

On the Unrestricted Hartree-Fock Wavefunction

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The unrestricted Hartree-Fock (UHF) wavefunction is analyzed and interpreted in configuration-interaction (CI) language. The results of the present study are as follows. (i) The UHF wavefunction includes only one type of the singly excited configurations [Eq. (20)], and thus the correlation effects included are very limited ones, compared with the usual CI treatment. (ii) The weight of the lowest contaminating spin function, included in the UHF wavefunction, decreases with increasing spin multiplicity. (iii) The annihilation of the lowest contaminating spin function little affects the electron density distributions and other physical quantities, the operators of which commute with the annihilation operator. (iv) In the UHF method, the "spin-appearing" (spin-polarization and spin-delocalization) mechanisms are clearly divided, and an approximate method to separate these contributions is generalized, and some discussions about spin annihilation are made.

I. INTRODUCTION

The unrestricted Hartree-Fock (UHF) method,¹ which takes account of correlation effects between electrons with different spins, has been extensively applied in the study of spin properties. Amos, Hall, and Snyder² examined the UHF wavefunction and connected it with the alternant molecular-orbital method and with the configuration-interaction method. Since the UHF wavefunction is not an eigenfunction of a spin-squared operator S^2 , they proposed to annihilate the lowest contaminating spin function after energy minimization.² However, the validity of annihilation after energy minimization is still questionable,³ and Sando and Harriman⁴ compared the spin densities associated with the various SCF methods.

Here, the UHF wavefunction is analyzed and interpreted in configuration-interaction language by means of the natural orbitals of the UHF wavefunction.^{2a} The charge-density and spin-density properties of the UHF wavefunction are studied and the generalization of the previous results,⁵ which provides a useful procedure to separate the UHF spin densities into components due to the mechanistic contributions (spin-polarization and spin-delocalization contributions), are carried out. Some discussions about spin annihilation are made in the last section.

II. BASIC THEORY

The unrestricted single-determinantal wavefunction built up of the p α -spin and q β -spin orbitals is written as

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

where φ_i and ϕ_i may be different, and we assume $p \geq q$ without loss of generality. The wavefunction (1) is an eigenfunction of an operator S_z , and its eigenvalue is $\frac{1}{2}s$ ($s = p - q$) in \hbar units,

$$S_z\Psi_{\text{UHF}} = \frac{1}{2}s\Psi_{\text{UHF}}. \quad (2)$$

As shown by Amos and Hall,^{2a} the unitary transformations of the unrestricted molecular orbitals (MO's) $\{\varphi_i\}$ and $\{\phi_j\}$ lead to the corresponding orbitals $\{\chi_i\}$ and $\{\eta_j\}$ which are orthonormal in each sets but have overlap between them when $i=j$,

$$\int \chi_i\eta_j d\tau = T_i\delta_{ij}. \quad (3)$$

By means of these corresponding orbitals, the UHF wavefunction is rewritten as^{4c}

$$\Psi_{\text{UHF}} = [(p+q)!]^{-1/2} \det\{\chi_1\alpha\chi_2\alpha\cdots\chi_p\alpha\eta_1\beta\eta_2\beta\cdots\eta_q\beta\}, \quad (4)$$

where we omitted the unimportant constant factor introduced by the unitary transformation. Furthermore, these corresponding orbitals are connected with the natural orbitals λ , μ , and ν , of the UHF wavefunction by the following equations^{2a}:

$$\begin{aligned} \chi_i &= a_i\lambda_i + b_i\nu_i, & i &= 1, \dots, q, \\ \eta_i &= a_i\lambda_i - b_i\nu_i, & i &= 1, \dots, q, \\ \chi_{q+i} &= \mu_i, & i &= 1, \dots, s, \end{aligned} \quad (5)$$

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¹ J. A. Pople and R. K. Nesbet, *J. Chem. Phys.* **22**, 571 (1954).

² (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).

³ W. Marshall, *Proc. Phys. Soc. (London)* **A78**, 113 (1961).

⁴ (a) K. M. Sando and J. E. Harriman, *J. Chem. Phys.* **47**, 180

(1967); (b) J. E. Harriman and K. M. Sando, *ibid.* **48**, 5138

(1968); (c) see also J. E. Harriman, *ibid.* **40**, 2827 (1964).

⁵ (a) T. Yonezawa, H. Nakatsuji, T. Kawamura, and H. Kato,

Chem. Phys. Letters **2**, 454 (1968). (b) T. Yonezawa, H. Nakatsuji,

T. Kawamura, and H. Kato, *J. Chem. Phys.* **51**, 669 (1969).

where

$$\begin{aligned} a_i &= [\tfrac{1}{2}(1+T_i)]^{1/2}, \\ b_i &= [\tfrac{1}{2}(1-T_i)]^{1/2}. \end{aligned} \quad (6)$$

These natural orbitals are orthogonal to each other and diagonalize the reduced density matrix^{2a}

$$\begin{aligned} \rho(1|2) &= \sum_i^q (1+T_i)\lambda_i^*(1)\lambda_i(2) \\ &+ \sum_i^q (1-T_i)\nu_i^*(1)\nu_i(2) + \sum_i^q \mu_i^*(1)\mu_i(2). \end{aligned} \quad (7)$$

Note that the natural orbitals are not changed by projection. Only the occupation numbers are changed by projection.^{4c} Moreover, the natural orbitals λ_i and μ_i are similar^{2c,5} to the restricted Hartree-Fock MO's.⁶

By using Eq. (5), the UHF wavefunction [Eq. (4)] may be expanded in the form of the limited configuration interaction,^{2c,7}

$$\Psi_{\text{UHF}} = C_{s/2}{}^{\text{rf}}\Psi_{s/2}{}^{\text{rf}} + C^{\text{se}}\Psi^{\text{se}} + C^{\text{de}}\Psi^{\text{de}} + C^{\text{te}}\Psi^{\text{te}} \dots, \quad (8)$$

where $\Psi_{s/2}{}^{\text{rf}}$ is the normalized restricted function with eigenvalue of S^2 , $\frac{1}{2}s(\frac{1}{2}s+1)$,

$$\Psi_{s/2}{}^{\text{rf}} = |\lambda_1\alpha\lambda_1\beta \dots \lambda_q\alpha\lambda_q\beta\mu_1\alpha\mu_2\alpha \dots \mu_s\alpha| \quad (9)$$

and its coefficient is given by

$$C_{s/2}{}^{\text{rf}} = \prod_{i=1}^q a_i^2. \quad (10)$$

Ψ^{se} and Ψ^{de} are the sums of the normalized singly excited and doubly excited configurations,

$$C^{\text{se}}\Psi^{\text{se}} = \sum_{i=1}^q C^{\text{se}}(ii^*)\Psi^{\text{se}}(ii^*), \quad (11)$$

$$C^{\text{se}}(ii^*) = \sqrt{2}N_i a_i b_i,$$

$$\Psi^{\text{se}}(ii^*) = |\lambda_1\alpha\lambda_1\beta \dots \nu_i\lambda_i(1/\sqrt{2})$$

$$\times (\alpha\beta + \beta\alpha) \dots \lambda_q\alpha\lambda_q\beta\mu_1\alpha\mu_2\alpha \dots \mu_s\alpha|, \quad (12)$$

and

$$\begin{aligned} C^{\text{de}}\Psi^{\text{de}} &= \sum_{i<j}^q \sum_{i'<j'}^q C^{\text{de}}(ii^*; jj^*)\Psi^{\text{de}}(ii^*; jj^*) \\ &+ \sum_i^q C_{s/2}{}^{\text{de}}(ii^*)\Psi_{s/2}{}^{\text{de}}(ii^*), \end{aligned} \quad (13)$$

$$C^{\text{de}}(ii^*; jj^*) = 2a_i b_i a_j b_j N_{ij},$$

$$\begin{aligned} \Psi^{\text{de}}(ii^*; jj^*) &= |\lambda_1\alpha\lambda_1\beta \dots \nu_i\lambda_i(1/\sqrt{2})(\alpha\beta + \beta\alpha) \dots \nu_j\lambda_j \\ &\times (1/\sqrt{2})(\alpha\beta + \beta\alpha) \dots \lambda_q\alpha\lambda_q\beta\mu_1\alpha \dots \mu_s\alpha|, \end{aligned} \quad (14)$$

$$C_{s/2}{}^{\text{de}}(ii^*) = b_i^2 N_i,$$

$$\Psi_{s/2}{}^{\text{de}}(ii^*) = |\lambda_1\alpha\lambda_1\beta \dots \nu_i\alpha\nu_i\beta \dots \lambda_q\alpha\lambda_q\beta\mu_1\alpha \dots \mu_s\alpha|,$$

⁶ C. C. J. Roothaan, Rev. Mod. Phys. 32, 179 (1960).

⁷ R. Lefebvre, H. H. Dearman, and H. M. McConnell, J. Chem. Phys. 32, 176 (1960).

where

$$N_i = \prod_{m=1(m \neq i)}^q a_m^2 = a_j^2 N_{ij},$$

$$N_{ij} = \prod_{m=1(m \neq i, j)}^q a_m^2.$$

The higher-order terms in Eq. (8) are written in the same manner as above. Note that the singly and doubly excited configurations given above are not eigenfunctions of the spin-squared operator S^2 , except $\Psi_{s/2}{}^{\text{de}}(ii^*)$.

III. SPIN FUNCTIONS INCLUDED IN THE UHF WAVEFUNCTION

As shown previously,^{5b} the b_i values in Eq. (6) are very small and then the relation, $C_{s/2}{}^{\text{rf}} > C^{\text{se}} > C^{\text{de}} \dots$, may be expected in Eq. (8). Therefore, the correlation effects included in the UHF wavefunction may be attributed mainly to the singly excited configurations expressed by Eqs. (11) and (12). This was certainly true in the cases previously studied.⁸ Here, we analyze this configuration and divide it into eigenfunctions with respect to the spin-squared operator S^2 .

We rewrite the singly excited configuration as

$$\begin{aligned} \Psi^{\text{se}}(ii^*) &= |\lambda_1\alpha\lambda_1\beta \dots \nu_i\lambda_i(1/\sqrt{2}) \\ &\times (\alpha\beta + \beta\alpha) \dots \lambda_q\alpha\lambda_q\beta\mu_1\alpha\mu_2\alpha \dots \mu_s\alpha| \\ &= |\nu_i\lambda_i(1/\sqrt{2})(\alpha\beta + \beta\alpha)\mu_1\alpha\mu_2\alpha \dots \mu_s\alpha| \end{aligned} \quad (15)$$

for brevity. It includes $s+2$ singly occupied orbitals, and is the eigenfunction of the operator S_z with eigenvalue $\frac{1}{2}s$. This configuration $\Psi^{\text{se}}(ii^*)$ may be expressed as

$$\Psi^{\text{se}}(ii^*) = \zeta\Psi_{s/2}{}^{\text{se}}(ii^*) + \xi\Psi_{(s/2)+1}{}^{\text{se}}(ii^*), \quad (16)$$

where the functions satisfy the following eigenvalue problems:

$$\begin{aligned} S^2\Psi_{s/2}{}^{\text{se}}(ii^*) &= \tfrac{1}{2}s(\tfrac{1}{2}s+1)\Psi_{s/2}{}^{\text{se}}(ii^*), \\ S_z\Psi_{s/2}{}^{\text{se}}(ii^*) &= \tfrac{1}{2}s\Psi_{s/2}{}^{\text{se}}(ii^*), \end{aligned} \quad (17)$$

$$\begin{aligned} S^2\Psi_{(s/2)+1}{}^{\text{se}}(ii^*) &= (\tfrac{1}{2}s+1)(\tfrac{1}{2}s+2)\Psi_{(s/2)+1}{}^{\text{se}}(ii^*), \\ S_z\Psi_{(s/2)+1}{}^{\text{se}}(ii^*) &= \tfrac{1}{2}s\Psi_{(s/2)+1}{}^{\text{se}}(ii^*). \end{aligned} \quad (18)$$

Obviously, there is only one function which satisfies the relation (18). It is expressed as

$$\begin{aligned} \Psi_{(s/2)+1}{}^{\text{se}}(ii^*) &= (s+2)^{-1/2} |\nu_i\lambda_i\mu_1 \dots \mu_s \\ &\times \{(\alpha\beta + \beta\alpha)\alpha \dots \alpha + \alpha\alpha \sum_{j=1}^s \alpha \dots \alpha\beta\alpha \dots \alpha\}|, \end{aligned} \quad (19)$$

where the second term in the braces means the sum

$$\begin{aligned} \sum_{j=1}^s \alpha \dots \alpha\beta\alpha \dots \alpha &= \beta\alpha\alpha \dots \alpha + \alpha\beta\alpha \dots \alpha \\ &+ \alpha\alpha\beta \dots \alpha + \dots + \alpha\alpha\alpha \dots \beta. \end{aligned}$$

⁸ For example, see Tables IV and V of Ref. 5(b).

Now, we determine the function which satisfies Eq. (17). There are $s+1$ such functions. Note that *all* of these $s+1$ functions are considered in the usual CI treatment. However, as shown in the Appendix, *only one* function among them satisfies Eq. (16) and it is given by

$$\begin{aligned} \Psi_{s/2}^{se}(ii^*) &= (s+2)^{-1/2} | \nu_i \lambda_i \mu_1 \cdots \mu_s \{ (\frac{1}{2}s)^{1/2} (\alpha\beta + \beta\alpha) \alpha \cdots \alpha \\ &\quad - (2/s)^{1/2} \alpha \alpha \sum_j \alpha \cdots \alpha \beta \alpha \cdots \alpha \} |. \end{aligned} \quad (20)$$

From Eqs. (19) and (20), the coefficients in Eq. (16) are given by

$$\zeta = [s/(s+2)]^{1/2}, \quad \xi = [2/(s+2)]^{1/2}, \quad (21)$$

as shown in the Appendix. Then Eq. (16) becomes

$$\begin{aligned} \Psi^{se}(ii^*) &= [s/(s+2)]^{1/2} \Psi_{s/2}^{se}(ii^*) \\ &\quad + [2/(s+2)]^{1/2} \Psi_{(s/2)+1}^{se}(ii^*). \end{aligned} \quad (22)$$

Equations (19), (20), and (22) show the nature of the correlation effects and of the contaminating spin function included in the UHF wavefunction: The correlation effect included in the UHF wavefunction is a very limited one, compared with the usual CI treatment. First, the UHF wavefunction includes only that type of singly excited configuration which is expressed by the transitions from λ_i to ν_i .²⁰ Second, only one spin function [Eq. (20)] among the $s+1$ spin functions [see Eq. (A1) in Appendix] is considered in the UHF wavefunction.

Note the following two limiting cases; when $s=0$ (singlet case), Eq. (22) reduces to

$$\Psi^{se}(ii^*) = \Psi_1^{se}(ii^*), \quad (23)$$

which shows that the singly excited configurations included in the UHF wavefunction are *all* due to the contaminating (triplet) spin function. Pople, McIver, and Ostlund⁹ exploited this fact in their finite perturbation methods. (Note that the spin-density operator and the spin-squared operator do not commute.) When $s = \infty$,

$$\Psi^{se}(ii^*) = \Psi_{s/2}^{se}(ii^*),$$

which shows that the singly excited configurations in the UHF wavefunction *do not* include the contaminating spin function. Since $\Psi_{s/2}^{rf}$ in Eq. (8) is the eigenfunction of S^2 with the eigenvalue $\frac{1}{2}s(\frac{1}{2}s+1)$, a conclusion is that the weight of the lowest contaminating spin state in the UHF wavefunction decreases with increasing spin multiplicity, $s+1$. However, as s increases, so decrease the correlation effects included in the UHF wavefunction, compared with the usual CI treatment. Of course, these discussions are valid only when the

singly excited configurations are important, as in the actual calculations reported previously.⁵ However, for the spin-density calculations, only the singly excited configuration expressed by Eq. (20) is important, and the other s spin functions and the doubly excited and higher-order configurations in Eq. (8) do not contribute to the first-order approximation of a perturbation theory (see Appendix).

To the first-order approximation of a perturbation theory, the coefficient $C^{se}(ii^*)$ of Eq. (11) may be written as^{2d}

$$\begin{aligned} C^{se}(ii^*) &= \sqrt{2N_i} a_i b_i \\ &= [s/(s+2)]^{1/2} \\ &\quad \times \frac{\langle \Psi_{s/2}^{rf} | \mathcal{H} | \Psi_{s/2}^{se}(ii^*) \rangle}{E^{rf} - [s/(s+2)]E_{s/2}^{se}(ii^*) - [2/(s+2)]E_{(s/2)+1}^{se}}, \end{aligned} \quad (24)$$

where \mathcal{H} is a Hamiltonian operator. Note that in the calculation of the spin densities of the σ -type atomic orbitals of the π -electron radicals, the numerator of Eq. (24) reduces to the σ - π -type electron repulsion integrals.

IV. DENSITY

Here, we discuss the density properties of the UHF wavefunction. The UHF electron density at position \mathbf{r} is calculated by applying the density operator

$$\mathbf{q}(\mathbf{r}) = \sum_k \delta(\mathbf{r}_k - \mathbf{r})$$

to Eq. (8),

$$\begin{aligned} q_{\text{UHF}}^r &= \langle \Psi_{\text{UHF}} | \mathbf{q}(\mathbf{r}) | \Psi_{\text{UHF}} \rangle \\ &= (C_{s/2}^{rf})^2 \langle \Psi_{s/2}^{rf} | \mathbf{q}(\mathbf{r}) | \Psi_{s/2}^{rf} \rangle \\ &\quad + 2C^{se} C_{s/2}^{rf} \langle \Psi_{s/2}^{rf} | \mathbf{q}(\mathbf{r}) | \Psi^{se} \rangle \\ &\quad + (C^{se})^2 \langle \Psi^{se} | \mathbf{q}(\mathbf{r}) | \Psi^{se} \rangle + \cdots \end{aligned} \quad (25)$$

The second term in Eq. (25) is calculated by using Eqs. (9) and (12),

$$\begin{aligned} C^{se} \langle \Psi_{s/2}^{rf} | \mathbf{q}(\mathbf{r}) | \Psi^{se} \rangle &= \sum_i^q C^{se}(ii^*) \langle \Psi_{s/2}^{rf} | \mathbf{q}(\mathbf{r}) | \Psi^{se}(ii^*) \rangle \\ &= \frac{1}{2} \sum_i^q C^{se}(ii^*) \{ \lambda_i(\mathbf{r}) \nu_i(\mathbf{r}) - \lambda_i(\mathbf{r}) \nu_i(\mathbf{r}) \} \\ &= 0. \end{aligned}$$

Similarly, all the off-diagonal elements included in the expansion (25) are zero. This is obvious from Eq. (7). Thus, Eq. (25) reduces to

$$\begin{aligned} q_{\text{UHF}}^r &= (C_{s/2}^{rf})^2 \langle \Psi_{s/2}^{rf} | \mathbf{q}(\mathbf{r}) | \Psi_{s/2}^{rf} \rangle \\ &\quad + (C^{se})^2 \langle \Psi^{se} | \mathbf{q}(\mathbf{r}) | \Psi^{se} \rangle + \cdots, \end{aligned} \quad (26)$$

which includes only the diagonal elements.

⁹ J. A. Pople, J. W. McIver, Jr., and N. S. Ostlund, J. Chem. Phys. **49**, 2960, 2965 (1968).

As shown previously,^{5b,8} the relation, $(C_{s/2}{}^{rf})^2 \gg (C^{so})^2$ holds fairly satisfactorily in the actual calculations. Therefore, Eq. (26) shows that the annihilation of the lowest contaminating spin function in the UHF wavefunction little affects the electron density distribution. This point was suggested by Amos,^{2b} Harri- man,^{4c} and by the present authors.¹⁰ Referring to Eq. (7), the above approximation, $(C_{s/2}{}^{rf})^2 \gg (C^{so})^2$, corresponds to omitting the second term in Eq. (7).

Note that the above conclusion is obtained more elegantly only from the knowledge that the charge- density operator commutes with the annihilation operator. This is easily generalized. Namely, all the UHF expectation values of the physical quantities, the operators of which commute with the annihilation operator, do not change much by annihilation, if $(C_{s/2}{}^{rf})^2 \gg [C_{(s/2)+1}{}^{so}(i^*)]^2$.

V. SPIN DENSITY

The UHF method is frequently applied to the spin- density calculations. Especially in π -electron radicals the correlation effects are essential to interpret the observed ESR hfs constants. The UHF spin density at the position \mathbf{r} is calculated by applying the following normalized spin-density operator¹²:

$$\rho(\mathbf{r}) = S_z^{-1} \sum_k S_{zk} \delta(\mathbf{r}_k - \mathbf{r}),$$

which do not commute with the annihilation operator, to Eq. (8). The result is

$$\begin{aligned} \rho_{\text{UHF}}^r &= \langle \Psi_{\text{UHF}} | \rho(\mathbf{r}) | \Psi_{\text{UHF}} \rangle \\ &= (C_{s/2}{}^{rf})^2 \langle \Psi_{s/2}{}^{rf} | \rho(\mathbf{r}) | \Psi_{s/2}{}^{rf} \rangle \\ &\quad + 2C^{so} C_{s/2}{}^{rf} \langle \Psi_{s/2}{}^{rf} | \rho(\mathbf{r}) | \Psi^{so} \rangle \\ &\quad + (C^{so})^2 \langle \Psi^{so} | \rho(\mathbf{r}) | \Psi^{so} \rangle + \dots \quad (27) \end{aligned}$$

From Eqs. (4) and (5), ρ_{UHF}^r is also written as

$$\rho_{\text{UHF}}^r = \frac{2}{S_z} \sum_{i=1}^s a_i b_i \lambda_i(\mathbf{r}) \nu_i(\mathbf{r}) + (2S_z)^{-1} \sum_{i=1}^s \mu_i(\mathbf{r})^2. \quad (28)$$

Equation (28) is very simple and has clear physical meaning about the "spin-appearing" mechanisms.⁵ The first term represents the contributions due to the "spin-polarization" (SP) mechanism, and the second term represents those due to the "spin-delocalization" (SD) mechanism. (The definitions of these terminologies were given previously.¹³) By calculating the terms in Eq. (27), we obtain the following descriptions

for each of the mechanistic contributions:

$$\begin{aligned} (\rho_{\text{UHF}}^r)_{\text{SD}} &= (2S_z)^{-1} \sum_{i=1}^s \mu_i(\mathbf{r})^2 \\ &= (C_{s/2}{}^{rf})^2 \rho^r(\text{rf} \frac{1}{2} s | \text{rf} \frac{1}{2} s) + (C^{so})^2 \rho^r(\text{se} | \text{se}) \\ &\quad + (C^{de})^2 \rho^r(\text{de} | \text{de}) + \dots, \quad (29) \end{aligned}$$

which contains only diagonal elements, and

$$\begin{aligned} (\rho_{\text{UHF}}^r)_{\text{SP}} &= \frac{2}{S_z} \sum_{i=1}^s a_i b_i \lambda_i(\mathbf{r}) \nu_i(\mathbf{r}) \\ &= 2C^{so} C_{s/2}{}^{rf} \rho^r(\text{rf} \frac{1}{2} s | \text{se}) + 2C^{de} C^{so} \rho^r(\text{se} | \text{de}) \\ &\quad + 2C^{de} C^{te} \rho^r(\text{de} | \text{te}) + \dots, \quad (30) \end{aligned}$$

which contains only off-diagonal elements. $\rho^r(\text{rf} \frac{1}{2} s | \text{se})$ is the matrix element between $\Psi_{s/2}{}^{rf}$ and Ψ^{so} with respect to the normalized spin-density operator $\rho(\mathbf{r})$.

VI. SPIN-APPEARING MECHANISMS

Here we derive the approximate equations which serve a useful procedure in the separation of the UHF spin densities into mechanistic (spin-polarization and spin-delocalization) contributions. For the special cases of doublet and triplet radicals, the results have already been reported.⁵

First, we assume that the second and higher terms in Eqs. (29) and (30) are negligibly small,

$$(\rho_{\text{UHF}}^r)_{\text{SD}} = (C_{s/2}{}^{rf})^2 \rho^r(\text{rf} \frac{1}{2} s | \text{rf} \frac{1}{2} s), \quad (31a)$$

$$(\rho_{\text{UHF}}^r)_{\text{SP}} = 2C^{so} C_{s/2}{}^{rf} \rho^r(\text{rf} \frac{1}{2} s | \text{se}), \quad (31b)$$

$$\rho_{\text{UHF}}^r = (\rho_{\text{UHF}}^r)_{\text{SD}} + (\rho_{\text{UHF}}^r)_{\text{SP}}. \quad (31c)$$

By using Eq. (22), Eq. (8) is rewritten as

$$\Psi_{\text{UHF}} = C_{s/2}{}^{rf} \Psi_{s/2}{}^{rf} + C_{s/2}{}^{so} \Psi_{s/2}{}^{so} + C_{(s/2)+1}{}^{so} \Psi_{(s/2)+1}{}^{so}, \quad (32)$$

where

$$C_{s/2}{}^{so} = [s/(s+2)]^{1/2} C^{so},$$

$$C_{(s/2)+1}{}^{so} = [2/(s+2)]^{1/2} C^{so}. \quad (33)$$

From Eqs. (9), (19), and (20), the equation

$$\rho^r[\text{rf} \frac{1}{2} s | \text{se}(\frac{1}{2} s + 1)] = (2/s)^{1/2} \rho^r(\text{rf} \frac{1}{2} s | \text{se} \frac{1}{2} s) \quad (34)$$

is obtained. By using Eqs. (32)–(34), the UHF spin density (ρ_{UHF}^r) is written as

$$\begin{aligned} \rho_{\text{UHF}}^r &= (C_{s/2}{}^{rf})^2 \rho^r(\text{rf} \frac{1}{2} s | \text{rf} \frac{1}{2} s) \\ &\quad + 2[1 + (2/s)] C_{s/2}{}^{rf} C_{s/2}{}^{so} \rho^r(\text{rf} \frac{1}{2} s | \text{se} \frac{1}{2} s). \quad (35) \end{aligned}$$

Similarly, by assuming that the renormalization constant associated with the annihilation of the lowest contaminating spin function is very close to unity, the spin densities obtained after single annihilation (asa) and after annihilation (aa)² are given by

$$\begin{aligned} \rho_{\text{asa}}^r &= (C_{s/2}{}^{rf})^2 \rho^r(\text{rf} \frac{1}{2} s | \text{rf} \frac{1}{2} s) \\ &\quad + 2(1 + s^{-1}) C_{s/2}{}^{rf} C_{s/2}{}^{so} \rho^r(\text{rf} \frac{1}{2} s | \text{se} \frac{1}{2} s) \end{aligned}$$

¹⁰ See Table III of Ref. 11.

¹¹ T. Yonezawa, H. Nakatsuji, T. Kawamura, and H. Kato, *Bull. Chem. Soc. Japan* **42**, No. 9 (1969).

¹² H. M. McConnell, *J. Chem. Phys.* **28**, 1188 (1958).

¹³ See Footnote 6 of Ref. 5(b).

TABLE I. Ratios of $(\rho_{\text{UHF}})_{\text{SP}} : (\rho_{\text{aaa}})_{\text{SP}} : (\rho_{\text{aa}})_{\text{SP}}$.

	Singlet $s=0$	Doublet $s=1$	Triplet $s=2$	Quartet $s=3$	Qunitet $s=4$...	$s=s$
$(\rho_{\text{UHF}})_{\text{SP}}$	2	3	4	5	6	...	$s+2$
$(\rho_{\text{aaa}})_{\text{SP}}$	1	2	3	4	5	...	$s+1$
$(\rho_{\text{aa}})_{\text{SP}}$	0	1	2	3	4	...	s

and

$$\rho_{\text{aa}}^r = (C_{s/2}^r)^2 \rho^r(\text{rf}\frac{1}{2}s | \text{rf}\frac{1}{2}s) + 2C_{s/2}^r C_{s/2}^{\text{re}} \rho^r(\text{rf}\frac{1}{2}s | \text{se}\frac{1}{2}s). \quad (36)$$

By comparing Eqs. (35) and (36) with Eq. (31), the mechanistic contributions are derived. The *SP contribution* is given by using ρ_{UHF} and ρ_{aa} as

$$\begin{aligned} (\rho_{\text{UHF}})_{\text{SP}} &= \frac{1}{2}s[1 + (2/s)](\rho_{\text{UHF}} - \rho_{\text{aa}}), \\ (\rho_{\text{aaa}})_{\text{SP}} &= \frac{1}{2}s(1 + s^{-1})(\rho_{\text{UHF}} - \rho_{\text{aa}}), \\ (\rho_{\text{aa}})_{\text{SP}} &= \frac{1}{2}s(\rho_{\text{UHF}} - \rho_{\text{aa}}), \end{aligned} \quad (37)$$

or, by using ρ_{UHF} and ρ_{aaa} as

$$\begin{aligned} (\rho_{\text{UHF}})_{\text{SP}} &= s[1 + (2/s)](\rho_{\text{UHF}} - \rho_{\text{aaa}}), \\ (\rho_{\text{aaa}})_{\text{SP}} &= s(1 + s^{-1})(\rho_{\text{UHF}} - \rho_{\text{aaa}}), \\ (\rho_{\text{aa}})_{\text{SP}} &= s(\rho_{\text{UHF}} - \rho_{\text{aaa}}). \end{aligned} \quad (38)$$

The *SD contribution* is calculated from Eq. (31c) as

$$(\rho)_{\text{SD}} = \rho - (\rho)_{\text{SP}}. \quad (39)$$

Note the fact that the SP contributions to the spin densities associated with the various stages of annihilation satisfy the relation,

$$(\rho_{\text{UHF}})_{\text{SP}} : (\rho_{\text{aaa}})_{\text{SP}} : (\rho_{\text{aa}})_{\text{SP}} = (s+2) : (s+1) : s \quad (40)$$

and

$$(\rho_{\text{UHF}})_{\text{SD}} = (\rho_{\text{aaa}})_{\text{SD}} = (\rho_{\text{aa}})_{\text{SD}}. \quad (41)$$

Table I shows the above relation [Eq. (40)] for some examples.

For special case of $s=0$ (singlet state), Eqs. (37) and (38) cannot be applied. However, in this case, from Eq. (23), the spin densities are all due to the contaminating (triplet) spin function and are due only to the SP mechanism. By the similar procedure as above, the spin densities obtained at various stages of annihilation are shown to hold the relation,

$$\rho_{\text{UHF}} : \rho_{\text{aaa}} : \rho_{\text{aa}} = 2 : 1 : 0. \quad (42)$$

This is the special case of Eq. (40).

VII. DISCUSSION

As may be noticed, Eq. (5) is very similar to the starting point of alternant molecular-orbital (AMO) method. λ_i and ν_i correspond to the bonding and antibonding AMO partners, respectively. Therefore, all the

results obtained by the present study apply to the *unprojected* AMO method. The extensive studies of the AMO method were given by Löwdin, de Heer, and Pauncz.¹⁴

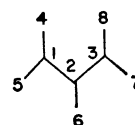
Now, we discuss the approximate method obtained in Sec. VI. Since the spin densities in the σ -type atomic orbitals of the π -electron radicals are due only to the SP mechanism, the approximate relation (40) holds for the total spin densities. Moreover, this relation may be used to check the validity of the approximations introduced in Sec. VI.^{5,11} For example, in the " π -quartet" state of the allyl radical,¹⁵ the values of

TABLE II. Spin density* in the " π -quartet" state of the allyl radical.^b

Atom	AO	ρ_{UHF}	ρ_{aa}	ρ_{aa} from Eqs. (40), (41)
C ₁ , C ₂	2S	0.051	0.031	0.031
	2P _x	0.000	0.000	0.000
	2P _y	0.003	0.002	0.002
	2P _z	0.355	0.354	0.355
C ₂	2S	0.054	0.033	0.033
	2P _x	0.000	0.000	0.000
	2P _y	0.005	0.003	0.003
	2P _z	0.377	0.376	0.377
H ₄ , H ₅	1S	-0.013	-0.008	-0.008
H ₆ , H ₇	1S	-0.012	-0.007	-0.007
H ₆	1S	-0.018	-0.010	-0.010

* About the method of calculation, see Ref. 13.

^b Numbering of atoms is as follows:



The geometry is C-C=1.40 Å, C-H=1.08 Å, and $\angle\text{HCH} = \angle\text{HCC} = \angle\text{CCC} = 120^\circ$.

¹⁴ (a) P.-O. Löwdin, Phys. Rev. **97**, 1509 (1955); (b) R. Pauncz, J. de Heer, and P.-O. Löwdin, J. Chem. Phys. **36**, 2247 (1962), and the succeeding papers; (c) R. Pauncz, *Alternant Molecular Orbital Method* (W. B. Saunders and Co., Philadelphia, Pa., 1967).

¹⁵ Note that in the " π -quartet" state of the allyl radical, the order of the proton spin densities (absolute values) is $\text{H}_6 > \text{H}_4 > \text{H}_5$, but, on the other hand, in the doublet allyl radical, it is $\text{H}_5 > \text{H}_4 > \text{H}_6$ and is reverse to the above. (Ref. 11.)

ρ_{aa} are compared with those calculated by Eqs. (40) and (41) from ρ_{UHF} (Table II). They agree very satisfactorily. For some doublet and triplet radicals, the examination of the method described in Sec. VI is carried out more rigorously in the previous reports.⁵

Equations (40) and (41) show approximately the theoretical relations existing among ρ_{UHF} , ρ_{aaa} , and ρ_{aa} . Thus, at present, we think it almost meaningless to discuss theoretically whether the annihilation of the lowest contaminating spin function "improves" the spin-density properties. For example, in the methyl radical, the spin densities in the σ -type atomic orbitals are due only to the SP mechanism,^{5a,11} then the relation,

$$\rho_{\text{UHF}}:\rho_{\text{aaa}}:\rho_{\text{aa}}=3:2:1,$$

can be expected transcendently. The computational examination of the validity of projection after energy minimization is carried out by Harriman and Sando.⁴ They reported that the spin densities obtained by the spin-extended SCF calculations are generally (but not always) closer to the unrestricted values.⁴

Another important aspect of the spin-density calculations (especially in the semiempirical ones) lies in their agreement with experiments. From the above standpoint and from Eq. (24), the problem, "which stages of annihilation are best recommended," depends very much on the choice of the integral values (especially on the choice of the σ - π -type electron repulsion integrals).¹⁶ In the conventional (semiempirical) calculations of the hfs constants (a), it may be approved to consider A of the following equation:

$$a = A\rho,$$

as a proportionality constant determined by "best fitting" the calculated spin densities with the observed hfs constants.^{11,17} However, from Eqs. (24), (40), and (41), we think it very difficult to determine both the values of A_{UHF} and A_{aa} , which reproduce satisfactorily the observed hfs constants from ρ_{UHF} and ρ_{aa} , respectively. A good example is the ethyl radical. Its methylene-group proton spin density is due only to the SP mechanism, and thus $(\rho_{\text{UHF}})_{\text{CH}_2} = 3(\rho_{\text{aa}})_{\text{CH}_2}$,^{11,18} while its methyl-group proton spin density (assuming free rotation) is due to both (SP and SD) mechanisms, and thus, $(\rho_{\text{UHF}})_{\text{CH}_3} \approx 1.2(\rho_{\text{aa}})_{\text{CH}_3}$ in our calculation¹¹ and $(\rho_{\text{UHF}})_{\text{CH}_3} \approx 1.4(\rho_{\text{aa}})_{\text{CH}_3}$ in the Pople, Beveridge, and Dobosh's calculation.¹⁸ This example shows that if one adjusts the semiempirical (σ - π -type) repulsion integrals¹⁶ so as to obtain a good correlation of the

UHF spin densities with the observed hfs constants, then only A_{UHF} is acceptable in the least-mean-square sense (and vice versa).¹¹

For some doublet and triplet radicals, the method stated in Sec. VI has been applied in order to clarify the "spin-appearing" mechanisms, and threw a new light on the nature of spin density.^{5,11}

APPENDIX

Here we determine the spin function which satisfies Eq. (17). There are $s+1$ such functions. The spin parts of them may be written as¹⁹

$$\begin{aligned} \Theta_{\frac{1}{2}, \frac{1}{2}, s; 1} &= (1/\sqrt{2})(\alpha \cdots \alpha \beta \alpha - \alpha \cdots \alpha \alpha \beta), \\ \Theta_{\frac{1}{2}, \frac{1}{2}, s; 2} &= 6^{-1/2}(2\alpha \cdots \beta \alpha \alpha - \alpha \cdots \alpha \beta \alpha - \alpha \cdots \alpha \alpha \beta), \\ &\vdots \\ \Theta_{\frac{1}{2}, \frac{1}{2}, s; s} &= [s(s+1)]^{-1/2}(s\alpha\beta\alpha \cdots \alpha - \alpha\alpha\beta \cdots \alpha - \cdots \\ &\quad - \alpha \cdots \beta \alpha \alpha - \alpha \cdots \alpha \beta \alpha - \alpha \cdots \alpha \alpha \beta), \\ \Theta_{\frac{1}{2}, \frac{1}{2}, s; s+1} &= [(s+1)(s+2)]^{-1/2}[(s+1)\beta\alpha\alpha \cdots \alpha - \alpha\beta\alpha \cdots \alpha \\ &\quad - \cdots - \alpha \cdots \beta \alpha \alpha - \alpha \cdots \alpha \beta \alpha - \alpha \cdots \alpha \alpha \beta]. \quad (A1) \end{aligned}$$

Among the above functions, we need only the functions which satisfy the following two demands: (a) The first two terms must have the form, $(\alpha\beta + \beta\alpha)\alpha \cdots \alpha$, except for a constant factor, (b) it must satisfy Eq. (16) with Eq. (19). From demand (a) only the last two functions are important. By taking linear combinations of these two functions, we obtain

$$\begin{aligned} [s/2(s+1)]^{1/2}\Theta_{\frac{1}{2}, \frac{1}{2}, s; 2; s} - [(s+2)/2(s+1)]^{1/2}\Theta_{\frac{1}{2}, \frac{1}{2}, s; 2; s+1} \\ = 1/\sqrt{2}(\alpha\beta - \beta\alpha)\alpha \cdots \alpha \quad (A2) \end{aligned}$$

and

$$\begin{aligned} [(s+2)/2(s+1)]^{1/2}\Theta_{\frac{1}{2}, \frac{1}{2}, s; 2; s} + [s/2(s+1)]^{1/2}\Theta_{\frac{1}{2}, \frac{1}{2}, s; 2; s+1} \\ = (s+2)^{-1/2}[(\frac{1}{2}s)^{1/2}(\alpha\beta + \beta\alpha)\alpha \cdots \alpha \\ - (2/s)^{1/2}\alpha\alpha \sum_i \alpha \cdots \alpha \beta \alpha \cdots \alpha]. \quad (A3) \end{aligned}$$

Between the above two functions, only the second satisfies the demands (a) and (b). Then, Eq. (20) follows.

From Eqs. (19) and (20), the coefficients ζ and ξ in Eq. (16) are determined. By comparing Eq. (16) with Eqs. (19) and (20), we obtain the following two relations:

$$(s+2)^{-1/2}[\xi + (\frac{1}{2}s)^{1/2}\zeta] = 1/\sqrt{2},$$

and

$$(s+2)^{-1/2}[\xi - (2/s)^{1/2}\zeta] = 0,$$

Thus, Eq. (21) follows.

¹⁹ See, for example, M. Kotani, A. Amemiya, E. Ishiguro, and T. Kimura, *Tables of Molecular Integrals* (Maruzen Co., Ltd., Tokyo, Japan, 1963), p. 5.

¹⁶ See the paragraph which includes Eq. (24).

¹⁷ (a) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Am. Chem. Soc.* **90**, 4201 (1968); (b) D. L. Beveridge and P. A. Dobosh, *J. Chem. Phys.* **48**, 5532 (1968).

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