

## Semi-empirical Unrestricted SCF-MO Treatment for Valence Electron Systems. I. Application to Small Doublet Radicals

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A semi-empirical SCF method for valence electron systems including a differential overlap previously proposed by the present authors is here extended to molecules with an open-shell structure. The unrestricted Hartree-Fock method is applied, and the one-centre and part of two-centre  $\sigma$ - $\pi$ -type exchange repulsion integrals, playing an essential role in spin-density calculations, are included in the calculations. The calculated spin densities are divided into the mechanistic (spin-polarization and spin-delocalization) contributions. The spin-polarization mechanism is shown to be important even in cases where the spin delocalization mechanism has usually been considered to be dominant (*e. g.*, ethyl and vinyl radicals). The calculated spin densities of  $\pi$ -electron radicals (methyl, ethyl, allyl, and *trans*-butadienyl anion radicals) and of  $\sigma$ -electron radicals (vinyl, formyl, NO<sub>2</sub>, CO<sub>2</sub><sup>-</sup>, CN) are discussed. Their *hfs* constants and mechanistic contributions are calculated; for the methyl and vinyl radicals these are shown to be strongly angular-dependent. The calculated potential curve and the *hfs* constants of the vinyl radical lead to the CCH<sub>2</sub> angle,  $\theta \approx 135^\circ$ ; furthermore, the H<sub>2</sub> and C <sub>$\beta$</sub>  *hfs* constants are shown to be negative. Generally, the calculated proton *hfs* constants agree satisfactorily with the experimental data and with other calculations except in the case of the formyl radical. The atomic dipoles of some  $\sigma$ -electron radicals are calculated, and some interesting features common to all the  $\sigma$ -electron radicals studied are found.

Recently semi-empirical SCF methods for valence electron systems have been generally applied<sup>1-6</sup> to calculations of certain physical and chemical

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1) a) J. A. Pople, D. P. Santry and G. A. Segal, *J. Chem. Phys.*, **43**, S129 (1965). b) J. A. Pople and G. A. Segal, *ibid.*, **44**, 3289 (1966). c) J. A. Pople, D. L. Beveridge and P. A. Dobosh, *ibid.*, **47**, 2026 (1967). d) J. A. Pople, D. L. Beveridge and P. A. Dobosh, *J. Am. Chem. Soc.*, **90**, 4201 (1968).

2) N. M. Atherton and A. Hinchliffe, *Mol. Phys.*, **12**, 349 (1967).

3) T. Yonezawa, H. Konishi and H. Kato, *This Bulletin*, **41**, 1031 (1968).

4) a) T. Yonezawa, K. Yamaguchi and H. Kato, *ibid.*, **40**, 535 (1967). b) T. Yonezawa, H. Konishi and H. Kato, *ibid.*, **40**, 1071 (1967). c) H. Kato, H. Konishi, H. Yamabe and T. Yonezawa, *ibid.*, **40**, 2761 (1967). d) T. Yonezawa, H. Nakatsuji and H. Kato, *J. Am. Chem. Soc.*, **90**, 1239 (1968).

5) a) T. Yonezawa, H. Nakatsuji, T. Kawamura and H. Kato, *This Bulletin*, **40**, 2211 (1967). b) T. Yonezawa, H. Nakatsuji, T. Kawamura and H. Kato, *Mol. Phys.*, **13**, 589 (1967).

properties of molecules. We have previously proposed a semi-empirical SCF method including differential overlaps for valence electron systems and applied it to various closed-shell molecules.<sup>4</sup> Here, we extend this method to molecules with an open-shell structure. As in the preliminary reports,<sup>5</sup> the unrestricted Hartree-Fock (UHF) method<sup>6</sup> is applied. Since the UHF wave function is not an eigenfunction of the spin-squared operator,  $S^2$ , the lowest contaminating spin functions are annihilated<sup>7</sup> after energy minimization.

The spin density calculated by the UHF method originates from two main mechanisms,<sup>8</sup> the spin-polarization (SP) and spin-delocalization (SD) mechanisms. In order to clarify the nature of the spin-density, these mechanistic contributions are

6) J. A. Pople and R. K. Nesbet, *J. Chem. Phys.*, **22**, 571 (1954).

7) a) T. Amos and G. G. Hall, *Proc. Roy. Soc. (London)*, **A263**, 483 (1961). b) A. T. Amos, *Mol. Phys.*, **5**, 91 (1962). c) T. Amos and L. C. Snyder, *J. Chem. Phys.*, **41**, 1773 (1964). d) L. C. Snyder and T. Amos, *ibid.*, **42**, 3670 (1965).

separated by the method reported previously.<sup>9)</sup> In  $\pi$ -electron radicals, the SP mechanism is dominant and is reduced to small  $\sigma$ - $\pi$ -type electron repulsion integrals. In the present calculation, the one-center and part of two-center  $\sigma$ - $\pi$ -type exchange repulsion integrals are included, although the latter was neglected previously.<sup>6)</sup>

The method is applied mainly to the spin-density calculations of  $\pi$ -electron radicals, such as the methyl, ethyl, allyl, and *s-trans*-butadienyl anion radicals, and of some  $\sigma$ -electron radicals, such as vinyl, formyl, NO<sub>2</sub>, CO<sub>2</sub><sup>-</sup> and CN radicals. The mechanistic contributions to the spin density are separated, and some interesting features of spin density are revealed. Lastly, the dipole moments of the  $\sigma$ -electron radicals are analyzed.

### Method

An unrestricted wavefunction for a system with  $p$   $\alpha$ -spin and  $q$   $\beta$ -spin electrons has the form:

$$\psi_{\text{unf}} = |\varphi_1^\alpha(1)\alpha(1)\cdots\varphi_p^\alpha(p)\alpha(p)\varphi_1^\beta(p+1)\beta(p+1)\cdots\varphi_q^\beta(q)\beta(q)|, \quad (1)$$

where  $n=p+q$ . For the doublet radicals considered here  $p=q+1$ . The molecular orbital is expanded as a linear combination of all the valence atomic orbitals (VAO's),  $\chi_r$ , of the constituent atoms:

$$\varphi_i^\alpha = \sum_r C_{ir}^\alpha \chi_r$$

and:

$$\varphi_i^\beta = \sum_r C_{ir}^\beta \chi_r. \quad (2)$$

The unrestricted SCF equations of the LCAO approximation are:

$$F^\alpha C_i^\alpha = \epsilon_i^\alpha S C_i^\alpha$$

and:

$$F^\beta C_i^\beta = \epsilon_i^\beta S C_i^\beta \quad (3)$$

in the usual notations.<sup>6)</sup>

**Estimation of Integral Values.** One of the main features of the unrestricted SCF theory is its inclusion of spin correlation, thus enabling us to calculate negative spin densities. In the case of  $\pi$ -electron radicals, the spin densities appearing in the  $\sigma$ -type AO's are due to the  $\sigma$ - $\pi$ -type spin-polarization mechanism.<sup>9,10)</sup> In order to study these radicals, the following exchange integrals are considered in the calculations:

(a) The one-center exchange repulsion integrals\*<sup>2</sup> are evaluated by the approximate relations:<sup>4c)</sup>

8) 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.*, in press. c) H. Nakatsuji, H. Kato and T. Yonezawa, *ibid.*, in press.

$$(sp|sp) = 0.045Z_A(ss|pp)$$

and:

$$(pp'|pp') = 0.011Z_A(pp|pp), \quad (4)$$

where  $s$  denotes the  $2s$  AO.

(b) A part of the two-center  $\sigma$ - $\pi$ -type exchange repulsion integrals is approximated by the following semi-empirical estimation:

$$\begin{aligned} (h\pi_X|h\pi_X)_{\text{semi-empirical}} &= k(h\pi_X|h\pi_X)_{\text{Slater}} \\ (\mu_X\bar{\pi}_{X'}|\mu_X\bar{\pi}_{X'})_{\text{semi-empirical}} &= k(\mu_X\bar{\pi}_{X'}|\mu_X\bar{\pi}_{X'})_{\text{Slater}} \quad (5) \\ (\mu_X\nu_{X'}|\mu_Y\nu_{Y'}) &= \{(\mu_X\nu_{X'}|\mu_X\nu_{X'}) \cdot (\mu_Y\nu_{Y'}|\mu_Y\nu_{Y'})\}^{1/2} \end{aligned}$$

where  $h$  is a hydrogen  $1s$  AO, where  $\mu$  is a  $2s$ ,  $2p\sigma$  or  $2p\pi$  AO, and where  $X$  and  $Y$  denote the first-row elements of the periodic table. The value of the parameter,  $k$ , is chosen so that the calculated proton, spin densities of the methyl and ethyl radicals obtained before annihilation may reasonably be compared with the experimental results; the value is equal to 0.58 throughout these calculations.\*<sup>3</sup> For the  $2s$  AO spin density of the carbon atom, the above two-center  $\sigma$ - $\pi$ -type exchange repulsion integrals are not so important as are those for the proton spin density.\*<sup>4</sup>

Note that many other two-center  $\sigma$ - $\pi$ -type electron repulsion integrals are omitted. However, the parameter  $k$ , introduced in Eq. (5), may effectively include these neglected integrals for the proton-spin density in the C-H bond;\*<sup>5</sup> this assumption will, however, break down for heteropolar cases such as for the N-H and O-H bonds,

9) a) H. M. McConnell, *J. Chem. Phys.*, **24**, 764 (1956). b) H. M. McConnell and D. B. Chesnut, *ibid.*, **27**, 984 (1957); **28**, 107 (1958). c) H. M. McConnell, *ibid.*, **28**, 1188 (1958). d) S. I. Weissman, *ibid.*, **25**, 890 (1956).

10) M. Karplus and G. K. Fraenkel, *J. Chem. Phys.*, **35**, 1312 (1961).

\*<sup>2</sup> The inclusion of one-center exchange repulsion integrals destroys the invariance<sup>1a)</sup> of the Mulliken approximation, since  $(pp|p'p') = (pp|pp) - 2(pp'|pp')$ . Therefore, the one-center exchange repulsion integrals are included in the method after the Mulliken approximation for  $(rs|tu)$  is completed, and the term  $-2(pp'|pp')$  is introduced as a correction to  $(pp|p'p')$ . Thus, the present method is invariant to rotation around local atomic axis.

\*<sup>3</sup> The ratios of the adopted one-center exchange integrals to the theoretical values calculated from Slater AO's are 0.51 for  $(pp'|pp')$  and 0.58 for  $(sp|sp)$ .

\*<sup>4</sup> For the methyl radical, the contributions of the one- and the two-center  $\sigma$ - $\pi$ -type exchange repulsion integrals are  $-0.0787$  and  $+0.0512$  for the proton-spin density, and  $0.1788$  and  $-0.0301$  for the carbon  $2s$  AO spin-density (before annihilation).

\*<sup>5</sup> The contribution of the  $\sigma$ - $\pi$ -type ionic integrals is zero if the C-H bond is assumed to be homopolar. For example, the configuration interaction treatment of the methyl radical, using the simple MO's based on the hybrid orbitals, showed that the contribution due to the two center  $\sigma$ - $\pi$ -type ionic integrals amounts to only 6% of the total proton spin density.

where the omitted  $\sigma$ - $\pi$  type ionic integrals may become important.

The method of estimating all the other integral values is the same as has been previously reported.<sup>4-5)</sup>

**Spin-polarization and Spin-delocalization Contributions.** As has been shown in previous papers,<sup>9)</sup> the spin-polarization (SP) contribution to the calculated spin density at the  $i$  position is given by the following equations for doublet radicals:

$$\begin{aligned}(\rho_{ba}^i)_{SP} &= \frac{3}{2}(\rho_{ba}^i - \rho_{aa}^i), \\ (\rho_{aa}^i)_{SP} &= \frac{1}{2}(\rho_{ba}^i - \rho_{aa}^i).\end{aligned}\quad (6)$$

$(\rho_{ba}^i)_{SP}$  is the SP contribution to the spin density,  $\rho_{ba}^i$ , calculated by the UHF method, and  $(\rho_{aa}^i)_{SP}$  is the SP contribution to the spin density,  $\rho_{aa}^i$ , obtained after annihilation.\*<sup>6</sup> The spin-delocalization (SD) contributions are the same for both stages (ba and aa) and are approximated<sup>9)</sup> by:

$$(\rho^i)_{SD} = \rho^i - (\rho^i)_{SP}. \quad (7)$$

#### Estimation of the Isotropic $hfs$ Constants.

The isotropic proton  $hfs$  constant,  $a$ , is expressed approximately by:  $a_H = A_H \rho_H$ ,<sup>9e)</sup> while the values for the first-row nuclei of the periodic table are given as the sum of the  $2s$  contribution ( $A_{2s(N)} \cdot \rho_{2s(N)}$ ) and of the inner  $1s$  contribution.

In the present calculations,  $A_H$  is regarded as a proportionality constant determined by "best fitting" the calculated spin densities (before annihilation) to the observed  $hfs$  constants.\*<sup>7</sup>  $A_H$  is set equal to 743 gauss throughout this paper. The  $2s$  contribution to the  $hfs$  constant of the  $^{13}C$  nucleus is calculated by setting  $A_{2s(C)} = 1110$  gauss.<sup>11)</sup> However, the present method does not give the quite important contributions to  $hfs$  constants by

\*<sup>6</sup> Hereafter, the spin densities calculated before and after annihilation will be written as  $\langle \rho \rangle_{ba}$  and  $\langle \rho \rangle_{aa}$ , and the charge densities, as  $\langle q \rangle_{ba}$  and  $\langle q \rangle_{aa}$ .  $\langle \rho \rangle_{ba}$  has the same meaning as the  $\rho_{uhf}$  in the previous paper.<sup>9)</sup>

\*<sup>7</sup> For the proton, the  $hfs$  constants calculated only from  $(\rho_h)_{ba}$  are compared with the experimental results. The reasons for this are as follows: As may be seen from Eq. (6), the SP contributions satisfy the relation:  $(\rho_{ba}^i)_{SP} = 3(\rho_{aa}^i)_{SD}$ , while the SD contributions satisfy  $(\rho_{ba}^i)_{SD} = (\rho_{aa}^i)_{SD}$ . For example, in the ethyl radical, the spin density of the  $H_1$  atom is due to both mechanisms, while that of the  $H_2$  atom is due only to the SP mechanism. (See Fig. 1 and Table 4.) Thus,  $\rho_{ba} \approx 1.2\rho_{aa}$  for the  $H_1$  atom and  $\rho_{ba} \approx 3\rho_{aa}$  for the  $H_2$  atom. This example shows that, if the  $\sigma$ - $\pi$ -type electron repulsion integrals are so adjusted that  $\rho_{ba}$  correlates well with the experimental values, then  $\rho_{aa}$  correlates poorly with the observed values in the least-mean-square's sense. For a comparison of the spin densities calculated by the various methods, see the article by Harriman and Sando (*J. Chem. Phys.*, **48**, 5138 (1968)).

11) J. R. Morton, *Chem. Revs.*, **64**, 453 (1964).

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

inner  $1s$  AO's.<sup>10,12)</sup> These contributions are opposite in sign to those of the  $2s$  AO's.<sup>10,12)</sup>

### Application of the Method

In this section we will present the results obtained by applying the above method to three types of radicals: 1) organic  $\pi$ -electron radicals, such as methyl, ethyl, allyl, and *trans*-butadienyl anion radicals; 2) organic  $\sigma$ -electron radicals, such as vinyl and formyl radicals, and 3) inorganic  $\sigma$ -electron radicals, such as  $NO_2$ ,  $CO_2^-$ , and  $CN$  radicals. The geometries and the numberings are illustrated in Fig. 1. In this section we will first show the general features common to the three types of radicals. Secondly, the characteristic features of each type of radical will be compared with the experimental results, and lastly, the dipole moments of the  $\sigma$ -electron radicals will be analyzed.

**General Features.** The calculated ionization potentials and electron affinities are given in Table 1, together with the experimental values. The calculated ionization potentials are generally larger than the observed values.

Table 2 gives the expectation values of the spin-squared operator,  $S^2$ , before and after the annihilation of the quartet spin function. The annihilation of the lowest contaminating spin state yields a sufficiently pure eigenstate of  $S^2$ . If the sextet and higher spin states are neglected, the UHF wavefunction for doublet radicals may be written as:

$$\psi_{uhf} = C_{1/2}\psi_{1/2} + C_{3/2}\psi_{3/2},$$

and the relative weight,  $(C_{3/2})^2/(C_{1/2})^2$ , may be calculated by:<sup>7)</sup>

$$(C_{3/2})^2/(C_{1/2})^2 = \frac{4\langle S^2 \rangle_{uhf} - 3}{15 - 4\langle S^2 \rangle_{uhf}}. \quad (8)$$

In the last column of Table 2, these values are given for various radicals; they are less than 0.04 for all the cases studied here.

That annihilation of the lowest contaminating spin state weakly influences the total charge densities<sup>7b)</sup> is shown in Table 3 for the methyl and  $NO_2$  radicals. This fact can be deduced generally.<sup>8e)</sup> However, the annihilation causes large changes in the spin-density distributions, as will be shown below.

**Organic  $\pi$ -Electron Radicals.** i) *Methyl Radical.* The geometry,  $hfs$  constants, and some other properties of the methyl radical have been examined theoretically<sup>14,10,12,13)</sup> and experimental-

13) a) M. Karplus, *J. Chem. Phys.*, **30**, 15 (1959).

b) D. M. Schrader and M. Karplus, *ibid.*, **40**, 1593 (1964).

c) D. M. Schrader, *ibid.*, **46**, 3895 (1967).

d) K. Morokuma, L. Pedersen and M. Karplus, *ibid.*, **48**, 4801 (1968).

e) D. L. Beveridge and K. Miller, *Mol. Phys.*, **14**, 401 (1968).

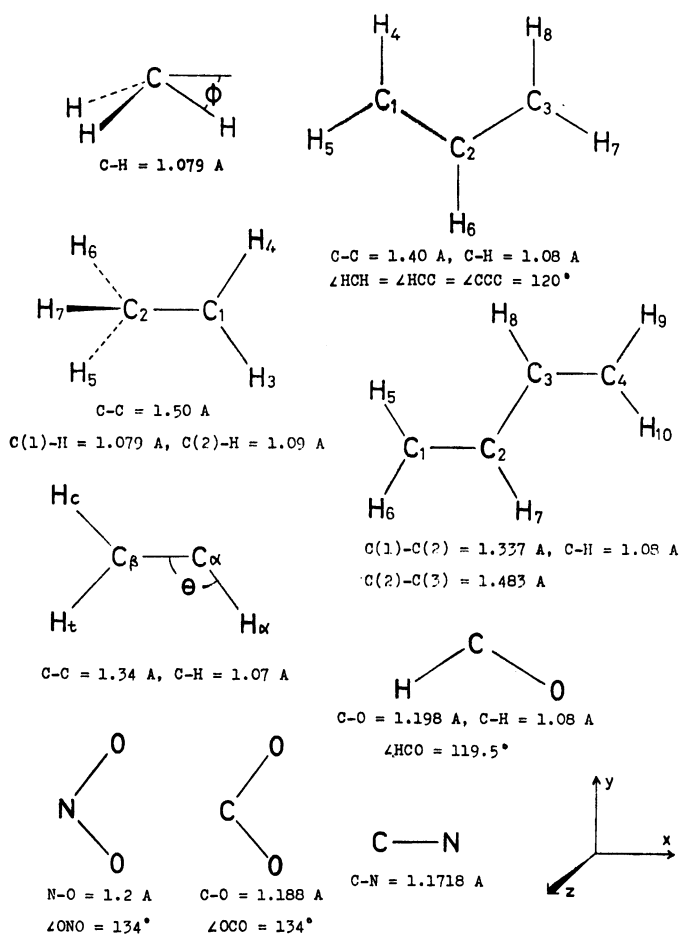


Fig. 1. Geometries (L. E. Sutton Ed., "Tables of Interatomic Distances and Configuration in Molecules and Ions," Chem. Soc. (London), (1956) and (1965)).

TABLE 1. IONIZATION POTENTIAL (*IP*) AND ELECTRON AFFINITY (*EA*) (eV)

Radical	<i>IP</i>		<i>EA</i>		Calcd
	Exptl.	Calcd	Exptl.	Calcd	
CH <sub>3</sub>	9.86, <sup>a)</sup> 9.95 <sup>a)</sup>	10.310	1.1, <sup>d)</sup> 1.4 <sup>e)</sup>	—	-0.813
C <sub>2</sub> H <sub>5</sub>	8.67, <sup>a)</sup> 8.78 <sup>a)</sup>	10.062	0.9, <sup>d)</sup> 0.94 <sup>e)</sup>	—	-0.690
C <sub>3</sub> H <sub>5</sub>	8.16, <sup>a)</sup> 8.755 <sup>a)</sup>	9.202	2.1, <sup>d)</sup> 2.21 <sup>e)</sup>	—	0.050
C <sub>4</sub> H <sub>6</sub> <sup>-</sup>	-0.34 <sup>b)</sup>	-0.164	—	—	-7.728
C <sub>2</sub> H <sub>3</sub>	9.45 <sup>e)</sup>	10.223	—	—	-0.665
HCO	9.82, <sup>a)</sup> 9.88 <sup>a)</sup>	9.854	—	—	0.200
NO <sub>2</sub>	11.3, <sup>a)</sup> 9.78 <sup>a)</sup>	11.967	2.34, <sup>f)</sup> 1.62 <sup>d)</sup>	—	2.18
CO <sub>2</sub> <sup>-</sup>	—	1.820	—	—	-8.041
CN	14.55, <sup>a)</sup> 15.13 <sup>a)</sup>	11.307	3.21 <sup>g)</sup>	—	0.445

a) R. W. Kiser, "Tables of Ionization Potentials", United States Atomic Energy Commission, TID-6142 (1960).

b) The value cited is the calculated *EA* of trans-butadiene: N. S. Hush and J. A. Pople, *Trans. Faraday Soc.*, **51**, 600 (1955).

c) F. W. McLafferty, "Mass Spectrometry of Organic Ions," Academic Press Inc., New York (1963), p. 240.

d) H. O. Pritchard, *Chem. Revs.*, **52**, 529 (1953); H. O. Pritchard and H. A. Skinner, *ibid.*, **55**, 745 (1955).

e) F. M. Page, Symp. Combust. 8-th, Pasadena, Calif., 1960, p. 160.

f) D. F. C. Morris, *J. Inorg. Nucl. Chem.*, **6**, 295 (1958).

g) J. T. Herron and V. H. Dibeler, *J. Am. Chem. Soc.*, **82**, 1555 (1960).

TABLE 2. THE EXPECTATION VALUES OF  $S^2$  BEFORE AND AFTER ANNIHILATION OF THE QUARTET SPIN FUNCTION

Radical	$\langle S^2 \rangle$		$\frac{(C_{3/2})^2}{(C_{1/2})^2}$ a)
	Before annihilation	After annihilation	
Methyl			
$\phi = 0.0^\circ$	0.7544	0.7500	0.0014
$6.0^\circ$	0.7542	0.7500	0.0014
$12.0^\circ$	0.7537	0.7500	0.0012
$19.47^\circ$	0.7529	0.7500	0.0010
Ethyl	0.7564	0.7500	0.0021
Allyl	0.8584	0.7510	0.0399
( <i>t</i> -Butadiene) <sup>-</sup>	0.7828	0.7502	0.0113
Vinyl			
$\theta = 120^\circ$	0.7880	0.7502	0.0132
$135^\circ$	0.7892	0.7503	0.0137
$150^\circ$	0.7906	0.7504	0.0142
$180^\circ$	0.7922	0.7506	0.0148
Formyl	0.7713	0.7502	0.0071
NO <sub>2</sub>	0.7563	0.7500	0.0021
CO <sub>2</sub> <sup>-</sup>	0.7529	0.7500	0.0009
CN	0.7562	0.7500	0.0020

a) See Eq. (8).

TABLE 3. TOTAL CHARGE DENSITIES OF THE CH<sub>3</sub> AND NO<sub>2</sub> RADICALS CALCULATED BEFORE AND AFTER ANNIHILATION

Atomic orbital	CH <sub>3</sub>		Atomic orbital	NO <sub>2</sub>	
	$\langle q \rangle_{ba}$	$\langle q \rangle_{aa}$		$\langle q \rangle_{ba}$	$\langle q \rangle_{aa}$
2s	1.1152	1.1126	2s(N)	1.4906	1.4900
2p <sub>x</sub> , 2p <sub>y</sub>	0.4200	0.4200	2p <sub>x</sub> (N)	1.0690	1.0686
2p <sub>y</sub>	1.0000	1.0000	2p <sub>y</sub> (N)	0.2588	0.2578
h	0.7611	0.7602	2p <sub>z</sub> (N)	0.7605	0.7603
			2s(O)	2.0238	2.0239
			2p <sub>x</sub> (O)	1.5712	1.5712
			2p <sub>y</sub> (O)	1.1459	1.1454
			2p <sub>z</sub> (O)	1.4142	1.4141

ly<sup>14</sup>) in great detail. In this paper we examine its structure, force constant, and *hfs* constants.

In Fig. 2, the calculated potential curve for the out-of-plane bending of the methyl radical is shown. The present calculation predicts a planar configura-

14) a) T. Cole, H. O. Pritchard, N. R. Davidson and H. M. McConnell, *Mol. Phys.*, **1**, 406 (1958). b) G. Herzberg and J. Shoosmith, *Can. J. Phys.*, **34**, 523 (1956). c) G. Herzberg, *Proc. Roy. Soc. (London)*, **A262**, 291 (1961). d) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963). e) R. W. Fessenden, *J. Phys. Chem.*, **71**, 74 (1967). f) W. L. S. Andrews and G. C. Pimentel, *J. Chem. Phys.*, **44**, 2527 (1966). g) D. E. Milligan and M. E. Jacox, *ibid.*, **47**, 5146 (1967).

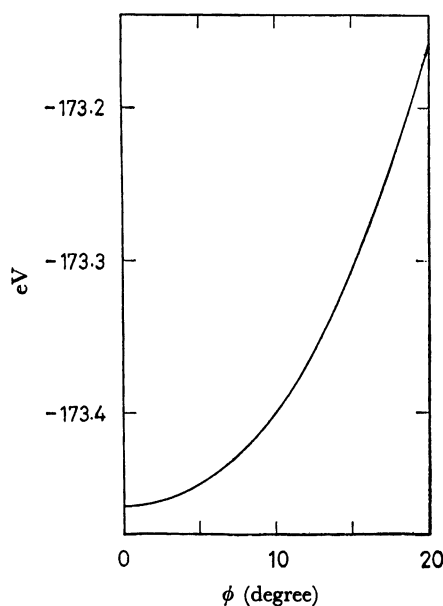


Fig. 2. Potential curve for out-of-plane bending of the methyl radical.

tion<sup>14</sup>) and gives a force constant of 0.183 mdyne/A, which is comparable with the experimental values, 0.2527 in a solid-argon matrix<sup>14f</sup>) and 0.177 in a nitrogen matrix.<sup>14g</sup>)

Recently, the isotope effects on the *hfs* constants of the methyl radicals have been reported by Fessenden,<sup>14e</sup>) the spin densities on both the proton and the carbon nuclei have been seen to increase with an increase in the angle  $\phi$  of Fig. 1. Here, we will examine the angular dependence of the spin densities in order to clarify the mechanism of these angular dependencies. The results are summarized in Table 4, while those for the carbon 2s AO are illustrated in Fig. 3. They predict reasonably well the angular dependences of the spin densities on both the hydrogen 1s and the carbon 2s AO's, which is in accordance with the experiments. Note that as the angle  $\phi$  increases, the  $(\rho_{2s(C)})_{SD}$  value increases, and that this increase exceeds the decreasing tendency of  $(\rho_{2s(C)})_{SP}$ , *vis.* Fig. 3. For the proton-spin density, the observed tendency may be explained by the increasing contribution of the SD mechanism with an increase in the angle. Note that the SP contribution is almost constant over the angular range considered and that the SD contribution is very small, even in the tetrahedral configuration.

In Table 5, these isotope effects of the methyl radicals are summarized and compared with the experimental values,<sup>14e</sup>) the temperature effects<sup>14b</sup>) are neglected and the calculated *hfs* constants are averaged over the zero-point vibration, and the force constant of the CH<sub>3</sub> radical obtained by Milligan and Jacox<sup>14g</sup>) is used for all the isotopical-

TABLE 4. SPIN DENSITIES IN THE METHYL RADICAL

Geometry $\phi$	Atomic orbital	Before annihilation			After annihilation		
		$\langle\rho\rangle_{ba}$	$(\rho)_{SP}$	$(\rho)_{SD}$	$\langle\rho\rangle_{aa}$	$(\rho)_{SP}$	$(\rho)_{SD}$
0°	2s(C)	0.1487	0.147	0.002 <sup>a)</sup>	0.0510	0.049	0.002 <sup>a)</sup>
	2p <sub>x</sub> (C), 2p <sub>z</sub> (C)	0.0115	0.012	0.000	0.0038	0.004	0.000
	2p <sub>y</sub> (C)	1.0000	0.000	1.000	0.9990	0.000	0.999
	h	-0.0275	-0.028	0.000	-0.0089	-0.009	0.000
6°	2s(C)	0.1523	0.143	0.009	0.0570	0.048	0.009
	2p <sub>x</sub> (C), 2p <sub>z</sub> (C)	0.0117	0.012	0.000	0.0039	0.004	0.000
	2p <sub>y</sub> (C)	0.9909	0.001	0.990	0.9897	0.000	0.990
	h	-0.0270	-0.028	0.001	-0.0084	-0.009	0.001
12°	2s(C)	0.1622	0.132	0.030	0.0739	0.044	0.030
	2p <sub>x</sub> (C), 2p <sub>z</sub> (C)	0.0126	0.013	0.000	0.0042	0.004	0.000
	2p <sub>y</sub> (C)	0.9653	0.003	0.962	0.9635	0.001	0.962
	h	-0.0258	-0.028	0.002	-0.0071	-0.009	0.002
19.47 <sup>ob)</sup>	2s(C)	0.1812	0.114	0.067	0.1052	0.038	0.067
	2p <sub>x</sub> (C), 2p <sub>z</sub> (C)	0.0145	0.015	0.000	0.0049	0.005	0.000
	2p <sub>y</sub> (C)	0.9164	0.004	0.912	0.9138	0.001	0.912
	h	-0.0241	-0.029	0.005	-0.0050	-0.010	0.005

a) This value must be zero by symmetry, and the error results from the approximation used to derive Eq. (7) (See Ref. 8).

b) Tetrahedral angle.

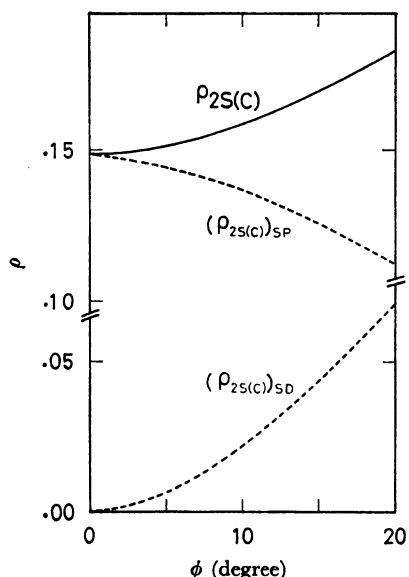


Fig. 3.  $\langle\rho_{2s(C)}\rangle_{ba}$  and its mechanistic contributions versus the bending angle  $\phi$  in the methyl radical. Only the curves obtained before annihilation are given, but the characteristic features are the same in both stages.

ly-substituted methyl radicals. As Table 5 shows, the rate of the change in the calculated *hfs* constants with an increase in the number of the deuterium atom is less than that required to explain the

observed *hfs* constants; this has also been noted by Morokuma, Pedersen and Karplus.<sup>13d)</sup> The vibrational corrections to the spin density are +0.0004 (0.29 gauss) and +0.0156~+0.0052 (17.31~5.77 gauss) for the hydrogen 1s AO and for the carbon 2s AO respectively. (See also Table 7.)

ii) *Ethyl, Allyl and Butadienyl Anion Radicals.* In this section, the spin densities of the ethyl, allyl, and *s-trans*-butadienyl anion radicals are discussed. The calculated spin densities and their mechanistic contributions are summarized in Table 6, while the proton *hfs* constants calculated from  $\langle\rho_n\rangle_{ba}$  are shown in Table 7.

Previously,<sup>8)</sup> the methyl proton *hfs* constants of the ethyl radical have been shown to be due to a major SD contribution and a minor SP contribution. When we assume the experimentally observed relation<sup>15)</sup> for the methyl proton *hfs* constant,  $a_H = B_0 + B_1 \cos^2\theta$ , where  $\theta$  is the rotational angle about the C-C single bond, the values of  $B_0$  and  $B_1$  may be calculated as -1.49 and 55.28 gauss respectively.\*<sup>8</sup> The average  $a_H$  value over the rotational angle,  $\theta$ , is 26.15 gauss, which may be compared with the observed value,<sup>14d)</sup> 26.87 gauss.

15) 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).

\*<sup>8</sup>  $B_0$  is calculated from the results previously reported (Ref. 8)).

TABLE 5. ISOTOPE EFFECTS FOR THE  $hfs$  CONSTANT (gauss)

Radical	$\langle \rho_h \rangle_{ba}$	$a_H$		Radical	$\langle \rho_{2s}(C) \rangle$		$\Delta a(^{13}C)^a$		
		Calcd	Exptl. <sup>b)</sup>		ba	aa	Calcd		Exptl. <sup>b)</sup>
							ba	aa	
$^{12}CH_3$	-0.0271 <sub>g</sub>	20.15	23.038	$^{13}CH_3$	0.1518 <sub>0</sub>	0.0562 <sub>3</sub>	0.00	0.00	0.00
$^{12}CH_2D$	-0.0271 <sub>f</sub>	20.17	23.10	$^{13}CH_2D$	0.1515 <sub>9</sub>	0.0558 <sub>7</sub>	-0.24	-0.41	-0.52
$^{12}CHD_2$	-0.0271 <sub>g</sub>	20.19	23.21	$^{13}CHD_2$	0.1513 <sub>5</sub>	0.0554 <sub>7</sub>	-0.50	-0.85	-1.28
$^{12}CD_3$	-0.0272 <sub>1</sub>	20.22	23.29 <sup>c)</sup>	$^{13}CD_3$	0.1511 <sub>0</sub>	0.0550 <sub>4</sub>	-0.78	-1.33	-2.36

a)  $\Delta a(^{13}C) = a(^{13}C) - a(^{13}C \text{ in } ^{13}CH_3)$ 

b) Ref. 14c.

c) The relation,  $a_H = 6.514a_D$ , is used.TABLE 6. SPIN DENSITIES IN THE ETHYL, ALLYL, AND *trans*-BUTADIENYL ANION RADICALS

Radical	Atomic orbital	Before annihilation			After annihilation		
		$\langle \rho \rangle_{ba}$	$(\rho)_{SP}$	$(\rho)_{SD}$	$\langle \rho \rangle_{aa}$	$(\rho)_{SP}$	$(\rho)_{SD}$
Ethyl	$2s(C_1)$	0.1614	0.159	0.002 <sup>a)</sup>	0.0555	0.053	0.002 <sup>a)</sup>
	$2p_z(C_1)$	1.0001	0.002	0.998	0.9985	0.001	0.998
	$2s(C_2)$	-0.0123	-0.012	0.000	-0.0040	-0.004	0.000
	$2p_z(C_2)$	-0.0130	-0.013	0.000	-0.0042	-0.004	0.000
	$h_3, h_4$	-0.0345	-0.035	0.000	-0.0111	-0.011	0.000
	$h_5, h_6$	0.0165	0.003	0.013	0.0142	0.001	0.013
	$h_7$	0.0724	0.020	0.052	0.0593	0.007	0.052
Allyl	$2s(C_1)$	0.0988	0.099	0.000	0.0335	0.034	0.000
	$2p_z(C_1)$	0.6840	0.173	0.511	0.5686	0.058	0.511
	$2s(C_2)$	-0.0534	-0.054	0.000	-0.0175	-0.018	0.000
	$2p_z(C_2)$	-0.3414	-0.356	0.015 <sup>a)</sup>	-0.1043	-0.119	0.015 <sup>a)</sup>
	$h_4, h_8$	-0.0188	-0.019	0.000	-0.0061	-0.006	0.000
	$h_5, h_7$	-0.0191	-0.019	0.000	-0.0062	-0.006	0.000
	$h_6$	0.0049	0.005	0.000	0.0016	0.002	0.000
Butadienyl Anion	$2s(C_1)$	0.0674	0.067	0.000	0.0228	0.022	0.000
	$2p_z(C_1)$	0.5022	0.095	0.407	0.4387	0.032	0.407
	$2s(C_2)$	0.0157	0.016	0.000	0.0053	0.005	0.000
	$2p_z(C_2)$	0.1330	-0.094	0.227	0.1957	-0.031	0.227
	$h_5, h_{10}$	-0.0132	-0.013	0.000	-0.0043	-0.004	0.000
	$h_6, h_9$	-0.0125	-0.013	0.000	-0.0041	-0.004	0.000
	$h_7, h_8$	-0.0070	-0.007	0.000	-0.0023	-0.002	0.000

a) See Ref. a) of Table 4.

The allyl radical has been extensively studied<sup>16)</sup> using the  $\pi$ -approximation method. The  $\pi$ -spin densities calculated by the UHF method by Berthier<sup>16a)</sup> are 0.812 for  $2p_z(C_1)$  and -0.619 for  $2p_z(C_2)$  AO, and the projected values<sup>16b)</sup> are 0.609 and -0.185 respectively. The corresponding values obtained by the present method are given in Table 6. The SP contribution to the spin density in the  $2p_z(C_1)$  AO is as great as 10–25%.<sup>16d)</sup> The spin

densities on the  $2p_z(C_2)$  and the  $h_6$  AO's are calculated to be negative and positive in sign respectively, which is in agreement with earlier theoretical works.<sup>16)</sup>

The electron-spin resonance study by Fessenden and Schuler<sup>14d)</sup> of the allyl radical in a liquid medium showed a slight difference in the  $hfs$  constants for the two methylene protons ( $H_4$  and  $H_5$  in Fig. 1). Obviously, McConnell's relation,<sup>9a)</sup>  $a_H = Q_H \rho_e^\pi$ , can not interpret this observed difference. However, the present valence electron treatment yields a small difference in the spin densities on the  $H_4$  and  $H_5$  nuclei. Therefore, the observed  $hfs$  constants of 13.93 and 14.83 gauss may be assigned

16) a) G. Berthier, *J. chim. Phys.*, **52**, 141 (1955).b) H. M. McConnell, *J. Chem. Phys.*, **29**, 244 (1958).c) C. Heller and T. Cole, *ibid.*, **37**, 243 (1962). d) D.Lazdins and M. Karplus, *ibid.*, **44**, 1600 (1966).

TABLE 7. ISOTROPIC PROTON  $hfs$  CONSTANTS

Radical	Position	$hfs$ Constant (gauss)	
		Calcd <sup>a)</sup>	Exptl. <sup>b)</sup>
Methyl ( $\phi=0^\circ$ )	H	-20.43	(-) 23.04
Ethyl	H(CH <sub>3</sub> )	-25.63	(-) 22.38
	H(CH <sub>2</sub> )	26.15 <sup>c)</sup>	(+) 26.87
Allyl	H <sub>4</sub> , H <sub>8</sub>	-13.97	(-) 13.93
	H <sub>5</sub> , H <sub>7</sub>	-14.19	(-) 14.83
	H <sub>6</sub>	3.64	(+) 4.06
<i>t</i> -Butadienyl Anion	H <sub>9</sub> , H <sub>10</sub>	-9.81	(-) 7.62
	H <sub>6</sub> , H <sub>9</sub>	-9.29	(-) 7.62
Vinyl ( $\theta=135^\circ$ )	H <sub>c</sub>	32.54	(+) 34
	H <sub>i</sub>	72.37	(+) 68
	H <sub>a</sub>	-15.83	(-) 16, (-) 13.4
Formyl	H	38.63	(+) 137.0

a) Calculated from  $\langle\rho\rangle_{ba}$ . See footnote \*6.

b) Refs. 14e, 18, and 22.

c) The relation,  $a_H = B_0 + B_1 \cos^2 \theta$ , is assumed.

to the H<sub>4</sub> (H<sub>6</sub>) and H<sub>5</sub> (H<sub>7</sub>) nuclei respectively. This assignment is the same as the one previously reported.<sup>5a)</sup> However, the recent calculations by Hincliffe and Atherton<sup>17)</sup> and by Pople, Beveridge, and Dobosh<sup>14d)</sup> gave an assignment opposite to that reported here. Further experimental work is necessary to settle this point.\*9

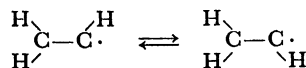
The proton  $hfs$  constants of the butadienyl anion radical have been observed by Levy and Myers.<sup>18)</sup> The calculated values, assuming the *s-trans* configuration, are shown in Table 6. The CH<sub>2</sub> protons of butadiene are non-equivalent and different  $hfs$  constants are predicted; this is in contrast to the observed identical  $hfs$  constants for these protons.<sup>18)</sup>

As is well known, the spin densities in the  $\sigma$ -type AO's of planar  $\pi$ -electron radicals and in the  $2p_z(C_2)$  AO of the allyl radical are due only to the SP mechanism. Therefore, the  $\langle\rho\rangle_{ba} = 3 \langle\rho\rangle_{sa}$  relation,<sup>7c,8)</sup> is fairly satisfactory, except for the  $2p_z(C_2)$  AO of the allyl radical.\*10

**Organic  $\sigma$ -Electron Radicals.** *i) Vinyl Radical.* The  $hfs$  constants of the vinyl radical have recently been observed,<sup>14d,14e,19)</sup> and its structure and the sign of the  $hfs$  constant of its  $\alpha$ -proton have

been intensely investigated.<sup>2,5a,19,20)</sup> Previously,<sup>5)</sup> we suggested that the  $hfs$  constant of the  $\alpha$ -proton is negative in sign. Here, we will examine theoretically the structure\*11 and the  $hfs$  constants of this radical.

The calculated potential curve with respect to the bending of the  $\theta$  angle of Fig. 1 is illustrated in Fig. 4. The minimum in the potential curve appears near  $135^\circ$ , the calculated barrier to inversion:



is 1.6 kcal/mol, which is comparable with the value,  $\sim 2$  kcal/mol, estimated by the ESR technique.<sup>14d)</sup>

One of the main features of the present method lies in its consistent applicability to the spin-density calculations of both  $\sigma$ - and  $\pi$ -electron radicals. Good examples in which the  $\sigma$ - $\pi$ -type SP mechanism, the "bulk" SP mechanism, and the SD mechanism are all competing with one another are the spin densities on the  $\alpha$ -hydrogen and the  $\alpha$ - and  $\beta$ -carbon atoms of the vinyl radical. None of these mechanisms can be ignored. This may be understood from the fact that the unpaired orbital of this radical

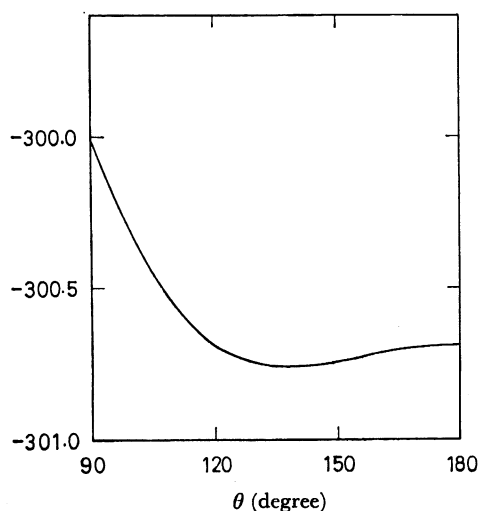


Fig. 4. Total energy (eV) on bending of  $CCH_2$  in the vinyl radical.

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

\*9 Recent experiments by Kochi and Krusic (*J. Am. Chem. Soc.*, **90**, 7157 (1968)) support the present assignment.

18) D. H. Levy and R. J. Myers, *J. Chem. Phys.*, **41**, 1062 (1964).

\*10 This exception may be attributed to the rather large value of  $(C_{3/2})^2/(C_{1/2})^2$  shown in Table 2, since the assumption used to derive Eq. (6) becomes crude in this case (see Ref. 8b).

19) E. L. Cochran, F. J. Adrian and V. A. Bowers, *J. Chem. Phys.*, **40**, 213 (1964).

20) a) W. T. Dixon, *Mol. Phys.*, **9**, 201 (1965). b) G. A. Peterson and A. D. McLachlan, *J. Chem. Phys.*, **45**, 628 (1966). c) R. S. Drago and H. Petersen, Jr., *J. Am. Chem. Soc.*, **89**, 5774 (1967). d) A. Hincliffe, *Theoret. chim. Acta (Berl.)*, **8**, 300 (1967). e) Y. Ellinger, A. Rassat, R. Subra and G. Berthier, *ibid.*, **10**, 289 (1968).

\*11 The present method predicts the angular geometry of ethylene in fair agreement with the experiment; this will be reported in detail at a later date.



at  $\theta=135^\circ$ , calculated with the open-shell restricted Hartree-Fock (RHF) method,<sup>\*12</sup> is

$$\begin{aligned} \varphi_{\text{rnf}} = & 0.2848(2s(C_\alpha)) + 0.3542(2p_x(C_\alpha)) \\ & + 0.8630(2p_y(C_\alpha)) - 0.0609(2s(C_\beta)) \\ & - 0.0664(2p_x(C_\beta)) + 0.0368(2p_y(C_\beta)) \\ & - 0.1910(h_c) + 0.2737(h_t) - 0.1319(h_a), \end{aligned}$$

and is mainly localized in the  $2p_x(C_\alpha)$  and  $2p_y(C_\alpha)$  AO's.

The spin densities and their mechanistic contributions are given in Table 8 for various configurations of the vinyl radical. The dependence of the carbon  $2s$  AO spin density on the  $\theta$  angle is illustrated in Fig. 5, while that of the proton spin density is illustrated in Fig. 6.

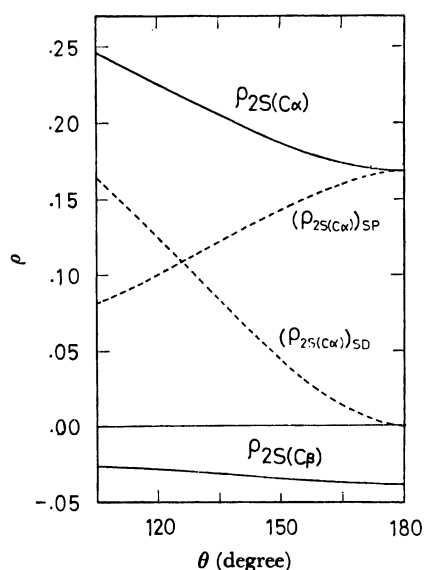


Fig. 5.  $2s$  AO spin densities of carbon atoms versus the bending of  $\text{CCH}_\alpha$  in the vinyl radical. Only the curves obtained before annihilation are shown, but the characteristic features are the same in both stages.

Figure 5 shows that the angular dependence of the SD contribution to the  $\alpha$ -carbon  $2s$  AO spin density is opposite to that of the SP contribution, and that it determines the dependence of the total spin density. At  $\theta=135^\circ$ ,  $\rho_{2s}(C_\alpha)$  is due to the 41–67% SD and 59–33% SP contributions. For the  $\beta$ -carbon atom, the angular dependence is exceptionally small and its  $2s$  AO spin density is always negative.

Figure 6 shows that the spin density on the  $\alpha$ -proton is the sum of the negative SP and the positive

\*12 C. C. J. Roothaan, *Rev. Mod. Phys.*, **32**, 179 (1960). The estimations of the integral values are the same as for the present UHF calculations, except that the two center  $\sigma$ - $\pi$ -type exchange repulsion integrals are not included in the RHF calculation.

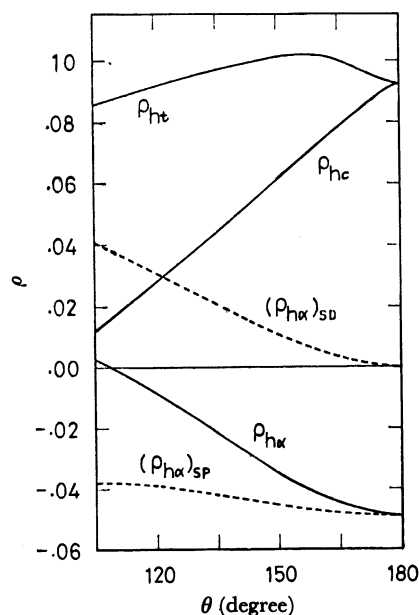


Fig. 6. Proton spin densities (ba) versus bending of  $\text{CCH}_\alpha$  in vinyl radical.

SD contributions. They depend oppositely on the angle  $\theta$ , and at  $\theta=135^\circ$ , where the minimum potential lies, the  $\alpha$ -proton spin density is due to the 97% SD and -197% SP contributions. For the *cis*- and *trans*-protons, their spin densities also show a large angular dependence, and they are also due to both the SD and SP mechanisms. At  $\theta=135^\circ$ , the spin density of the *trans*-proton is due to the 73% SD and 27% SP contributions, while that of the *cis*-proton is due to the 80% SD and 20% SP contributions.

The calculated proton *hfs* constants at the minimum potential ( $\theta=135^\circ$ ) are  $a_{\text{Hc}}=32.54$ ,  $a_{\text{Ht}}=72.37$ , and  $a_{\text{Ha}}=-15.83$  gauss (Table 7). These values agree satisfactorily with the experimental values. Moreover, as may be seen in Table 8 and Fig. 6, the calculated proton *hfs* constants obtained near  $\theta=135^\circ$  agree most reasonably with the experimental values, thus lending support to the vinyl radical configuration with  $\theta=135^\circ$ .

Note that the calculated *hfs* constant of the  $\alpha$ -proton is negative in sign.<sup>5a)</sup> However, recent INDO calculations by Pople, Beveridge and Dobosh<sup>1d)</sup> have predicted the opposite sign. Further experimental work, such as with isotope effects,<sup>14e)</sup> will be necessary to settle this point. Figures 5 and 6 will be very useful when one experimentally determines the sign of the  $\alpha$ -proton *hfs* constant. When the  $\alpha$ -proton is replaced by deuterium, a smaller *hfs* constant (except for a constant factor  $g_{\text{H}}/g_{\text{D}}=6.514$ ) should be observed if  $a_{\text{Ha}}$  is negative, and *vice versa*.

Let us now comment on the recent theoretical spin-density studies of the vinyl radical, in which

TABLE 8. SPIN DENSITIES IN THE VINYL RADICAL

Geometry $\theta$	Atomic orbital	Before annihilation			After annihilation		
		$\langle \rho \rangle_{\text{ba}}$	$(\rho)_{\text{SP}}$	$(\rho)_{\text{SD}}$	$\langle \rho \rangle_{\text{aa}}$	$(\rho)_{\text{SP}}$	$(\rho)_{\text{SD}}$
120°	2s(C <sub>α</sub> )	0.2251	0.100	0.125	0.1581	0.033	0.125
	2s(C <sub>β</sub> )	-0.0286	-0.033	0.004	-0.0063	-0.011	0.004
	<i>h<sub>c</sub></i>	0.0286	0.005	0.024	0.0255	0.002	0.024
	<i>h<sub>t</sub></i>	0.0913	0.024	0.067	0.0752	0.008	0.067
	<i>h<sub>a</sub></i>	-0.0083	-0.039	0.031	0.0175	-0.013	0.031
135°	2s(C <sub>α</sub> )	0.2051	0.122	0.083	0.1240	0.041	0.083
	2s(C <sub>β</sub> )	-0.0315	-0.035	0.004	-0.0082	-0.012	0.004
	<i>h<sub>c</sub></i>	0.0438	0.009	0.035	0.0381	0.003	0.035
	<i>h<sub>t</sub></i>	0.0974	0.026	0.071	0.0799	0.009	0.071
	<i>h<sub>a</sub></i>	-0.0213	-0.042	0.021	0.0064	-0.014	0.021
150°	2s(C <sub>α</sub> )	0.1870	0.143	0.044	0.0917	0.048	0.044
	2s(C <sub>β</sub> )	-0.0348	-0.037	0.002	-0.0102	-0.012	0.002
	<i>h<sub>c</sub></i>	0.0614	0.013	0.048	0.0525	0.004	0.048
	<i>h<sub>t</sub></i>	0.1013	0.027	0.074	0.0832	0.009	0.074
	<i>h<sub>a</sub></i>	-0.0345	-0.045	0.011	-0.0042	-0.015	0.011
180°	2s(C <sub>α</sub> )	0.1690	0.166	0.003 <sup>a)</sup>	0.0583	0.055	0.003 <sup>a)</sup>
	2s(C <sub>β</sub> )	-0.0384	-0.038	0.000	-0.0125	-0.013	0.000
	<i>h<sub>c</sub>, h<sub>t</sub></i>	0.0926	0.023	0.070	0.0774	0.008	0.070
	<i>h<sub>a</sub></i>	-0.0487	-0.050	0.001 <sup>a)</sup>	-0.0153	-0.017	0.002 <sup>a)</sup>

a) See Ref. a) of Table 4.

only the SD contribution was taken into account.<sup>20b,20c)</sup> For instance, if the SP mechanism is neglected, the  $\alpha$ -proton spin density will be about +0.021 ( $(\rho_{\text{H}\alpha})_{\text{SD}}$  shown in Table 8), which is of the same magnitude, but of the opposite sign, as the present result, -0.0213. Thus, even if the SP contribution is neglected, a value which is apparently reasonable in magnitude can be obtained for the  $\alpha$ -proton spin density. Furthermore, neglect of the SP contribution leads to serious errors in the calculation of the spin densities even of other protons and of the carbon 2s AO's, as is shown in Table 8, Fig. 5, and Fig. 6. This is probably true for other  $\sigma$ -electron radicals as well; namely, one should not neglect the spin polarization mechanism even in  $\sigma$ -electron radicals, especially in AO's near the radical-center atom.<sup>8b,20a)</sup>

ii) *Formyl Radical.* Recently, the results of a non-empirical UHF calculation of the formyl radical *hfs* constants have been reported by Hincliffe and Cook<sup>21)</sup> to be in good agreement with the experimental values.<sup>22)</sup> However, most of the semi-empirical MO calculations<sup>1d,2,20b,20d)</sup> have

failed to yield such a large proton *hfs* constant as was experimentally observed value, 137.0 gauss.<sup>22)</sup> As may be seen in Table 9, the present result for the proton *hfs* constant is also disappointing. It is necessary to examine the present result to determine its failing by comparing it with the result of the non-empirical calculation.

From the  $(\rho)_{\text{SD}}$  shown in Table 9 we can see that the unpaired orbital consists mainly of the  $2p_y(\text{C})$  and  $2p_y(\text{O})$  AO's. This implies that the SP mechanism is very important to the *hfs* constant of this radical. The nonempirical calculation of the proton *hfs* constant gave 154.58 gauss before annihilation and 133.95 gauss after single annihilation. The SP and SD contributions calculated from these values (see Eq. (20) of the previous report.<sup>8b)</sup>) are 61.89 and 92.69 gauss before annihilation. In the present calculations, they are -5.94 and 44.58 gauss respectively. Very large differences exist in both contributions. The SP contributions of both methods differ especially even in sign. The reason for this is perhaps that  $\sigma$ - $\pi$ -type exchange repulsion integrals other than those included in the present calculation (especially the two center  $\sigma$ - $\pi$ -type ionic integrals which make a positive contribution to the proton *hfs* constant) can not be neglected in this case.

**Inorganic  $\sigma$ -Electron Radicals.** We chose here, as sample calculations for the inorganic  $\sigma$ -electron radicals, the isoelectronic NO<sub>2</sub> and CO<sub>2</sub><sup>-</sup> radicals, where the spin densities on the VAO's

21) A. Hincliffe and D. B. Cook, *Chem. Phys. Letters*, **1**, 217 (1967).

22) a) F. J. Adrian, E. L. Cochran and V. A. Bowers, *J. Chem. Phys.*, **36**, 1661 (1962). b) J. A. Brivati, N. Keen and M. C. R. Symons, *J. Chem. Soc.*, **1962**, 237. c) F. J. Adrian, E. L. Cochlan and V. A. Bowers, *J. Chem. Phys.*, **44**, 4626 (1966).

TABLE 9. SPIN DENSITIES IN THE FORMYL RADICAL

Atomic orbital	Before annihilation			After annihilation		
	$\langle\rho\rangle_{ba}$	$(\rho)_{SP}$	$(\rho)_{SD}$	$\langle\rho\rangle_{aa}$	$(\rho)_{SP}$	$(\rho)_{SD}$
2s(C)	0.1603	0.029	0.131	0.1409	0.010	0.131
2p <sub>x</sub> (C)	-0.0169	-0.021	0.004	-0.0029	-0.007	0.004
2p <sub>y</sub> (C)	0.5028	-0.014	0.517	0.5124	-0.005	0.517
2p <sub>z</sub> (C)	-0.1118	-0.114	0.002 <sup>a)</sup>	-0.0356	-0.038	0.002 <sup>a)</sup>
h	0.0522	-0.008	0.060	0.0574	-0.003	0.060
2s(O)	0.1106	0.109	0.002	0.0378	0.036	0.002
2p <sub>x</sub> (O)	0.0593	0.020	0.039	0.0457	0.007	0.039
2p <sub>y</sub> (O)	0.4802	0.012	0.468	0.4725	0.004	0.468
2p <sub>z</sub> (O)	0.1310	0.128	0.003 <sup>a)</sup>	0.0457	0.043	0.003 <sup>a)</sup>

a) See Ref. a) of Table 4.

TABLE 10. SPIN DENSITIES IN NO<sub>2</sub>, CO<sub>2</sub><sup>-</sup>, AND CN RADICALS

Radical	Atomic orbital	$\langle\rho\rangle_{ba}$	$\langle\rho_{SP}\rangle_{ba}$	$\langle\rho_{SD}\rangle_{ba}$	$\langle\rho\rangle_{aa}$	Experimental <sup>a)</sup>
NO <sub>2</sub>	2s(N)	0.1900	0.057	0.133	0.1522	0.106, 0.097
	2p <sub>x</sub> (N)	0.4576	0.001	0.457	0.4570	0.452, 0.371
	2p <sub>z</sub> (N)	0.0497	0.049	0.000	0.0169	0.019
	2s(O)	0.0505	0.048	0.003	0.0185	—
	2p <sub>x</sub> (O)	0.3495	0.012	0.337	0.3412	—
	2p <sub>z</sub> (O)	-0.0250	-0.025	0.000	-0.0082	—
CO <sub>2</sub> <sup>-</sup>	2s(C)	0.2652	0.012	0.253	0.2571	0.14
	2p <sub>x</sub> (C)	0.5421	-0.006	0.548	0.5460	0.66
	2p <sub>z</sub> (C)	0.0131	0.013	0.000	0.0044	0.08
	2s(O)	0.0641	0.056	0.008	0.0271	—
	2p <sub>x</sub> (O)	0.2746	0.008	0.267	0.2690	—
	2p <sub>z</sub> (O)	-0.0080	-0.008	0.000	-0.0026	—
CN	2s(C)	0.0884	-0.026	0.115	0.1060	—
	2p <sub>x</sub> (C)	0.3377	-0.003	0.341	0.3398	—
	2p <sub>y</sub> (C), 2p <sub>z</sub> (C)	-0.0494	-0.050	0.001	-0.0162	—
	2s(N)	0.0876	0.054	0.034	0.0515	—
	2p <sub>x</sub> (N)	0.4994	0.006	0.493	0.4956	—
	2p <sub>y</sub> (N), 2p <sub>z</sub> (N)	0.0563	0.056	0.000	0.0191	—

a) Ref. 23a.

are assumed from the anisotropy of the ESR parameters<sup>23)</sup> and the CN radical, which is especially interesting in its dipole moment. Table 10 summarizes the spin densities calculated on the various VAO's of these radicals, along with those estimated from the experiments.<sup>23)</sup> The NO<sub>2</sub> spin densities theoretically calculated by McEwen<sup>24a)</sup> and by

23) a) P. W. Atkins, N. Keen and M. C. R. Symons, *J. Chem. Soc.*, **1962**, 2873. b) H. Zeldes and R. Livingston, *J. Chem. Phys.*, **35**, 563 (1961). c) H. Zeldes and R. Livingston, *ibid.*, **37**, 3017 (1962). d) D. W. Ovenall and D. H. Whiffen, *Proc. Chem. Soc.*, **1960**, 420. e) D. W. Ovenall and D. H. Whiffen, *Mol. Phys.*, **4**, 135 (1961). f) J. A. Brivati, N. Keen, M. C. R. Symons and P. A. Trevalion, *Proc. Chem. Soc.*, **1961**, 66.

Green and Linnett<sup>24b)</sup> gave small magnitudes (0.263 and 0.222 respectively) for the spin density on the 2p<sub>x</sub>(N) AO, but the present method gave  $\rho_{2p_x(N)} = 0.457$ , which is in closer agreement with the experimental estimations.

Table 10 shows that the present calculation qualitatively predicts almost all features of the spin densities of the isoelectronic NO<sub>2</sub> and CO<sub>2</sub><sup>-</sup> radicals. For example, the spin density on the 2p<sub>x</sub>(N) AO of NO<sub>2</sub> is smaller than that on the 2p<sub>x</sub>(C) AO of CO<sub>2</sub><sup>-</sup>, the delocalization of the unpaired spin to oxygens is greater in NO<sub>2</sub> than in CO<sub>2</sub><sup>-</sup>, etc.

24) a) K. L. McEwen, *J. Chem. Phys.*, **32**, 1801 (1960). b) M. Green and J. W. Linnett, *Trans. Faraday Soc.*, **57**, 1 (1961).

Note that the  $2s$  spin densities shown in the last column of Table 10 are estimated from the observed values without paying any attention to the inner  $1s$  contributions. Hence, these  $2s$  contributions cannot be compared directly with the calculated contributions.

**Analyses of Dipole Moments of  $\sigma$ -Electron Radicals.** The dipole moment of a neutral molecule may be expressed approximately as the sum of the atomic dipole ( $\mu_{AD}$ ) and the charge dipole ( $\mu_{CD}$ ). The atomic dipole ( $x$ -direction) of the first-row atoms of the periodic table is given by:

$$\mu_{AD}(x) = -7.3370 \sum_A (P_{sp(x)}^A / \zeta_A)$$

in debye units, and the charge dipole is:

$$\mu_{CD}(x) = 4.8029 \sum_A (Z_A - N_A) x_A,$$

if we adopt the Mulliken approximation:

$$\langle \chi_r | x | \chi_s \rangle = \frac{1}{2} S_{rs} \{ \langle \chi_r | x | \chi_r \rangle + \langle \chi_s | x | \chi_s \rangle \}.$$

$\zeta_A$  is the Slater exponent, and  $N_A$  is the atomic population of the  $A$  atom.  $P_{sp(x)}^A$  is the off-diagonal density matrix element between the  $2s$  and  $2p_x$  AO's of the  $A$  atom.

The analyses of the dipole moment of vinyl, formyl,  $\text{NO}_2$ , and CN radicals are given in Table 11; they were obtained by using the values obtained before annihilation.  $\mu_{AD}^\alpha$  and  $\mu_{AD}^\beta$  are the contributions to the atomic dipole from all the occupied  $\alpha$ - and  $\beta$ - spin orbitals respectively. These contributions may be further divided into those due to the first-row atoms in the molecule. As is shown in the forth and fifth columns of the table,  $\mu_{AD}^\alpha$  due

to the radical center atom (*e.g.*,  $\text{C}_\alpha$  in vinyl) surpasses the  $\mu_{AD}^\beta$  due to the other atoms and the  $\mu_{AD}^\alpha$  values of all the constituent atoms. The values of  $\mu_{AD}^\alpha$  (HO) in the sixth column give contributions to the atomic dipole only from the highest occupied (HO)  $\alpha$ -spin orbital. Note that the  $\mu_{AD}^\alpha$  (HO) at the radical-center atom makes the dominant contribution to  $\mu_{AD}^\alpha$  and even to  $\mu_{AD}$ . Thus, the most unstable HO orbital of the  $\sigma$ -electron radical extends considerably out of the molecule from the radical center atom. The direction of the  $-\mu_{AD}^\alpha$  (HO) of the vinyl radical is  $113^\circ$  from the  $\text{C}_\alpha$ - $\text{C}_\beta$  bond.

In  $\text{NO}_2$  and CN radicals, the contributions due to the charge dipole cancel those due to the atomic dipole. In the CN radical especially, these two contributions are almost the same in magnitude, but reverse in direction, so the resultant dipole moment is very small. This should be compared with the well-known example of the CO molecule, where its atomic dipole surpasses its charge dipole and makes it a powerful ligand in the chemistry of metal complexes. The calculated dipole moment of  $\text{NO}_2$  is  $-1.301$  debye, which is too large if compared with the observed value,  $-0.29$  debye. However, the above qualitative discussion will not be altered by more rigorous calculations.

### Summary and Conclusions

As has been seen in the previous sections, the semi-empirical method for valence electron systems including differential overlap can be satisfactorily extended to systems with open-shell structures.

TABLE 11. ANALYSES OF DIPOLE MOMENTS OF  $\sigma$ -ELECTRON RADICALS (in debye units)

Radical	Atom	Direction	Analyses of atomic dipole				Total
			$\mu_{AD}^\alpha$ <sup>a)</sup>	$\mu_{AD}^\beta$	$\mu_{AD}^\alpha$ (HO) <sup>b)</sup>	$\mu_{AD}$ <sup>c)</sup>	
Vinyl ( $\theta=135^\circ$ )	$\text{C}_\alpha$	$x$	-0.36	0.06	-0.31	-0.31	$\mu_{AD}=0.68$ $\mu_{CD}=0.52$ $\mu=1.19$
		$y$	-0.85	0.16	-0.71	-0.69	
	$\text{C}_\beta$	$x$	0.16	0.09	-0.02	0.24	
		$y$	0.01	0.01	-0.01	0.02	
Formyl	C	$x$	0.31	0.36	-0.13	0.67	$\mu_{AD}=1.42$ $\mu_{CD}=3.07$ $\mu=3.16$
		$y$	-1.58	-0.36	-1.09	-1.93	
	O	$x$	-0.36	-0.55	0.01	-0.91	
		$y$	0.23	0.30	0.04	0.53	
$\text{NO}_2$ <sup>d)</sup>	N	$x$	1.17	0.32	0.59	1.49	$\mu_{AD}=0.52$ $\mu_{CD}=-1.83$ $\mu=-1.30$
	O	$x$	-0.17	-0.31	0.02	-0.48	
CN	C	$x$	1.87	0.90	1.03	2.77	$\mu_{AD}=1.13$ $\mu_{CD}=-1.18$ $\mu=-0.05$
	N	$x$	-1.01	-0.63	-0.31	-1.64	

a)  $\mu_{AD}^\alpha$  denotes the contribution to atomic dipole ( $\mu_{AD}$ ) from all the occupied  $\alpha$ -spin orbitals.

b)  $\mu_{AD}^\alpha$ (HO) denotes the contribution to atomic dipole from the highest occupied  $\alpha$ -spin orbital.

c)  $\mu_{AD} = \mu_{AD}^\alpha + \mu_{AD}^\beta$ .

d) The experimental value is  $-0.29$  debye; C. H. Townes and A. L. Schawlow, "Microwave Spectroscopy," McGraw-Hill Book Co., New York (1955).

The results of the present study are as follows:

(1) The separation of the mechanistic contributions to spin density makes it possible to enter into detailed discussions of the nature of the spin density; *e.g.*, the spin-polarization mechanism is shown to be very important even when the spin-localization mechanism has hitherto been considered dominant (*e.g.*, ethyl and vinyl radicals).

(2) A good correlation between the calculated  $hf_s$  constants and the configurations of radicals is found for methyl and vinyl radicals. The geometry of the vinyl radical is predicted to be  $\theta \simeq 135^\circ$  from both the potential curve and the calculated  $hf_s$  constants. Since there are many radicals with known  $hf_s$  constants, but with

unknown configurations, the agreement between the configuration expected from the calculated potential curve and that expected from the calculated  $hf_s$  constants is ideal for a reliable prediction of the configuration of the radical from the theoretical point of view.

(3) The analyses of the atomic dipole moments of the  $\sigma$ -electron radicals revealed some interesting features. For example, the highest occupied orbitals of these  $\sigma$ -electron radicals make decisive contributions to the total atomic dipole.

The calculations were carried out on a HITAC 5020 E computer at the computation center of the University of Tokyo.

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