July, 1975] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48 (7), 2025—2032 (1975) 2025

# Electron Pair Concept and an Extension of the Penney-Dirac Bond Order

Takashi Okada and Takayuki Fueno
*Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560*

(Received March 24, 1975)

The density functions representing electron pairs are extracted from two-electron density matrices by operating irreducible tensor operators in a two-electron spin space. Properties of these functions are examined, and the generalized Penney-Dirac bond orders are defined between atomic orbitals. Significance of the bond orders in chemical valence problems is discussed.

The concept of electron pair first introduced by Lewis[1)] has long been accepted as the concisest and most fundamental notion of chemical valence. Ever since Heitler and London[2)] and Sugiura[3)] unveiled the nature of chemical binding of the hydrogen molecule, quantum theory has gained a great deal of success in the description of bondings in molecules as well as electron pairs. Thus, in valence bond theory, the electron pair concept is cast into the premise that an electron pair bond is associated with perfect singlet pairing of spins of electrons in the valence orbitals of the atoms concerned. The picture of electron pair bond was further extended by the introduction of the resonance concept.[4)] On the other hand, molecular orbital theory in its simplest form explains the electron pair concept from the viewpoint that for each chemical bond there exists a bonding orbital which is occupied by two electrons in a singlet spin coupling. The methods of equivalent orbitals[5)] and localized orbitals[6)] are considered to be a reformulation of Lewis' concept in the molecular orbital formalism.

The recent development of computers has made more exact and complicated wavefunctions available, and more sophisticated types of wavefunctions which preserve the electron pair concept have been examined by several authors.[7)] However, all these attempts to interpret the electron pair concept are still liable to depend upon the forms of the wavefunctions adopted. It is desirable to reformulate Lewis' concept in terms of fundamental quantities that may be applicable to general types of wavefunctions.

For this purpose, the reduced density matrices, which were introduced by Hushimi[8)] and developed by Löwdin[9)] and McWeeny,[10)] would be the most adequate tool. The first- and second-order reduced density matrices (hereafter referred to as 1- and 2-matrices, respectively) are defined, in the Löwdin normalization,[9)] for an $N$-electron wavefunction $\Psi(x_1, x_2\, x_3, \cdots x_N)$ by the expressions

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

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

The diagonal elements of 1-matrix, $\rho^{(1)}(x_1;\ x_1)$, are interpreted as the electron density at point $x_1$. A number of useful valence concepts such as various types of populations,[11)–14)] valence atomic orbitals[10,15)] and force concept,[16)] have emerged from 1-matrix. By contrast, 2-matrix has hitherto been scarcely employed in electronic structure interpretations despite its fundamental importance.[17)]

In this article, we consider Lewis' electron pairs as singlet coupled pairs of electrons possible in an $N$-electron system and intend to extract these pairs from the total $N(N-1)/2$ pairs represented by 2-matrix. First, we will obtain the distribution of these pairs in an $N$-electron singlet state by applying to 2-matrix the operator, $-(4/3)\boldsymbol{S}(1)\cdot\boldsymbol{S}(2)$, which was used to define the Penney-Dirac bond order.[18)] Then, we will define generalized bond orders from this distribution, which will prove to give spinless 1-matrix on integration. The characteristics of the pair distribution and the bond order will be examined. Finally, we will extend the formulation to nonsinglet states by introducing spin density as well as triplet coupled electron pairs.

## I. Definitions of the Spin Coupling Matrix $Q^0$ and the Bond Order $P^0_{ab}$ in a Singlet State

In the Dirac vector model,[19,20)] the problem of permutation degeneracy is replaced by vector couplings between spin angular momenta. The Hamiltonian is equivalent to

$$H = \text{const.} - \frac{1}{2}\sum_{a>b}(1+4\boldsymbol{s}_a\cdot\boldsymbol{s}_b)J_{ab} \tag{3}$$

the summation being over all pairs. Here, $J_{ab}$ is the exchange integral between orbitals $a$ and $b$, and $\boldsymbol{s}_a$ is the spin vector of an electron in orbital $a$.

If the spins in orbitals $a$ and $b$ are antiparallel, as in the hydrogen molecule, $\boldsymbol{s}_a\cdot\boldsymbol{s}_b=-3/4$. However, if the spins are mutually random, $\boldsymbol{s}_a\cdot\boldsymbol{s}_b=0$. Penney defined the fractional bond order $P_{ab}$ by a linear interpolation between the two limits. Thus,

$$P_{ab} = -(4/3)\overline{\boldsymbol{s}_a\cdot\boldsymbol{s}_b} \tag{4}$$

$$= (1+2\partial E/\partial J_{ab})/3 \tag{5}$$

Equation (5) shows that, once the energy has been obtained as a function of exchange integrals, the Penney-Dirac bond orders are easy to compute.[21)] This definition of $P_{ab}$ may be extended to general types of wavefunctions.[17)]

Alternatively, we may think of a bonding electron pair as a pair of electrons with singlet coupled spins and generalize the original idea of Penney by operating $-(4/3)\boldsymbol{S}(1)\cdot\boldsymbol{S}(2)$ to 2-matrix for an $N$-electron singlet system. We define a matrix $Q^0$ with space variables alone such that[22-24]

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

where $r_i$ and $s_i$ are the space and spin variables, respectively. The spinless matrix $Q^0$ may be termed the spin coupling matrix.

For an eigenstate of $\boldsymbol{S}^2$ and $\boldsymbol{S}_z$ (with $M_s=0$), 2-matrix can always be decomposed into four components:[24]

$$\begin{aligned}\rho^{(2)}(x_1, x_2; x_1', x_2') &= P_2^{\tau_1\tau_1}\tau_1(s_1, s_2)\tau_1{}^*(s_1', s_2') \\ &+ P_2^{\tau_2\tau_2}\tau_2(s_1, s_2)\tau_2{}^*(s_1', s_2') + P_2^{\tau_3\tau_3}\tau_3(s_1, s_2)\tau_3{}^*(s_1', s_2') \\ &+ P_2^{\sigma\sigma}\sigma(s_1, s_2)\sigma^*(s_1', s_2')\end{aligned} \tag{7}$$

where $P_2^{\tau_1\tau_1}$, *etc.*, are the space functions that depend on $r_1$, $r_2$, $r_1'$, $r_2'$. The four possible spin functions are abbreviated as $\tau_1$, $\tau_2$, $\tau_3$ and $\sigma$:

$$\begin{aligned}\tau_1 &= \alpha(1)\alpha(2) \\ \tau_2 &= \beta(1)\beta(2) \\ \tau_3 &= [\alpha(1)\beta(2)+\beta(1)\alpha(2)]/\sqrt{2} \\ \sigma &= [\alpha(1)\beta(2)-\beta(1)\alpha(2)]/\sqrt{2}\end{aligned} \tag{8}$$

For a singlet state, three functions $P_2^{\tau_1\tau_1}$, $P_2^{\tau_2\tau_2}$ and $P_2^{\tau_3\tau_3}$ are identical,[24] so that they can be written as $P_2^{\tau\tau}$. Considering $\overline{\boldsymbol{S}(1)\cdot\boldsymbol{S}(2)}=-3/4$ and $1/4$ for singlet and triplet pairs, respectively, the $Q^0$ matrix is represented by

$$Q^0(r_1, r_2; r_1', r_2') = P_2^{\sigma\sigma} - P_2^{\tau\tau} \tag{9}$$

When we operate $-4\boldsymbol{S}_z(1)\cdot\boldsymbol{S}_z(2)$ on 2-matrix and integrate over spin variables, we obtain a quantity equal to

$$P_2^{zz} = P_2^{\sigma\sigma} + P_2^{\tau_3\tau_3} - P_2^{\tau_1\tau_1} - P_2^{\tau_2\tau_2} \tag{10}$$

For a singlet state, this quantity coincides with that of the $Q^0$ matrix (Eq. (9)). $\boldsymbol{S}_z(1)\cdot\boldsymbol{S}_z(2)$ givens an expectation value 1/4 for parallel spins and $-1/4$ for antiparallel spins. Thus, we may interpret the $Q^0$ matrix of a singlet state as indicating the difference in the probabilities of two electrons at $r_1$ and $r_2$ being with antiparallel and parallel spins. Note that the terms *antiparallel* and *parallel* are used strictly as an attribute of $\boldsymbol{S}_z(1)\cdot\boldsymbol{S}_z(2)$, whereas the *singlet* and *triplet* pairs are defined on the basis of $\boldsymbol{S}(1)\cdot\boldsymbol{S}(2)$.

On the other hand, the following trace conditions hold[24]:

$$\mathrm{Tr}P_2^{\sigma\sigma} = N(N+2)/8 - S(S+1)/2 \tag{11}$$

$$\frac{1}{3}\mathrm{Tr}(P_2^{\tau_1\tau_1}+P_2^{\tau_2\tau_2}+P_2^{\tau_3\tau_3}) = N(N-2)/8+S(S+1)/6 \tag{12}$$

Therefore, the trace for our $Q^0$ matrix is given by:

$$\mathrm{Tr}Q^0(r_1, r_2; r_1', r_2') = N/2 - 2S(S+1)/3 \tag{13}$$

We regard the $N/2$ pairs represented by the $Q^0$ matrix in a singlet state ($S=0$) as electron pairs in the chemical sense.

It seems natural to base bond orders on the $Q^0$ matrix. To this end, we use a normalized atomic orbital basis set ($a$, $b$, $c$,$\cdots$) and introduce spatial "Heitler-London-like" geminals among these atomic orbitals:

$$\begin{aligned}S_{aa}(r_1, r_2) &= a(r_1)a(r_2) \\ S_{ab}(r_1, r_2) &= [a(r_1)b(r_2)+b(r_1)a(r_2)]/\sqrt{2} \\ T_{ab}(r_1, r_2) &= [a(r_1)b(r_2)-b(r_1)a(r_2)]/\sqrt{2}\end{aligned} \tag{14}$$

$S_{ab}$ and $T_{ab}$ are not necessarily normalized; the overlaps between atomic orbitals are generally nonzero. Using Eq. (14), we define the bond orders $P_{aa}^0$ and $P_{ab}^0$ as

$$\begin{aligned}P_{aa}^0 &= \int S_{aa}^*(r_1, r_2)Q^0(r_1, r_2; r_1', r_2')S_{aa}(r_1', r_2')\mathrm{d}r_1\mathrm{d}r_2\mathrm{d}r_1'\mathrm{d}r_2' \\ &= \int a^*(r_1)a^*(r_2)Q^0(r_1, r_2; r_1', r_2')a(r_1')a(r_2')\mathrm{d}r_1\mathrm{d}r_2\mathrm{d}r_1'\mathrm{d}r_2' \\ P_{ab}^0 &= \int S_{ab}^*(r_1, r_2)Q^0(r_1, r_2; r_1', r_2')S_{ab}(r_1', r_2')\mathrm{d}r_1\mathrm{d}r_2\mathrm{d}r_1'\mathrm{d}r_2' \\ &+ \int T_{ab}^*(r_1, r_2)Q^0(r_1, r_2; r_1', r_2')T_{ab}(r_1', r_2')\mathrm{d}r_1\mathrm{d}r_2\mathrm{d}r_1'\mathrm{d}r_2' \\ &= 2\int a^*(r_1)b^*(r_2)Q^0(r_1, r_2; r_1', r_2')a(r_1')b(r_2')\mathrm{d}r_1\mathrm{d}r_2\mathrm{d}r_1'\mathrm{d}r_2'\end{aligned} \tag{15}$$

By definition of Eq. (15), we may assign the bond order $P_{aa}^0$ and $P_{ab}^0$ to ionic and covalent terms, respectively. It should be noted that the bond orders proposed in this paper are not directly related to bond strength but are some topological indices concerning the electron spin coupling.

## II. Characteristics of the Bond Order

Our bond orders and $Q^0$ matrix have been derived from 2-matrix, and so it is useful to investigate their relations with 1-matrix. By integrating the $Q^0$ matrix of a singlet state with respect to the second electron, we obtain the following relation:

$$P_1(r_1; r_1') = 2\int Q^0(r_1, r_2; r_1', r_2)\mathrm{d}r_2 \tag{16}$$

where $P_1(r_1; r_1')$ is the ordinary spinless 1-matrix defined by

$$P_1(r_1; r_1') = \int_{s_1=s_1'} \rho^{(1)}(x_1; x_1')\mathrm{d}s_1 \tag{17}$$

The proof of Eq. (16) will be given in the Appendix.

Equation (16) means that the spatial distribution of $N$ electrons in $N/2$ paris as represented by the $Q^0$ matrix is identical to the charge density distribution, which has been accepted as a fundamental quantity in usual theories of molecular electronic structure.

The physical meaning of Eq. (16) becomes apparent when this relation is considered on the atomic orbital basis. The spinless 1-matrix is expanded by atomic orbital basis set ($a$, $b$,$\cdots$) in the following way:

$$P_1(r_1; r_1') = \sum_{a,b}\gamma_{ab}^0 a(r_1)b^*(r_1') \tag{18}$$

If we assume an orthogonalized atomic orbital basis set (OAO set), the integration over the one-electron Hilbert space can be divided into subspaces of the atomic orbitals involved. Then, from Eqs. (15), (16) and (18), we obtain

$$\begin{aligned}\gamma_{aa}^0 &= \int a^*(r_1)P_1(r_1; r_1')a(r_1')\mathrm{d}r_1\mathrm{d}r_1' \\ &= 2\sum_b\int a^*(r_1)b^*(r_2)Q^0(r_1, r_2; r_1', r_2')a(r_1')b(r_2')\mathrm{d}r_1\mathrm{d}r_2\mathrm{d}r_1'\mathrm{d}r_2' \\ &= 2P_{aa}^0 + \sum_{b\neq a}P_{ab}^0\end{aligned} \tag{19}$$

Once we have calculated bond orders on OAO basis, the electron population of each AO is easily computed according to Eq. (19). The contribution is two electrons from the ionic term and one electron from the covalent terms, in agreement with usual chemical concepts.

A similiar relation obtains for $\gamma^0_{ab}$, if we define $P^0_{\substack{ac\\bc}}$ as follows:

$$P^0_{\substack{ac\\bc}} = \int S^*_{ac}(r_1, r_2)Q^0(r_1, r_2; r_1', r_2')S_{bc}(r_1', r_2')\mathrm{d}r_1\mathrm{d}r_2\mathrm{d}r_1'\mathrm{d}r_2'$$
$$+ \int T^*_{ac}(r_1, r_2)Q^0(r_1, r_2; r_1', r_2')T_{bc}(r_1', r_2')\mathrm{d}r_1\mathrm{d}r_2\mathrm{d}r_1'\mathrm{d}r_2' \tag{20}$$

The resulting $\gamma^0_{ab}$ is

$$\gamma^0_{ab} = \sqrt{2}(P^0_{\substack{aa\\ba}}+P^0_{\substack{ab\\bb}}) + \sum_{c\neq a.b} P^0_{\substack{ac\\bc}} \tag{21}$$

The meaning of Eq. (21) is to be discussed in a later section.

For single-determinant wavefunctions, 2-matrix can be expressed in terms of the products of 1-matrix.

$$\rho^{(2)}(x_1, x_2; x_1', x_2') = \frac{1}{2}\Big\{\rho^{(1)}(x_1; x_1')\rho^{(1)}(x_2; x_2')$$
$$-\rho^{(1)}(x_2; x_1')\rho^{(1)}(x_1; x_2')\Big\} \tag{22}$$

By a straight manipulation using Eq. (18) we obtain the following expression for $Q^0$ matrix:

$$Q^0(r_1, r_2; r_1', r_2') = \frac{1}{4}\sum_{a.b.c.d}\gamma^0_{ad}\gamma^0_{bc}a(r_1)b(r_2)c^*(r_1')d^*(r_2') \tag{23}$$

The corresponding expressions for bond orders are

$$P^0_{aa} = n^{0\,2}_{aa}/4,\ P^0_{ab} = n^{0\,2}_{ab}/2 \tag{24}$$

where $n^0_{aa}$ and $n^0_{ab}$ are the diagonal and the off-diagonal elements of $\boldsymbol{n}^0$ matrix,

$$\boldsymbol{n}^0 = \boldsymbol{s}\gamma^0\boldsymbol{s} \tag{25}$$

which was first defined by Davidson[13)] and further discussed by Roby[14)] in electronic population analysis. Here $\boldsymbol{s}$ is the ordinary overlap matrix between atomic orbitals and $\gamma^0$ is the matrix whose elements are $\gamma^0_{ab}$ given in Eq. (18). On an OAO basis set, $\boldsymbol{n}^0$ simply reduces to $\gamma^0$.

We immediately see that Wiberg's bond indices[25)]

$$W_{aa} = \gamma^{0\,2}_{aa},\ W_{ab} = \gamma^{0\,2}_{ab} \tag{26}$$

are simply related to our bond orders. Further, the bond index partitioning of atomic charge proposed by Trindle[26)] may be regarded as a special case of Eq. (19), and the localization procedure by bond index maximization[27)] has a clear physical meaning that each localized orbital contributes most to covalent electron pairing between the atomic orbitals concerned.

More generally, molecular wavefunctions are expressed as a linear combination of determinants made up of orthonormal spin orbitals. It will be convenient, therefore, to evaluate the $Q^0$ matrix elements and bond orders explicitly for these wavefunctions.

We consider a many-determinant wavefunction,

$$\Psi = \sum_\kappa a_\kappa\Phi_\kappa \tag{27}$$

The density matrix for the case of the present concern is a simple weighted sum of the transition density matrices connecting all different pairs of determinants which arise from the expansion.

$$Q^0(\kappa\lambda|r_1, r_2; r_1', r_2') = \binom{N}{2}\int_{s_1=s_1',\,s_2=s_2'}\Phi_\kappa(x_1, x_2, \cdots x_N)$$
$$\times\left(-\frac{4}{3}\boldsymbol{S}(s_1)\cdot\boldsymbol{S}(s_2)\right)\Phi_\lambda^*(x_1', x_2', \cdots x_N)\mathrm{d}s_1\mathrm{d}s_2\mathrm{d}x_3\cdots\mathrm{d}x_N \tag{28}$$

$$Q^0(r_1, r_2; r_1', r_2') = \sum_{\kappa,\lambda}a_\kappa a_\lambda^* Q^0(\kappa\lambda|r_1, r_2; r_1', r_2') \tag{29}.$$

We denote by $P^0_{aa}(\kappa\lambda)$ and $P^0_{ab}(\kappa\lambda)$ the bond orders pertaining to $Q^0(\kappa\lambda|r_1,r_2; r_1',r_2')$. Thus

$$P^0_{aa} = \sum_{\kappa,\lambda}a_\kappa a_\lambda^* P^0_{aa}(\kappa\lambda) \text{ and } P^0_{ab} = \sum_{\kappa,\lambda}a_\kappa a_\lambda^* P^0_{ab}(\kappa\lambda) \tag{30}$$

The transition densities and bond orders for determinants representing spin orbital configurations,

$$\kappa = (\phi_1\theta_1, \phi_2\theta_2, \cdots, \phi_i\theta_i, \cdots) \text{ and}$$
$$\kappa' = (\phi_1'\theta_1', \phi_2'\theta_2', \cdots, \phi_i'\theta_i', \cdots)$$

follow at once from Slater's rules:

(i) $\kappa = \kappa' = (\phi_1\theta_1, \phi_2\theta_2, \cdots, \phi_i\theta_i, \cdots)$

$$Q^0(\kappa\kappa|r_1, r_2; r_1', r_2') = \frac{1}{2}\sum_{i,j}\{\varepsilon_1\phi_i(r_1)\phi_j(r_2)\phi_i^*(r_1')\phi_j^*(r_2')$$
$$-\varepsilon_2\phi_j(r_1)\phi_i(r_2)\phi_i^*(r_1')\phi_j^*(r_2')\}$$

$$P^0_{aa}(\kappa\kappa) = \frac{1}{2}\sum_{i,j}(\varepsilon_1-\varepsilon_2)c_{ia}{}^2c_{ja}{}^2$$

$$P^0_{ab}(\kappa\kappa) = \frac{1}{2}\sum_{i,j}\{\varepsilon_1(c_{ia}{}^2c_{jb}{}^2+c_{ja}{}^2c_{ib}{}^2)-2\varepsilon_2c_{ia}c_{ib}c_{ja}c_{jb}\}$$

(ii) $\kappa = (\phi_1\theta_1, \phi_2\theta_2, \cdots, \phi_i\theta_i, \cdots, \phi_j\theta_j \cdots)$
$\kappa' = (\phi_1\theta_1, \phi_2\theta_2, \cdots, \phi_i'\theta_i, \cdots, \phi_j\theta_j, \cdots)$

$$Q^0(\kappa\kappa'|r_1, r_2; r_1', r_2') = \frac{1}{2}\sum_{j\neq i}\{\varepsilon_1\phi_i(r_1)\phi_j(r_2)\phi_i'^*(r_1')\phi_j^*(r_2')$$
$$+\varepsilon_1\phi_j(r_1)\phi_i(r_2)\phi_j^*(r_1')\phi_i'^*(r_2')$$
$$-\varepsilon_2\phi_j(r_1)\phi_i(r_2)\phi_i'^*(r_1')\phi_j^*(r_2')$$
$$-\varepsilon_2\phi_i(r_1)\phi_j(r_2)\phi_j^*(r_1')\phi_i'^*(r_2')\}$$

$$P^0_{aa}(\kappa\kappa') = \sum_{j\neq i}(\varepsilon_1-\varepsilon_2)c_{ja}{}^2c_{ia}c_{i'a}$$
$$P^0_{ab}(\kappa\kappa') = \sum_{j\neq i}\{\varepsilon_1(c_{jb}{}^2c_{ia}c_{i'a}+c_{ja}{}^2c_{ib}c_{i'b})$$
$$-\varepsilon_2c_{ja}c_{jb}(c_{ia}c_{i'b}+c_{ib}c_{i'a})\}$$

(iii) $\kappa = (\phi_1\theta_1, \phi_2\theta_2, \cdots, \phi_i\theta_i, \cdots, \phi_j\theta_j, \cdots)$
$\kappa' = (\phi_1\theta_1, \phi_2\theta_2, \cdots, \phi_i'\theta_i, \cdots, \phi_j'\theta_j, \cdots)$

$$Q^0(\kappa\kappa'|r_1, r_2; r_1', r_2') = \frac{1}{2}\{\varepsilon_1\phi_i(r_1)\phi_j(r_2)\phi_i'^*(r_1')\phi_j'^*(r_2')$$
$$+\varepsilon_1\phi_j(r_1)\phi_i(r_2)\phi_j'^*(r_1')\phi_i'^*(r_2')$$
$$-\varepsilon_2\phi_i(r_1)\phi_j(r_2)\phi_j'^*(r_1')\phi_i'^*(r_2')$$
$$-\varepsilon_2\phi_j(r_1)\phi_i(r_2)\phi_i'^*(r_1')\phi_j'^*(r_2')\}$$

$$P^0_{aa}(\kappa\kappa') = (\varepsilon_1-\varepsilon_2)c_{ia}c_{ja}c_{i'a}c_{j'a}$$
$$P^0_{ab}(\kappa\kappa') = \varepsilon_1(c_{ia}c_{jb}c_{i'a}c_{j'b}+c_{ib}c_{ja}c_{i'b}c_{j'a})$$
$$-\varepsilon_2(c_{ia}c_{jb}c_{i'b}c_{j'a}+c_{ib}c_{ja}c_{i'a}c_{j'b})$$

In all the above equations, $\varepsilon_1$ and $\varepsilon_2$ are defined as follows:

If $\phi_i$ and $\phi_j$ have the same spin,

$$\varepsilon_1 = \varepsilon_2 = -1/3;$$

If $\phi_i$ and $\phi_j$ have different spins,

$$\varepsilon_1 = 1/3 \text{ and } \varepsilon_2 = -2/3.$$

$c_{ia}$, *etc.*, are the overlap between orbital $\phi_i$ and atomic orbital $a$

$$c_{ia} = \langle\phi_i|a\rangle = \sum_b d_{ib}s_{ab} \tag{31}$$

$d_{ib}$ being the usual LCAO coefficients.

For a special case in which $\kappa=\kappa'=(\phi_1\alpha,\ \phi_1\beta,\cdots\phi_i\alpha,\ \phi_i\beta\cdots)$, the bond orders $P^0_{aa}(\kappa\kappa)$ and $P^0_{ab}(\kappa\kappa)$ reduce to

$$P^0_{aa}(\kappa\kappa) = (\sum_i c_{ia}{}^2)^2 \tag{32}$$

$$P^0_{ab}(\kappa\kappa) = 2(\sum_i c_{ia}c_{ib})^2 \tag{33}.$$

Noting that

$$\gamma^0_{\mu\nu} = 2\sum_i d_{i\mu}d_{i\nu}, \tag{34}$$

Eqs. (32) and (33) can readily be verified to be identical with Eq. (24) for a single determinant case.

Incidentally, it will be appropriate to define an atom-atom bond order, $P^0_{\mathrm{AB}}$, as a simple sum of the bond orders between the atomic orbitals on atoms A and B

$$P^0_{\mathrm{AB}} = \sum_a^{\text{on A}} \sum_b^{\text{on B}} P^0_{ab} \tag{35}.$$

If atomic orbitals on a given atom are assumed to be orthogonal, as is usually the case, the atom-atom bond order remains invariant under a unitary transformation of AO basis within each atom. This invariance is easily derived from the fact that the one-electron Hilbert space for each atom is constant under the transformation.

## III. Bond Order and Molecular Binding

As has already been stated, the bond order defined in the present paper has no bearing with energy derivatives but is a topological index of spin coupling. Thus, the bond order of dissociated hydrogen molecule is 1 but there exists no energy stabilization. None the less, it is expected that one may gain some insight into molecular binding, using the present bond order concept.

In molecular orbital theory the binding energy is ascribed to resonance integrals, $\beta_{ab}$. Slater[28] and McWeeny[29] pointed out that this integral is also responsible for molecular binding in valence bond theory. Generally, the expression of total electronic energy contains a term $\sum_{a.b}\gamma^0_{ab}\beta_{ab}$, and $\gamma^0_{ab}$ is considered to be some measure of binding. Fortunately, the electronic structure of stable molecules can well be represented by a single-determinant wavefunction. In this case the bond order, $P^0_{ab}$, simply reduces to $\gamma^0_{ab}{}^2/2$. Therefore, $P^0_{ab}$ might also be a measure of binding, which varies more sharply than $\gamma^0_{ab}$.

In this connection, use of an effective one-electron Hamiltonian

$$h(1) = T(1) + V_a(1) + V_b(1) \tag{36}$$

is suggestive. The expectation values of this hamiltonian between "Heitler-London-like" geminals are

$$\langle S_{ab}|h(1)|S_{ab}\rangle = (E_a+E_b+2s_{ab}\beta_{ab})/2 \tag{37}$$

and

$$\langle T_{ab}|h(1)|T_{ab}\rangle = (E_a+E_b-2s_{ab}\beta_{ab})/2 \tag{38}$$

which show that the energy stabilization, $s_{ab}\beta_{ab}$, results if electrons in $a$ and $b$ couple into a singlet pair, whereas there appears a repulsive interaction of $-s_{ab}\beta_{ab}$ in triplet coupling. It can be concluded that the bond order, $P^0_{ab}$, which assures a net stabilization roughly proportional to $s^2_{ab}$, is a certain measure of the latent capability with which an electron pair can enter into covalent binding when the overlap between the relevant atomic orbitals becomes sufficiently large.

On the OAO basis set, we must turn to Eq. (21). $P^0_{\substack{aa\\ba}}$, $P^0_{\substack{ab\\bb}}$ and $P^0_{\substack{ac\\bc}}$ are interpreted as an intensity of resonance between the corresponding structures of electron pairing. Because $\gamma^0_{ab}$ is a sum of many such terms, examination of its significance in chemical binding is somewhat boring to make. However, in single-determinant wavefunctions each term in Eq. (21) takes a simple form:

$$P^0_{\substack{aa\\ba}} = \gamma^0_{aa}\gamma^0_{ab}/2\sqrt{2},\quad P^0_{\substack{ab\\bb}} = \gamma^0_{bb}\gamma^0_{ab}/2\sqrt{2},$$

$$P^0_{\substack{ac\\bc}} = \gamma^0_{ac}\gamma^0_{bc}/2 \tag{39}$$

Substituting these expressions into Eq. (21), we obtain

$$\gamma^0_{ab} = (\gamma^0_{aa}+\gamma^0_{bb})\gamma^0_{ab}/2 + \sum_{c\neq a.b}\gamma^0_{ac}\gamma^0_{bc}/2 \tag{40}.$$

When the sum of populations on $a$ and $b$ equals 2, as is generally expected in electron pair bonds, $\gamma^0_{ab}$ can in effect be imparted to $P^0_{\substack{aa\\ba}}$ and $P^0_{\substack{ab\\bb}}$ only. This result verifies the picture that the resonance between covalent and ionic structures is responsible for chemical binding depicted on the OAO basis.

## IV. Extension to a Doublet State

It is desired to extend the analysis of electron pairs in previous sections to nonsinglet states. As can be seen from Eq. (13), the trace of the $Q^0$ matrix for these states is no longer equal to the number of singlet pairs. Obviously, we must add a certain quantity to make up the difference.

In this section we consider doublet states with $N$ electrons which would be interpreted as $(N-1)/2$ pairs plus one odd electron. Integration of the $Q^0$ matrix over the second electron yields

$$P_1(r_1;r_1') - D_s(r_1;r_1') = 2\int Q^0(r_1,r_2;r_1',r_2)\mathrm{d}r_2 \tag{41}$$

where $D_s(r_1;r_1')$ is a normalized spin density matrix[30,31] defined by

$$D_s(r_1;r_1') = \frac{1}{M_s}\int_{s_1=s_1'} \mathbf{S}_z(s_1)\rho^{(1)}(x_1;x_1')\mathrm{d}s_1 \tag{42}$$

The relationship (41) will be proved in the Appendix.

Equation (41) can be interpreted as an indication that the electron distribution may be decomposed to $(N-1)/2$ pairs and an odd electron. The former distribution is represented by the same $Q^0$ matrix as in singlet states while the latter comes from the spin density matrix.

For an electron distribution represented by Eq. (41) the electron population on each atomic orbital is expressed by bond orders and spin density as follows:

$$\gamma^0_{aa} = 2P^0_{aa} + \sum_{b\neq a}P^0_{ab} + \gamma^s_{aa} \tag{43}$$

where $\gamma^s_{aa}$ is an expansion coefficient of the spin density matrix

$$D_S(r_1;r_1') = \frac{1}{2S}\sum_{a.b}\gamma^s_{ab}a(r_1)b^*(r_1'). \tag{44}$$

As an example, we consider a linear $H_3$ system and show the distributions of one electron pair and one odd electron obtained from the HMO solution. Two configurations were considered: (a) an $H_2$ molecule plus an H radical; and (b) the linear symmetrical $H_3$ radical. The various bond quantities are as shown in Fig. 1.

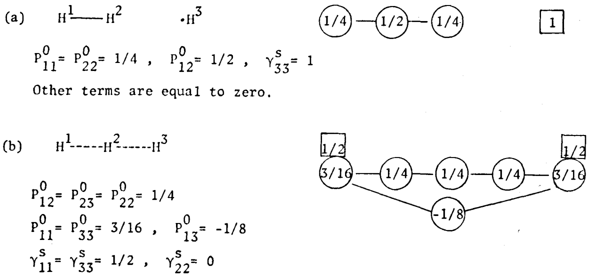


Fig. 1. Distribution of bond quantities in the linear $H_3$ molecule. The quantities pertaining to electron pairs and odd electrons are shown in circles and squares, respectively.

## V. States with Higher Spin Multiplicities

We may interpret the electronic structure of an $N$-electron system having a resultant spin $S \geq 1$ in the following two fashions. One is a system comprising $(N/2-S)$ electron pairs and $2S$ odd electrons while the other is $N/2$ pairs in which $(N/2-S)$ pairs are singlet type and the remaining $S$ pairs are triplet type. Here we proceed along the latter line.

We now must seek for a density function which represents the distribution of triplet type pairs. The triplet type pairs of the present concern should be anisotropic ones which give the total spin angular momentum $S$, and are the origin of spin-spin dipolar interactions.[23,31,32] Further, it is preferred that this density function does not depend on the axis of spin quantization.

To meet these requirements, it seems appropriate to introduce the normalized spin-spin coupling function, $D_{SS}(r_1,r_2;r_1',r_2')$, defined by McWeeny.[31] This function is obtained by operating an irreducible tensor operator of rank 2, $3\boldsymbol{S}_z\cdot\boldsymbol{S}_z-\boldsymbol{S}\cdot\boldsymbol{S}$, to 2-matrix:

$$D_{SS}(r_1,r_2;r_1',r_2') = \frac{2}{S(2S-1)}\int_{s_1=s_1',s_2=s_2'}(3\boldsymbol{S}_z(s_1)\cdot\boldsymbol{S}_z(s_2) - \boldsymbol{S}(s_1)\cdot\boldsymbol{S}(s_2))\rho^{(2)}_{\mathrm{st}}(x_1,x_2;x_1',x_2')ds_1ds_2 \tag{45}$$

where the subscript st on 2-matrix denotes that a standard state with $\langle S_z\rangle = S$ is assumed. It has been shown that the function is invariant against different $\langle S_z\rangle$ values. The four spin functions in Eq. (8) are eigenfunctions of this operator.

$$3\boldsymbol{S}_z(s_1)\cdot\boldsymbol{S}_z(s_2)-\boldsymbol{S}(s_1)\cdot\boldsymbol{S}(s_2)\begin{cases}\tau_1(s_1,s_2) = \frac{1}{2}\tau_1(s_1,s_2)\\ \tau_2(s_1,s_2) = \frac{1}{2}\tau_2(s_1,s_2)\\ \tau_3(s_1,s_2) = -\tau_3(s_1,s_2)\\ \sigma(s_1,s_2) = 0\ \sigma(s_1,s_2)\end{cases} \tag{46}$$

Obviously, neither of the electron pairs in singlet and random couplings contributes to $D_{SS}$.

We obtain $D_S(r_1;r_1')$ by integrating $D_{SS}(r_1,r_2;r_1',r_2')$ over the second electron.

$$D_S(r_1;r_1') = \int D_{SS}(r_1,r_2;r_1',r_2)dr_2 \tag{47}$$

On the other hand, the $Q^0$ matrix, upon integration, gives the following relation,

$$P_1(r_1;r_1') - \frac{4}{3}S(S+1)D_S(r_1;r_1') = 2\int Q^0(r_1,r_2;r_1',r_2)dr_2 \tag{48}$$

Equations (47) and (48) will be proved in the Appendix.

We are now at the position to define a matrix, $Q^2$, representing the distribution of triplet type pairs. It is most advantageous to define it by

$$Q^2(r_1,r_2;r_1',r_2') = \frac{2}{3}S(S+1)D_{SS}(r_1,r_2;r_1',r_2') \tag{49}$$

which leads to a simple relation

$$P_1(r_1;r_1') = 2\int\{Q^0(r_1,r_2;r_1',r_2) + Q^2(r_1,r_2;r_1',r_2)\}dr_2 \tag{50}$$

We define the corresponding bond order, $P^2_{ab}$, from $Q^2$ matrix as in Eq. (15).

$$P^2_{ab} = 2\int a^*(r_1)b^*(r_2)Q^2(r_1,r_2;r_1',r_2')a(r_1')b(r_2')dr_1dr_2dr_1'dr_2' \tag{51}$$

On the OAO basis, the electron population on each atomic orbital is expressed by $P^0_{aa}$, $P^0_{ab}$ and $P^2_{ab}$:

$$\gamma^0_{aa} = 2P^0_{aa} + \sum_{b\neq a}(P^0_{ab}+P^2_{ab}) \tag{52}$$

Alternatively, in chemical interpretations, it is preferred that negative values are assigned to triplet coupled electron pairs. When we regard $N/2$ pairs as comprising $(N/2-S)$ singlet pairs and $S$ triplet pairs, it is appropriate to use the following density function

$$Q^T = Q^0(r_1,r_2;r_1',r_2') + [(S-2)/(S+1)]Q^2(r_1,r_2;r_1',r_2') \tag{53}$$

and the bond order

$$P^T_{ab} = P^0_{ab} + [(S-2)/(S+1)]P^2_{ab} \tag{54}$$

On the OAO basis set, the sum of these bond orders is equal to $(N/2-2S)$, which is the difference in number between the singlet and triplet pairs.

In single-determinant wavefunctions with a definite spin angular momentum $S$, $Q^0$ and $Q^2$ matrices take the following forms:

$$Q^0(r_1,r_2;r_1',r_2') = \frac{1}{12}\sum_{a.b.c.d}(3\gamma^0_{ad}\gamma^0_{bc}-\gamma^s_{ad}\gamma^s_{bc}-2\gamma^s_{ac}\gamma^s_{bd}) \times a(r_1)b(r_2)c^*(r_1')d^*(r_2') \tag{55}$$

$$Q^2(r_1,r_2;r_1',r_2') = \frac{S+1}{3(2S-1)}\sum_{a.b.c.d}(\gamma^s_{ac}\gamma^s_{bd}-\gamma^s_{ad}\gamma^s_{bc}) \times a(r_1)b(r_2)c^*(r_1')d^*(r_2') \tag{56}$$

If we define $\boldsymbol{n}^s$ matrix by $\boldsymbol{n}^s = \boldsymbol{s}\gamma^s\boldsymbol{s}$ as in Eq. (25), the bond orders resulting from Eqs. (55) and (56) are

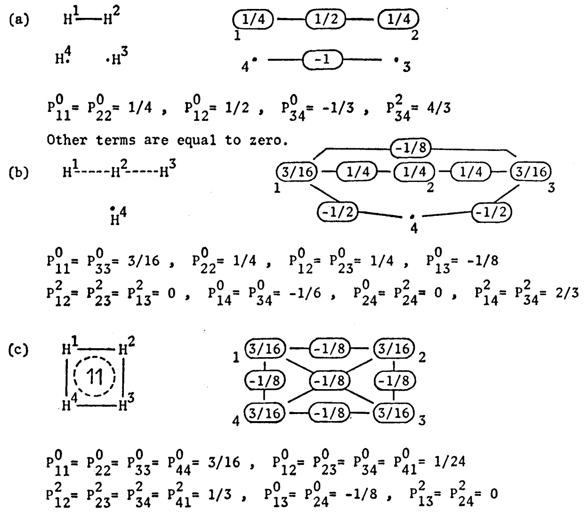
$$P^0_{aa} = ({n^0_{aa}}^2-{n^s_{aa}}^2)/4 \tag{57}$$

$$P^0_{ab} = (3{n^0_{ab}}^2-{n^s_{ab}}^2-2n^s_{aa}n^s_{bb})/6 \tag{58}$$

$$P^2_{ab} = [2(S+1)/3(2S-1)](n^s_{aa}n^s_{bb}-{n^s_{ab}}^2) \tag{59}$$

These generalized bond orders can be applied to singlet and doublet states as well.

We conclude the context by considering the $H_4$ system in a triplet state as an example. Three possible configurations are examined: (a) an $H_2$ molecule plus two H atoms; (b) an $H_3$ linear symmetrical doublet radical plus one H atom; and (c) an $H_4$ square planar configuration. The bond orders defined by Eq. (54) were calculated in the simple HMO approximation. The results are collected in Fig. 2.



$P^0_{11} = P^0_{22} = 1/4$ , $P^0_{12} = 1/2$ , $P^0_{34} = -1/3$ , $P^2_{34} = 4/3$

Other terms are equal to zero.

$P^0_{11} = P^0_{33} = 3/16$ , $P^0_{22} = 1/4$ , $P^0_{12} = P^0_{23} = 1/4$ , $P^0_{13} = -1/8$

$P^2_{12} = P^2_{23} = P^2_{13} = 0$ , $P^0_{14} = P^0_{34} = -1/6$ , $P^0_{24} = P^2_{24} = 0$ , $P^2_{14} = P^2_{34} = 2/3$

$P^0_{11} = P^0_{22} = P^0_{33} = P^0_{44} = 3/16$ , $P^0_{12} = P^0_{23} = P^0_{34} = P^0_{41} = 1/24$

$P^2_{12} = P^2_{23} = P^2_{34} = P^2_{41} = 1/3$ , $P^0_{13} = P^0_{24} = -1/8$ , $P^2_{13} = P^2_{24} = 0$

Fig. 2. Distribution of bond quantities in the triplet $H_4$ molecule. The bond orders defined by Eq. (54) are depicted.

## VI. Concluding Remarks

We have shown in this introductory study that the electron pair concept as used in chemistry can be characterized adequately by the spin coupling matrices $Q^0$ and $Q^2$. These matrices in turn permit definitions of the generalized Penney-Dirac bond orders, from which the covalent and ionic characters of chemical binding can immediately be understood.

On the other hand, the contact nuclear spin-spin coupling constants are known to be a measure of the covalent bonding character.[33-35] Also, it has been shown implicitly that the bond order $P^0_{ab}$ can be related to nuclear spin-spin coupling constants, provided a mean excitation energy approximation is adopted.[23,36-38] The situation endorses the usefulness of the bond order here defined.

The allowed and forbidden characters of chemical reactions are also a problem of current interest. Continuity of the bond order along reaction path has successfully been used for this purpose in connection with the space and spin symmetry conservations.[39,25] It was particularly with such uses for reactivity problems in mind that we decided to undertake the present analytical study. The concept of electron pair shift as was put forth by Robinson and Ingold[40] will be treated in a succeeding paper.

The authors would like to thank Dr. K. Yamaguchi for his helpful discussions.

TABLE 1. $\Phi^0_{ij}(r_1,r_2;\ r_1{}',r_2{}')$ AND $\Phi^2_{ij}(r_1,r_2,;\ r_1{}',r_2{}')$ IN TERMS OF "HEITLER-LONDON-LIKE" BASIS (STANDARD STATES)

| | $Q^0$ | $[3(2S-1)/4(S+1)]Q^2$ |
|---|---|---|
| (a) $\phi_i \neq \phi_j;\ \phi_{i'} \neq \phi_{j'}$ | | |
| (i) Same island, $p_{ij}=-1$ | $S_{ij}S'^{*}_{ij}$ | 0 |
| (ii) Same island, $p_{ij}=+1$ | $-\frac{1}{2}(S_{ij}S'^{*}_{ij}+T_{ij}T'^{*}_{ij})$ | 0 |
| (iii) Different islands | $\frac{1}{4}(S_{ij}S'^{*}_{ij}-T_{ij}T'^{*}_{ij})$ | 0 |
| (iv) $i$ in island, $j$ in $O$-chain | $\frac{1}{4}(S_{ij}S'^{*}_{ij}-T_{ij}T'^{*}_{ij})$ | 0 |
| (v) Same $O$-chain, $p_{ij}=-1$ | $S_{ij}S'^{*}_{ij}$ | 0 |
| (vi) Same $O$-chain, $p_{ij}=+1$ | $-\frac{1}{2}(S_{ij}S'^{*}_{ij}+T_{ij}T'^{*}_{ij})$ | 0 |
| (vii) Different $O$-chains, $p_{ij}=+1$ | $-\frac{1}{3}T_{ij}T'^{*}_{ij}$ | $\frac{1}{2}T_{ij}T'^{*}_{ij}$ |
| (viii) Different $O$-chains, $p_{ij}=-1$ | $\frac{1}{2}S_{ij}S'^{*}_{ij}-\frac{1}{6}T_{ij}T'^{*}_{ij}$ | $-\frac{1}{2}T_{ij}T'^{*}_{ij}$ |
| (ix) Different $E$-chains, $p_{ij}=+1$ | $-\frac{1}{2}S_{ij}S'^{*}_{ij}-\frac{1}{6}T_{ij}T'^{*}_{ij}$ | $-\frac{1}{2}T_{ij}T'^{*}_{ij}$ |
| (x) Different $E$-chains, $p_{ij}=-1$ | $\frac{1}{2}S_{ij}S'^{*}_{ij}+\frac{1}{6}T_{ij}T'^{*}_{ij}$ | $\frac{1}{2}T_{ij}T'^{*}_{ij}$ |
| (b) $\phi_i \neq \phi_j;\ \phi_{i'}=\phi_{j'}$ or $\phi_i=\phi_j;\ \phi_{i'} \neq \phi_{j'}$ | | |
| (xi) Same island | $\frac{1}{\sqrt{2}}S_{ij}S'^{*}_{ij}$ | 0 |
| (xii) Same $O$-chain | $\frac{1}{\sqrt{2}}S_{ij}S'^{*}_{ij}$ | 0 |
| (c) $\phi_i=\phi_j;\ \phi_{i'}=\phi_{j'}$ | | |
| (xiii) Same island | $S_{ij}S'^{*}_{ij}$ | 0 |

## Appendix

Our purpose is to prove Eqs. (47) and (48).

$$D_S(r_1;r_1') = \int D_{SS}(r_1,r_2;r_1',r_2)\mathrm{d}r_2 \tag{47}$$

$$P_1(r_1;r_1') - \frac{4}{3}S(S+1)D_S(r_1;r_1') = 2\int Q^0(r_1,r_2;r_1',r_2)\mathrm{d}r_2 \tag{48}$$

Both Eqs. (16) and (41) are special cases of Eq. (48).

To derive these relations it is convenient to use the results obtained by Cooper and McWeeny,[41,42] who expressed a wavefunction of configuration interaction type in the form

$$\Psi = \sum_{\kappa} a_{\kappa}\Psi_{\kappa} \tag{60}$$

where the $\Psi_{\kappa}$ are general spin-coupled functions of valence bond type arising from arbitrary orbital configurations. They derived the general expressions of various transition density functions for any pair of standard states $\kappa$ and $\lambda$. From Eq. (4.2) in reference (41) we can easily write $Q^0$ and $Q^2$ matrices in the following form:

$$Q(\kappa\lambda|r_1,r_2;r_1',r_2') = M_{\kappa\lambda}\Delta_{\kappa\lambda}\sum_{i,j}^{\text{(pairs)}}\xi_{ij}\Phi_{ij}(r_1,r_2;r_1',r_2') \tag{61}$$

where $\Phi_{ij}$ is expressed in terms of the "Heitler-London-like" geminals as used in Eq. (14). The $\Phi_{ij}$ 's relevant to $Q^0$ and $Q^2$ matrices are listed in Table 1. For other symbols, original papers by Cooper and McWeeny are to be referred.

On the other hand, the $P_1$ and $D_S$ matrices are written in the forms

$$P_1(\kappa\lambda|r_1;r_1') = M_{\kappa\lambda}\Delta_{\kappa\lambda}\sum_{i=1}^{N}\xi_i\phi_i(r_1)\phi_{i'}^*(r_1') \tag{62}$$

$$D_S(\kappa\lambda|r_1;r_1') = (1/S)M_{\kappa\lambda}\Delta_{\kappa\lambda}\sum_{i=1}^{N}\xi_i x_i\phi_{i1}(r_1)\phi_{i'}^*(r_1') \tag{63}$$

where $x_i = \frac{1}{2}p_i$ if $i$ is in an $O$-chain

$= 0$ otherwise.

It should be noted that no contribution occurs in this category if there are two or more orbital differences, or if any $E$-chain occurs.

The relations (47) and (48) are replaced by similar relations among the transition densities for each pair of standard states $\kappa$ and $\lambda$. The two-body terms expressed by "Heitler-London-like" geminals give the following one-body terms by integrating over the second electron.

$$\int S_{ij}(r_1,r_2)S_{ij}'^*(r_1',r_2)\mathrm{d}r_2 =$$

$$\varepsilon\{\phi_i(r_1)\phi_{i'}^*(r_1')\delta_{\phi_j\phi_{j'}} + \phi_j(r_1)\phi_{j'}^*(r_1')\delta_{\phi_i\phi_{i'}}\} \tag{64}$$

where

$\varepsilon = 1/2$ for $\phi_i \neq \phi_j$; $\phi_{i'} \neq \phi_{j'}$ or $\phi_i = \phi_j$; $\phi_{i'} = \phi_{j'}$

$\varepsilon = 1/\sqrt{2}$ for $\phi_i \neq \phi_j$; $\phi_{i'} = \phi_{j'}$ or $\phi_i = \phi_j$; $\phi_{i'} \neq \phi_{j'}$

$$\int T_{ij}(r_1,r_2)T_{ij}'^*(r_1',r_2)\mathrm{d}r_2 =$$

$$\frac{1}{2}\{\phi_i(r_1)\phi_{i'}^*(r_1')\delta_{\phi_j\phi_{j'}} + \phi_j(r_1)\phi_{j'}^*(r_1')\delta_{\phi_i\phi_{i'}}\} \tag{65}.$$

It is verified from the above equations that $Q^0$ and $Q^2$ densities between standard states with more than two orbital differences do not contribute to the $P_1$ and $D_S$ densities.

The proof is given for a case with no orbital difference. The contributions to $\phi_i(r_1)\phi_i^*(r_1')$ from $Q^0$ densities are obtained from Table 1 as follows.

[$i$ in island]

$$\left.\begin{array}{ll}\text{(i), (xiii)}\rightarrow & \frac{1}{2}\phi_i\phi_i^* \\ \text{(ii)} \rightarrow & -\frac{1}{2}\phi_i\phi_i^* \\ \text{(iii), (iv)}\rightarrow & 0\end{array}\right\} - \frac{1}{2}\phi_i\phi_i^*$$

The number of pairs with $p_{ij} = -1$ is always more than that with $p_{ij} = +1$ by one, so that the sum of the above terms is $\phi_i\phi_i^*/2$.

[$i$ in $O$-chain]

$$\begin{array}{lcc} & p_i=1 & p_i=-1 \\ \text{(iv)} \rightarrow 0 & & \\ \left.\begin{array}{ll}\text{(v)} \rightarrow & \frac{1}{2}\phi_i\phi_i^* \\ \text{(vi)} \rightarrow & -\frac{1}{2}\phi_i\phi_i^*\end{array}\right\} - & 0 & \phi_i\phi_i^* \\ \left.\begin{array}{ll}\text{(vii)} \rightarrow & -\frac{1}{6}\phi_i\phi_i^* \\ \text{(viii)} \rightarrow & \frac{1}{6}\phi_i\phi_i^*\end{array}\right\} - & -\frac{1}{6}\phi_i\phi_i^* & \frac{1}{6}\phi_i\phi_i^*\end{array}$$

The results of summation are obtained by counting the number of pairs with $p_{ij} = +1$ and $p_{ij} = -1$. Further, the number of $O$-chains is equal to $2S$, where $S(S+1)$ is the eigenvalue of the $S^2$ operator. We get the expression of one-body terms in the following forms:

$$p_i = +1 \qquad \frac{1-2S}{6}\phi_i\phi_i^*$$

$$p_i = -1 \qquad \frac{2S+5}{6}\phi_i\phi_i^*$$

[$i$ in $E$-chain]

$$\left.\begin{array}{ll}\text{(ix)} \rightarrow & -\frac{1}{3}\phi_i\phi_i^* \\ \text{(x)} \rightarrow & \frac{1}{3}\phi_i\phi_i^*\end{array}\right\} - 0$$

The one-body terms from (ix) and (x) always cancel each other, so we can disregard the transition densities if any $E$-chain occurs.

On the other hand, the left-hand side of Eq. (48) is expressed by

$$M_{\kappa\lambda}\Delta_{\kappa\lambda}\sum_{i=1}^{N}\{1-\frac{4}{3}(S+1)\times\frac{1}{2}p_i\}\phi_i(r_1)\phi_i^*(r_1') \tag{66}$$

where the second term in blackets is counted only if $i$ is in $O$-chains. The expression (66) completely agrees with twice the sum of the various terms derived above.

We may obtain the contributions to $\phi_i(r_1)\phi_i^*(r_1')$ from $Q^2$ densities similarly.

[$i$ in $O$-chain]

$$\begin{array}{lcc} & p_i=1 & p_i=-1 \\ \left.\begin{array}{ll}\text{(vii)} \rightarrow & \frac{1}{4}\phi_i\phi_i^* \\ \text{(viii)} \rightarrow & -\frac{1}{4}\phi_i\phi_i^*\end{array}\right\} - & \frac{1}{4}\phi_i\phi_i^* & -\frac{1}{4}\phi_i\phi_i^*\end{array}$$

[$i$ in $E$-chain]

$$\left.\begin{array}{ll}\text{(ix)} \rightarrow & -\frac{1}{4}\phi_i\phi_i^* \\ \text{(x)} \rightarrow & \frac{1}{4}\phi_i\phi_i^*\end{array}\right\} - 0$$

Then $[(2S-1)p_i/4]\phi_i(r_1)\phi_i^*(r_1')$ is the result of summation among all $O$-chains. Then, from Eq. (49) we obtain

$$\int D_{SS}(\kappa\lambda|r_1, r_2; r_1', r_2)\mathrm{d}r_2 = M_{\kappa\lambda}\varDelta_{\kappa\lambda} \sum_{i}^{\text{in } O\text{-chain}} (1/2S)p_i\phi_i(r_1)\phi_i^*(r_1')$$
$$= D_S(\kappa\lambda|r_1; r_1')$$

The proof for the case with one orbital difference can be obtained in a similar way and hence omitted.

## References

1) G. N. Lewis, "Valence and the Structure of Atoms and Molecules," (1923), New York, Chemical Catalog Co.

2) W. Heitler and F. London, *Z. Phys.*, **44**, 455 (1927).

3) Y. Sugiura, *ibid.*, **45**, 484 (1927).

4) L. Pauling, "The Nature of the Chemical Bond," Cornell Univ. Press, New York (1940).

5) J. Lennard-Jones, *Proc. Roy. Soc., Ser. A*, **198**, 1, 14 (1949).

6) C. Edmiston and K. Ruedenberg, *Rev. Mod. Phys.*, **35**, 457 (1963).

7) For examples; J. M. Parks and R. G. Parr, *J. Chem. Phys.*, **28**, 335 (1958): W. A. Goddard, III, *Phys. Rev.*, **157**, 81 (1967): W. A. Goddard, III, T. H. Dunning, Jr., W. J. Hunt, and P. J. Hay, *Accounts Chem. Res.*, **6**, 368 (1973): K. J. Miller and K. Ruedenberg, *J. Chem. Phys.*, **48**, 3444 (1968).

8) K. Husimi, *Proc. Phys. Math. Soc. Japan*, **22**, 264 (1940).

9) P.-O. Löwdin, *Phys. Rev.*, **97**, 1474 (1955).

10) R. McWeeny, *Rev. Mod. Phys.*, **32**, 335 (1960).

11) C. A. Coulson, *Proc. Roy. Soc., Ser. A*, **169**, 413 (1939); A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, Inc., New York (1961).

12) R. McWeeny, *J. Chem. Phys.*, **19**, 1614 (1951); R. S. Mulliken, *ibid.*, **23**, 1833 (1955).

13) E. R. Davidson, *ibid.*, **46**, 3320 (1967).

14) K. R. Roby, *Mol. Phys.*, **27**, 81 (1974); *Theoret. Chim. Acta*, **33**, 105 (1974) and references therein.

15) K. Ruedenberg, *Rev. Mod. Phys.*, **34**, 326 (1962).

16) B. M. Deb, *ibid.*, **45**, 22 (1973).

17) C. A. Coulson and R. G. A. R. MacLagan, *Adv. Chem. Phys.*, **21**, 303 (1971); R. G. A. R. MacLagan, *Mol. Phys.*, **22**, 821 (1971).

18) W. G. Penney, *Proc. Roy. Soc., Ser. A*, **158**, 306 (1937).

19) P. A. M. Dirac, *ibid.*, *Ser. A*, **123**, 714 (1929).

20) J. Van Vleck and A. Sherman, *Rev. Mod. Phys.*, **7**, 167 (1935).

21) D. Clarkson, C. A. Coulson, and T. H. Goodwin, *Tetrahedron*, **19**, 2153 (1963).

22) The $Q^0$ matrix is the same as the $D_{\mathrm{st}}$ matrix defined by McWeeny and Mizuno[23] and the $R_2^0$ matrix defined by Kutzelnigg,[24] if proper multiplicative constants are included. The superscript 0 is attached because $\boldsymbol{S}(1)\cdot\boldsymbol{S}(2)$ is an irreducible tensor operator of rank 0.

23) R. McWeeny and Y. Mizuno, *Proc. Roy. Soc., Ser. A*, **259**, 554 (1961).

24) W. Kutzelnigg, *Z. Naturforsch.*, **18a**, 1058 (1963); **20a**, 168 (1965).

25) K. B. Wiberg, *Tetrahedron*, **24**, 1083 (1968).

26) C. Trindle, *J. Amer. Chem. Soc.*, **91**, 219 (1969).

27) C. Trindle, *ibid.*, **92**, 3251 (1970).

28) J. C. Slater, *J. Chem. Phys.*, **19**, 220 (1951).

29) R. McWeeny, *Proc. Roy. Soc., Ser. A*, **223**, 63, 306 (1953).

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

31) R. McWeeny, *ibid.*, **42**, 1717 (1965).

32) A. D. McLachlan, *Mol. Phys.*, **5**, 51 (1962).

33) J. B. Stothers, "Carbon-13 NMR Spectroscopy," Academic Press, New York (1971).

34) M. H. Chisholm, H. C. Clark, L. E. Manzer, and J. B. Stothers, *J. Amer. Chem. Soc.*, **94**, 5087 (1972).

35) T. Ibusuki and Y. Saito, *Chem. Lett.*, **1973**, 1255.

36) H. M. McConnell, *J. Chem. Phys.*, **24**, 460 (1956).

37) L. Salem, "The Molecular Orbital Theory of Conjugated Systems," W. A. Benjamin, Inc., New York (1966).

38) M. Barfield and M. Karplus, *J. Amer. Chem. Soc.*, **91**, 1 (1969), and references therein.

39) K. Yamaguchi, *Chem. Phys. Lett.*, **28**, 93 (1974).

40) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Bell, London (1953).

41) I. L. Cooper and R. McWeeny, *J. Chem. Phys.*, **45**, 226 (1966).

42) I. L. Cooper, *ibid.*, **50**, 2166 (1969).