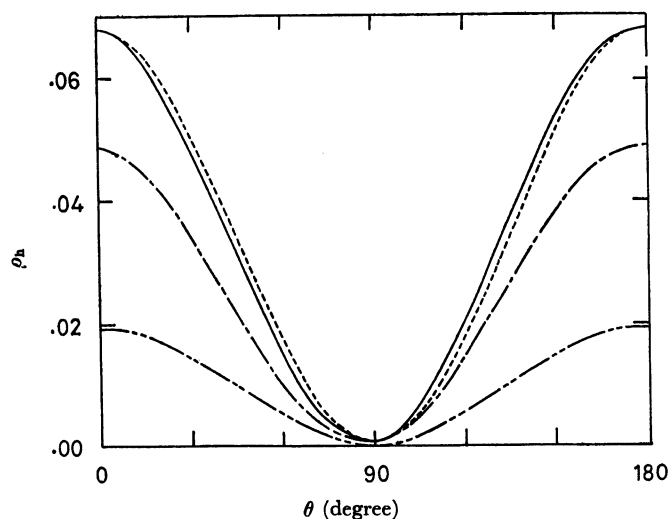
Fig. 2. Angular dependence of the β-proton spin density of the n-propyl radical.

——, ρ_{uhf}; · —, $(\rho_{uhf})_{SD}$; -·-—, $(\rho_{uhf})_{SP}$; -----, ρ calculated from Eq. (2)

TABLE 2. ANGULAR DEPENDENCE OF THE MECHANISTIC CONTRIBUTIONS[a]

Radical	B_0 [b]	B_1	$(B_1)_{SP}$	$(B_1)_{SD}$	ρ_C^π
Ethyl	−1.5	55.4	16.0	39.4	1.000
ι-Propyl	0.6	50.0	13.7	36.3	1.000
cis-1-Methylallyl	−0.5	49.2	21.4	27.9	0.689
trans-1-Methylallyl	−0.5	50.7	21.7	29.0	0.694
2-Methylallyl	1.6	44.1	44.1	0.0	−0.345
Toluene anion	4.1	39.1	39.1	0.0	−0.135
Toluene cation	−1.0	63.4	23.8	39.6	0.383

a) The values of B are given in gauss unit.
b) $B_0 = (B_0)_{SP}$

$0.005 \cos^2\theta$, and $(\rho_{uhf})_{SP} = -0.001 + 0.013 \cos^2\theta$.

Among the methyl-substituted allyl radicals, the 2-methylallyl radical is of great interest. Since the singly-occupied π-orbital of this radical has a node on the C_2 atom, the spin density of the methyl group is expected to be due only to the SP mechanism and to be negative in sign. This is certainly true, as Tables 2 and 3 show. Thus, the angular dependence of the methyl proton spin density of the 2-methylallyl radical is well represented *only* by

TABLE 3. THE METHYL PROTON SPIN DENSITY OF THE 2-METHYLALLYL RADICAL

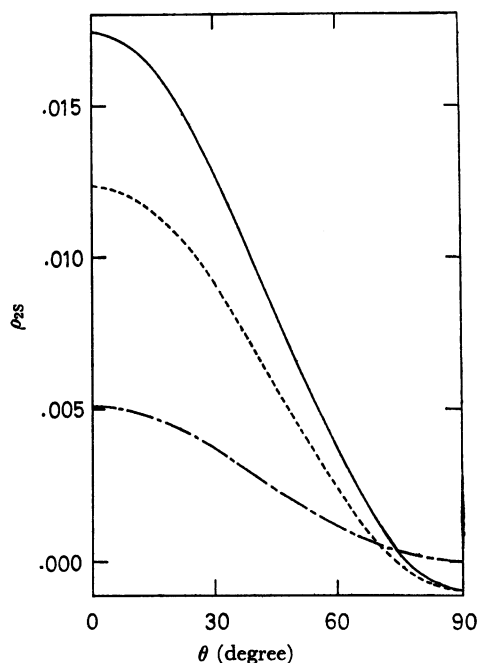| Angle	UHF spin density			AA
θ	ρ_{uhf}	$(\rho)_{SP}$	$(\rho)_{SD}$	From Eq.(2)or(3)	ρ_{AA}
0	−0.020	−0.020	0.000	(−0.020)	−0.006
30	−0.016	−0.016	0.000	−0.016	−0.005
60	−0.006	−0.006	0.000	−0.006	−0.002
90	−0.001	−0.001	0.000	(−0.001)	0.000

Fig. 3. Angular dependence of the $2s$ AO spin density of the γ-carbon atom of the n-propyl ridical.

——, ρ_{uhf}; · —, $(\rho_{uhf})_{SD}$; -----, $(\rho_{uhf})_{SP}$

Eq. (3), as is shown in Table 3.

For the other methyl-substituted allyl radicals (cis-1-methylallyl and trans-1-methylallyl), the situations are similar to that of the ethyl radical. The SD contributions to the methyl proton spin densities of these radicals are nearly 60%, small compared with those of the ethyl radical (See Table 2). Much

TABLE 4. THE METHYL PROTON SPIN DENSITY OF THE TOLUENE ION-RADICALS

Species	Angle θ	UHF spin density						AA ρ_{aa}
		ρ_{uhf}	From Eq. (2)	$(\rho)_{SP}$	From Eq. (3)	$(\rho)_{SD}$	From Eq. (4)	
Anion	0	−0.008	(−0.008)	−0.008	(−0.008)	0.000	0.000	−0.003
	30	−0.006	−0.006	−0.006	−0.006	0.000	0.000	−0.002
	45	−0.004	−0.005	−0.004	−0.005	0.000	0.000	−0.001
	60	−0.003	−0.003	−0.003	−0.003	0.000	0.000	−0.001
	90	−0.001	(−0.001)	−0.001	(−0.001)	0.000	0.000	0.000
Cation	0	0.033	(0.033)	0.012	(0.012)	0.021	(0.021)	0.025
	30	0.024	0.025	0.009	0.009	0.015	0.016	0.018
	45	0.016	0.016	0.006	0.006	0.010	0.010	0.012
	60	0.007	0.008	0.002	0.003	0.005	0.005	0.006
	90	−0.001	(−0.001)	−0.001	(−0.001)	0.000	0.000	0.000

as with the above examples, the angular dependences of the SP and SD contributions are well represented by Eqs. (3) and (4). The values of B in these equations are given in Table 2.

The methyl-proton spin densities of the toluene-ion radicals are summarized in Table 4. Although the tolune ions have nearly degenerate symmetric and antisymmetric electronic states with respect to the C_2 operation, only their ground electronic states (the symmetric electronic state for the cation and the antisymmetric state for the anion) are calculated for the present purposes. For the antisymmetric state of the anion radical, its singly-occupied π-orbital has a node on the 1-carbon (the carbon to which the methyl group is attached); therefore, the spin density of the methyl proton is due only to the SP mechanism and is negative, similar to that of the 2-methylallyl radical. By referring to Table 4, Eq. (3) is found to apply satisfactorily. For the symmetric state of the cation radical, the SD contribution to the methyl proton spin density is nearly 60%. As is shown in Table 3, Eqs. (2), (3), and (4) hold very satisfactorily. The values of B in these equations are given in Table 2. Note that the B_1 values of the anion and cation differ greatly.

One conclusion from Table 2 is that the methyl proton spin densities are composed of a major (60—75%) SD contribution and of a minor (25—40%) SP contribution, except for the special cases of the 2-methylallyl radical and the antisymmetric state of the toluene anion. Note that the B values of the 2-methylallyl and toluene anion radicals, in which only the SP mechanism is important, deviate greatly from the average B values. Another conclusion of the present study is that the observed relation, (2), can be interpreted as the sum of Eqs. (3) and (4), and that this relation may also hold for the $2s$ AO spin density of the γ-carbon atom (as is shown in the case of the n-propyl radical).

hfs Constants. The proton hfs constants[8]

8) Proton hfs constants are calculated by multiplying ρ_{uhf} by 743 gauss.

calculated by assuming the free rotation of the methyl group are compared with the experimental results in Tables 5 and 6. Although the toluene ions have nearly degenerate electronic states, the calculated values given in Table 5 correspond only to the lower electronic states (the symmetric state for the cation and the antisymmetric state for the anion). For a more rigorous discussion of the hfs constants, the thermal and vibronic coupling effects must be considered,[1d] as Purins and Karplus did recently.[9] Note, however, that the inclusion of

TABLE 5. CALCULATED PROTON hfs CONSTANTS

Radical	Position	hfs constant	
		Calcd.[a]	Exptl.
Ethyl	α-H	−25.6	(−)22.38[b]
	β-H	26.2	(+)26.87[b]
n-Propyl	α-H	−25.3	(−)22.08[b]
	β-H	25.6	(+)33.2[b]
	γ-H	−1.8	(−)0.38[b]
Toluene anion[c]	o-H	−9.0	(−)5.12[d]
	m-H	−9.6	(−)5.45[d]
	p-H	−0.1	(−)0.59[d]
	H(CH$_3$)	−3.2	(+)0.79[d]
Toluene cation[e]	o-H	−2.7	—
	m-H	−1.1	—
	p-H	−9.1	—
	H(CH$_3$)	11.8	—

a) The calculated values are obtained by assuming free rotation of the methyl group about the C–C single bond.

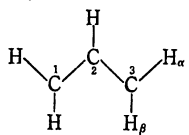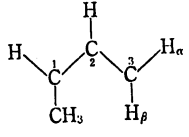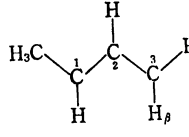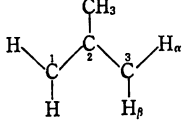b) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

c) Only the antisymmetric electronic state is calculated.

d) J. R. Bolton, A. Carrington, A. Forman and L. E. Orgel, *Mol. Phys.*, **5**, 43 (1962).

e) Only the symmetric electronic state is calculated.

9) a) D. Purins and M. Karplus, *J. Chem. Phys.*, **50**, 241 (1969). b) D. Purins and M. Karplus, *J. Amer. Chem. Soc.*, **90**, 6275 (1968).

TABLE 6. PROTON *hfs* CONSTANT OF THE ALLYL
AND METHYL-SUBSTITUTED ALLYL RADICALS

Radical	Position	*hfs* constant	
		Calcd.[a]	Exptl.[b]
Allyl			
	$H_{1,3\alpha}$	−14.19	(−) 14.81
	$H_{1,3\beta}$	−13.97	(−) 13.90
	H_2	3.64	(+) 4.06
cis-1-Methylallyl			
	$H(CH_3)$	16.80	(+) 14.01
	$H_{1\alpha}$	−18.87	(−) 14.17
	H_2	4.49	(+) 3.83
	$H_{3\alpha}$	−13.89	(−) 14.94
	$H_{3\beta}$	−13.64	(−) 13.52
trans-1-Methylallyl			
	$H(CH_3)$	17.22	(+) 16.43
	$H_{1\beta}$	−18.99	(−) 13.83
	H_2	3.97	(+) 3.85
	$H_{3\alpha}$	−14.12	(−) 14.78
	$H_{3\beta}$	−13.91	(−) 13.83
2-Methylallyl			
	$H(CH_3)$	− 7.89	(−) 3.19
	$H_{1,3\alpha}$	−13.97	(−) 14.68
	$H_{1,3\beta}$	−13.74	(−) 13.82

a) The calculated values are obtained by assuming free rotation of the methyl group about the C–C single bond.

b) J.K. Kochi and P.J. Krusic, *J. Amer. Chem. Soc.*, **90**, 7157 (1968).

these effects, which are expressed by the weighted mean of the *hfs* constants of the symmetric and antisymmetric electronic states, will improve the calculated *hfs* constants of the toluene anion.[10]

Since Fessenden and Schuler[11] observed the different *hfs* constants for the terminal methylene protons of the allyl radical, the observed *hfs* constants have been assigned theoretically by several investigators.[6,12–14] This finding was of particular interest since the well-known McConnell rule cannot interpret the observed difference. Recently, how-

ever, Kochi and Krusic[15] settled this assignment by observing the *hfs* constants of the methyl-substituted allyl radicals; they proved that the assignment by the present authors[6,12] was correct. Here, we calculated the proton *hfs* constants of these methyl-substituted allyl radicals. The results are summarized in Table 6. The assignments of the *hfs* constants of the $H_{3\alpha}$ and $H_{3\beta}$ protons of the *cis*- and *trans*-1-methylallyl radicals agree with the experimental results, although the differences in the calculated *hfs* constants of these two protons are rather small compared with the experimental values. In the 2-methylallyl radical, the methyl-proton *hfs* constants are calculated to be due only to the SP mechanism and to be negative in sign. The calculated *hfs* constants of the $H_{1\alpha}$ proton of the *cis*-form and of the $H_{1\beta}$ proton of the *trans*-form are too large (absolute value) compared with the experimental values.

Origin of the Angular Dependence. Here, we shall give a molecular orbital description of the angular dependences expressed by Eqs. (2), (3), and (4). For the present purposes the configuration interaction (CI) treatment may be most suitable. As has been shown previously, the UHF wave-function is expressed by the following CI form to a first-order approximation:[7]

$$\Psi_{uhf} = \Psi^{rf} + \sum_i C^{so}(ii^*) \, \Psi^{so}(ii^*), \qquad (6)$$

where the second term is due to the spin polarization perturbation. Ψ^{rf} is the restricted function composed of the natural orbitals,[16,4b] λ_i and μ, of the UHF wave-function and Ψ^{so} (ii^*) represents the normalized singly-excited configuration expressed by the one-electron jump from λ_i to ν_i:

$$\Psi^{rf} = |\lambda_1\alpha \, \lambda_1\beta \cdots \lambda_q\alpha \, \lambda_q\beta\mu\alpha|$$

$$\Psi^{so}(ii^*) =$$

$$|\lambda_1\alpha \, \lambda_1\beta \cdots \nu_i\lambda_i \frac{1}{\sqrt{2}} (\alpha\beta + \beta\alpha) \cdots \lambda_q\alpha\lambda_q\beta\mu\alpha| \qquad (7)$$

$2q+1$ is the number of electrons in the radical. The natural orbitals, λ, μ, and ν, correspond, respectively, to the doubly-occupied, singly-occupied, and unoccupied orbitals of the restricted function, Ψ^{rf}, and are orthonormal to each other.[16] Note that λ_i and ν_i correspond to the bonding and antibonding partner MO's of the alternant molecular orbital method.[16,4b]

From Eq. (6), the SP and SD contributions to the UHF spin density are given by[4b]:

$$(\rho_{uhf})_{SD} = \langle\Psi^{rf}|\rho|\Psi^{rf}\rangle = \mu^2 \qquad (8)$$

10) The observed *hfs* constant of the methyl proton of the toluene anion is positive in sign; E. de Boer and J. P. Colpa, *J. Phys. Chem.*, **71**, 21 (1967).

11) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

12) T. Yonezawa, H. Nakatsuji, T. Kawamura and H. Kato, This Bulletin, **40**, 2211 (1967).

13) A. Hincliffe and H. M. Atherton, *Mol. Phys.*, **13**, 89 (1967).

14) J. A. Pople, D. L. Beveridge and P. A. Dobosh, *J. Amer. Chem. Soc.*, **90**, 4201 (1968).

15) J. K. Kochi and P. J. Krusic, *ibid.*, **90**, 7157 (1968).

16) a) A. T. Amos and G. G. Hall, *Proc. Roy. Soc.*, Ser. A, **263**, 483 (1961). b) T. Amos and L.C. Snyder, *J. Chem. Phys.*, **41**, 1773 (1964).

TABLE 7.   UHF NATURAL ORBITALS, λ AND μ OF THE ETHYL RADICAL

AO	λ						μ
	$1(\sigma_1)$	$2(\sigma_2)$	$3(\bar{\pi}_1)$	$4(\pi_1)$	$5(\bar{\pi}_2)$	$6(\sigma_3)$	$7(\pi_2)$
Configuration[a]							
Y(1C)	0.000	0.000	0.310	0.000	−0.341	0.000	0.000
Z(1C)	0.000	0.000	0.000	0.038	0.000	0.001	1.000
Y(2C)	0.000	0.000	0.340	0.000	0.312	0.000	0.000
Z(2C)	−0.001	0.000	0.000	0.458	0.000	0.003	0.013
h(5H)	0.167	−0.118	−0.356	−0.307	−0.410	0.082	0.115
h(6H)	0.167	−0.118	0.356	−0.307	0.410	0.082	0.115
h(7H)	0.161	−0.115	0.000	0.614	0.000	0.089	−0.229
Configuration[b]							
Y(1C)	0.000	0.000	0.310	0.000	−0.341	0.000	0.000
Z(1C)	0.000	0.000	0.000	0.038	0.000	0.000	1.000
Y(2C)	0.001	0.000	0.340	0.000	0.313	−0.003	0.000
Z(2C)	0.000	0.000	0.000	0.458	0.000	0.000	0.013
h(5H)	0.163	−0.116	−0.206	−0.531	−0.237	0.086	0.198
h(6H)	0.163	−0.116	−0.206	0.531	−0.237	0.086	−0.198
h(7H)	0.169	−0.119	0.411	0.000	0.474	0.079	0.000

a) Configuration I
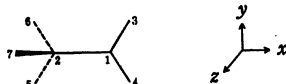
b) Configuration II
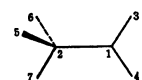
TABLE 8.   COEFFICIENTS OF THE SINGLY EXCITED CONFIGURATIONS,
$C^{se}(ii^*)$ OF THE ETHYL RADICAL

Geometry[a]	Coefficients, C^{se} (ii^*)					
	11*	22*	33*	44*	55*	66*
Configuration I	0.0013	0.0292	0.0043	0.0049	0.0031	0.0130
Configuration II	0.0015	0.0292	0.0042	0.0048	0.0032	0.0130

a) See footnotes a and b of Table 7.

and:

$$(\rho_{uhf})_{SP} = 2\sum_i C^{se}(ii^*) <\Psi^{rf}|\rho|\Psi^{se}(ii^*)>$$

$$= 2\sqrt{2}\sum_i C^{se}(ii^*)\ \lambda_i \nu_i,\qquad (9)$$

where ρ is the spin-density operator.

Now let us enter upon a description of the angular dependence of the methyl group proton spin density. In Table 7 the natural orbitals, λ and μ, of the ethyl radical, as calculated by the present method, are given for the two rotational configurations, and in Table 8 the coefficients of the singly-excited configurations, $C^{se}(ii^*)$, are summarized.[4] Table 8 shows that the coefficients, $C^{se}(ii^*)$, are almost independent of the rotational angle, θ. Thus, we have only to consider the angular dependence of the AO coefficients of the natural orbitals.

The local-group orbitals constructed from the three hydrogen $1s$ AO's of the methyl group may be written as:

$$\phi_\sigma = h_1 + h_2 + h_3,$$
$$\phi_{\bar\pi} = h_1 - h_2,\qquad (10)$$
$$\phi_\pi = h_1 + h_2 - 2h_3.$$

ϕ_σ is totally symmetric about the rotation, while $\phi_{\bar\pi}$ and ϕ_π are the quasi-π-orbitals and are perpendicular to each other. Thus, the angular dependence of the coefficients of the one particular hydrogen $1s$ AO, h, in various molecular orbitals (i) may be grouped into the following three types:

σ-type: $a_i \cdot h$,
$\bar\pi$-type: $b_i \sin \theta \cdot h$,   (11)
π-type: $c_i \cos \theta \cdot h$,

where a_i, b_i, and c_i are the AO coefficients of the molecular orbital, i, at $\theta=90°$ or at $\theta=0°$. In Table 7 the orbitals are divided into the above three groups.   For the π-electron radicals, the angular dependence of the coefficient of the methyl hydrogen is, of course, of the π-type. Hence, the

SD contribution to the methyl-proton spin density is given by:

$$(\rho_{uhf})_{SD} = c_\mu{}^2 \cos^2\theta. \tag{12}$$

From Eqs. (9) and (11) the SP contribution is similarly expressed by:

$$
\begin{aligned}
(\rho_{uhf})_{SP} &= 2\sqrt{2}\,\{\textstyle\sum_i^\sigma C^{se}(ii^*)\ a_i a_i{}^* \\
&\quad + \textstyle\sum_i^{\bar\pi} C^{se}(ii^*)\ b_i b_i{}^*\ \sin^2\theta \\
&\quad + \textstyle\sum_i^\pi C^{se}(ii^*)\ c_i c_i{}^*\ \cos^2\theta\} \\
&= (\rho_0)_{SP} + (\rho_1)_{SP}\cos^2\theta, \tag{13}
\end{aligned}
$$

where:

$$(\rho_0)_{SP} = 2\sqrt{2}\,\{\textstyle\sum_i^\sigma C^{se}(ii^*)\ a_i a_i{}^* + \textstyle\sum_i^{\bar\pi} C^{se}(ii^*)\ b_i b_i{}^*\}$$

$$(\rho_1)_{SP} = 2\sqrt{2}\,\{\textstyle\sum_i^\pi C^{se}(ii^*)\ c_i c_i{}^* - \textstyle\sum_i^{\bar\pi} C^{se}(ii^*)\ b_i b_i{}^*\}.$$

$\sum^\pi$ denotes the summation over the π-type orbitals. Eqs. (12) and (13), and the sum of them, correspond to Eqs. (4), (3), and (2) respectively.

Note here that the conditions for the local symmetry orbitals expressed by Eq. (10) (the conditions for the definite grouping of MO's by Eq. (11)) are not satisfactorily fulfilled in cases of poor symmetry,[17] and that, in the usual CI treatment, the transitions other than $i{\to}i^*$ (i and i^* have, of course, the same type of local symmetry) must be included.[18] (Compare this with Eq. (6)). In

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17) For example, the condition of the local symmetry expressed by Eq. (10) is already broken in the ethyl radical (See Table 7). However, the relations (2), (3) and (4) are very satistactory as shown in the previous section.

18) A. L. H. Chung, *J. Chem. Phys.*, **46**, 3144 (1967).

these cases, Eqs. (12) and (13) may include types of angular-dependent terms other than $\cos^2\theta$. One example of the poor symmetry is the n-propyl radical, where the curves obtained by Eqs. (2), (3), and (4) deviate slightly from the calculated curves. Nevertheless, the relations (2), (3), and (4) are still good approximations to the angular dependences of the β-proton spin density of the n-propyl radical (See Fig. 2).

The effects of the inclusion of the $i{\to}j^*$ ($i{\neq}j$) transitions are not certainly determined numerically by the present study, but they can be estimated as follows. The $i{\to}j^*$ transitions may be grouped into two groups; one is composed of the transitions where i and j^* have the same local symmetry, and the other is composed of the transitions where i and j^* have different local symmetries. By including the former type of transition, the angular dependence expressed by Eq. (13) is not altered. Only the coefficients may be changed. For the latter type of transition, which may produce types of angular-dependent terms other than $\cos^2\theta$, their CI coefficients, $C^{se}(ij^*)$, can be expected from symmetry considerations to be very small. Thus, the inclusion of the $i{\to}j^*$ ($i{\neq}j$) transitions will not much alter the type of angular dependence expressed by Eq. (13).