

SPIN POLARIZATION AND SPIN DELOCALIZATION  
IN UNRESTRICTED HARTREE-FOCK METHOD

T. YONEZAWA, H. NAKATSUJI, T. KAWAMURA and H. KATO

*Department of Hydrocarbon Chemistry, Faculty of Engineering,  
Kyoto University, Sakyo-ku, Kyoto, Japan*

Received 16 September 1968

A theory for the separation of the spin density calculated with the unrestricted Hartree-Fock method into the two components due to the spin polarization and spin delocalization mechanisms is given and applied to methyl, ethyl and vinyl radicals.

The unrestricted Hartree-Fock (UHF) method based on a spin polarized self-consistent field single determinant wave function [1] has been widely used for the spin density calculations of many organic and inorganic radicals. However, the unrestricted Hartree-Fock method, compared with the configuration interaction or perturbation methods, does not provide the information about the spin density appearing mechanisms such as the spin polarization (SP) and spin delocalization (SD) mechanisms\*. In the present communication, we propose a procedure to separate the spin density calculated with the UHF method and those obtained with the annihilation method [3] into components due to the SP mechanism and to the SD mechanism.

Here we follow closely the results given by Snyder and Amos [4]. The total wave function of the UHF method is written by the  $p$   $\alpha$ -spin orbitals and the  $q$   $\beta$ -spin orbitals and we assume  $p > q$  without loss of generality. The unitary transformation of the unrestricted molecular orbitals (MO's) gives the corresponding MO's,  $\chi_i$  and  $\eta_i$ , which are closely related to the natural orbitals,  $\lambda$ ,  $\nu$  and  $\mu$ :

$$\chi_i = \lambda_i(1 - \Delta_i^2)^{\frac{1}{2}} + \nu_i\Delta_i, \quad i = 1, \dots, q;$$

$$\eta_i = \lambda_i(1 - \Delta_i^2)^{\frac{1}{2}} - \nu_i\Delta_i, \quad i = 1, \dots, q;$$

$$\chi_i = \mu_i, \quad i = q + 1, \dots, p; \quad (1)$$

where

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

Using eq. (1), we can rewrite the UHF single determinant as the following for doublet radicals ( $p = q + 1$ )

$$\Psi_{\text{UHF}} = C_{\frac{1}{2}}^{\text{rf}} \Psi_{\frac{1}{2}}^{\text{rf}} + C_{\frac{1}{2}}^{\text{se}} \Psi_{\frac{1}{2}}^{\text{se}} + C_{\frac{3}{2}}^{\text{se}} \Psi_{\frac{3}{2}}^{\text{se}} + C_{\frac{1}{2}}^{\text{de}} \Psi_{\frac{1}{2}}^{\text{de}} + \dots, \quad (2)$$

where

$$\Psi_{\frac{1}{2}}^{\text{rf}} = |\lambda_1 \alpha \lambda_1 \beta \lambda_2 \alpha \lambda_2 \beta \dots \lambda_q \alpha \lambda_q \beta \mu \rho \alpha| \quad (3)$$

and  $\Psi_{\frac{1}{2}}^{\text{se}}$  and  $\Psi_{\frac{3}{2}}^{\text{se}}$  are the sums of the singly excited doublet and quartet configurations resulting from the excitation of an electron from  $\lambda_i$  to  $\nu_j$ .

By assuming  $C_{\frac{1}{2}}^{\text{rf}} \approx 1 \gg C_{\frac{1}{2}}^{\text{se}}, C_{\frac{3}{2}}^{\text{se}}$ , and by neglecting the doubly excited configuration  $\Psi_{\frac{1}{2}}^{\text{de}}$  and higher terms, the spin density of the UHF method at the position  $i$  can be written as\*

$$\rho_{\text{UHF}}^i \approx \rho^i(\text{rf}_{\frac{1}{2}} | \text{rf}_{\frac{1}{2}}) + 2C_{\frac{1}{2}}^{\text{se}} \rho^i(\text{rf}_{\frac{1}{2}} | \text{se}_{\frac{1}{2}}) + 2C_{\frac{3}{2}}^{\text{se}} \rho^i(\text{rf}_{\frac{1}{2}} | \text{se}_{\frac{3}{2}}). \quad (4)$$

From the following relations [4]

\* The spin density operator and the spin squared operator do not commute.

\* To avoid confusion, see ref. [2], we give a provisional definition of the spin delocalization and spin polarization mechanisms used in this communication. The former means the spin density appearing mechanism due to the singly occupied orbitals of the best restricted total wave function and the latter is defined as that due to the correlation between electron spins. This definition of the SP and SD mechanisms is identical with that used by Colpa and de Boer.

Table 1  
Spin polarization and spin delocalization in the calculated spin density

| Radical | Atomic Orbital                  | $(\rho_{\text{uhf}})_{\text{sp}}$ | $(\rho_{\text{uhf}})_{\text{sd}}$ | $(\rho_{\text{aa}})_{\text{sp}}$ | $(\rho_{\text{aa}})_{\text{sd}}$ | $\rho_{\text{rhf}}$ |
|---------|---------------------------------|-----------------------------------|-----------------------------------|----------------------------------|----------------------------------|---------------------|
| Methyl  | 2Sc                             | 0.147( 99) *                      | 0.002( 1)                         | 0.049( 96)                       | 0.002( 4)                        | 0.000               |
|         | H                               | -0.028(100)                       | 0.000( 0)                         | -0.009( 100)                     | 0.000( 0)                        | 0.000               |
| Ethyl   | 2Sc <sub>1</sub>                | 0.159( 99)                        | 0.002( 1)                         | 0.053( 95)                       | 0.002( 5)                        | 0.000               |
|         | 2Sc <sub>2</sub>                | -0.012(100)                       | 0.000( 1)                         | -0.004( 100)                     | 0.000( 0)                        | 0.000               |
|         | H <sub>3</sub>                  | -0.035(100)                       | 0.000( 0)                         | -0.012( 100)                     | 0.000( 0)                        | 0.000               |
|         | H <sub>4</sub>                  | -0.035(100)                       | 0.000( 0)                         | -0.012( 100)                     | 0.000( 0)                        | 0.000               |
|         | H <sub>5</sub> , H <sub>6</sub> | 0.014( 26)                        | 0.040( 74)                        | 0.005( 11)                       | 0.040( 89)                       | 0.041               |
|         | H <sub>7</sub>                  | -0.002(100)                       | 0.000( 0)                         | -0.001( 100)                     | 0.000( 0)                        | 0.000               |
|         | Vinyl<br>$\theta = 135^\circ$   | 2Sc $\alpha$                      | 0.122( 59)                        | 0.083( 41)                       | 0.041( 33)                       | 0.083( 67)          |
|         | 2Sc $\beta$                     | -0.035(111)                       | 0.004(-11)                        | -0.012( 146)                     | 0.004(-46)                       | 0.004               |
|         | Hc                              | 0.009( 21)                        | 0.035( 79)                        | 0.003( 8)                        | 0.035( 92)                       | 0.036               |
|         | Ht                              | 0.026( 27)                        | 0.071( 73)                        | 0.009( 11)                       | 0.071( 89)                       | 0.075               |
|         | H $\alpha$                      | -0.042(197)                       | 0.021(-97)                        | -0.014(-218)                     | 0.021(318)                       | 0.017               |

\* The values in parentheses show the percentages of the contributions.  $100 \cdot (\rho^i)_{\text{sp}} / \rho^i$  and  $100 \cdot (\rho^i)_{\text{sd}} / \rho^i$ , respectively.

$$\sqrt{2}C_{\frac{1}{2}}^{\text{se}} = C_{\frac{3}{2}}^{\text{se}}; \quad \rho^i(\text{rf}_{\frac{1}{2}} | \text{se}_{\frac{3}{2}}) = \sqrt{2}\rho^i(\text{rf}_{\frac{1}{2}} | \text{se}_{\frac{1}{2}}),$$

eq. (4) reduces to

$$\rho_{\text{UHF}}^i = \rho^i(\text{rf}_{\frac{1}{2}} | \text{rf}_{\frac{1}{2}}) + 3\sqrt{2}C_{\frac{3}{2}}^{\text{se}}\rho^i(\text{rf}_{\frac{1}{2}} | \text{se}_{\frac{1}{2}}) \quad (5)$$

and similarly, the spin densities after single annihilation ( $\rho_{\text{asa}}$ ) and after annihilation ( $\rho_{\text{aa}}$ ) are [3]

$$\rho_{\text{asa}}^i = \rho^i(\text{rf}_{\frac{1}{2}} | \text{rf}_{\frac{1}{2}}) + 2\sqrt{2}C_{\frac{3}{2}}^{\text{se}}\rho^i(\text{rf}_{\frac{1}{2}} | \text{se}_{\frac{1}{2}}), \quad (6)$$

$$\rho_{\text{aa}}^i = \rho^i(\text{rf}_{\frac{1}{2}} | \text{rf}_{\frac{1}{2}}) + \sqrt{2}C_{\frac{3}{2}}^{\text{se}}\rho^i(\text{rf}_{\frac{1}{2}} | \text{se}_{\frac{1}{2}}). \quad (7)$$

Referring to eq. (3), it may be clear that the first terms of eqs. (5) - (7) represent the contributions due to the SD mechanism and the second terms represent approximately those due to the SP mechanism. It may be noteworthy, however, that the unpaired orbital we mean is the natural orbital,  $\mu_i$ , in eq. (1) and that the  $\Psi_{\frac{1}{2}}^{\text{se}}$  in eq. (2) includes only the limited configurations like  $|\lambda_i \rightarrow \nu_i|$ , based on the natural orbitals, and does not include those expressed as  $|\lambda_i \rightarrow \nu_j|$  ( $i \neq j$ ) [3]. The natural orbitals  $\lambda$ ,  $\mu$  and  $\nu$  are not identical but closely similar to the best restricted orbitals as pointed out by Amos and Snyder [3], and this point will be examined numerically in table 1 by comparing the results obtained with the UHF method to those with the open shell restricted Hartree-Fock (RHF) method [5].

From eqs. (5) - (7), we obtain the results

$$(\rho_{\text{UHF}}^i)_{\text{sp}} = \frac{3}{2}(\rho_{\text{UHF}}^i - \rho_{\text{aa}}^i), \quad (8)$$

$$(\rho_{\text{asa}}^i)_{\text{sp}} = \rho_{\text{UHF}}^i - \rho_{\text{aa}}^i, \quad (9)$$

$$(\rho_{\text{aa}}^i)_{\text{sp}} = \frac{1}{2}(\rho_{\text{UHF}}^i - \rho_{\text{aa}}^i), \quad (10)$$

where  $(\rho_{\text{UHF}}^i)_{\text{sp}}$  is the SP contribution to the spin density calculated with the UHF method, and  $(\rho_{\text{asa}}^i)_{\text{sp}}$  and  $(\rho_{\text{aa}}^i)_{\text{sp}}$  are those to  $\rho_{\text{asa}}^i$  and  $\rho_{\text{aa}}^i$ , respectively. The SD contributions are, therefore, written in common as

$$(\rho^i)_{\text{sd}} = \rho^i - (\rho^i)_{\text{sp}}. \quad (11)$$

When only the SP mechanism is the source of the spin density as in the case of the  $\sigma$ -type atomic orbitals of the methyl radical, eqs. (8) - (10) give

$$\rho_{\text{UHF}}^i = \frac{3}{2}\rho_{\text{asa}}^i = 3\rho_{\text{aa}}^i, \quad (12)$$

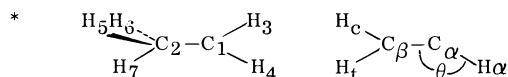
as was pointed out by Amos and Snyder.

A semi-empirical unrestricted SCF-MO method for valence electron systems including differential overlap proposed by the present authors [6] gave spin densities listed in table 2. As is well known, the spin densities on the  $\sigma$ -type atomic orbitals of the methyl radical are due only to the SP mechanism and therefore, relation (12) holds fairly satisfactorily.

By using the values shown in table 2, the contributions of the SP and SD mechanisms to spin

Table 2  
Spin densities calculated before and after annihilation  
of the quartet spin functions

| Radical                           | Atomic Orbital *                | $\rho_{\text{uhf}}^{**}$ | $\rho_{\text{aa}}$ |
|-----------------------------------|---------------------------------|--------------------------|--------------------|
| Methyl                            | 2Sc                             | 0.1487                   | 0.0510             |
|                                   | H                               | -0.0275                  | -0.0089            |
| Ethyl                             | 2Sc <sub>1</sub>                | 0.1314                   | 0.0555             |
|                                   | 2Sc <sub>2</sub>                | -0.0123                  | -0.0040            |
|                                   | H <sub>3</sub>                  | -0.0345                  | -0.0111            |
|                                   | H <sub>4</sub>                  | -0.0345                  | -0.0111            |
|                                   | H <sub>5</sub> , H <sub>6</sub> | 0.0538                   | 0.0442             |
|                                   | H <sub>7</sub>                  | -0.0020                  | -0.0007            |
| Vinyl<br>$\theta = 135^\circ$ *** | 2Sc $\alpha$                    | 0.2051                   | 0.1240             |
|                                   | 2Sc $\beta$                     | -0.0315                  | -0.0082            |
|                                   | H $c$                           | 0.0438                   | 0.0381             |
|                                   | H $t$                           | 0.0974                   | 0.0799             |
|                                   | H $\alpha$                      | -0.0213                  | 0.0064             |



\*\* To compare with the experimentally observed proton hyperfine coupling constants, the proportionality constant, 743 gauss, determined by the best fit method is recommended.

\*\*\* The most stable configuration calculated with the present method.

densities are calculated from eqs. (8) - (11) and the results are summarized in table 1. Moreover, the spin density calculated by the RHF method ( $\rho_{\text{RHF}}$ ) may be regarded as a reasonable measure of the validity of the SD contribution obtained by the above method \*, and therefore, the values

\* Eqs. (8) - (11) are correct only when the contributions due to the higher terms neglected in eq. (4) are negligibly small.

of  $\rho_{\text{RHF}}$  are given in the last column of table 1. It may be seen that the SD contributions calculated by the UHF method agree reasonable with those obtained by the RHF method. In the ethyl radical, the spin densities on H<sub>5</sub> and H<sub>6</sub> atoms are due to 25 - 10% SP and 75 - 90% SD contributions and those of the other atoms are chiefly due to the SP mechanism. In the vinyl radical, both mechanisms are important, and especially for the  $\alpha$ -hydrogen atom, the calculated spin density is the result of the large cancelling contributions of both mechanisms. It may be said based on the present results that extended Hückel type calculations [7, 8] of the vinyl radical, where only the SD mechanism is considered, have some doubt as has been mentioned by Dixon [9].

More details of the above method and its extension to the triplet state will be described elsewhere in the near future.

## REFERENCES

- [1] J. A. Pople and R. K. Nesbet, J. Chem. Phys. 22 (1954) 571.
- [2] J. P. Colpa, E. de Boer, D. Lazdins and M. Karplus, J. Chem. Phys. 47 (1967) 3098.
- [3] T. Amos and L. C. Snyder, J. Chem. Phys. 41 (1964) 1773.
- [4] L. C. Snyder and T. Amos, J. Chem. Phys. 42 (1965) 3670.
- [5] C. C. J. Roothaan, Rev. Mod. Phys. 32 (1960) 179.
- [6] T. Yonezawa, H. Nakatsuji, T. Kawamura and H. Kato, Bull. Chem. Soc. Japan 40 (1967) 2211; Mol. Phys. 13 (1967) 589.
- [7] G. A. Peterson and A. D. McLachlan, J. Chem. Phys. 45 (1966) 628.
- [8] R. S. Drago and H. Petersen Jr., J. Am. Chem. Soc. 89 (1967) 5774.
- [9] W. T. Dixon, Mol. Phys. 9 (1965) 201.