

## Spin Polarization and Spin Delocalization in Unrestricted Hartree-Fock Method

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A method to separate the spin density calculated with the unrestricted Hartree-Fock method into components due to spin-polarization and spin-delocalization mechanisms is presented, and applied to some doublet and triplet radicals. The results are examined by means of the UHF natural orbitals and of the open-shell restricted Hartree-Fock orbitals, and the validity of the method is confirmed.

### I. INTRODUCTION

The unrestricted Hartree-Fock (UHF) method based on a spin-polarized self-consistent-field single-determinant wavefunction<sup>1</sup> is widely used for spin-density calculations. However, compared with configuration-interaction or perturbation methods,<sup>2,3</sup> the UHF method does not usually provide information about "spin-appearing" mechanisms<sup>4</sup> such as spin-polarization (SP) and spin-delocalization (SD) mechanisms.<sup>5-7</sup>

In a previous communication,<sup>7</sup> we proposed a procedure to separate the spin density calculated with the UHF method ( $\rho_{\text{UHF}}$ ) and that obtained after the annihilation method<sup>8</sup> ( $\rho_{\text{asa}}$  and  $\rho_{\text{aa}}$ )<sup>9</sup> into components due to the SP mechanism ( $\rho_{\text{SP}}$ ) and to the SD mechanism ( $\rho_{\text{SD}}$ ). For doublet radicals, the results are

$$\begin{aligned}(\rho_{\text{UHF}})_{\text{SP}} &= \frac{3}{2}(\rho_{\text{UHF}} - \rho_{\text{aa}}), \\ (\rho_{\text{asa}})_{\text{SP}} &= \rho_{\text{UHF}} - \rho_{\text{aa}}, \\ (\rho_{\text{aa}})_{\text{SP}} &= \frac{1}{2}(\rho_{\text{UHF}} - \rho_{\text{aa}}),\end{aligned}\quad (1)$$

where  $(\rho_{\text{UHF}})_{\text{SP}}$  denotes the SP contribution to the spin density calculated with the UHF method and  $(\rho_{\text{asa}})_{\text{SP}}$  and  $(\rho_{\text{aa}})_{\text{SP}}$  are those to  $\rho_{\text{asa}}$  and  $\rho_{\text{aa}}$ , respec-

tively. The spin-delocalization contribution is approximated as the difference

$$(\rho)_{\text{SD}} = \rho - (\rho)_{\text{SP}}. \quad (2)$$

Furthermore, the validity of this approach was confirmed by comparing the SD contributions calculated by Eq. (2) with those obtained by the open-shell restricted Hartree-Fock method.<sup>10</sup>

The separation of the unrestricted spin density into mechanistic contributions is also possible by means of the natural orbitals of the UHF method. Here, we compare the results obtained by the above method with those calculated from the natural orbitals of the UHF method.<sup>8a</sup> In the next section, an extension of the above method to triplet states is described and some assumptions in the formalism are examined. Then, we apply the method to typical doublet and triplet radicals in Sec. III. The conclusion of the present study is given in Sec. IV.

### II. THEORY

The total wavefunction of the UHF method is written by a single determinant in which the  $\alpha$ -spin orbitals  $\{\varphi_i\}$  may be different from the  $\beta$ -spin orbitals  $\{\phi_i\}$ ;

$$\begin{aligned}\Psi_{\text{UHF}} &= [(\rho+q)!]^{-1/2} \det\{\varphi_1(1)\alpha(1)\varphi_2(2)\alpha(2) \\ &\quad \cdots \varphi_p(p)\alpha(p)\phi_1(p+1)\beta(p+1)\phi_2(p+2)\beta(p+2) \\ &\quad \cdots \phi_q(p+q)\beta(p+q)\},\end{aligned}\quad (3)$$

where we assume  $p \geq q$  without loss of generality. For doublet radicals,  $p=q+1$ , and for triplet radicals,  $p=q+2$ . As shown by Amos and Hall<sup>8a</sup> and by Amos and Snyder,<sup>8b</sup> the unitary transformations of the unrestricted molecular orbitals (MO's)  $\{\varphi_i\}$  and  $\{\phi_i\}$  give the corresponding MO's  $\{\chi_i\}$  and  $\{\eta_i\}$ , respectively. These are closely related to the natural orbitals  $\lambda$ ,  $\mu$ , and  $\nu$  by the following equations:

$$\begin{aligned}\chi_i &= \lambda_i(1 - \Delta_i^2)^{1/2} + \nu_i \Delta_i, & i=1, \dots, q, \\ \eta_i &= \lambda_i(1 - \Delta_i^2)^{1/2} - \nu_i \Delta_i, & i=1, \dots, q, \\ \chi_i &= \mu_i, & i=q+1, \dots, p,\end{aligned}\quad (4)$$

<sup>1</sup> J. A. Pople and R. K. Nesbet, *J. Chem. Phys.* **22**, 571 (1964).  
<sup>2</sup> (a) A. D. McLachlan, *Mol. Phys.* **3**, 233 (1960). (b) S. Aono and J. Higuchi, *Progr. Theoret. Phys.* **28**, 589 (1962). (c) J. P. Malrieu, *J. Chem. Phys.* **46**, 1654 (1967). (d) A. L. H. Chung, *ibid.* **46**, 3144 (1967).

<sup>3</sup> J. P. Colpa and E. de Boer, *Mol. Phys.* **7**, 333 (1964), and the references cited in this paper.

<sup>4</sup> By "spin-appearing" mechanism, we mean the mechanism by which the spin-density distribution occurs.

<sup>5</sup> (a) D. Lazdins and M. Karplus, *J. Chem. Phys.* **44**, 1600 (1966). (b) J. P. Colpa, E. de Boer, D. Lazdins, and M. Karplus, *ibid.* **47**, 3098 (1967).

<sup>6</sup> To avoid confusion [see Ref. 5(b)] we provisionally define the spin-delocalization and spin-polarization mechanisms used here. The former means the "spin-appearing" mechanism due to the singly occupied orbitals of the *best* restricted wavefunction, and the latter is defined as that due to correlation between electron spins. This definition of the SP and SD mechanisms is identical with that given by Colpa and de Boer in Ref. 5(b).

<sup>7</sup> T. Yonezawa, H. Nakatsuji, T. Kawamura, and H. Kato, *Chem. Phys. Letters* **2**, 454 (1968).

<sup>8</sup> (a) 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).

<sup>9</sup> Here we follow the notations used by Amos and Snyder.<sup>8b</sup> The suffixes "asa" and "aa" mean "after single annihilation" and "after annihilation," respectively.

<sup>10</sup> C. C. J. Roothaan, *Rev. Mod. Phys.* **32**, 179 (1960).

where

$$\Delta_i = \frac{(1-T_i)^{1/2}}{\sqrt{2}}, \quad \int \chi_i \eta_j d\tau = T_i \delta_{ij}.$$

As seen in Eq. (4), the corresponding orbitals of the UHF method are related to the alternant MO's proposed by Löwdin,<sup>11</sup> and the natural orbitals  $\lambda$  and  $\mu$  are closely related to the restricted MO's, as noted by Amos and Snyder.<sup>10</sup> In this treatment, we assume that the natural orbitals  $\mu$  are closely similar to the *unpaired orbitals* of the restricted open-shell method,<sup>12</sup> and this point will be verified later. (See Table VIII.)

Now, we extend the method described previously<sup>7</sup> to the triplet state. As shown by Snyder and Amos,<sup>10</sup> we can rewrite the UHF single determinant, using Eq. (4), in the following manner for the triplet state ( $p=q+2$ ):

$$\Psi_{\text{UHF}} = C_{2/2}{}^{rf} \Psi_{2/2}{}^{rf} + C_{2/2}{}^{se} \Psi_{2/2}{}^{se} + C_{4/2}{}^{se} \Psi_{4/2}{}^{se} + C_{2/2}{}^{de} \Psi_{2/2}{}^{de} + \dots, \quad (5)$$

where  $\Psi_{2/2}{}^{rf}$  is the normalized restricted function built up of the natural orbitals  $\lambda$  and  $\mu$ :

$$\Psi_{2/2}{}^{rf} = |\lambda_1 \alpha \lambda_1 \beta \lambda_2 \alpha \lambda_2 \beta \dots \lambda_q \alpha \lambda_q \beta \mu_{q+1} \alpha \mu_{q+2} \alpha|, \quad (6)$$

and its coefficient is given by

$$C_{2/2}{}^{rf} = \prod_{i=1}^q (1 - \Delta_i^2). \quad (7)$$

$\Psi_{2/2}{}^{se}$  and  $\Psi_{4/2}{}^{se}$  are sums of the singly excited triplet and quintet configurations, resulting from excitation from  $\lambda_i$  to  $\nu_i$ ;

$$\Psi_{2/2}{}^{se} = \frac{1}{C_{2/2}{}^{se}} \sum_{i=1}^q \Delta_i (1 - \Delta_i^2)^{1/2} N_i^{1/2} [ \dots \nu_i \lambda_i (\alpha\beta + \beta\alpha) \dots \mu_{q+1} \alpha \mu_{q+2} \alpha | - | \dots \nu_i \alpha \lambda_i \alpha \dots \mu_{q+1} \mu_{q+2} (\alpha\beta + \beta\alpha) | ], \quad (8)$$

$$\Psi_{4/2}{}^{se} = \frac{1}{C_{4/2}{}^{se}} \sum_{i=1}^q \Delta_i (1 - \Delta_i^2)^{1/2} N_i^{1/2} [ \dots \nu_i \lambda_i (\alpha\beta + \beta\alpha) \dots \mu_{q+1} \alpha \mu_{q+2} \alpha | + | \dots \nu_i \alpha \lambda_i \alpha \dots \mu_{q+1} \mu_{q+2} (\alpha\beta + \beta\alpha) | ], \quad (9)$$

where

$$N_i = \prod_{j=1, j \neq i}^q (1 - \Delta_j^2),$$

and their coefficients are given by

$$C_{2/2}{}^{se} = C_{4/2}{}^{se} = \left( \sum_{i=1}^q \Delta_i^2 (1 - \Delta_i^2) N_i^2 \right)^{1/2}. \quad (10)$$

Here we consider the expectation value of the normalized spin-density operator,<sup>13</sup>  $\rho^i = S_z^{-1} \sum_i S_{zi} \delta(\mathbf{r}_i - \mathbf{r}^i)$ . By

assuming  $C_{2/2}{}^{rf} \gg C_{2/2}{}^{se}$ ,  $C_{4/2}{}^{se}$  and by neglecting the doubly excited configuration  $\Psi_{1/2}{}^{de}$  and higher terms,<sup>14</sup> we obtain

$$\begin{aligned} \rho_{\text{UHF}}^i &= (C_{2/2}{}^{rf})^2 \rho^i [\text{rf}(2/2) | \text{rf}(2/2)] \\ &+ 2C_{2/2}{}^{rf} C_{2/2}{}^{se} \rho^i [\text{rf}(2/2) | \text{se}(2/2)] \\ &+ 2C_{2/2}{}^{rf} C_{4/2}{}^{se} \rho^i [\text{rf}(2/2) | \text{se}(4/2)], \quad (11) \end{aligned}$$

where  $\rho^i [\text{rf}(2/2) | \text{se}(2/2)]$  denotes the matrix element between  $\Psi_{2/2}{}^{rf}$  and  $\Psi_{2/2}{}^{se}$  with respect to the normalized spin-density operator. From Eq. (10) and from the relation

$$\rho^i [\text{rf}(2/2) | \text{se}(2/2)] = \rho^i [\text{rf}(2/2) | \text{se}(4/2)],$$

Eq. (11) reduces to

$$\begin{aligned} \rho_{\text{UHF}}^i &= (C_{2/2}{}^{rf})^2 \rho^i [\text{rf}(2/2) | \text{rf}(2/2)] \\ &+ 4C_{2/2}{}^{rf} C_{2/2}{}^{se} \rho^i [\text{rf}(2/2) | \text{se}(2/2)]. \quad (12) \end{aligned}$$

Similarly, the spin densities after single annihilation ( $\rho_{\text{aa}}^i$ ) and after annihilation ( $\rho_{\text{aaa}}^i$ ) are written as

$$\begin{aligned} \rho_{\text{aa}}^i &= (C_{2/2}{}^{rf})^2 \rho^i [\text{rf}(2/2) | \text{rf}(2/2)] \\ &+ 3C_{2/2}{}^{rf} C_{2/2}{}^{se} \rho^i [\text{rf}(2/2) | \text{se}(2/2)] \end{aligned}$$

and

$$\begin{aligned} \rho_{\text{aaa}}^i &= (C_{2/2}{}^{rf})^2 \rho^i [\text{rf}(2/2) | \text{rf}(2/2)] \\ &+ 2C_{2/2}{}^{rf} C_{2/2}{}^{se} \rho^i [\text{rf}(2/2) | \text{se}(2/2)]. \quad (13) \end{aligned}$$

From the definition given in Ref. 6, the first terms of Eqs. (12) and (13) represent the contributions due to the SD mechanism, and the second terms represent those due to the SP mechanism. Note that  $\Psi_{2/2}{}^{se}$  and  $\Psi_{4/2}{}^{se}$  given by Eqs. (8) and (9) include only the limited configurations like  $|\lambda_i \rightarrow \nu_i|$ , the excited configuration, where  $\lambda_i$  is replaced by  $\nu_i$ , and do not include those expressed by  $|\lambda_i \rightarrow \nu_j|$  ( $i \neq j$ ),  $|\mu_i \rightarrow \nu_j|$ , and  $|\lambda_i \rightarrow \mu_j|$ , and that the occupation number of  $\mu$  is unity. [See Eq. (4).] Moreover, Eqs. (12) and (13) show that the annihilation of the lowest contaminating spin state (quintet state in this case) affects only the SP contributions.

From Eqs. (12) and (13), we obtain the results for *triplet radicals*. By using the values of  $\rho_{\text{aa}}^i$ , the SP contributions are calculated from

$$\begin{aligned} (\rho_{\text{UHF}}^i)_{\text{SP}} &= 2(\rho_{\text{UHF}}^i - \rho_{\text{aa}}^i), \\ (\rho_{\text{aa}}^i)_{\text{SP}} &= \frac{3}{2}(\rho_{\text{UHF}}^i - \rho_{\text{aa}}^i), \\ (\rho_{\text{aaa}}^i)_{\text{SP}} &= \rho_{\text{UHF}}^i - \rho_{\text{aa}}^i, \quad (14) \end{aligned}$$

<sup>11</sup> P.-O. Löwdin, Phys. Rev. **97**, 1509 (1955).

<sup>12</sup> Strictly speaking, this assumption should be that the *unitarily transformed* natural orbitals  $\mu$  are closely similar to the unpaired orbitals of the RHF wavefunction.

<sup>13</sup> H. M. McConnell, J. Chem. Phys. **28**, 1188 (1958).

<sup>14</sup> This assumption corresponds to neglecting contributions from  $\rho^i [\text{se}(2/2) | \text{se}(2/2)]$  and  $\rho^i [\text{se}(4/2) | \text{se}(4/2)]$ , etc. In other words, this corresponds to omission of part of the second- and higher-order terms with respect to the spin-correlation perturbation.

and by using  $\rho_{\text{aaa}}^i$ , from

$$\begin{aligned}(\rho_{\text{UHF}}^i)_{\text{SP}} &= 4(\rho_{\text{UHF}}^i - \rho_{\text{aaa}}^i), \\ (\rho_{\text{aaa}}^i)_{\text{SP}} &= 3(\rho_{\text{aaa}}^i - \rho_{\text{aaa}}^i), \\ (\rho_{\text{aa}}^i)_{\text{SP}} &= 2(\rho_{\text{UHF}}^i - \rho_{\text{aaa}}^i).\end{aligned}\quad (15)$$

The SD contribution in the triplet state is given by

$$\frac{1}{2} [ |\mu_{q+1}(\mathbf{r}^i)|^2 + |\mu_{q+2}(\mathbf{r}^i)|^2 ],$$

since the occupation number of  $\mu$  is unity. But in the present approximation (see Ref. 14), this is given by

$$\begin{aligned}(\rho^i)_{\text{SD}} &= (C_{2/2}^{\mathbf{r}^i})^2 \rho^i [ \text{rf}(2/2) | \text{rf}(2/2) ] \\ &= \frac{1}{2} (C_{2/2}^{\mathbf{r}^i})^2 [ |\mu_{q+1}(\mathbf{r}^i)|^2 + |\mu_{q+2}(\mathbf{r}^i)|^2 ],\end{aligned}\quad (16)$$

and is calculated from

$$(\rho)_{\text{SD}} = \rho - (\rho)_{\text{SP}},\quad (17)$$

without a knowledge of the natural orbitals  $\mu_i$ . When only the SP mechanism is the source of spin density as is the case of spin densities in the  $\sigma$ -type atomic orbitals of the planar  $\pi \rightarrow \pi^*$  triplet state of ethylene, Eq. (14) leads to

$$\rho_{\text{UHF}}^i = \frac{4}{3} \rho_{\text{aaa}}^i = 2\rho_{\text{aa}}^i.\quad (18)$$

For *doublet radicals*, the results have been reported previously.<sup>7</sup> However, it may be convenient to summarize the results here. The SP contributions to the spin densities are calculated by using  $\rho_{\text{UHF}}$  and  $\rho_{\text{aa}}$  from

$$\begin{aligned}(\rho_{\text{UHF}}^i)_{\text{SP}} &= \frac{3}{2} (\rho_{\text{UHF}}^i - \rho_{\text{aa}}^i), \\ (\rho_{\text{aaa}}^i)_{\text{SP}} &= \rho_{\text{UHF}}^i - \rho_{\text{aa}}^i, \\ (\rho_{\text{aa}}^i)_{\text{SP}} &= \frac{1}{2} (\rho_{\text{UHF}}^i - \rho_{\text{aa}}^i),\end{aligned}\quad (19)$$

and by using  $\rho_{\text{UHF}}$  and  $\rho_{\text{aaa}}$  from

$$\begin{aligned}(\rho_{\text{UHF}}^i)_{\text{SP}} &= 3(\rho_{\text{UHF}}^i - \rho_{\text{aaa}}^i), \\ (\rho_{\text{aaa}}^i)_{\text{SP}} &= 2(\rho_{\text{UHF}}^i - \rho_{\text{aaa}}^i), \\ (\rho_{\text{aa}}^i)_{\text{SP}} &= \rho_{\text{UHF}}^i - \rho_{\text{aaa}}^i.\end{aligned}\quad (20)$$

The SD contributions are also given by Eq. (17). When only the SP mechanism is important, the spin densities calculated by the three methods satisfy the following relation:

$$\rho_{\text{UHF}}^i = \frac{3}{2} \rho_{\text{aaa}}^i = 3\rho_{\text{aa}}^i,\quad (21)$$

as pointed out by Amos and Snyder.<sup>8a</sup>

The separation of the UHF spin densities into mechanistic contributions is also possible by means of the natural orbitals of the UHF method, which is more direct than the above method. In this method, the mechanistic contributions can be calculated directly from Eq. (5) for triplet states, and for doublet radicals from [see Eq. (2) in the previous paper<sup>7</sup>]

$$\Psi_{\text{UHF}} = C_{1/2}^{\mathbf{r}^i} \Psi_{1/2}^{\mathbf{r}^i} + C_{1/2}^{\text{oo}} \Psi_{1/2}^{\text{oo}} + C_{3/2}^{\text{oo}} \Psi_{3/2}^{\text{oo}} + \dots,\quad (22)$$

TABLE I. Comparison of UHF orbitals, UHF natural orbitals, and RHF orbitals of the methyl radical.

Symmetry	Coefficient	$T_i$
UHF Orbitals		
$\alpha$ -Spin orbitals		
$a_1'$	$0.7950S + 0.1129(h_2 + h_3 + h_4)$	
	$0.4645X - 0.5153(h_3 - h_4)$	
$e'$	$0.4645Y + 0.5950h_2 - 0.2975(h_3 + h_4)$	
$a_2''$	$1.0000Z$	
$\beta$ -Spin orbitals		
$a_1'$	$0.6951S + 0.1642(h_2 + h_3 + h_4)$	
	$0.4520X - 0.5249(h_3 - h_4)$	
$e'$	$0.4520Y + 0.6061h_2 - 0.3030(h_3 + h_4)$	
UHF Natural orbitals		
$a_1'$	$0.7454S + 0.1386(h_2 + h_3 + h_4)$	0.9979
	$0.4582X - 0.5201(h_3 - h_4)$	1.0000
$e'$	$0.4582Y + 0.6005h_2 - 0.3002(h_3 + h_4)$	1.0000
$a_2''$	$1.0000Z$	
RHF Orbitals		
$a_1'$	$0.7462S + 0.1382(h_2 + h_3 + h_4)$	
	$0.4686X - 0.5121(h_3 - h_4)$	
$e'$	$0.4686Y + 0.5914h_2 - 0.2957(h_3 + h_4)$	
$a_2''$	$1.0000Z$	

where the coefficients are given by

$$C_{1/2}^{\mathbf{r}^i} = \prod_{i=1}^q (1 - \Delta_i^2)$$

and

$$\begin{aligned}C_{1/2}^{\text{oo}} &= (1/\sqrt{2}) C_{3/2}^{\text{oo}} \\ &= (\frac{2}{3})^{1/2} \left( \sum_{j=1}^q [\Delta_j (1 - \Delta_j^2)^{1/2} N_j]^2 \right)^{1/2}.\end{aligned}\quad (23)$$

The SD contribution, which is compared with the one obtained by the above method, is given by Eq. (16) for triplet states, and by the following equation for doublet radicals:

$$(\rho^i)_{\text{SD}} = (C_{1/2}^{\mathbf{r}^i})^2 |\mu_{q+1}(\mathbf{r}^i)|^2.\quad (24)$$

On the other hand, the SP contribution may be calculated by applying the spin-density operator to Eq. (5) or to Eq. (22). However, this is rather impractical, since the natural orbital  $\nu_i$  is given by<sup>8a</sup>

$$\nu_i = (\chi_i - \eta_i) / \sqrt{2(1 - T_i)^{1/2}},$$

where  $T_i$  is always very close to unity. (For example, see Tables I and II.) A more straightforward way than

TABLE II. Comparison of UHF orbitals, UHF natural orbitals, and RHF orbitals of the  $\pi \rightarrow \pi^*$  triplet state of planar ethylene.

Symmetry	Coefficient	$T_i$
UHF Orbitals		
$\alpha$ -Spin orbitals		
$a_g$	$0.6014(S_1+S_2) - 0.0096(X_1-X_2) - 0.0088(h_3+h_4+h_5+h_6)$	
$b_{2u}$	$0.4987(S_1-S_2) - 0.1188(X_1+X_2) + 0.2067(h_3+h_4-h_5-h_6)$	
$b_{2u}$	$0.3396(Y_1+Y_2) + 0.3081(h_3-h_4-h_5+h_6)$	
$b_{1g}$	$0.3240(Y_1-Y_2) + 0.4274(h_3-h_4+h_5-h_6)$	
$a_g$	$-0.0682(S_1+S_2) - 0.5069(X_1-X_2) + 0.2129(h_3+h_4+h_5+h_6)$	
$b_{1u}$	$0.6271(Z_1+Z_2)$	
$b_{2g}$	$0.8283(Z_1-Z_2)$	
$\beta$ -Spin orbitals		
$a_g$	$0.5357(S_1+S_2) + 0.0242(X_1-X_2) + 0.0441(h_3+h_4+h_5+h_6)$	
$b_{2u}$	$0.4682(S_1-S_2) - 0.1258(X_1+X_2) + 0.2497(h_3+h_4-h_5-h_6)$	
$b_{2u}$	$0.3245(Y_1+Y_2) + 0.3213(h_3-h_4-h_5+h_6)$	
$b_{1g}$	$0.3119(Y_1-Y_2) + 0.4353(h_3-h_4+h_5-h_6)$	
$a_g$	$0.0851(S_1+S_2) + 0.5014(X_1-X_2) - 0.2196(h_3+h_4+h_5+h_6)$	
UHF Natural orbitals		
$a_g$	$0.5531(S_1+S_2) - 0.0620(X_1-X_2) + 0.0472(h_3+h_4+h_5+h_6)$	0.9971
$b_{2u}$	$0.4537(S_1-S_2) - 0.1223(X_1+X_2) + 0.2283(h_3+h_4-h_5-h_6)$	0.9977
$b_{2u}$	$0.3321(Y_1+Y_2) + 0.3147(h_3-h_4-h_5+h_6)$	0.9998
$b_{1g}$	$0.3180(Y_1-Y_2) + 0.4313(h_3-h_4+h_5-h_6)$	1.0000
$a_g$	$-0.1541(S_1+S_2) - 0.5003(X_1-X_2) + 0.2120(h_3+h_4+h_5+h_6)$	1.0000
$b_{1u}$	$0.6271(Z_1+Z_2)$	
$b_{2g}$	$0.8283(Z_1-Z_2)$	
RHF Orbitals		
$a_g$	$0.5626(S_1+S_2) - 0.0004(X_1-X_2) + 0.0259(h_3+h_4+h_5+h_6)$	
$b_{2u}$	$0.4495(S_1-S_2) - 0.1245(X_1+X_2) + 0.2294(h_3+h_4-h_5-h_6)$	
$b_{2u}$	$0.3376(Y_1+Y_2) + 0.3099(h_3-h_4-h_5+h_6)$	
$b_{1g}$	$0.3253(Y_1-Y_2) + 0.4266(h_3-h_4+h_5-h_6)$	
$a_g$	$-0.0905(S_1+S_2) - 0.5030(X_1-X_2) + 0.2174(h_3+h_4+h_5+h_6)$	
$b_{1u}$	$0.6271(Z_1+Z_2)$	
$b_{2g}$	$0.8283(Z_1-Z_2)$	

this is to use the equation

$$(\rho)_{\text{SP}} = \rho - (\rho)_{\text{SD}} \quad (25)$$

In the present paper, we also calculate the mechanistic contributions by this method and compare the results with those obtained with Eqs. (14)–(20). Hereafter we call the method based on Eqs. (14)–(20) as “annihilation method (AN method)” and the one based on Eqs. (16), (24), and (25) as “natural-orbital method (NO method).”

In the formulations of Eqs. (14)–(18) for triplet states and in those of Eqs. (19)–(21) for doublet radicals described previously,<sup>7</sup> we set the following two assumptions: One is that the natural orbitals  $\mu$  are closely similar to the unpaired orbitals of the *best* restricted molecular orbitals, and the other is that the coefficients in Eq. (5) satisfy the relation  $C_{2/2}^{\text{f}} \gg C_{2/2}^{\text{oe}}, C_{4/2}^{\text{oe}}$ . (See also Ref. 14.) Now, we examine these assumptions. In Tables I and II the natural orbitals of the UHF method calculated for the methyl radical and

TABLE III. Comparison of the UHF natural orbitals  $\mu$  and the RHF unpaired orbitals.<sup>a</sup>

Radical	AO <sup>b</sup>	UHF $\rho^i[\text{rf}(1/2)   \text{rf}(1/2)]$	RHF $\rho^i(\text{RHF}   \text{RHF})$	Triplet state	AO <sup>b</sup>	UHF $\rho^i[\text{rf}(2/2)   \text{rf}(2/2)]$	RHF $\rho^i(\text{RHF}   \text{RHF})$
Ethyl	$2P_x(\text{C}_1)$	1.000	0.999	H <sub>2</sub> CO	$2P_x(\text{C})$	0.525	0.525
	$2P_x(\text{C}_2)$	0.000	0.000	( $\pi \rightarrow \pi^*$ )	$2P_x(\text{O})$	0.525	0.525
	$5h, 6h$	0.039	0.041				
Vinyl	$2S(\text{C}_\alpha)$	0.090	0.081	H <sub>2</sub> CO	$2P_y(\text{C})$	0.000	0.000
	$2P_x(\text{C}_\alpha)$	0.118	0.125	( $n \rightarrow \pi^*$ )	$2P_x(\text{C})$	0.407	0.438
	$2P_y(\text{C}_\alpha)$	0.739	0.745		$2P_y(\text{O})$	0.484	0.483
	$2S(\text{C}_\beta)$	0.008	0.004		$2P_x(\text{O})$	0.226	0.187
	$2P_x(\text{C}_\beta)$	0.001	0.004		$h$	0.022	0.023
	$2P_y(\text{C}_\beta)$	0.000	0.001				
	$h_a$	0.053	0.037				
	$h_t$	0.071	0.075				
	$h_u$	0.020	0.017				

<sup>a</sup> Only the coefficients of the diagonal elements of the AO spin-density matrix are given. (See Ref. 13.)

<sup>b</sup> The values of the AO's other than those given in this table are zero by symmetry.

for the  $\pi \rightarrow \pi^*$  triplet state of ethylene are compared<sup>15</sup> with the MO's obtained by the open-shell restricted Hartree-Fock (RHF) method.<sup>10</sup> (The method of calculations and estimations of integral values are described in Ref. 16.) Since the wavefunction obtained with the Roothaan's open-shell method may be regarded as the *best* RHF wavefunction within the approximations introduced in the integral estimations, it provides a good criterion of the restricted configuration [Eq. (6)] included in the UHF wavefunction. As seen in Tables I and II, the natural orbitals of the UHF method accord satisfactorily well with the MO's obtained by the RHF method. Note that, in the cases shown in Tables I and II, the unpaired orbitals are uniquely determined by symmetry requirements. In Table III, the natural orbitals  $\mu$  of some doublet and triplet radicals are compared with the unpaired orbitals of the RHF method. Generally, they are very close to each other, except some large differences which lie in the  $h_c$  AO of the vinyl radical and in the  $2P_x(\text{C})$  and  $2P_x(\text{O})$  AO's of the  $n \rightarrow \pi^*$  triplet state of formaldehyde.

<sup>15</sup> In the cases of the methyl radical and the  $\pi \rightarrow \pi^*$  triplet state of planar ethylene, each orbital belongs to different symmetry representation except the  $a_g$  orbitals in the  $\pi \rightarrow \pi^*$  triplet state, so we can compare directly the calculated UHF natural orbitals, having degenerate  $T_i$  values, with the MO's obtained by the RHF method.

<sup>16</sup> T. Yonezawa, H. Nakatsuji, T. Kawamura, and H. Kato, "Semi-empirical Unrestricted SCF-MO Treatment for Valence Electron Systems. I. Application to Small Doublet Radicals," Bull. Chem. Soc. Japan (to be published). The methods of estimating the integral values in the present UHF calculations are the same as those in this paper. In the RHF calculations, the two-center  $\sigma$ - $\pi$ -type exchange repulsion integrals are omitted. Since these integrals are very small in magnitude, they don't affect the SD contributions. Hence, the SD contributions calculated by both methods can be directly compared.

However, the agreement to this order between the UHF natural orbitals and the RHF orbitals is rather surprising, considering the large differences in the variation processes of both methods. This lends support to the first assumption that the natural orbitals  $\mu$  are closely similar to the unpaired orbitals of the best restricted molecular orbitals. Referring to Tables I and II, we see that the natural-orbital coefficients are always the median in magnitude of those of the  $\alpha$ - and  $\beta$ -spin orbitals of the UHF method.

Then, we examine the second assumption: From the  $T_i$  values shown in the last column of Tables I and II, the coefficients of the singly excited configurations in Eqs. (5) and (22) are calculated, and they are summarized in Table IV for doublet radicals, while those for triplet states are listed in Table V. Generally speaking, the second assumption that the coefficient of the restricted configuration is much larger than the coefficients of the singly excited configurations is good and the magnitude of error due to this assumption is  $\sim (C^{oe})^2/C^{oe}$ .<sup>17</sup> As described in Ref. 14, this assumption

<sup>17</sup> The magnitude of error due to this assumption can also be estimated approximately by calculating the weight of mixing of the lowest contaminating spin state into the UHF total wavefunction, and this is calculated for doublet radicals by

$$[C(\text{quartet})/C(\text{doublet})]^2 \approx (4 \langle S^2 \rangle_{\text{UHF}} - 3) / (15 - 4 \langle S^2 \rangle_{\text{UHF}})$$

and for triplet states by

$$[C(\text{quintet})/C(\text{triplet})]^2 \approx (\langle S^2 \rangle_{\text{UHF}} - 2) / (6 - \langle S^2 \rangle_{\text{UHF}}),$$

where  $\langle S^2 \rangle_{\text{UHF}}$  is the expectation value of the UHF total wavefunction with respect to the spin-squared operator. These values are 0.00217 and 0.01372 for ethyl and vinyl radicals, and 0.00583 and 0.00472 for the  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  triplet states of formaldehyde. They correspond reasonably well with the values shown in Tables IV and V. See also the succeeding paper (Ref. 16).

TABLE IV. Coefficients in doublet radicals.

Radical	$C_{1/2}^{rf}$	$C_{1/2}^{so}$		$C_{3/2}^{so}$	
		$\sigma \rightarrow \sigma^*$ Type	$\pi \rightarrow \pi^*$ Type	$\sigma \rightarrow \sigma^*$ Type	$\pi \rightarrow \pi^*$ Type
Methyl	0.9989	0.0269	...	0.0373	...
Ethyl	0.9984	0.0327	...	0.0464	...
Vinyl	0.9901	0.0260	0.0763	0.0367	0.1079

corresponds to omission of part of the second and higher terms with respect to the spin-correlation perturbation, and the errors in the final results are seen by comparing the SD contributions calculated by the AN and NO methods given in Tables VI–VIII. An examination of this point is discussed more fully in the next section.

### III. DISCUSSION OF THE RESULTS

#### A. Doublet Radicals

In this section, we apply the AN Method to doublet radicals such as ethyl and vinyl radicals (geometries and numberings are illustrated in Fig. 1.) and compare the results with those obtained by the NO method. (About the method of the UHF and RHF calculations and estimations of integral values, see Ref. 16.) The UHF natural orbitals are calculated by means of the method given by Amos and Hall.<sup>8a</sup> The UHF calculations of the spin densities of the ethyl and vinyl radicals were recently reported by Pople, Beveridge, and Dobosh<sup>18</sup> and by Atherton and Hincliffe,<sup>19</sup> respectively, who considered all the valence electrons of the constituent atoms. Here, we also apply the AN method to their results, and compare them with the present ones.

In Table VI, the UHF spin densities and their mechanistic contributions in ethyl radical calculated by the AN method are compared with those obtained by the NO method, and with the values obtained by applying the AN method to the INDO results of Pople, Beveridge, and Dobosh.<sup>18</sup> Since the AN method is derived by assuming  $C_{1/2}^{rf} \gg C_{1/2}^{so}$ ,  $C_{3/2}^{so}$ , the calculated mechanistic contributions include some small errors as seen by the nonzero SD contributions in the  $2S(C_1)$

and  $2P_x(C_2)$  AO's, which must be zero by symmetry. Nevertheless, the SD contributions calculated by the AN method agree fairly well with those obtained by means of the NO method and of the RHF method (the fourth column of Table III). This is a direct proof that the natural orbital of the UHF method is closely similar to the unpaired orbital of the restricted open-shell method, and that the contributions to spin densities from part of the second- and higher-order terms with respect to the spin-correlation perturbation<sup>14</sup> are negligibly small. The UHF spin densities on the atomic orbitals, where the NO method gives zero spin density, are due only to the SP mechanism. Hence, in these positions, the relation [Eq. (21)]  $\rho_{UHF} = 3\rho_{sa}$  holds fairly satisfactorily, and this is also true for the INDO calculations.<sup>18</sup>

The UHF spin densities on the  $H_5$  and  $H_6$  protons obtained before annihilation are due to 26% SP and 74% SD contributions in the present calculation, and the mechanistic separation of the INDO results predicts 47% SP and 53% SD contributions. Anyway, the SP mechanism contributes much to the spin densities on these protons. Lazdins and Karplus<sup>5a</sup> pointed out

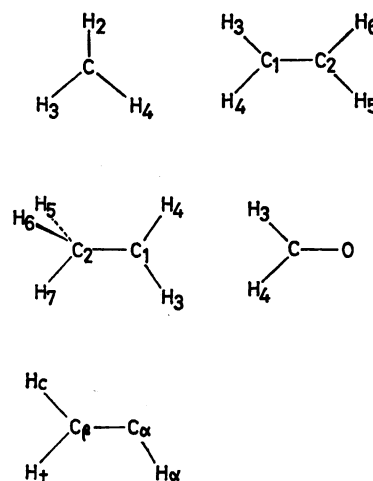


FIG. 1. Geometries [L. E. Sutton (Ed.), Chem. Soc. (London), Spec. Publ. 11 (1956); 18 (1965)]. For methyl radical, C–H = 1.079 Å; for ethyl, C–C = 1.50 Å, C(1)–H = 1.079 Å, C(2)–H = 1.09 Å; for vinyl, C–C = 1.34 Å, C–H = 1.07 Å,  $\angle CCH(\alpha) = 135^\circ$ ; for ethylene triplet radical, C–C = 1.337 Å, C–H = 1.086 Å,  $\angle HCH = 117.3^\circ$ ; for formaldehyde, C–H = 1.12 Å, C–O = 1.21 Å,  $\angle HCH = 118^\circ$ .

TABLE V. Coefficients in triplet radicals.

Triplet radical	$C_{2/2}^{rf}$	$C_{2/2}^{so}$	$C_{4/2}^{so}$
Ethylene ( $\pi \rightarrow \pi^*$ )	0.9973	0.0520	0.0520
Formaldehyde ( $n \rightarrow \pi^*$ )	0.9942	0.0761	0.0761
( $\pi \rightarrow \pi^*$ )	0.9953	0.0684	0.0684

<sup>18</sup> J. A. Pople, D. L. Beveridge, and P. A. Dobosh, J. Chem. Phys. **47**, 2026 (1967).

<sup>19</sup> N. M. Atherton and A. Hincliffe, Mol. Phys. **12**, 349 (1967).

TABLE VI. SP and SD mechanism in ethyl radical.<sup>a</sup>

Atom	AO	AN Method						NO Method ( $\rho$ ) <sub>SD</sub>
		Before annihilation			After annihilation			
		( $\rho$ ) <sub>UEF</sub>	( $\rho$ ) <sub>SP</sub>	( $\rho$ ) <sub>SD</sub>	( $\rho$ ) <sub>aa</sub>	( $\rho$ ) <sub>SP</sub>	( $\rho$ ) <sub>SD</sub>	
A. Present								
			$\langle S^2 \rangle = 0.7565$				$\langle S^2 \rangle = 0.7500$	
C <sub>1</sub>	2S	0.161	0.159	0.002	0.055	0.053	0.002	0.000
	2P <sub>x</sub>	0.042	0.042	0.000	0.014	0.014	0.000	0.000
	2P <sub>y</sub>	0.015	0.015	0.000	0.005	0.005	0.000	0.000
	2P <sub>z</sub>	1.000	0.002	0.998	0.999	0.001	0.998	0.997
C <sub>2</sub>	2S	-0.012	-0.012	0.000	-0.004	-0.004	0.000	0.000
	2P <sub>x</sub>	-0.047	-0.048	0.001	-0.015	-0.016	0.001	0.000
	2P <sub>y</sub>	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	2P <sub>z</sub>	-0.013	-0.013	0.000	-0.004	-0.004	0.000	0.000
	3h	-0.035	-0.035	0.000	-0.011	-0.012	0.000	0.000
	4h	-0.035	-0.035	0.000	-0.011	-0.012	0.000	0.000
	5h, 6h	0.054	0.014	0.040	0.044	0.005	0.040	0.039
	7h	-0.002	-0.002	0.000	-0.001	-0.001	0.000	0.000
B. Pople, Beveridge, and Dobosh <sup>b</sup>								
			$\langle S^2 \rangle = 0.7573$				$\langle S^2 \rangle = 0.7500$	
C <sub>1</sub>	2S	0.049	0.048	0.001	0.017	0.016	0.001	...
	2P <sub>x</sub>	0.028	0.028	0.000	0.009	0.009	0.000	...
	2P <sub>y</sub>	0.030	0.030	0.000	0.010	0.010	0.000	...
	2P <sub>z</sub>	0.926	0.010	0.916	0.919	0.003	0.916	...
C <sub>2</sub>	2S	-0.015	-0.015	0.000	-0.005	-0.005	0.000	...
	2P <sub>x</sub>	-0.033	-0.033	0.000	-0.011	-0.011	0.000	...
	2P <sub>y</sub>	-0.013	-0.012	0.001	-0.005	-0.004	0.001	...
	2P <sub>z</sub>	-0.046	-0.048	0.002	-0.014	-0.016	0.002	...
	3h	-0.037	-0.037	0.000	-0.012	-0.012	0.000	...
	4h	-0.038	-0.038	0.000	-0.013	-0.013	0.000	...
	5h, 6h	0.075	0.035	0.040	0.051	0.012	0.040	...
	7h	0.003	0.003	0.000	0.001	0.001	0.000	...

<sup>a</sup> Geometry and numbering are illustrated in Fig. 1.<sup>b</sup> Reference 18.

this fact in the valence-bond languages.<sup>5b</sup> Some attention was also given to this point by Colpa and de Boer<sup>3</sup> and by Pople, Beveridge, and Dobosh,<sup>18</sup> but they estimated the SP contribution to the methyl-proton spin density from the one on the H<sub>7</sub> atom in the configuration illustrated in Fig. 1. Since there is no reason<sup>20</sup>

<sup>20</sup> The SP mechanism also shows a large angular dependence, and the manner of dependence is written to a good approximation as  $(\rho)_{SP} = (\rho^0)_{SP} + (\rho^1)_{SP} \cos^2\theta$ . This point will be discussed more fully in the near future.

to believe that the SP mechanism has no angular dependence on the rotation about the C-C single bond, this kind of estimation of the SP mechanism is certainly erroneous and leads to too small values.<sup>21</sup>

From Table VI, we notice that the INDO results are rather similar, except for the SP contribution in the 2S(C<sub>1</sub>) AO, to those of the present authors. This is

<sup>21</sup> Colpa and de Boer<sup>3</sup> estimated about 3% SP contribution, and Pople, Beveridge, and Dobosh<sup>18</sup> estimated 7% SP contribution from the results quoted in Table VI.

TABLE VII. SP and SD mechanisms in vinyl radical.<sup>a</sup>

Atom	AO	AN Method						NO Method ( $\rho$ ) <sub>SD</sub>
		Before annihilation			After annihilation			
		( $\rho$ ) <sub>UHF</sub>	( $\rho$ ) <sub>SP</sub>	( $\rho$ ) <sub>SD</sub>	( $\rho$ ) <sub>AN</sub>	( $\rho$ ) <sub>SP</sub>	( $\rho$ ) <sub>SD</sub>	
A. Present ( $\angle CCH_\alpha = 130^\circ$ ) <sup>b</sup>								
			$\langle S^2 \rangle = 0.7892$				$\langle S^2 \rangle = 0.7503$	
C <sub><math>\alpha</math></sub>	2S	0.205	0.122	0.083	0.124	0.041	0.083	0.088
	2P <sub><i>x</i></sub>	0.153	0.026	0.127	0.136	0.009	0.127	0.116
	2P <sub><i>y</i></sub>	0.748	0.017	0.731	0.737	0.006	0.731	0.724
	2P <sub><i>z</i></sub>	0.196	0.188	0.008	0.070	0.063	0.007	0.000
C <sub><math>\beta</math></sub>	2S	-0.031	-0.035	0.004	-0.008	-0.012	0.004	0.008
	2P <sub><i>x</i></sub>	-0.028	-0.033	0.005	-0.006	-0.011	0.005	0.001
	2P <sub><i>y</i></sub>	-0.012	-0.014	0.002	-0.003	-0.005	0.002	0.000
	2P <sub><i>z</i></sub>	-0.193	-0.198	0.005	-0.061	0.066	0.005	0.000
	<i>h<sub>c</sub></i>	0.044	0.009	0.035	0.038	0.003	0.035	0.052
	<i>h<sub>t</sub></i>	0.097	0.026	0.071	0.080	0.009	0.071	0.070
	<i>h<sub><math>\alpha</math></sub></i>	-0.021	-0.042	0.021	0.006	-0.014	0.021	0.020
B. Atherton and Hincliffe ( $\angle CCH_\alpha = 160^\circ$ ) <sup>c</sup>								
			$\langle S^2 \rangle = 0.7634$				$\langle S^2 \rangle = 0.7501$	
C <sub><math>\alpha</math></sub>	2S	0.031	-0.006	0.037	0.035	-0.002	0.037	...
	2P <sub><i>x</i></sub>	0.027	-0.007	0.034	0.031	-0.002	0.033	...
	2P <sub><i>y</i></sub>	0.766	0.017	0.749	0.755	0.006	0.749	...
	<i>h<sub>c</sub></i>	0.115	0.055	0.060	0.079	0.018	0.060	...
	<i>h<sub>t</sub></i>	0.174	0.079	0.095	0.121	0.026	0.095	...
	<i>h<sub><math>\alpha</math></sub></i>	0.028	0.011	0.017	0.020	0.004	0.016	...

<sup>a</sup> Geometry is given in Fig. 1.<sup>b</sup> Reference 22.<sup>c</sup> Reference 19.

very interesting, considering the large differences of these two methods. (See Refs. 16 and 18.)

Now, we discuss the spin densities of the vinyl radical.<sup>22</sup> In Table VII, the UHF spin densities and their mechanistic contributions calculated by the AN method are compared with those obtained from the NO method. As seen from the values given in the last two columns, the SD contributions calculated by these two methods agree satisfactorily except the ones in the *h<sub>c</sub>* AO. The differences in these two set of values are attributed to the assumption  $C_{1/2}^{rf} \gg C_{1/2}^{se}$ ,  $C_{3/2}^{se}$ , and are nearly  $100 \times (C^{se})^2 / (C^{se})\%$  of the value of ( $\rho$ )<sub>UHF</sub>. (See Table IV.) Referring to Table III, the SD contributions calculated by the AN method agree satis-

factorily well with those obtained by the RHF wavefunction. Hence, the errors due to the two assumptions set in the previous section almost cancel in this case.

In the lower part of Table VII, the SP and SD contributions in the CNDO/2 results of Atherton and Hincliffe<sup>19</sup> are calculated by means of the AN method. Although the SD contributions obtained by both authors are rather similar, the SP contributions are quite different, especially in the AO's near the radical center atom. The most remarkable differences exist in the 2S(C <sub>$\alpha$</sub> ) and *h <sub>$\alpha$</sub>*  AO's, and both results differ even in sign. The most probable reason of these differences is that in the CNDO/2 method the one-center exchange repulsion integrals are neglected, while in the present method the one-center (and part of the two-center)  $\sigma$ - $\pi$ -type exchange repulsion integrals, which are important to the SP mechanism, are included. (See Ref. 16.) Since, referring to Table III, the natural

<sup>22</sup> In the succeeding paper,<sup>16</sup> the angular configuration of vinyl radical is examined. The most probable configuration expected from both the potential curve and the calculated hfs constants is  $\angle CCH_\alpha = 135^\circ$ . (See Fig. 1.)



TABLE VIII. Normalized spin densities<sup>a</sup> and their SP and SD contributions in triplet state.<sup>b</sup>

Triplet state	Atom	AO	AN Method						NO Method ( $\rho$ ) <sub>SD</sub>
			Before annihilation			After annihilation			
			( $\rho$ ) <sub>UHF</sub>	( $\rho$ ) <sub>SP</sub>	( $\rho$ ) <sub>SD</sub>	( $\rho$ ) <sub>aa</sub>	( $\rho$ ) <sub>SP</sub>	( $\rho$ ) <sub>SD</sub>	
<b>C<sub>2</sub>H<sub>4</sub></b>			$\langle S^2 \rangle = 2.0109$			$\langle S^2 \rangle = 2.0001$			
$(\pi \rightarrow \pi^*)^3$	C	2S	0.077	0.075	0.002	0.040	0.038	0.002	0.000
		2P <sub>x</sub>	0.002	0.002	0.000	0.001	0.001	0.000	0.000
		2P <sub>y</sub>	0.009	0.009	0.000	0.005	0.005	0.000	0.000
		2P <sub>z</sub>	0.540	0.001	0.539	0.539	0.000	0.539	0.537
		h	-0.020	-0.020	0.000	-0.010	-0.010	0.000	0.000
<b>H<sub>2</sub>CO</b>			$\langle S^2 \rangle = 2.0188$			$\langle S^2 \rangle = 2.0001$			
$(\pi \rightarrow \pi^*)^3$	C	2S	0.072	0.070	0.002	0.037	0.035	0.002	0.000
		2P <sub>x</sub>	-0.009	-0.011	0.002	-0.003	-0.005	0.002	0.000
		2P <sub>y</sub>	0.007	0.007	0.000	0.003	0.003	0.000	0.000
		2P <sub>z</sub>	0.525	0.002	0.523	0.524	0.001	0.523	0.520
	O	2S	0.090	0.088	0.002	0.047	0.045	0.002	0.000
		2P <sub>x</sub>	0.015	0.014	0.001	0.008	0.007	0.001	0.000
		2P <sub>y</sub>	0.008	0.008	0.000	0.004	0.004	0.000	0.000
		2P <sub>z</sub>	0.525	0.002	0.523	0.524	0.001	0.523	0.520
	h	-0.028	-0.028	0.000	-0.014	-0.014	0.000	0.000	
<b>H<sub>2</sub>CO</b>			$\langle S^2 \rangle = 2.0232$			$\langle S^2 \rangle = 2.0001$			
$(n \rightarrow \pi^*)^3$	C	2S	0.052	0.049	0.003	0.027	0.024	0.003	0.000
		2P <sub>x</sub>	-0.013	-0.017	0.004	-0.005	-0.009	0.004	0.000
		2P <sub>y</sub>	-0.006	-0.006	0.000	-0.003	-0.003	0.000	0.000
		2P <sub>z</sub>	0.407	0.002	0.405	0.406	0.001	0.405	0.402
	O	2S	0.113	0.108	0.005	0.059	0.054	0.005	0.000
		2P <sub>x</sub>	0.025	0.023	0.002	0.014	0.012	0.002	0.000
		2P <sub>y</sub>	0.484	0.003	0.481	0.482	0.001	0.481	0.478
		2P <sub>z</sub>	0.226	0.002	0.224	0.225	0.001	0.224	0.223
	h	0.017	-0.006	0.023	0.020	-0.003	0.023	0.022	

<sup>a</sup> Reference 13.<sup>b</sup> Geometries are given in Fig. 1.

orbital  $\mu$  and the unpaired orbital of the RHF wavefunction are mainly composed of the  $2P_x(C_\alpha)$  and  $2P_y(C_\alpha)$  AO's, inclusion of these integrals is essential even in the  $\sigma$ -electron radicals like the vinyl radical, as in the  $\pi$ -electron radicals.<sup>16</sup>

### B. Triplet State

The "spin-appearing" mechanisms in triplet states are very similar<sup>23</sup> as in doublet radicals, and the definition of these mechanisms is completely the same as in doublet radicals. (See Ref. 6.) Here, we apply the AN method to the UHF spin densities of some triplet

radicals such as the  $\pi \rightarrow \pi^*$  triplet states of ethylene and formaldehyde and the  $n \rightarrow \pi^*$  triplet state of formaldehyde. (The geometries are illustrated in Fig. 1.)

In Table VIII, the mechanistic contributions to the UHF spin densities in the triplet state calculated by the AN method are summarized and compared with the SD contributions calculated from the NO method. By comparing the SD contributions calculated by these two methods, the validity of the assumption ( $C_{2/2}^{\uparrow\uparrow} \gg C_{2/2}^{\uparrow\downarrow}, C_{4/2}^{\uparrow\downarrow}$ ) is examined. The largest error is 0.005 in the  $2S(O)$  AO in the  $n \rightarrow \pi^*$  triplet state of formaldehyde, and is 4% of the value of ( $\rho$ )<sub>UHF}. Moreover, the UHF spin densities in the AO's, where zero SD contributions are expected from the symmetry</sub>

<sup>23</sup> A. D. McLachlan, Mol. Phys. 5, 53 (1962).

requirement, satisfy the relation [Eq. (18)]  $\rho_{\text{UHF}}^{\uparrow} = 2\rho_{\text{aa}}^{\uparrow}$  to good approximation.

In the present calculation of triplet states, their ground-state geometries are consistently used. Since the excited-state configurations are quite different<sup>24</sup> from the ground-state ones in the cases of ethylene and formaldehyde, the spin densities reported here do not correspond to the real ones. Nevertheless, the spin densities in the  $\pi \rightarrow \pi^*$  triplet state of ethylene in the planar configuration has foremost importance in the study of  $\pi \rightarrow \pi^*$  triplet states of conjugated hydrocarbons. The situation is very similar to that of the methyl radical in the study of conjugated radicals. Close similarities are found between the  $\pi \rightarrow \pi^*$  triplet state of ethylene and the  $\pi$ -electron radical such as ethyl radical. Referring to Tables VI and VIII, we see that the ratios of the spin densities,  $\rho_{2S(C)}/\rho_{2P_z(C)}$  and  $\rho_h/\rho_{2P_z(C)}$ , in the  $\pi \rightarrow \pi^*$  triplet state of ethylene are closely similar to  $\rho_{2S(C_1)}/\rho_{2P_z(C_1)}$  and  $\rho_{h_3}/\rho_{2P_z(C_1)}$ , in ethyl radical.

The unpaired orbitals of the  $n \rightarrow \pi^*$  triplet state of formaldehyde are calculated by the RHF method to be

$$\psi_n = 0.9828P_y(O) + 0.0206P_y(C) - 0.2139(h_3 - h_4)$$

and

$$\psi_{\pi^*} = 0.8220P_z(O) - 0.4173P_z(C).$$

The  $n$ -type orbital is mainly localized on the  $2P_y(O)$  AO and lies in the molecular plane, while the  $\pi^*$  orbital has its node in this plane. This situation is very interesting, namely, the  $n \rightarrow \pi^*$  triplet state of formaldehyde

in this configuration has both characteristic features of the  $\sigma$ - and  $\pi$ -electron radicals, and may be regarded as the starting point for a study of the  $n \rightarrow \pi^*$  triplet state of heteroconjugated molecules. A prominent difference between the spin densities of the planar  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  triplet states of formaldehyde exists in their proton spin densities. That of the former is negative in sign and that of the latter is positive in sign, and they are comparable in magnitude. The positive proton spin density in the  $n \rightarrow \pi^*$  triplet state of formaldehyde is due to the delocalization of the  $n$ -type unpaired orbital  $\psi_n$  above.

#### IV. CONCLUSION

As seen in the previous sections, the validity of the AN method, proposed to separate the UHF spin densities into mechanistic contributions, is confirmed. Since the SP and SD mechanisms are quite different and very important origins of the spin density, the present method to calculate their contributions is very useful in order to clarify the nature of spin density. Note that, when the lowest contaminating spin state in the UHF wavefunction is annihilated to improve the spin density,<sup>8</sup> the information about the "spin-appearing" mechanisms is obtained at the same time by means of the AN method. The generalization of the method to any multiplicity is simple.<sup>25</sup> Some applications of the method to doublet radicals are given in the succeeding paper.<sup>16</sup>

<sup>24</sup> G. Herzberg, *Molecular Spectra and Molecular Structure* (D. Van Nostrand Co., Inc., New York, 1966), Vol. 3.

<sup>25</sup> H. Nakatsuji, H. Kato, and T. Yonezawa, "On the Unrestricted Hartree-Fock Wavefunction," *J. Chem. Phys.* (to be published).