

*Original Investigations***Distribution of Odd Electrons in Ground-State Molecules**

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A density function  $D(r) = 2\gamma(r, r) - \int \gamma(r, r')\gamma(r', r) dr'$ , where  $\gamma(r, r')$  is a spinless first-order density matrix, has been proposed as fundamental formula representing the spatial distribution of odd electrons in molecules. The bonding properties of  $\pi$  electrons in some representative triatomic species have been examined in the light of  $D(r)$ . The density function can also be used successfully to assess the diradical character of unstable singlet ground-state molecules.

**Key words:** Electron pair splitting – Odd electrons, distribution of – Triatomic species – Diradical character

**1. Introduction**

When electron correlation is utterly ignored, each orbital in the singlet ground state of atoms and molecules can be considered to be doubly occupied by a pair of electrons having  $\alpha$  and  $\beta$  spins. The concept of such a double occupancy of spatial orbitals has provided a useful guiding principle to the understanding of electronic structures of stable molecules, as is endorsed by the success of the restricted Hartree-Fock (RHF) theory [1]. However, the concept apparently breaks down when the electron correlation is duly taken into account [2]. An RHF orbital is then more or less split into two spatial orbitals, each of which now accommodates either one of the paired electrons separately. An electron pair will thus be split spatially to assume a partial odd-electron character even in a singlet ground-state molecule. The nature of such split electron pairs should have a particularly significant bearing on the properties of the so-called singlet diradical species [3] as well as the transition state of certain concerted reactions [4].

The electronic structure of molecular systems involving the electron pair splitting can be represented satisfactorily well by some specific wavefunctions such as the

generalized valence bond (GVB) wavefunction [5]. Yet, it seems desirable to invent a general method of drawing information about the splitting of electron pairs from exact or any trial wavefunctions. Particular efforts along this line are the main purpose of the present work. It is also a formal complement to our general considerations [6] of Lewis' electron pair concept.

## 2. Definition of the Odd Electron Density

Consider a singlet ground state. The first-order reduced density matrix [7] is written as

$$\rho^{(1)}(x, x') = \frac{1}{2}\gamma(r, r')[\alpha(s)\alpha(s') + \beta(s)\beta(s')], \quad (1)$$

where  $r$  and  $s$  respectively denote the space and spin coordinates and where  $\gamma(r, r')$  is the spinless first-order density matrix. The necessary and sufficient condition [7] for a wavefunction to be reduced to a single Slater determinant is

$$\begin{aligned} \rho^{(1)}(x, x') - \int \rho^{(1)}(x, x'')\rho^{(1)}(x'', x) dx'' &= \frac{1}{4}[2\gamma(r, r') \\ &- \int \gamma(r, r'')\gamma(r'', r') dr''] [\alpha(s)\alpha(s') + \beta(s)\beta(s')] = 0. \end{aligned} \quad (2)$$

It follows that

$$2\gamma(r, r') - \gamma^2(r, r') = 0 \quad (3)$$

where  $\gamma^2(r, r')$  has been defined as

$$\gamma^2(r, r') = \int \gamma(r, r'')\gamma(r'', r') dr''. \quad (4)$$

Equation (3) means that the natural orbitals [7] should be doubly occupied, as long as the wavefunction for which  $\langle S^2 \rangle = 0$  can be represented by a single Slater determinant. On the contrary, when the exact wavefunction cannot be expressed by one determinant alone,  $2\gamma(r, r') - \gamma^2(r, r')$  should be nonzero. In such latter cases, at least one of the natural orbital pairs must be split to a certain extent. Thus, a spinless density function defined as

$$D(r, r') = 2\gamma(r, r') - \gamma^2(r, r') \quad (5)$$

is expected to provide a theoretical clue to the spatial splitting of electron pairs in a given molecular system. Each counterpart electron of an electron pair which is thus split to occupy different portions of space orthogonally will hereafter be referred to as an "odd electron". The extent of generation of such odd electrons and their distribution in molecules are the central problem of our present concern.

Let us concern ourselves here primarily with the diagonal element of Eq. (5). We will express the diagonal element as

$$D(r) = 2\gamma(r) - \gamma^2(r). \quad (6)$$

The density function  $D(r)$  can be expanded diagonally in terms of the natural orbitals  $\phi_k$ 's and their occupation numbers  $n_k$ 's ( $0 \leq n_k \leq 2$ ). The result is written as

$$D(r) = \sum_k n_k(2 - n_k) \phi_k^*(r) \phi_k(r). \quad (7)$$

Equation (7) indicates that the intensity factor of a natural orbital  $\phi_k$  contributing to the density function  $D(r)$  is  $n_k(2 - n_k)$ . Obviously, the factor  $n_k(2 - n_k)$  takes a maximal value of 1 when  $n_k = 1$ , and diminishes monotonously down to 0 as  $n_k$  approaches 0 or 2. This could be taken as an implication that  $n_k(2 - n_k)$  is the probability that the electron(s) in  $\phi_k$  is left unpaired as if it were an odd electron in the singly occupied molecular orbital of a doublet radical. Our density function  $D(r)$  could then be regarded as a formal expression giving the spatial distribution of the total odd electrons in a given molecule.

In open-shell ground states, unpaired spin densities do exist at the outset. The first-order density matrix is

$$\rho^{(1)}(x, x') = \gamma_\alpha(r, r') \alpha(s) \alpha(s') + \gamma_\beta(r, r') \beta(s) \beta(s'), \quad (8)$$

the spinless first-order density matrix being written as

$$\gamma(r, r') = \gamma_\alpha(r, r') + \gamma_\beta(r, r'). \quad (9)$$

In this case, the density function for odd electrons  $D(r)$  is formally expressed as

$$D(r) = 2\gamma(r) - \gamma^2(r) \\ = 2[\{\gamma_\alpha(r) - \gamma_\alpha^2(r)\} + \{\gamma_\beta(r) - \gamma_\beta^2(r)\}] + (\gamma_\alpha - \gamma_\beta)^2(r) \quad (10)$$

where the term  $(\gamma_\alpha - \gamma_\beta)^2(r)$  is the diagonal element of the integrated square (Eq. (4)) of the customary spin density function  $\gamma_\alpha(r) - \gamma_\beta(r)$ . Clearly,  $\gamma_\alpha(r) - \gamma_\beta(r)$  is due to the presence of unpaired spin(s) in the ground configuration. In cases where the wavefunction happens to be given by a single determinant, we have

$$\gamma_\alpha(r) - \gamma_\alpha^2(r) = 0, \quad \gamma_\beta(r) - \gamma_\beta^2(r) = 0, \quad (11)$$

which give an obvious result for the unpaired spin(s):

$$D(r) = (\gamma_\alpha - \gamma_\beta)^2(r). \quad (12)$$

Thus, the unpaired spin(s) has already been incorporated in our  $D(r)$  as a part of the odd electron density. It is the first term of the right-hand side of Eq. (10) that represents the splitting of paired electrons themselves.

With the distribution function  $D(r)$  at hand, we can readily calculate the populations of the odd electrons on given atomic sites in a given molecule. Thus,  $D(r)$  is expanded over the atomic orbitals  $\{\chi_t(r)\}$ :

$$D(r) = \sum_t \sum_u d_{tu} \chi_t^*(r) \chi_u(r). \quad (13)$$

After the manner of Mulliken [8], the atomic-orbital population of odd electrons can be defined by

$$D_t = \sum_u d_{tu} \langle \chi_t | \chi_u \rangle. \quad (14)$$

The gross population on atom A is simply a sum

$$D_A = \sum_i^A D_i. \quad (15)$$

Needless to say, the total sum of  $D_A$ 's over the atoms involved should be finite:

$$\sum_A D_A = \text{Tr } D(r) \leq N, \quad (16)$$

where  $N$  is the total number of electrons.

### 3. Applications to Some Specific Orbital Theories

Prior to the application of the theory to existing molecules, we will here derive the expressions of  $D(r)$  pertinent to a few typical orbital theories. It is hoped that such expressions will assist a proper understanding of the features of numerical results for molecules which will be presented in Sect. 4.

#### 3.1. Doubly Occupied Orbital CI Wavefunction

For the sake of simplicity, we choose the configuration-interaction (CI) wavefunction composed of doubly occupied (DO) spatial orbitals [9]

$$\Psi = C_0 \Phi_0 + \sum_i^{\text{occ}} \sum_a^{\text{unocc}} C_i^a \Phi_{ii}^{aa}, \quad (16)$$

where  $\Phi_0$  stands for the ground configuration and  $\Phi_{ii}^{aa}$  is a Slater determinant having two ( $\alpha$ - and  $\beta$ -spin) virtual orbitals  $\phi_a$  in place of two occupied ones  $\phi_i$ . From Eq. (7),  $D(r)$  becomes

$$D(r) = 4 \sum_i^{\text{occ}} \left[ \sum_a^{\text{unocc}} (C_i^a)^2 - \left\{ \sum_a^{\text{unocc}} (C_i^a)^2 \right\}^2 \right] \phi_i^*(r) \phi_i(r) \\ + 4 \sum_a^{\text{unocc}} \left[ \sum_i^{\text{occ}} (C_i^a)^2 - \left\{ \sum_i^{\text{occ}} (C_i^a)^2 \right\}^2 \right] \phi_a^*(r) \phi_a(r). \quad (17)$$

In the simplest DOCI theory, we only consider the highest occupied (HO) and the lowest vacant (LV) MO's as the  $\phi_i$  and  $\phi_a$ , respectively. Further, if we reoptimize  $\phi_{\text{HO}}$  and  $\phi_{\text{LV}}$  simultaneously with  $C_{\text{HO}}^{\text{LV}}$ , the optimized double-configuration (ODC) version [10] will be obtained. In either case, Eq. (17) is simplified into

$$D(r) = 4(C_{\text{HO}}^{\text{LV}})^2 [1 - (C_{\text{HO}}^{\text{LV}})^2] [\phi_{\text{HO}}^*(r) \phi_{\text{HO}}(r) + \phi_{\text{LV}}^*(r) \phi_{\text{LV}}(r)]. \quad (18)$$

The expression is useful for the consideration of the diradical character of singlet molecules, as will be discussed later.

#### 3.2. Singlet UHF Wavefunction

By use of the corresponding orbitals [11], the unrestricted Hartree-Fock (UHF)

wavefunction for a singlet state can be written as [12]

$$\Psi = |a_1 \bar{b}_1 a_2 \bar{b}_2 \dots|, \quad (19)$$

where the bar denotes  $\beta$ -spin orbitals. The corresponding orbitals satisfy the following relation :

$$\langle a_k | b_l \rangle = S_k \delta_{kl}. \quad (20)$$

Since the UHF wavefunction is a single Slater determinant,  $D(r)$  should consist only of the spin density term. Thus,

$$D(r) = (\gamma_\alpha - \gamma_\beta)^2(r) = \sum_k \{a_k^*(r)a_k(r) + b_k^*(r)b_k(r) - S_k[a_k^*(r)b_k(r) + b_k^*(r)a_k(r)]\}. \quad (21)$$

Equation (21) suggests separate contributions of  $a_k(r)$  and  $b_k(r)$  to the  $D(r)$  function. The spatial splitting of the  $\alpha$ - and  $\beta$ -spin electrons is thus apparent in this case.

### 3.3. Generalized Valence Bond (GVB) Wavefunction

The GVB wavefunction [5] has also been applied to the studies of diradical species [13]. It is generally written as

$$\Psi = \mathcal{A} a_1(1)b_1(2)(\alpha\beta - \beta\alpha)a_2(3)b_2(4)(\alpha\beta - \beta\alpha) \dots \quad (22)$$

where  $\mathcal{A}$  is an antisymmetrizing operator. The orbitals  $a_k$  and  $b_k$  constitute a pair, and every pair is orthogonal to others, i.e.,  $\langle a_k | a_l \rangle = \langle b_k | b_l \rangle = \langle a_k | b_l \rangle = 0$  ( $k \neq l$ ).

Use of Eq. (22) leads to

$$D(r) = \sum_k \frac{1 - S_k^2}{(1 + S_k^2)^2} \{a_k^*(r)a_k(r) + b_k^*(r)b_k(r) - S_k[a_k^*(r)b_k(r) + b_k^*(r)a_k(r)]\}. \quad (23)$$

Aside from the factor  $(1 - S_k^2)/(1 + S_k^2)^2$ , Eq. (23) is identical in form with Eq. (21). It is likely that the UHF and GVB theories provide similar distribution patterns of split spins, insofar as the spatial orbitals used in these theories do not differ appreciably.

## 4. Numerical Examples

In this section, we will apply the present theory to some existing three-atom species and to the transition state of concerted reactions.

### 4.1. Triatomic Species

A few triatomic three-electron  $\pi$  systems (together with their two- and four-electron family systems) were chosen as examples. They include allyl radical  $C_3H_5$  ( $C_3H_5^+$ ,  $C_3H_5^-$ ), formyl radical  $HCO_2$  ( $HCO_2^+$ ,  $HCO_2^-$ ), nitric oxide  $NO_2$  ( $NO_2^+$ ,  $NO_2^-$ ) and ozone cation  $O_3^+$  ( $O_3^{2+}$ ,  $O_3$ ). For all of these species, various types of wavefunctions were calculated on a common basis set by Linnett *et al.* [14]. Among others, their RHF, full-CI and Heitler–London (HL) wavefunctions will be adopted for our

**Table 1.** Odd  $\pi$  electron populations in some ground-state triatomic species

Wave-function	$C_3H_5$		$HCO_2$		$NO_2$		$O_3^+$	
	$C_t^a$	$C_c^b$	O	C	O	N	$O_t^a$	$O_c^b$
Two-electron systems								
RHF	0	0	0	0	0	0	0	0
CI	0.164	0.141	0.239	0.158	0.214	0.162	0.393	0.306
HL	0.296	0.593	0.351	0.701	0.398	0.795	0.444	0.889
Three-electron systems								
RHF	0.500	0	0.500	0	0.500	0	0.500	0
CI	0.663	0.326	0.632	0.265	0.675	0.350	0.859	0.719
HL	0.871	0.742	0.909	0.817	0.939	0.878	0.968	0.936
Four-electron systems								
RHF	0	0	0	0	0	0	0	0
CI	0.188	0.141	0.295	0.133	0.295	0.163	0.411	0.297
HL	0.296	0.593	0.351	0.701	0.398	0.795	0.444	0.889

<sup>a</sup> Terminal atoms.<sup>b</sup> Central atom.**Table 2.** Overlap integrals between the atomic orbitals<sup>a</sup>

	$O_3$	$NO_2$	$HCO_2$	$C_3H_5$
	$O_1-O_2-O_3$	$O_1-N_2-O_3$	$O_1-C_2-O_3$	$C_1-C_2-C_3$
$\langle \chi_1   \chi_2 \rangle$	0.12179	0.17005	0.21130	0.25995
$\langle \chi_1   \chi_3 \rangle$	0.00862	0.01137	0.00865	0.03887

<sup>a</sup> These overlap integrals are common to the ionized states of given systems.

present purpose. The populations of odd  $\pi$  electrons calculated therefrom are summarized in Table 1.

The salient points noticed in Table 1 are the following:

- 1) The odd electron populations given by the HL method is always larger than those given by the CI treatment, as is expected. The populations obtained from the RHF wavefunction reflect the unpaired spin term, Eq. (12), only.
- 2) In the CI case, the results for the two- and four-electron systems nearly coincide with each other. In either system, the splitting of pairs is due almost exclusively to that of the highest occupied MO.
- 3) In both the CI and HL treatments, all the triatomic species examined have a fairly large odd electron density on their central atoms.
- 4) Roughly speaking, the population of odd electrons increases with the decreasing overlap  $\langle \chi_a | \chi_b \rangle$  between the neighboring atomic orbitals (Table 2).
- 5) For  $O_3^+$  the total population (2.437) calculated by the CI method exceeds 2, indicative of a partial triradical character.

As has been shown in the above examples,  $D(r)$  could be used for the comparisons of the features of various model wavefunctions. For preciser displays of these features, it will be more advantageous to use contour density maps of  $D(r)$ .

#### 4.2. Concerted Reactions

We here treat two types of cycloaddition reactions. One is a  $(2_s + 2_s)$  cyclodimerization of ethylene, which is a typical orbital-symmetry forbidden reaction. The other is a  $(2_s + 2_s + 2_s)$  allowed reaction of three ethylenes to give cyclohexane. The wavefunctions of these two concerted reactions were traced by Porter and Raff [15] and by Wilson and Wang [16], respectively. The latter workers noted that in forbidden reactions the occupation numbers of the natural orbitals normally show a crossing between the orbitals of high and low occupation numbers but that no such crossing takes place in allowed reactions. The crossing should naturally be accompanied by the generation of odd electrons.

The populations of odd electrons on a carbon atom at the transition states were calculated by use of the occupation numbers given by Wilson and Wang [16]. The results were 0.55 and 0.2 for the  $(2_s + 2_s)$  and  $(2_s + 2_s + 2_s)$  reactions, respectively. In the allowed reaction, apparently more electrons are kept paired during the course of bond interchange.

#### 4.3. Diradical Character

In connection with the foregoing argument, it seems particularly interesting to consider the diradical character of singlet species. The diradical character is believed to show up also in the intermediary state of the Woodward-Hoffmann forbidden reactions [4].

Hayes and Siu [17] defined the diradical character by

$$y = 2(C_{\text{HO}}^{\text{LV}})^2, \quad (24)$$

where  $(C_{\text{HO}}^{\text{LV}})^2$  is the weight of the doubly excited configuration due to the electron transition from the highest occupied to the lowest unoccupied molecular orbital. Although Eq. (24) can well be understood intuitively, it is yet unsatisfactory on the following three grounds:

- 1) Virtual molecular orbitals to be made use of in the CI calculation can always be transformed unitarily among them [18], so that no uniqueness can be attached to the values of  $(C_{\text{HO}}^{\text{LV}})^2$ .
- 2) The existence of more than two odd electrons as in a triradical should not be precluded in general cases.
- 3) It provides no information at all about the distribution of odd electrons.

All these ambiguities can be removed by use of our  $D(r)$ . To clarify the situation, let us consider the  $D(r)$  function in the DOCI approximation, Eq. (18). Obviously, the trace of  $D(r)$

$$\text{Tr } D(r) = 8(C_{\text{HO}}^{\text{LV}})^2 [1 - (C_{\text{HO}}^{\text{LV}})^2] \quad (25)$$

satisfies

$$0 \leq \text{Tr } D(r) \leq 2, \quad (26)$$

as long as

$$0 \leq (C_{\text{HO}}^{\text{LV}})^2 \leq \frac{1}{2}. \quad (27)$$

Hence, one half of  $\text{Tr } D(r)$  must correspond to the diradical character

$$y_D = \left(\frac{1}{2}\right) \text{Tr } D(r). \quad (28)$$

The  $y_D$  here defined is always larger than or equal to the Hayes–Siu quantity, Eq. (24), so far as the condition (27) is satisfied. The diradical characters of the various two-electron systems obtained by the full CI treatment were 0.546, 0.295, 0.318 and 0.235 for  $\text{O}_3^{2+}$ ,  $\text{NO}_2^+$ ,  $\text{HCO}_2^+$  and  $\text{C}_3\text{H}_3^+$ , respectively.

The diradical character which can be defined likewise from Eq. (17) should be more general than that based on Eq. (18). The UHF and GVB expressions, Eqs. (21) and (23), may also be used. In either of these latter formalisms, it is apparent that the diradical character of a singlet state stems from the splittings of the corresponding orbital pairs. Clearly, the diradical character should be the greater, the smaller the orbital overlap  $S_k$  is.

## 5. Concluding Remarks

We have defined a density function  $D(r)$  which describes the distribution of odd electrons in molecules. The definition is based on the spinless first-order density matrix, so that it precludes all the uncertainties originating from the arbitrariness in selecting the basis sets, virtual orbitals and configurations. Use of the density function sheds light on the nature of thermal reactions as well as isolated molecules. It is emphasized that the traditional term “diradical” is a physically acceptable one. Further, in the sense that  $D(r)$  expresses the distribution of electrons still capable of forming a new pairing, it could also be taken as a conceptual generalization of Coulson’s free valence [19].

Although we have defined  $D(r)$  for the ground state only, it may also be applicable to excited states. However, in the virtual orbital approximation, excited singlet and triplet states of homopolar molecules cannot be distinguished; the former state should be zwitterionic [3] (not necessarily identical with zwitterion itself) while the latter, diradical. In such a case, recourse to the second-order density matrix would be unavoidable.

## References

1. Roothaan, C. C. J.: *Rev. Mod. Phys.* **23**, 69 (1951); **32**, 179 (1960)
2. Sinanoğlu, O.: *J. Chem. Phys.* **36**, 706 (1962)
3. Salem, L., Rowland, C.: *Angew Chem. Intern. Ed.* **11**, 92 (1972)
4. Woodward, R. B., Hoffmann, R.: *The conservation of orbital symmetry*. New York: Academic Press 1970



5. Hunt, W. J., Hay, P. J., Goddard III, W. A.: *J. Chem. Phys.* **57**, 738 (1972)
6. Okada, T., Fueno, T.: *Bull. Chem. Soc. Japan* **48**, 2025 (1975); **49**, 1524 (1976)
7. Löwdin, P.-O.: *Phys. Rev.* **97**, 1474 (1955); **97**, 1490 (1955)
8. Mulliken, R. S.: *J. Chem. Phys.* **23**, 1833 (1955); **23**, 1841 (1955); **23**, 2338 (1955)
9. Weinhold, F., Wilson Jr., E. B.: *J. Chem. Phys.* **46**, 2752 (1967)
10. Das, G., Wahl, A. C.: *J. Chem. Phys.* **44**, 87 (1966)
11. Amos, A. T., Hall, G. G.: *Proc. Roy. Soc. (London)* **A263**, 483 (1961)
12. Koutecký, J.: *J. Chem. Phys.* **46**, 2443 (1967)
13. Goddard III, W. A., Dunning Jr., T. H., Hay, P. J.: *Acc. Chem. Res.* **6**, 368 (1973)
14. Hirst, D. M., Linnett, J. W.: *J. Chem. Soc.* 1035 (1962); 3844 (1962); 1068 (1963); Hirst, D. M., Linnett, J. W.: *J. Chem. Phys.* **43**, S74 (1965); Kirchhoff, W. H., Farron, J., Linnett, J. W.: *J. Chem. Phys.* **42**, 1410 (1965); Gould, R. D., Linnett, J. W.: *Trans. Faraday Soc.* **59**, 1001 (1963)
15. Porter, R. N., Porter, L. M.: *J. Chem. Phys.* **50**, 5216 (1969)
16. Wilson, E. B., Wang, P. S. C.: *Chem. Phys. Letters* **15**, 400 (1972)
17. Hayes, E. F., Siu, A. K. Q.: *J. Am. Chem. Soc.* **93**, 2090 (1971)
18. Kelly, H. P.: *Phys. Rev.* **136**, B896 (1964); Huzinaga, S., Arnau, C.: *Phys. Rev.* **1**, 1285 (1970); *J. Chem. Phys.* **54**, 1948 (1971); Hunt, W. J., Goddard III, W. A.: *Chem. Phys. Letters* **3**, 414 (1969); Morokuma, K., Iwata, S.: *Chem. Phys. Letters* **16**, 192 (1972)
19. Burkitt, F. H., Coulson, C. A., Longuet-Higgins, H. C.: *Trans. Faraday Soc.* **47**, 553 (1951)

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