

# Symmetry Properties of One- and Two-Electron Correlation Functions in the Many-Electron Theory of Atoms and Molecules\*

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(Received 11 July 1966)

The symmetry properties of the many-electron wavefunctions containing unlinked clusters are shown to follow directly from those of the wavefunctions with one- and two-electron correlations occurring one at a time for both closed- and nonclosed-shell states. The separate calculation and symmetry properties of distinct pair functions in general nonclosed- and closed-shell states are discussed. The symmetry considerations carry over to the localized-orbital+localized-pair-function descriptions.

## I. INTRODUCTION

THE symmetry properties of the many-electron wavefunctions<sup>1-9</sup> are related quite simply to the symmetry properties of the spin orbitals, one-electron correlation functions, and pair correlation functions from which the wavefunctions are constructed. The symmetry properties follow rigorously from the methods of derivation, the "method of partial orthogonalizations"<sup>6</sup> for closed-shell states and in each order of perturbation theory<sup>8,10,11</sup> (for closed- and nonclosed-shell states) once the symmetry properties of the uncorrelated  $\phi_0$  part are specified. The properties of the first-order pair functions  $u_{ij}^{(1)}$  for closed shells and the transformation from "*B*(*ij*)-type pairs" to "irreducible pairs" have been given previously.<sup>2,10,11</sup> The transformations of the "pairs to all orders"  $u_{ij}$  in the closed-shell variational theory have also been discussed<sup>2,6</sup> as well as the spin properties in four-electron systems.<sup>12</sup>

In this paper (a) we show how the symmetry properties of the many-electron wavefunctions containing unlinked clusters ( $\chi'_s$ ) follow from those of the wavefunctions with one- and two-electron correlations occurring one at a time ( $\chi_s$ ) for both closed- and

open-shell states; (b) we discuss further the symmetry and separate calculation of distinct pair functions in general nonclosed- and closed-shell states; and (c) we also show that these symmetry considerations carry over to the localized-orbital + localized-pair-function descriptions.

## II. SYMMETRY PROPERTIES OF PAIR FUNCTIONS AND CLOSED-SHELL STATES

The "many-electron theory" approximate wavefunction for a closed-shell state is given by<sup>1</sup>

$$\phi_0 + \chi'_s = \mathcal{Q} \left[ (12 \cdots N) \left( 1 + 2^{-1/2} \sum_{1 \leq i < j}^N \frac{u_{ij}}{(ij)} + 2^{-1} \sum_{i < j}^N \sum_{k < l}^N \frac{u_{ij} u_{kl}}{(ijkl)} + \cdots \right) \right]. \quad (1)$$

$(i < k; \text{ both } i, j \neq k, l)$

The 1, 2,  $\dots$ ,  $N$  denote spin orbitals, the  $u_{ij}$  denote pair correlation functions, and  $\mathcal{Q}$  denotes the anti-symmetrization operator. When does  $\phi_0 + \chi'_s$  (especially the parts of  $\chi'_s$  with products of two or more pair functions) have the same symmetry properties as the exact wavefunction ( $^1S$  for atoms)? Assuming that  $\phi_0$ ,

$$\phi_0 = \mathcal{Q}(12 \cdots N) \quad (2)$$

has the correct symmetry, we demonstrate the following result.

$\phi_0 + \chi'_s$  has the same symmetry properties as the exact wavefunction if, and only if, the pair functions  $u_{ij}$  have the same symmetry properties as the anti-symmetrized pairs of spin orbitals they replace. Thus, for example, the  $(2p)^2$  pairs for neon satisfy:

- (a)  $(u_{2p,\alpha,2p,\beta} + u_{2p,\alpha,2p,\beta} + u_{2p,\alpha,2p,\beta})/\sqrt{3}$  is a  $^1S$  function;
- (b)  $u_{2p,\alpha,2p,\alpha}$  is a  $^3P$  function with  $M_L = M_S = 1$ ;
- (c)  $(u_{2p,\alpha,2p,\beta} + u_{2p,\beta,2p,\alpha})/\sqrt{2}$  is the  $(M_L = 1; M_S = 0)$  component of the  $^3P$  in (b) above; and so forth.

\* Supported by a grant from the National Science Foundation.  
† Part of this work was done under a National Science Foundation Postdoctoral Fellowship at Yale in 1964.

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<sup>1</sup> O. Sinanoğlu, *J. Chem. Phys.* **36**, 706 (1962).

<sup>2</sup> O. Sinanoğlu, *J. Chem. Phys.* **36**, 3198 (1962).

<sup>3</sup> O. Sinanoğlu and D. F. Tuan, *J. Chem. Phys.* **38**, 1740 (1963).

<sup>4</sup> D. F. Tuan and O. Sinanoğlu, *J. Chem. Phys.* **41**, 2677 (1964).

<sup>5</sup> V. McKoy and O. Sinanoğlu, *J. Chem. Phys.* **41**, 2689 (1964).

<sup>6</sup> O. Sinanoğlu, *Advan. Chem. Phys.* **6**, 315 (1964).

<sup>7</sup> H. J. Silverstone and O. Sinanoğlu, in *Modern Quantum Chemistry—Istanbul Lectures*, O. Sinanoğlu, Ed. (Academic Press Inc., New York, 1965), Pt. 2, Interactions.

<sup>8</sup> H. J. Silverstone and O. Sinanoğlu, *J. Chem. Phys.* **44**, 1899 (1966).

<sup>9</sup> H. J. Silverstone and O. Sinanoğlu, *J. Chem. Phys.* **44**, 3608 (1966).

<sup>10</sup> O. Sinanoğlu, *Phys. Rev.* **122**, 493 (1961).

<sup>11</sup> O. Sinanoğlu, *Proc. Roy. Soc. (London)* **A260**, 379 (1961).

<sup>12</sup> H. B. Levine, M. Geller, and H. S. Taylor, *J. Chem. Phys.* **40**, 595 (1964).

To formulate our theorem more precisely, we introduce some of the notation and results of group theory.<sup>13</sup> Let  $G$  denote the group of (space and spin) coordinate transformations  $R$  which commute with the electronic Hamiltonian. That  $\psi$  is the exact wavefunction for a closed-shell state implies

$$R\psi = \psi. \tag{3}$$

We assume that the  $N$  spin orbitals form a basis for a unitary representation  $\Gamma$  of  $G$ ;

$$R | k \rangle = \sum_{j=1}^N \Gamma_{jk}(R) | j \rangle, \quad (k=1, 2, \dots, N), \tag{4}$$

and that  $\phi_0$  (like  $\psi$ ) is also invariant under all  $R$  in  $G$

$$R\phi_0 = \mathcal{G} \{ (R1) (R2) \dots (RN) \} = (\det | \Gamma_{ij}(R) |) \phi_0 = \phi_0. \tag{5}$$

[Since the "many-electron theory"  $\phi_0$  is a Hartree-Fock determinant of symmetry orbitals (e.g., the angular dependence of the orbitals for atoms is given by single spherical harmonics), Eqs. (4) and (5) are automatically satisfied.] Note that we use a single symbol  $R$  to represent the change of coordinates of a single particle, the corresponding  $N$ -electron transformation, and the transformation induced on the spin orbitals.

From Eqs. (1), (3), and (5), one sees that  $R\chi'_s$  must equal  $\chi'_s$  for all  $R$  in  $G$ , so that, given Eqs. (1)-(5), a

mathematical statement of the theorem described above is

*Theorem:*  $R\chi'_s = \chi'_s$ , for all  $R$  in  $G$ , if, and only if,

$$R\hat{u}_{ij} = \sum_{1 \leq k < l \leq N} [\Gamma_{ki}(R)\Gamma_{lj}(R) - \Gamma_{kj}(R)\Gamma_{li}(R)] \hat{u}_{kl}; \tag{6}$$

( $1 \leq i < j \leq N$ ).

The proof is greatly simplified by the use of second quantized formalism.<sup>14,15</sup> Denote by  $a_k^\dagger$  and  $a_k$  the creation and annihilation operators for Spin Orbital  $k$ . Similarly, denote by  $b_{ij}^\dagger$  the creation operator for the pair function  $\hat{u}_{ij}$ . If  $\hat{u}_{ij}$  is defined in configuration-interaction language by

$$\hat{u}_{ij} = \sum_{N < k < l < \infty} C_{kl}{}^{ij} B(kl), \tag{7}$$

$$B(kl) = [k(\mathbf{x}_1)l(\mathbf{x}_2) - l(\mathbf{x}_1)k(\mathbf{x}_2)]/\sqrt{2}, \tag{8}$$

then  $b_{ij}^\dagger$  is given by

$$b_{ij}^\dagger = \sum_{N < k < l < \infty} C_{kl}{}^{ij} a_k^\dagger a_l^\dagger. \tag{9}$$

[Note that  $\hat{u}_{ij}$  is taken to be one-electron orthogonal<sup>1</sup> to the  $N$  occupied spin orbitals, i.e.,  $\hat{u}_{ij}$  consists entirely of "double excitations," as is implied by the lower limits of the summation indices in Eqs. (7) and (9).] Then,  $\phi_0$  and  $\chi'_s$  are given in second quantized notation by

$$\phi_0 = a_1^\dagger a_2^\dagger \dots a_N^\dagger | 0 \rangle, \tag{10}$$

$$\phi_0 + \chi'_s = (1 + \sum_{1 \leq i < j} b_{ij}^\dagger a_j a_i + \sum_{1 \leq i < j} \sum_{1 \leq k < l} b_{ij}^\dagger a_j a_i b_{kl}^\dagger a_l a_k + \dots) a_1^\dagger a_2^\dagger \dots a_N^\dagger | 0 \rangle. \tag{11a}$$

( $i < k; i, j \neq k, l$ )

Equation (11a) can be written in the compact form

$$\phi_0 + \chi'_s = e^U \phi_0, \tag{11b}$$

where

$$U = \sum_{1 \leq i < j} b_{ij}^\dagger a_j a_i, \tag{12}$$

and  $| 0 \rangle$  denotes the "vacuum" state.

Now if  $R(\phi_0 + \chi'_s) = \phi_0 + \chi'_s$ , then since  $R\phi_0 = \phi_0$  and  $Re^U \phi_0 = \exp(RUR^{-1})R\phi_0 = \exp(RUR^{-1})\phi_0$ ,

$$R(\phi_0 + \chi'_s) - (\phi_0 + \chi'_s) = (Re^U - e^U)\phi_0 = [\exp(RUR^{-1}) - e^U]\phi_0 = 0, \tag{13}$$

which [along with Eqs. (4), (9), and the absence of  $(b_{ij}^\dagger)^2$  and  $(b_{ij}^\dagger b_{ik}^\dagger)$  terms<sup>15b</sup>] implies that

$$(RUR^{-1} - U)\phi_0 = 0. \tag{14}$$

<sup>13</sup> V. Heine, *Group Theory in Quantum Mechanics* (Pergamon Press, Inc., New York, 1960).  
<sup>14</sup> L. D. Landau and E. M. Lifshitz, *Quantum Mechanics* (Addison-Wesley Publ. Co., Inc., Reading, Mass., 1958).  
<sup>15</sup> (a) H. Primas, in *Modern Quantum Chemistry—Istanbul Lectures*, O. Sinanoğlu, Ed. (Academic Press Inc., New York, 1965), Pt. 2, Interactions. (b) In the power series expansion of  $e^U$ , terms such as  $(b_{ij}^\dagger a_j a_i)^2$  and  $(b_{ij}^\dagger a_j a_i)(b_{ik}^\dagger a_k a_i)$  vanish. See, for instance: Ref. 15(a); F. Coester, *Nucl. Phys.* **7**, 421 (1958); F. Coester and H. Kummel, *ibid.* **17**, 477 (1960).

So clearly we must focus our attention on the transformation properties of  $U$ :

$$RUR^{-1} - U = \sum_{i < j}^N (Rb_{ij}^\dagger R^{-1})(Ra_j R^{-1})(Ra_i R^{-1}) - \sum_{k < l}^N b_{kl}^\dagger a_l a_k. \tag{15}$$

From Eq. (4),

$$Ra_k^\dagger R^{-1} = \sum_{j=1}^N \Gamma_{jk}(R) a_j^\dagger, \quad (k=1, 2, \dots, N) \tag{16}$$

$$Ra_k R^{-1} = \sum_{j=1}^N \Gamma_{jk}^*(R) a_j, \quad (k=1, 2, \dots, N) \tag{17}$$

[where (\*) denotes complex conjugate] so that

$$RUR^{-1} - U = \sum_{k < l}^N \left\{ \sum_{i < j}^N (Rb_{ij}^\dagger R^{-1}) [\Gamma_{ij}^*(R) \Gamma_{ki}^*(R) - \Gamma_{kj}^*(R) \Gamma_{li}^*(R)] - b_{kl}^\dagger \right\} a_l a_k. \tag{18}$$

Both  $k$  and  $l$  are occupied in  $\phi_0$ , but no spin orbital appearing in the expansion of  $b_{kl}^\dagger$  [Eq. (9)] is occupied in  $\phi_0$ . Thus, for Eq. (14) to hold, the coefficient of  $a_l a_k$  in Eq. (18) must vanish:

$$\sum_{i < j}^N (Rb_{ij}^\dagger R^{-1}) [\Gamma_{ij}^*(R) \Gamma_{ki}^*(R) - \Gamma_{kj}^*(R) \Gamma_{li}^*(R)] - b_{kl}^\dagger = 0, \quad (1 \leq k < l \leq N). \tag{19}$$

Because the representation is (by hypothesis) unitary, Eq. (19) is equivalent to

$$Rb_{mn}^\dagger R^{-1} = \sum_{k < l}^N [\Gamma_{km}(R) \Gamma_{ln}(R) - \Gamma_{lm}(R) \Gamma_{kn}(R)] b_{kl}^\dagger, \quad (m < n \leq N), \tag{20}$$

which is just the second quantized version of Eq. (6). Thus we have proven the necessity of Eq. (6).

The sufficiency is proved by noting that Eq. (6) is equivalent [because of Eqs. (18)-(20)] to

$$RUR^{-1} = U, \tag{21}$$

which implies Eq. (13) is valid. Q.E.D.

Another way of stating the above theorem is that  $\chi'$  has the right symmetry properties if, and only if,  $\chi$  (no unlinked clusters) has. Also, the theorem can be applied to other types of wavefunctions which can be written as in Eq. (1) or as in a special case of Eq. (1) such as to the so-called "separated-pair theory"<sup>16</sup> wavefunction.

Perhaps it should also be remarked that the terminology "unlinked cluster" used in this work has an entirely different meaning from the same words that occur in Goldstone perturbation theory.<sup>17</sup> In the Goldstone terminology, an "unlinked part" in a graph contributing to the wavefunction refers to "any part of a graph which is completely disconnected from the rest of the graph and which has no external lines attached..."<sup>17</sup> Here "unlinked cluster" refers to terms

in the wavefunction which are *analogous* to graphs in the Goldstone theory whose "disconnected parts" would have external lines, viz., graphs *without unlinked parts*.

### III. SYMMETRY PROPERTIES OF NONCLOSED-SHELL STATES

The discussion of symmetry properties of nonclosed-shell states is complicated by degeneracy and a multi-configurational  $\phi_0$ . Apart from the symmetry properties of  $\phi_0$  and the one-electron correlation functions, the main change in the relationship of the symmetry properties of the pair functions to those of  $\phi_0 + \chi$  is that Eq. (6) is a sufficient but not a necessary condition.

In general,  $\psi$  is one of  $n$  degenerate exact wavefunctions ( $\psi_1 \equiv \psi, \psi_2, \dots, \psi_n$ ) transforming irreducibly (except for accidental degeneracy) under  $G$ :

$$R\psi_j = \sum_{i=1}^n \Lambda_{ij}(R) \psi_i. \tag{22}$$

[For atoms,  $n = (2L+1)(2S+1)$ , and the  $\psi_i$  might differ, say, in only the quantum numbers  $M_L$  and  $M_S$ .] One must discuss the symmetry properties of all  $n\psi_i$  together.

The "many-electron theory" nonclosed-shell approxi-

<sup>16</sup> A. C. Hurley, J. E. Lennard-Jones, and J. A. Pople, Proc. Roy. Soc. (London) **A220**, 446 (1953).

<sup>17</sup> J. Goldstone, Proc. Roy. Soc. (London) **A239**, 267 (1957).

mate wavefunction<sup>7,9</sup> is given by

$$\phi_0 + \chi'_{d} = \sum_{K=1}^{\binom{M}{N}} C_K (\Delta_K + \chi'_K), \tag{23}$$

$$\Delta_K = \mathcal{A}(k_1 k_2 \cdots k_N), \tag{24}$$

$$\begin{aligned} \chi'_K = \mathcal{A} \left\{ (k_1 k_2 \cdots k_N) \left[ \sum_{a=1}^N \frac{\hat{f}_{k_a}^{(P)K}}{(k_a)} \left( 1 + 2^{-1/2} \sum_{1 \leq b < c \leq N} \frac{\hat{u}_{k_b k_c}^K}{(k_b k_c)} + 2^{-1} \sum_{b < c} \sum_{d < e} \frac{\hat{u}_{k_b k_c}^K \hat{u}_{k_d k_e}^K}{(k_b k_c k_d k_e)} + \cdots \right) \right. \right. \\ \quad (b, c \neq a) \quad (b < d; b, c \neq d, e; b, c, d, e \neq a) \\ + \sum_{1 \leq a < b \leq N} \sum_{m=1}^M \frac{m \hat{f}_{k_a k_b}^{K; m}}{(k_a k_b)} \left( 1 + 2^{-1/2} \sum_{i < j} \frac{\hat{u}_{ij}^K}{(ij)} \right. \\ \quad (m \neq k_1, k_2, \dots, k_N) \quad (i, j = k_1, k_2, \dots, k_N, m; \text{ but } \neq k_a, k_b) \\ + 2^{-1} \sum_{i < j} \sum_{l < p} \frac{\hat{u}_{ij}^K \hat{u}_{lp}^K}{(ijlp)} + \cdots \left. \right) \\ \quad (i < l; i, j \neq l, p; i, j, l, p = k_1, k_2, \dots, k_N, m; \text{ but } \neq k_a k_b) \\ \left. + 2^{-1/2} \sum_{1 \leq a < b \leq N} \frac{\hat{u}_{k_a k_b}^K}{(k_a k_b)} + 2^{-1} \sum_{a < b} \sum_{c < d} \frac{\hat{u}_{k_a k_b}^K \hat{u}_{k_c k_d}^K}{(k_a k_b k_c k_d)} + \cdots \right] \}. \tag{25} \\ (a < c; a, b \neq c, d) \end{aligned}$$

Accordingly, there are  $n$  such approximate wavefunctions,  $\phi_{0,i} + \chi'_{d,i}$ , ( $i=1, 2, \dots, m$ ), ( $\phi_{0,1} + \chi'_{d,1} \equiv \phi_0 + \chi'_d$ ). [The  $\hat{f}_i^{(P)K}$  represent spin, symmetry and/or configuration polarizations of the spin orbitals, the  $\hat{f}_{ij,k}^K$  semi-internal correlations, and the  $\hat{u}_{ij}^K$  pair correlations. The reader is referred to Refs. 8 and 9 for details.] We develop below some general conditions under which the  $\phi_{0,i} + \chi'_{d,i}$  will also transform (like the exact  $\psi_i$ ) according to Eq. (22).

Consider first the spin orbitals and  $\phi_0$ . The spin orbitals are restricted<sup>7-9</sup> to be symmetry spin orbitals, i.e., they transform irreducibly under  $G$ :

$$R |k\rangle = \sum_j^{(\lambda)} \Gamma_{jk}^{(\lambda)}(R) |j\rangle. \tag{26}$$

In Eq. (26),  $k$  belongs to the irreducible representation

$\lambda$ , and the summation is only over those spin orbitals  $j$  which belong to the same irreducible representation. The number of spin orbitals in  $\Delta_k$  from each irreducible representation defines the *configuration* of  $\Delta_k$ . Under  $G$  a  $\Delta_k$  is transformed only into determinants of the same configuration. Consequently, symmetry may dictate the relative values of the  $C_K$  for determinants of the same configuration. How to determine the relative values of the  $C_K$  for a single configuration is discussed in elementary textbooks on atomic structure and is not considered here. (The relative values of the  $C_K$  for different configurations are determined<sup>7-9</sup> by the variational principle.) See Eq. (65) of Ref. (9) for a formal illustration.

Next consider the one-electron correlation functions. Denote the part of  $\chi'_{d,i}$  containing only single  $\hat{f}$ 's by  $\chi_{f,i}$ :

$$\chi_{f,i} \equiv \sum_K C_K \mathcal{A} \left\{ (k_1 k_2 \cdots k_N) \left[ \sum_{a=1}^N \frac{\hat{f}_{k_a}^{(P)K}}{(k_a)} + \sum_{1 \leq a < b} \sum_{l=1}^M \frac{l \hat{f}_{k_a k_b}^{K; l}}{(k_a k_b)} \right] \right\}. \tag{27} \\ (l \neq k_1, k_2, \dots, k_N)$$

It is a simple vector-coupling problem to determine the correct symmetry properties for the  $\hat{f}$ 's. It does not seem possible, especially in view of the "polarizing" nature of the  $\hat{f}_k^{(P)K}$ , to relate the symmetry properties of the  $\hat{f}$ 's to the spin orbitals they replace. Note, however, that there is no loss of generality to treat  $\chi_{f,i}$  configuration by configuration and to determine together the symmetry properties of all the  $\hat{f}^K$  arising from determinants of a single configuration. A formal illustration of the symmetry properties of  $\hat{f}$ 's is given by Eqs. (67)–(69) of Ref. (9).

The symmetry properties of the pair functions can be related, as in the closed-shell case, directly to those

of the spin orbitals they replace. Consider first the simplified approximate wavefunction  $\phi_0 + \chi'_s$ —the anonymous-parentage case.<sup>7,9</sup>  $\phi_0 + \chi'_s$  can be written in second quantized notation as

$$\phi_{0,i} + \chi'_{s,i} = e^U (\phi_{0,i} + \chi_{f,i}), \tag{28}$$

where

$$U = \sum_{1 \leq i < j} b_{ij}^\dagger a_j a_i. \tag{29}$$

Note that  $U$  contains all pairs from the set of  $M$  spin orbitals ( $M \geq N =$  number of electrons), and that the same set of pair functions  $\hat{u}_{ij} = \hat{u}_{ij}^{K \leftarrow b} \hat{u}_{ij}^\dagger$  [Eq. (9)]

( $K$  is irrelevant in the anonymous-parentage approximation<sup>9</sup>) is used for all  $n\chi'_{s,i}$ . From the proof of the theorem in the closed-shell case, in particular Eqs. (11)–(21), we see that the following result is valid: If the coefficients  $C_K$  and the  $\hat{f}_i^{(P)K}$  and  $\hat{f}_{ij;k}^K$  have been chosen so that the  $\phi_{0,i}+\chi'_{f,i}$  have the correct transformation properties [Eq. (22)], and if the  $\hat{u}_{ij}$  obey the same transformation law [Eq. (6) with the upper limits on the sums replaced by  $M$ ] as the spin orbitals they replace, then the  $\phi_{0,i}+\chi'_{s,i}$  have the correct transformation properties [Eq. (22)].

Conditions for which the  $\phi_{0,i}+\chi'_{d,i}$  transform correctly may be formulated by treating  $\phi_{0,i}+\chi'_{d,i}$  configuration by configuration. We only state the results; the proof is a straightforward extension of the above. (1) Assume that the  $\phi_{0,i}+\chi'_{f,i}$  have the correct symmetry properties configuration by configuration. (2) Let  $K$  denote the configuration (rather than the determinant), let  $\lambda$  denote the irreducible representation of Spin Orbital  $j$ ,  $\mu$  that of  $k$ , and let  $l$  run over the  $\lambda$  irreducible representation and  $m$  over the  $\mu$  irreducible representation. If

$$R\hat{u}_{jk}^K = \sum_l^{(\lambda)} \sum_m^{(\mu)} \Gamma_{lj}^{(\lambda)}(R) \Gamma_{mk}^{(\mu)}(R) \hat{u}_{lm}^K; \quad (\text{for } \lambda \neq \mu), \quad (30)$$

$$R\hat{u}_{jk}^K = \sum_l^{(\lambda)} \sum_m^{(\lambda)} \{ \Gamma_{lj}^{(\lambda)} \Gamma_{mk}^{(\lambda)} - \Gamma_{mj}^{(\lambda)} \Gamma_{lk}^{(\lambda)} \} \hat{u}_{lm}^K; \quad (l < m) \quad (\text{for } \lambda = \mu), \quad (31)$$

then equations similar to Eqs. (28), (29), and (21) hold for each configuration contributing to  $\phi_{0,i}$ , and  $\phi_{0,i}+\chi'_{d,i}$  will also transform like  $\psi_i$  [Eq. (22)].

Unlike the closed-shell case, however, the conditions stated above [in particular, Eqs. (30) and (31)] are not necessary ones, as can be seen by a trivial example. Suppose  $\phi_0$  has the form

$$\phi_0 = 3^{-1/2} \alpha \{ (2p_x)^2 + (2p_y)^2 + (2p_z)^2 \}. \quad (32)$$

There are three possible pair functions, but only their sum enters  $\chi'_{d,i}$ . Two can be chosen arbitrarily, and in particular in a way consistent with Eq. (31), provided the third is chosen to make the sum come out right (<sup>1</sup> $S$ ).

#### IV. ON THE CALCULATION OF PAIR FUNCTIONS HAVING CORRECT SYMMETRY PROPERTIES BY VARIATIONAL METHODS

In the case of perturbation theory, variational methods for calculating pair functions separately give the first-order  $\hat{u}_{ij}^{(1)}$  satisfying Eqs. (6), (30), and (31). This is true both for “ $B(ij)$ -type pairs” and for “irre-

ducible pairs”.<sup>2,10,11</sup> A recent statement to the contrary in the literature<sup>18</sup> is incorrect.<sup>19</sup>

Outside of perturbation theory, with “pairs to all orders,” the transformation of the variational energy expression from “ $B(ij)$ -type pairs” to “irreducible pairs” involves a reapportionment of the energy between pairs and triangle parts.<sup>2</sup> Which type of pairs may give the smaller triangles part depends on the system. In either case the number of distinct pairs<sup>1,2,11</sup> to be obtained is of the order of  $N$ , the number of electrons, in the closed-shell case. Once one pair is obtained, several others differing only in  $M_L$ ,  $M_S$  components, and/or spatial orientation have the same  $\epsilon_{ij}$ .

One method of calculation is to minimize the  $\epsilon_{ij}^{\text{irr}}$  for one-component  $\hat{u}_{ij}^{\text{irr}}$  (e.g., with given  $M_L$ ,  $M_S$ ) of each distinct irreducible set.<sup>2</sup> Then the  $\chi'_{s,i}$  will automatically have the same symmetry as  $\phi_0$ .

Another method which yields  $\hat{u}_{ij}$  with exact over-all  $\chi'_{s,i}$  symmetry properties is to pick one independent pair [say  $(2p_x\alpha)(2p_y\alpha)$  in  $F$ ], and obtain its  $\hat{u}_{ij}$  by minimizing  $\epsilon'_{ij}$ . This  $\hat{u}_{ij}$  contains certain irreducible correlation functions. Obtain a second  $\hat{u}_{kl}$  (say  $\hat{u}_{2p_x,2p_y\beta}$ ) by minimizing  $\epsilon'_{kl}$ , but do not vary any of the irreducible components already fixed by  $\hat{u}_{ij}$  (<sup>3</sup> $P$  component in our example). Proceed until all the distinct  $\hat{u}_{ij}$ 's have been calculated. This procedure is simplified further if in a calculation, triangles will be neglected, by minimizing separately the  $\epsilon'_{ij}$  with a distinct set of  $\hat{u}_{ij}$ 's in any type of description, not just an “irreducible-pair” description, since then the transformed energies are the same to within the order of effects neglected already.

#### V. PAIR FUNCTIONS FOR LOCALIZED ORBITALS

The closed-shell Hartree–Fock (HF) determinant can be written as a determinant of localized orbitals,  $\eta_\nu$ , obtained from the HF orbitals by a unitary transformation:

$$\eta_\nu = \sum_{k=1}^N t_{\nu k} \dagger | k \rangle, \quad (33)$$

$$| k \rangle = \sum_{\nu=1}^N t_{k\nu} \eta_\nu, \quad (34)$$

$$\phi_0 = \alpha \{ 12 \cdots N \} = \det(\mathbf{t}) \alpha \{ \eta_1 \eta_2 \cdots \eta_N \}. \quad (35)$$

By replacing pairs of localized orbitals by localized pair

<sup>18</sup> V. McKoy, J. Chem. Phys. **43**, 1605 (1965). [see also: M. Geller, H. S. Taylor, and H. B. Levine, J. Chem. Phys. **43**, 1727 (1965)].

<sup>19</sup> For instance, on the right-hand side of Eq. (5) of Ref. 18, a term in a trial  $\tilde{\chi}_1$  of spurious symmetry would not contribute to the first term in this equation and would give a positive contribution to the second term. Therefore, when  $\tilde{\chi}_1$  is varied to minimize the  $\tilde{E}_2$ , the spurious term will drop out (along with its positive-valued contribution to  $\tilde{E}_2$ ), in apparent contradiction with the statement made four lines below this equation. Similar remarks apply to minimizing  $\tilde{\epsilon}_{ij}^{(2)}$  to get  $\hat{u}_{ij}^{(1)}$ . [The choice of two-electron basis functions with correct symmetry properties for use in variational calculations has been discussed recently by H. F. King, J. Chem. Phys. **46**, 705 (1967).]

functions  $\hat{\mu}_{\nu\zeta}$ , we obtain<sup>6,20</sup> a localized approximate  $\chi$ :

$$\chi'_s(\text{localized}) = \alpha \left\{ (\eta_1 \eta_2 \cdots \eta_N) \left[ 2^{-1/2} \sum_{1 \leq \nu < \zeta}^N \frac{\hat{\mu}_{\nu\zeta}}{(\eta_\nu \eta_\zeta)} \right. \right. \\ \left. \left. + 2^{-1} \sum_{1 \leq \nu < \zeta}^N \sum_{1 \leq \sigma < \tau}^N \frac{\hat{\mu}_{\nu\zeta} \hat{\mu}_{\sigma\tau}}{(\eta_\nu \eta_\zeta \eta_\sigma \eta_\tau)} + \cdots \right] \right\} \quad (36)$$

$(\nu < \sigma; \nu, \zeta \neq \sigma, \tau)$

<sup>20</sup> O. Sinanoğlu, in *Modern Quantum Chemistry—Istanbul Lectures*, O. Sinanoğlu, Ed. (Academic Press Inc., New York, 1965), Pt. 2.

The identity of  $\chi'_s$  (localized) with  $\chi'_s$  [Eq. (1)] is the subject of the following theorem:  $\chi'_s$  (localized) =  $\det(\mathbf{t})\chi'_s$  [Eq. (1)], if, and only if, the localized pair functions  $\hat{\mu}_{\nu\zeta}$  are determined from the  $\hat{u}_{ij}$  by

$$\hat{\mu}_{\nu\zeta} = \sum_{1 \leq k < l}^N (t_{\nu k}^\dagger t_{\zeta l}^\dagger - t_{\nu l}^\dagger t_{\zeta k}^\dagger) \hat{u}_{kl} \quad (37)$$

The proof follows immediately upon consideration that  $U$  [Eqs. (11) and (12)] is invariant under the transformation to localized orbitals [Eq. (33)] if, and only if, Eq. (37) holds.

### Electron Recombination in Hydrocarbon-Oxygen Reactions behind Shock Waves

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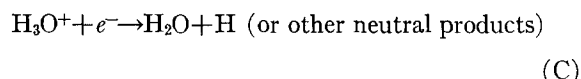
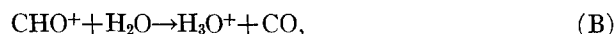
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(Received 15 August 1966)

The rate of recombination of electrons with ions behind shock waves in argon containing dilute lean mixtures of hydrocarbons and oxygen has been measured with a microwave system. The recombination reaction was found to be two body, as evidenced by insensitivity of the recombination coefficient  $\alpha$  to changes in pressure and concentration; and the recombination coefficient for acetylene-oxygen and methane-oxygen mixtures was found to depend upon temperature as  $T^{-1.98}$  between 2500° and 5000°K. Extrapolating to room temperature gives a value of  $\alpha = 1.3 \times 10^{-5}$  cm<sup>3</sup>/sec, consistent with the electron removal process being a dissociative recombination involving a complex ion. In the case of acetylene, the reaction is probably a previously proposed scheme:  $\text{H}_3\text{O}^+ + e^- \rightarrow$  neutral products. Measurements made at a temperature of about 3800°K, using ethane, ethylene, propane, and benzene, gave recombination coefficients similar in magnitude to those obtained for the acetylene and methane, consistent with the recombining ion being the same for all these hydrocarbon-oxygen reactions.

#### I. INTRODUCTION

MASS-spectrometer measurements in lean acetylene-oxygen flames have led to a proposal for the mechanism of production and removal of chemi-ions as follows<sup>1</sup>:



Although there is some disagreement as to the validity of Reaction A, and as to  $\text{CHO}^+$  as the primary ion, the  $\text{H}_3\text{O}^+$  ion is recognized as the dominant ion persisting after the main reaction,<sup>1-3</sup> so that during the final removal process  $[\text{H}_3\text{O}^+] = [e^-]$ . For a dissociative recombination process like (C), involving only two charged species, a recombination coefficient  $\alpha$ , in-

dependent of pressure or concentration, may be defined by<sup>4</sup>

$$de/dt = -\alpha e^2 \quad (1)$$

or

$$(1/e) - (1/e_0) = \alpha t, \quad (2)$$

where  $e_0$  is electron density at time  $t=0$ .

Measured at room temperature, the value of  $\alpha$  is about  $10^{-7}$  cm<sup>3</sup>/sec for a diatomic ion like  $\text{N}_2^+$  and a little higher, or about  $10^{-6}$  cm<sup>3</sup>/sec, for a more complex ion like  $\text{N}_4^+$ .<sup>5</sup> Few measurements of recombination rates at room temperature are available for complex ions, and none for  $\text{H}_3\text{O}^+$ .

The predicted temperature dependence of  $\alpha$  takes the form<sup>4</sup>

$$\alpha \propto T^{-3/2} f(T), \quad (3)$$

where the functional form of  $f(T)$  is determined by details of potential curve crossings of the ion and the unstable intermediate molecule.<sup>5</sup>

<sup>1</sup> J. A. Green and T. M. Sugden, *Symp. Combust.* 9th, Cornell Univ., Ithaca, N.Y., 1962, 607 (1963).

<sup>2</sup> H. F. Calcote, in Ref. 1, p. 622.

<sup>3</sup> H. F. Calcote, S. C. Kurzius, and W. J. Miller, *Symp. Combust.* 10th, Cambridge Univ., 1964, 605 (1965).

<sup>4</sup> D. R. Bates and A. Dalgarno, in *Atomic and Molecular Processes*, D. R. Bates, Ed. (Academic Press Inc., New York, 1962), Sec. 7.

<sup>5</sup> M. A. Biondi, T. R. Connor, C. S. Weller, and W. H. Kasner, in Ref. 3, p. 597.