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# Electronic Population Analysis Based on the Electron Pair Concept

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The electronic population in molecular systems is analyzed on the basis of the spin coupling matrix. A proposal is made to define the pair-coupling population which is directly related to the electron pair concept. The theory is applied to the examinations of various types of wave functions used for three-centered two-, three-, and four-electron systems. The results permit clear comparisons of the characteristics of the various wave functions examined.

Recent progress in computer technology has made it possible to determine molecular electronic wave functions in fairly good accuracy. However, such wave functions are generally too intricate in form to permit naive interpretation by chemical intuition. Thus, a systematic procedure for obtaining a maximum insight into any type of wave function is necessitated. The first- and second-order reduced density matrices (hereafter referred to as 1- and 2-matrices, respectively) are the most appropriate starting point in this respect, because they contain enough information to specify the electronic structures in question. In particular, population analysis applied to the density matrices affords an interpretation of electronic structure in chemical language. Thus far, spinless 1- and 2-matrices have been successfully analyzed in several articles.[1-5)]

In this paper, we analyze the spin coupling matrices, $Q^0$ and $Q^2$, and therefrom define the pair-coupling populations between AO's. The spin coupling matrices are directly related to the electron pair concept as studied in a previous paper.[6)] Accordingly, the analysis of pair-coupling populations is expected to shed light on the classical Lewis-Langmuir theory as well as the valence bond interpretation. The specific examples which we will here investigate are the $\pi$-electron systems of $C_3H_5$, $NO_2$, $HCO_2$, and $O_3$ with 2 to 4 $\pi$-electrons. Population analysis has been carried out for various types of wave functions calculated by Linnett and coworkers.[7-10)] The pair-coupling populations, together with the conventional populations so far employed, have been examined for each wave function. The results are compared, and the characteristics of molecules discussed.

## I. Population Analysis

The 1- and 2-matrices in the Löwdin normalization[11)] for an $N$-electron wave function $\Psi(x_1,x_2,\cdots x_N)$ are given by

$$\rho^{(1)}(x_1\,;\,x_1') = N\int\Psi(x_1,x_2,\cdots x_N)\times\Psi^*(x_1',x_2,\cdots x_N)\mathrm{d}x_2\cdots\mathrm{d}x_N \tag{1}$$

$$\rho^{(2)}(x_1,x_2\,;\,x_1',x_2') = \binom{N}{2}\int\Psi(x_1,x_2,x_3,\cdots x_N)\times\Psi^*(x_1',x_2',x_3,\cdots x_N)\mathrm{d}x_3\cdots\mathrm{d}x_N \tag{2}$$

The population analysis is to be made on spin-free density functions, so that we will make use of the following types of density matrices with space variables alone:

$$P_1(r_1\,;\,r_1') = \int_{s_1=s_1'}\rho^{(1)}(x_1\,;\,x_1')\mathrm{d}s_1 \tag{3}$$

$$Q_S(r_1\,;\,r_1') = 2\int_{s_1=s_1'}S_z(s_1)\rho_{\mathrm{st}}{}^{(1)}(x_1\,;\,x_1')\mathrm{d}s_1 \tag{4}$$

$$P_2(r_1,r_2\,;\,r_1',r_2') = \int_{s_1=s_1',s_2=s_2'}\rho^{(2)}(x_1,x_2\,;\,x_1',x_2')\mathrm{d}s_1\mathrm{d}s_2 \tag{5}$$

$$Q^0(r_1,r_2\,;\,r_1',r_2') = \int_{s_1=s_1',s_2=s_2'}(-4/3)\boldsymbol{S}(s_1)\cdot\boldsymbol{S}(s_2)\times\rho^{(2)}(x_1,x_2\,;\,x_1',x_2')\mathrm{d}s_1\mathrm{d}s_2 \tag{6}$$

$$Q^2(r_1,r_2\,;\,r_1',r_2') = \frac{4(S+1)}{3(2S-1)}\int_{s_1=s_1',s_2=s_2'}[3\boldsymbol{S}_z(s_1)\cdot\boldsymbol{S}_z(s_2)-\boldsymbol{S}(s_1)\cdot\boldsymbol{S}(s_2)]\rho_{\mathrm{st}}{}^{(2)}(x_1,x_2\,;\,x_1',x_2')\mathrm{d}s_1\mathrm{d}s_2 \tag{7}$$

where $r_i$ and $s_i$ are the space and spin variables, respectively, and where the subscript st denotes that a standard state with $\langle S_z\rangle=S$ is assumed.

The density functions defined as the diagonal elements of the spinless matrices (3) to (7) possess clear physical meanings. Thus, $P_1(r_1)$ and $P_2(r_1,r_2)$ stand for the charge and pair-electron densities. $Q_S(r_1)$ represents the spin density distribution. $Q^0(r_1,r_2)$ and $Q^2(r_1,r_2)$ are the spin-coupling functions,[6)] which respectively denote the distributions of singlet- and triplet-type electron pairs.

In performing the population analysis, we assume that these density functions can be expanded by an atomic orbital basis set $(a,b,c,\cdots)$. The charge density function $P_1(r_1)$ is then expressed as follows:

$$P_1(r_1) = \sum_{a,b}\gamma_1(a|b)a(r_1)b^*(r_1) \tag{8}$$

The expansion coefficients $\gamma_1(a|b)$ lead to Mulliken's *gross* and *net populations*,[2)] $q_a$ and $q_{aa}$, for atomic orbital $a$ as well as the *overlap population*[2)] $q_{ab}$ between atomic orbitals $a$ and $b$:

$$q_a = \sum_b\gamma_1(a|b)s_{ab} \tag{9a}$$

$$q_{aa} = \gamma_1(a|a) \tag{9b}$$

$$q_{ab} = 2\gamma_1(a|b)s_{ab} \tag{9c}$$

where $s_{ab}$ is the overlap integral between $a$ and $b$. Populations of a total of $N$ electrons are subject to the following constraints:

$$\sum_a q_a = N \tag{10a}$$

$$\sum_a q_{aa} + \sum\sum_{a>b} q_{ab} = N \tag{10b}$$

A similar partitioning procedure may be used for the other density functions. First, from the spin density function expressed in the form

$$Q_S(r_1) = \sum_{a,b} \delta_s(a|b)a(r_1)b^*(r_1), \tag{11}$$

we define the *spin population*:

$$q_a{}^s = \sum_b \delta_s(a|b)s_{ab} \tag{12}$$

Clearly, $q_a{}^s$ should satisfy the relationship:

$$\sum_a q_a{}^s = 2S. \tag{13}$$

Second, the two-particle density functions are expanded as follows:

$$P_2(r_1,r_2) = \sum_{a,b,c,d} \gamma_2(ab|cd)a(r_1)b(r_2)c^*(r_1)d^*(r_2) \tag{14}$$

$$Q^0(r_1,r_2) = \sum_{a,b,c,d} \delta^0(ab|cd)a(r_1)b(r_2)c^*(r_1)d^*(r_2) \tag{15}$$

$$Q^2(r_1,r_2) = \sum_{a,b,c,d} \delta^2(ab|cd)a(r_1)b(r_2)c^*(r_1)d^*(r_2) \tag{16}$$

from which we define the *pair populations*[12]

$$P_{aa} = \sum_{c,d} \gamma_2(aa|cd)s_{ac}s_{ad} \tag{17a}$$

$$P_{ab} = 2\sum_{c,d} \gamma_2(ab|cd)s_{ac}s_{bd} \tag{17b}$$

and the *pair-coupling populations.*

$$Q^0_{aa} = \sum_{c,d} \delta^0(aa|cd)s_{ac}s_{ad} \tag{18a}$$

$$Q^0_{ab} = 2\sum_{c,d} \delta^0(ab|cd)s_{ac}s_{bd} \tag{18b}$$

$$Q^2_{ab} = 2\sum_{c,d} \delta^2(ab|cd)s_{ac}s_{bd} \tag{19}$$

Obviously,

$$P_{aa} = Q^0_{aa}, \tag{20}$$

$$Q^2_{aa} = 0, \tag{21}$$

because the two electrons in the same AO have to be singlet coupled with each other.

The total sums of the above-defined two-particle populations are also bound. The pertinent relationships are as follows:

$$\sum_a P_{aa} + \sum_{a>b}\sum P_{ab} = N(N-1)/2 \tag{22}$$

$$\sum_a Q^0_{aa} + \sum_{a>b}\sum Q^0_{ab} = N/2 - 2S(S+1)/3 \tag{23}$$

$$\sum_{a>b}\sum Q^2_{ab} = 2S(S+1)/3 \tag{24}$$

It should be noted that a somewhat different method of population analysis has been proposed by Davidson[4] and Roby.[5] According to their proposal, the electronic population on each AO is defined as

$$n^0_{aa} = \sum_{b,c} s_{ab}\gamma_1(b|c)s_{ca} \tag{25}$$

The quantity $n^0_{aa}/N$ is interpreted as expressing the probability that an electron belongs to orbital $a$. In this formalism, however, an electron in orbital $a$ may be found simultaneously in orbital $b$, if $a$ and $b$ are not orthogonal to each other. Extension of this last method to two-particle density functions is easy. For example, the pair-coupling population is expressible in the form:

$$P^0_{ab} = 2\sum_{c,d,e,f} s_{ac}s_{bd}\delta^0(cd|ef)s_{ea}s_{fb} \tag{26}$$

The quantity is what we called the *generalized Penney-Dirac bond order* in a previous paper.[6] In this paper, however, we will not consider such populations as shown in Eqs. 25 and 26. For these populations, simple relations such as Eqs. 10a, 13 and 22—24 and as those that would be discussed in the next section do not hold.

## II. Characteristics of the Populations

In a singlet state, the $Q^0$ function yields the charge density function by integrating over the second electron.[6]

$$P_1(r_1) = 2\int Q^0(r_1,r_2)\mathrm{d}r_2 \tag{27}$$

By expanding both sides of the above equation with respect to AO's and comparing the corresponding terms, we obtain the following relationship:

$$S=0: q_a = 2Q^0_{aa} + \sum_{b\neq a} Q^0_{ab} \tag{28a}$$

Thus, the gross population of each AO may be regarded as being composed of twice the ionic pair-coupling population on that AO and the sum of the covalent pair-coupling populations relevant to the same AO. This relationship is similar to that obtained on an orthogonalized AO basis set.[6] Analogous relations exist in the states with higher spin multiplicities.

$$S=\frac{1}{2}: \quad q_a = 2Q^0_{aa} + \sum_{b\neq a} Q^0_{ab} + q^s_a \tag{28b}$$

$$S\geqq 1: \quad q_a = 2Q^0_{aa} + \sum_{b\neq a} (Q^0_{ab}+Q^2_{ab}) \tag{28c}$$

The pair populations can likewise be related with the gross population.[12] The corresponding equations take the following forms:

$$P_1(r_1) = \frac{2}{N-1}\int P_2(r_1,r_2)\mathrm{d}r_2 \tag{29}$$

$$q_a = \frac{1}{N-1}(2P_{aa} + \sum_{b\neq a} P_{ab}) \tag{30}$$

For single-determinantal wave functions, 2-matrix can be expressed in terms of the products of 1-matrix. Hence, the pair and pair-coupling populations are expressed by

$$\begin{aligned}
Q^0_{aa} &= P_{aa} = \{(q_a)^2-(q^s_a)^2\}/4 \\
Q^0_{ab} &= \{3(\boldsymbol{\gamma}_1\boldsymbol{s})_{ab}(\boldsymbol{\gamma}_1\boldsymbol{s})_{ba}-(\boldsymbol{\delta}_s\boldsymbol{s})_{ab}(\boldsymbol{\delta}_s\boldsymbol{s})_{ba}-2q^s_aq^s_b\}/6 \\
Q^2_{ab} &= \{2(S+1)/3(2S-1)\}\{q^s_aq^s_b-(\boldsymbol{\delta}_s\boldsymbol{s})_{ab}(\boldsymbol{\delta}_s\boldsymbol{s})_{ba}\} \\
P_{ab} &= \{2q_aq_b-(\boldsymbol{\gamma}_1\boldsymbol{s})_{ab}(\boldsymbol{\gamma}_1\boldsymbol{s})_{ba}-(\boldsymbol{\delta}_s\boldsymbol{s})_{ab}(\boldsymbol{\delta}_s\boldsymbol{s})_{ba}\}/2
\end{aligned} \tag{31}$$

where $\boldsymbol{s}$ is the ordinary overlap matrix between AO's and where $\boldsymbol{\gamma}_1$ and $\boldsymbol{\delta}_s$ are the matrices composed of the expansion coefficients which appear in Eqs. 8 and 11, respectively.

The various populations investigated so far can be converted to atomic quantities by summing up the appropriate orbital populations. The resulting atomic and interatomic populations are invariant for the hybridization of AO's when the atomic orbitals on each atom are, as is usually the case, mutually orthogonal.

## III. Applications to Three-center Systems

To illustrate the use of the population analysis above proposed, we apply it to various types of wave functions. The wave functions to be examined are those for the three-center systems calculated by Linnett and coworkers.[7–10] These have been chosen merely for the simplicity of arguments. The applications will clarify essential differences encountered on going from simple two-center cases to many-center problems. The sample systems here treated are the $\pi$-electron part of the allyl,[7] $NO_2$,[8] and $HCO_2$[9] radicals ($N=3$) as well as their cations ($N=2$) and anions ($N=4$). Ozone[10] ($N=4$) and its cation ($N=3$) and dication ($N=2$) will also be examined.

*(A) Two-electron Systems.* The three atomic orbitals involved are denoted as *a*, *b*, and *c*. The following basic functions constitute a complete set for the $^1A_1$ representation of the *a–b–c* system:

$$\begin{aligned} \Phi_1^{(2)} &= (a,b) + (b,a) + (b,c) + (c,b) \\ \Phi_2^{(2)} &= (a,c) + (c,a) \\ \Phi_3^{(2)} &= (a,a) + (c,c) \\ \Phi_4^{(2)} &= (b,b) \end{aligned} \tag{32}$$

Here, $(a,b)$, for example, denotes a Slater determinant of the form:

$$(a,b) = \frac{1}{\sqrt{2}} \begin{vmatrix} a(1)\alpha(1) & b(1)\beta(1) \\ a(2)\alpha(2) & b(2)\beta(2) \end{vmatrix} \tag{33}$$

In all the Slater determinants the order of the spin function is $\alpha\beta$.

The wave function optimized over all these functions will be referred to as the configuration-interaction (CI) function $\Psi_{CI}^{(2)}$. In addition, the following approximate functions, each involving a smaller number of variational parameters, are considered.

1. Simple molecular orbital (MO) function:

$$\Psi_{MO}^{(2)} = (a+kb+c,\, a+kb+c) \tag{34}$$

2. Alternant molecular orbital (AMO) function[13]:

$$\Psi_{AMO}^{(2)} = (a+k_1b+c,\, a+k_2b+c) + (a+k_2b+c,\, a+k_1b+c) \tag{35}$$

3. Valence bond (VB) functions:
Heitler-London type (HL)

$$\Psi_{HL}^{(2)} = (a,b) + (b,a) + (b,c) + (c,b) \tag{36}$$

Coulson-Fischer type (CF)

$$\Psi_{CF}^{(2)} = (a+kb,\, b+ka) + (b+ka,\, a+kb) + (c+kb,\, b+kc) + (b+kc,\, c+kb) \tag{37}$$

Bond orbital type (BO)

$$\Psi_{BO}^{(2)} = (a+kb,\, a+kb) + (c+kb,\, c+kb) \tag{38}$$

4. Nonpaired spatial orbital (NP) functions:
Symmetrical form (NPA)

$$\Psi_{NPA}^{(2)} = (a+kb,\, kb+c) + (kb+c,\, a+kb) \tag{39}$$

Unsymmetrical form (NPB)

$$\Psi_{NPB}^{(2)} = (a+kb,\, b+kc) + (b+kc,\, a+kb) + (ka+b,\, kb+c) + (kb+c,\, ka+b) \tag{40}$$

In Eqs. 34 to 40, *k*'s are the variational parameters and the functions are not normalized.

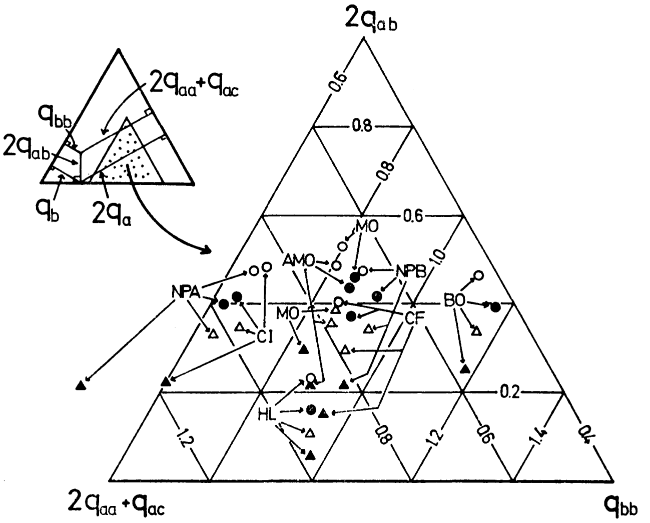


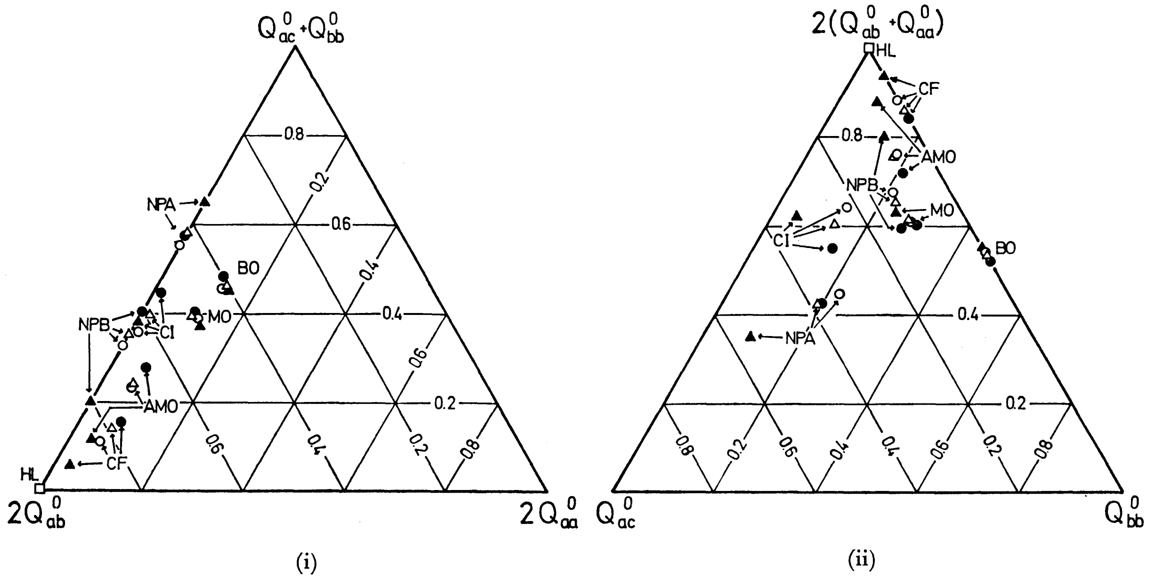
Fig. 1. The net and overlap populations for two-electron systems.
○: $C_3H_5^+$, △: $NO_2^+$, ●: $HCO_2^+$, ▲: $O_3^{2+}$
The length of the perpendicular from each point onto a base line shows the value of the population indicated at the opposite vertex.

The results of population analysis are shown in Figs. 1 and 2. The density distributions have been partitioned according to Eqs. 10b and 23. In two-electron systems, the function $P_2(r_1,r_2)$ is identical with $Q^0(r_1,r_2)$, so that there is no difference between the pair and pair-coupling populations. The numerical value for the population indicated at one vertex is equal to the length of the perpendicular onto the opposing base line (see Fig. 1). The sum of the lengths of three perpendiculars is invariant at any point. Thus, the gross populations $q_a$ and $q_b$ can be read simply as the lengths of the two perpendiculars drawn from the point at which the $q_{ab}$ perpendicular intersects with the horizontal base line.

Let us first compare the results of the CI calculations for the four species: $C_3H_5^+$, $NO_2^+$, $HCO_2^+$ and $O_3^{2+}$. The polarity of molecules is reflected in the gross population $q_a$, which decreases in the order: $O_3^{2+} > HCO_2^+ \sim NO_2^+ > C_3H_5^+$. The overlap population $q_{ab}$, which corresponds to the strength of the bond *a–b*, decreases in the order: $C_3H_5^+ > HCO_2^+ > NO_2^+ > O_3^{2+}$. The pair-coupling populations shown in Fig. 2 are shifted regularly for $C_3H_5^+$, $NO_2^+$, and $HCO_2^+$; the populations, $Q^0_{ab}$ and $Q^0_{ac}$, decrease and increase, respectively, in that order. $O_3^{2+}$ has a characteristic feature that $Q^0_{bb}$ is very small.

The shortcomings of the approximate functions compared with the CI treatment can readily be seen from Figs. 1 and 2. The molecular orbital method generally gives too large weights to the ionic terms $Q^0_{aa}$ and $Q^0_{bb}$. Moreover, $q_b$ is overestimated. In the AMO method, the value of $Q^0_{bb}$ is improved, but the weight of the covalent term $Q^0_{ab}$ is unduly increased. In this latter sense, the AMO method cannot be regarded as an improvement over the MO method.

The valence bond functions (HL, CF, and BO) impart no weight to $Q^0_{ac}$. The variational parameters



(i) (ii)

Fig. 2. The pair-coupling populations for two-electron systems.
○: $C_3H_5^+$, △: $NO_2^+$, ●: $HCO_2^+$, ▲: $O_3^{2+}$

introduced in the CF and BO functions serve to improve the value of $q_{ab}$ as compared with the HL function, but this is so only at sacrifice of the polarity to be predicted.

The methods of nonpaired spatial orbitals provide relatively good values for the ionic terms $Q^0_{aa}$ and $Q^0_{bb}$, reflecting the success of Linnett's idea to incorporate the Coulomb type correlation. Another advantage of $\Psi_{NPA}^{(2)}$ is, as can be seen from Fig. 1, the results that the charge distributions calculated by this method are close to those obtained by the CI treatment.

*(B) Three-electron Systems.* We shall adopt the convention that each Slater determinant has the spin function $\alpha\beta\alpha$. The basic functions are represented by:

$$\begin{aligned} \Phi_1^{(3)} &= 2(a,b,c) + (a,c,b) + (b,a,c) \\ \Phi_2^{(3)} &= (a,a,c) + (a,c,c) \\ \Phi_3^{(3)} &= (a,b,b) + (b,b,c) \\ \Phi_4^{(3)} &= (a,a,b) + (b,c,c) \end{aligned} \tag{41}$$

The expressions for the approximate functions are as follows:

1. Simple molecular orbital (MO) function:

$$\Psi_{MO}^{(3)} = (a+kb+c, a+kb+c, a-c) \tag{42}$$

2. Alternant molecular orbital (AMO) function:

$$\Psi_{AMO}^{(3)} = \boldsymbol{O}(a+k_1b+c, a+k_2b+c, a-c) \tag{43}$$

3. Valence bond functions:

Heitler-London type (HL)

$$\Psi_{HL}^{(3)} = \{(a,b,c)+(a,c,b)\} + \{(a,b,c)+(b,a,c)\} \tag{44}$$

Coulson-Fischer type (CF)

$$\begin{aligned} \Psi_{CF}^{(3)} = &(a+kb, ka+b, c) + (ka+b, a+kb, c) \\ &- (kb+c, b+kc, a) - (b+kc, kb+c, a) \end{aligned} \tag{45}$$

Bond orbital type (BO)

$$\Psi_{BO}^{(3)} = (a+kb, a+kb, c) + (a, kb+c, kb+c) \tag{46}$$

4. Nonpaired spatial orbital functions:

A type (NPA)

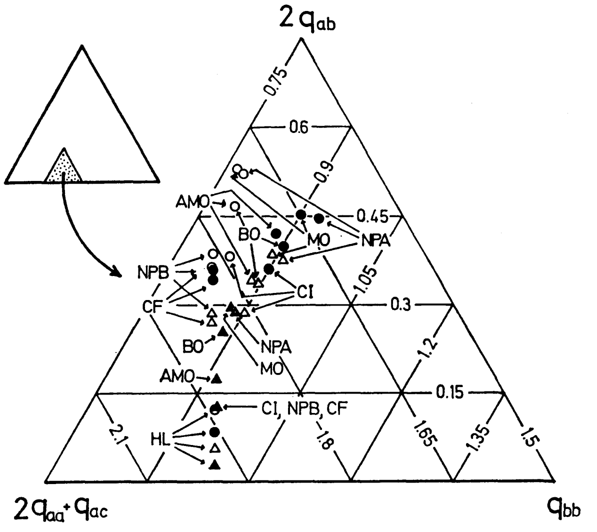


Fig. 3. The net and overlap populations for three-electron systems.
○: $C_3H_5$, △: $NO_2$, ●: $HCO_2$, ▲: $O_3^+$

$$\Psi_{NPA}^{(3)} = \boldsymbol{O}(ka+b, b+kc, c) \tag{47}$$

B type (NPB)

$$\Psi_{NPB}^{(3)} = \boldsymbol{O}(a+kb, b+kc, c) \tag{48}$$

where $\boldsymbol{O}$ is the projection operator to the $^2A_2$ state.

Figures 3 to 5 show the various populations obtained from the functions, $P_1(r_1)$, $Q^0(r_1,r_2)$, and $P_2(r_1,r_2)$, respectively. The pair populations $P_{aa}$ and $P_{bb}$ always take the same values as those of pair-coupling populations. Also, the relation, $Q^0_{ac}=(-1/2)Q^0_{ab}$, holds in these systems, so that we have shown only the sum of these pair-coupling populations in Fig. 4.

The results of the CI treatment characterize the $O_3^+$ ion as having extremely small overlap and ionic pair-coupling populations, thus indicating that the HL picture would be adequate for this species. For the other three radicals, the value of $Q^0_{bb}$ becomes larger

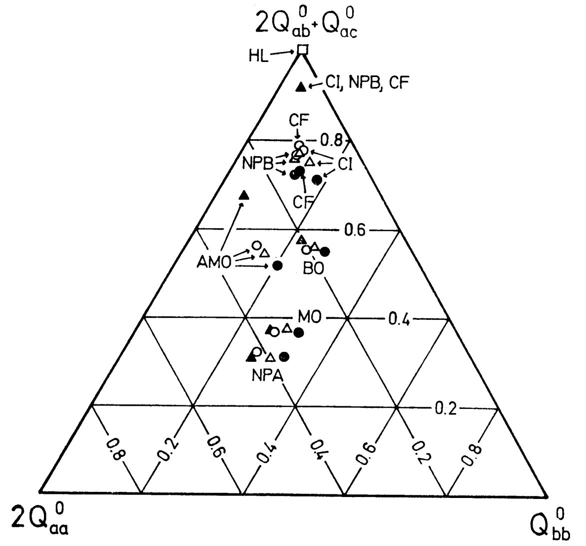


Fig. 4. The pair-coupling populations for three-electron systems.

○: $C_3H_5$, △: $NO_2$, ●: $HCO_2$, ▲: $O_3^+$

There exists a relation, $Q^0_{ac} = -\frac{1}{2}Q^0_{ab}$, so that these populations are not shown separately.

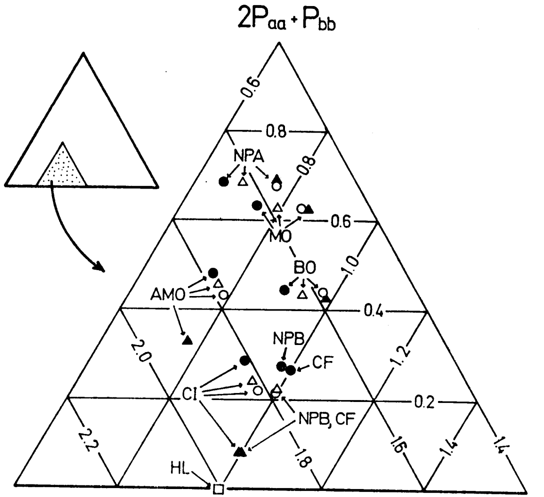


Fig. 5. The pair populations for three-electron systems.

○: $C_3H_5$, △: $NO_2$, ●: $HCO_2$, ▲: $O_3^+$

The pair populations $P_{aa}$ and $P_{bb}$ are identical respectively with the pair-coupling populations $Q^0_{aa}$ and $Q^0_{bb}$ shown in Fig. 4.

in the order, $C_3H_5<NO_2<HCO_2$, while the covalent pair-coupling population decreases simultaneously in the same order.

In the light of the above CI results, we examine the outcomings from the various approximate wave functions. Both $\Psi_{CF}^{(3)}$ and $\Psi_{NPB}^{(3)}$, providing the results close to each other, give good values for $q_{ab}$, $2Q^0_{ab}+Q^0_{ac}$, and $2Q^0_{aa}+Q^0_{bb}$. The shortcomings of these functions are that the ratios $(Q^0_{aa}/Q^0_{bb})$ and $(P_{ab}/P_{ac})$ are unreasonable and hence that the polarity of each species is not well reflected in the gross populations.

By contrast, all the other functions except $\Psi_{HL}^{(3)}$ give reasonable results for the above ratios. Thus, it may be suggested that a good wave function would result, if one combines the improvements from $\Psi_{HL}^{(3)}$ with the functions $\Psi_{CF}^{(3)}$ as well as $\Psi_{BO}^{(3)}$. For all kinds of populations, the AMO method gives much better results than does the MO treatment.

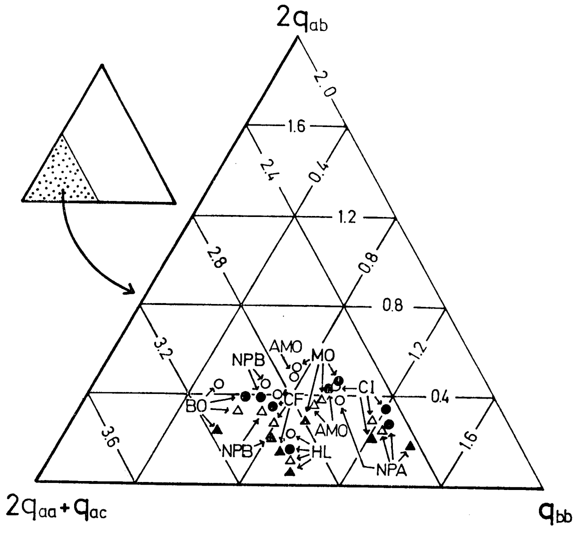


Fig. 6. The net and overlap populations for four-electron systems.

○: $C_3H_5^-$, △: $NO_2^-$, ●: $HCO_2^-$, ▲: $O_3$

*(C) Four-electron Systems.* The order of the spin functions in all the Slater determinants is given as $\alpha\beta\alpha\beta$.

The basic functions pertinent to four-electron systems are

$$\begin{aligned} \Phi_1^{(4)} &= (a,a,b,c)+(a,a,c,b)+(c,c,b,a)+(c,c,a,b) \\ \Phi_2^{(4)} &= (a,b,b,c)+(c,b,b,a) \\ \Phi_3^{(4)} &= (a,a,c,c) \\ \Phi_4^{(4)} &= (a,a,b,b)+(c,c,b,b) \end{aligned} \tag{49}$$

The approximate wave functions to be considered are as follows:

1. Simple molecular orbital (MO) function:

$$\Psi_{MO}^{(4)} = (a+kb+c,\ a+kb+c,\ a-c,\ a-c) \tag{50}$$

2. Alternant molecular orbital (AMO) function:

$$\begin{aligned} \Psi_{AMO}^{(4)} = {} & (a+k_1b+c,\ a+k_2b+c,\ a-c,\ a-c) \\ & +(a+k_2b+c,\ a+k_1b+c,\ a-c,\ a-c) \end{aligned} \tag{51}$$

3. Valence bond functions:

Heitler-London type (HL)

$$\Psi_{HL}^{(4)} = (a,a,b,c)+(a,a,c,b)+(c,c,b,a)+(c,c,a,b) \tag{52}$$

Coulson-Fischer type (CF)

$$\begin{aligned} \Psi_{CF}^{(4)} = {} & (a+kb,\ ka+b,\ c,c)+(ka+b,\ a+kb,\ c,\ c) \\ & +(c+kb,\ kc+b,\ a,\ a)+(kc+b,\ c+kb,\ a,\ a) \end{aligned} \tag{53}$$

Bond orbital type (BO)

$$\Psi_{BO}^{(4)} = (a+kb,\ a+kb,\ c,\ c)+(c+kb,\ c+kb,\ a,\ a) \tag{54}$$

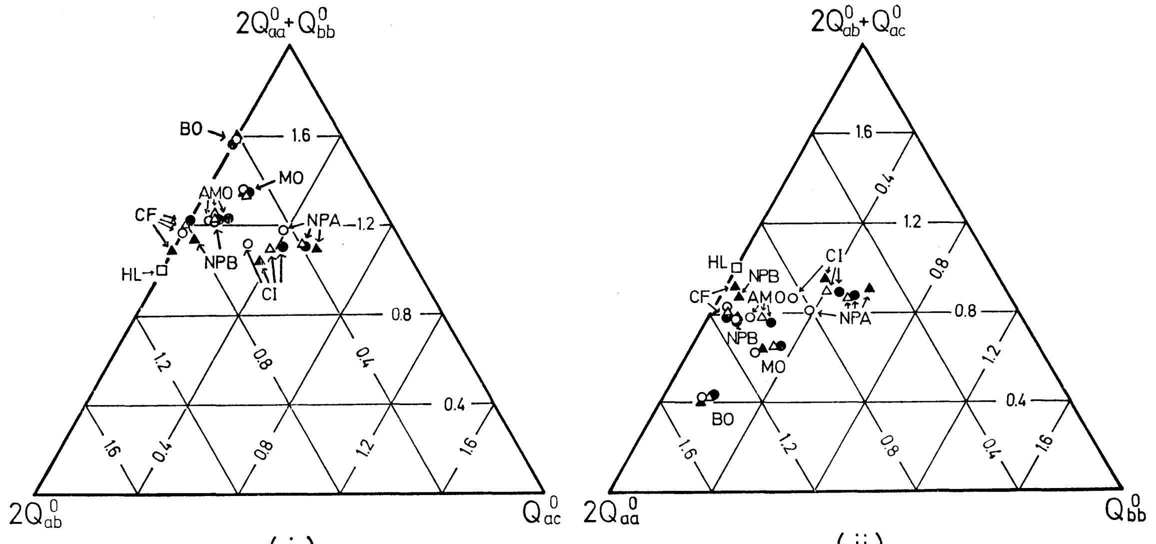
4. Nonpaired spatial orbital functions:

Symmetrical form (NPA)

$$\Psi_{NPA}^{(4)} = \boldsymbol{O}(a,\ a+kb,\ kb+c,\ c) \tag{55}$$

Unsymmetrical form (NPB)

$$\Psi_{NPB}^{(4)} = \boldsymbol{O}(\boldsymbol{a},\ a+kb,\ b+kc,\ c) \tag{56}$$



( i ) ( ii )

Fig. 7. The pair-coupling populations for four-electron systems.
○: $C_3H_5^-$, △: $NO_2^-$, ●: $HCO_2^-$, ▲: $O_3$

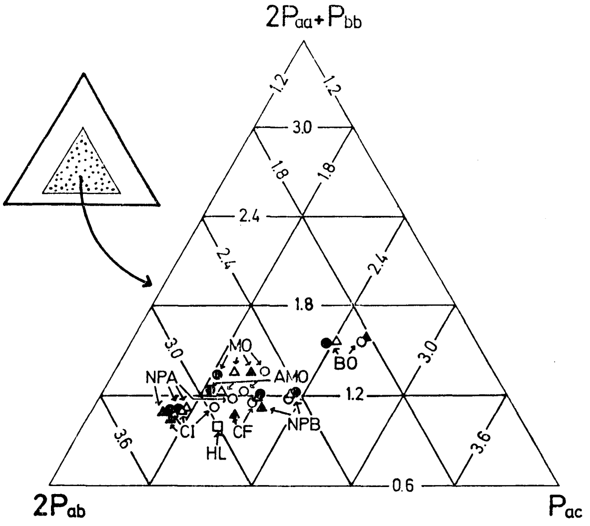


Fig. 8. The pair populations for four-electron systems.
○: $C_3H_5^-$, △: $NO_2^-$, ●: $HCO_2^-$, ▲: $O_3$
The pair populations for $P_{aa}$ and $P_{bb}$ are identical respectively with $Q^0_{aa}$ and $Q^0_{bb}$ in Fig. 7(ii).

Figures 6 to 8 show the results of population analysis for $C_3H_5^-$, $NO_2^-$, $HCO_2^-$, and $O_3$. It can be said from Fig. 6 that $C_3H_5^-$ concentrates its charge on the terminal atoms, while $O_3$ tends to have small values of $q_{ab}$. In Figs. 7 and 8, plots for the three ions $C_3H_5^-$, $NO_2^-$, and $HCO_2^-$, show a simple pattern that the three ratios, $(Q^0_{ab}/Q^0_{ac})$, $(Q^0_{aa}/Q^0_{bb})$, and $(P_{ac}/P_{ab})$, decrease in that order. The $O_3$ molecule shows a general trend that it takes relatively small values for the ionic pair-coupling populations, $Q^0_{aa}$ and $Q^0_{bb}$.

Compared with other species, the value of $Q^0_{ac}$ for $O_3$ is not particularly large. Therefore, it will be inadequate to attribute the well-known biradical character of ozone to the weight of the long-bond canonical structure, so far as Linnett's wave functions are concerned.

The function $\Psi_{NPA}{}^{(4)}$ appears to be the best of the approximate wave functions here examined, even though it fails to reproduce the CI results for ozone. The populations calculated from $\Psi_{CF}{}^{(4)}$ and $\Psi_{NPB}{}^{(4)}$ are nearly equal to each other. These latter wave functions can well give small ionic populations for ozone but do not improve other populations obtained by the HL treatment. The AMO treatment gives larger values for $Q^0_{ab}$ than does the MO method, thus reducing the ionic pair-coupling populations. However, the improvements are still unsatisfactory.

## IV. Concluding Remarks

We have shown in this study that the method of electronic population analysis can be extended to the analysis of the spin coupling matrices, by defining the pair-coupling populations. Interpretations of the electronic structure of molecules by the pair-coupling populations are similar to those by the resonance hybrid picture in the valence bond theory. The present method thus permits ready understandings of the characteristics of bonds by chemical intuition and yet is free from the arbitrariness in selecting the canonical structures.

It has frequently been found in the applications to three-center systems that an approximate wave function does not necessarily bring about improvements in populations, even when it improves energy. Of course, Linnett's wave functions are approximate ones even in the CI treatment. Nevertheless, the results for each species treated by use of various wave functions correctly demonstrate the characteristics of the molecular electronic structures to be represented by these wave functions. It should be emphasized that basic properties of the pair-electron density function $P_2(r_1,r_2)$ could best be understood when it is looked at, as in this work, in the light of the distribution of pair-coupling populations in molecules.

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