

# An analysis of VB structures in MO wave functions I

## The ground state of some conjugated hydrocarbons

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**Summary.** A new method for the resolution of an antisymmetrized product of molecular orbitals into VB structures is proposed. Here VB structures are projected from a single Slater determinant associated with the ground state using the first-order density matrix. The present theory is applied to the ground state of some conjugated hydrocarbons, and special attention is paid to the covalent type VB structures.

**Key words:** Spin distribution – Density matrix – VB structure

### 1 Introduction

Most chemists have been accustomed to the molecular structural formula that shows the covalent chemical bond by the line and the ionic site by the minus or plus sign. Although the conception of the structural formula becomes obscure in LCAO MOs, it remains explicitly in the valence bond (VB) method and some interesting studies based on the VB method have been reported [1–3]. In spite of this advantage, the VB method has been less used than the LCAO MO treatment because of its complexity incidental to the practical calculation. Therefore, the attempt to draw out the graphical image of a molecule hidden in the LCAO MO results should be meaningful for chemists. A successful attempt is the localized molecular orbitals (LMO) method, and some kinds of localization conditions have been proposed [4, 5]. The LMO method is based on the concept that a molecule is considered as an assembly of “two center–two electron molecules” (conventional chemical bond). Consequently, LMOs may be classified to the covalent type VB structure from a viewpoint of the VB theory. A series of studies based on the LMO method [4, 6, 7] have been proposed by Ruedenberg and co-workers [8, 9]. They have also analyzed the delocalization energy and aromatic stability in terms of localized  $\pi$ -orbitals [10, 11].

Cantu has proposed the decomposing method of a determinantal function into VB components, and he has paid much attention to the spin degeneracy problem of linearly independent VB functions [12]. On the other hand, Hiberty et al. have proposed the direct expansion method of MO wave functions into VB wave functions [13–15]. However, there are still two complicated problems concerning “electron correlation” and “spin degeneracy”. In order to solve these problems, Gerratt et al.

have studied from a standpoint of the spin-coupled valence bond theory, and they have presented the important general remarks on MO–CI and VB wave functions [16].

As our analysis is based on the idea of decomposing the molecule into the components of VB structures, it is closely related to the studies for analyzing the partial structure in a molecule. The benzene character in the aromatic hydrocarbons has been analyzed based on the idea of expanding the MO functions of the parent molecule by the reference ones [17]. The idea has been followed by the configuration analysis [18], the energy decomposition [19], and other studies. An analysis of VB structures in MOs has been proposed utilizing the bond index [20] and applied to some molecules of ground state structures [21]. This method has also been applied to the excited states of butadiene [22]. These studies have shown that the bond index is intimately related to the chemical bond. The relation between the density matrix and the electron pair concept has been studied, and the chemical bond has been discussed [23, 24]. Mathematical relations among various bond orders has been clarified by using the topological index [25]. It has also been suggested that the partial structures are related to the bond order calculated by using the selected MOs [26]. For the resonance energy, many studies have been reported in the framework of  $\pi$ -electron theory [27–29]. On the basis of the graph theory [30], the resonance energy has been defined and the correlative results with the previous works have been reported [31]. On the other hand, a method for analyzing the partial structures in a molecule has been proposed by adopting a model Hamiltonian [32].

Building from the direct expansion method [13] proposed by Hiberty et al., we present a method for analyzing the VB structures in the MO representation. First, we will show that VB structures are derived from an antisymmetrized products of molecular orbitals and each coefficient is expressed in terms of first-order reduced density matrices obtained from MO functions. Next, the simple method to rewrite the dependent VB structures as a linear combination of the independent VB structures will be proposed.

In this paper, “spin distribution” is used for the determinant constructed from AOs or the corresponding figure. “VB structure” is defined as the wave function written as the products of  $2 \times 2$  determinantal functions that show the ethylenic bonds or the ionic sites. Our theory is applicable to any  $\pi$ -electron system and can encompass excited states.

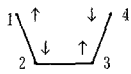
## 2 Method

### 2.1 The spin distribution (SD) and the determinant constructed from AOs

The following discussion will be restricted within the framework equal numbers  $2n$  of electrons and AOs as for Hückel MO theory of neutral conjugated hydrocarbons. We consider the ground state of a molecule which is written as a single Slater determinant. Supposing that the molecular orbitals  $\{\psi_1, \psi_2, \dots, \psi_n\}$  are already obtained, each MO is expressed as a linear combination of AOs

$$\psi_i(1) = \sum_{r=1}^{2n} C_{ir} \cdot \chi_r(1), \quad (1)$$

where  $\chi_r$  is the  $r$ th AO and  $C_{ir}$  is the LCAO coefficient. The ground state wave function  $\Psi$  is given as the antisymmetrized products of molecular orbitals where  $\psi$



$$\begin{vmatrix} q_{12} & q_{14} \\ q_{32} & q_{34} \end{vmatrix} = 0.2500$$

**Fig. 1.** An example of the spin distribution and coefficient for butadiene. The determinantal expression corresponds to Eq. (10)

$$\Psi = N |\psi_1(1)\bar{\psi}_1(2)\psi_2(3)\bar{\psi}_2(4)\dots\bar{\psi}_n(2n)|, \quad (2)$$

and  $\bar{\psi}$  are used for  $\alpha$  and  $\beta$  spin MOs, respectively, and  $N$  is the normalization constant  $N = 1/\sqrt{(2n)!}$ . Applying Eq. (1) to each  $\psi_i$  in Eq. (2),  $\Psi$  can be expanded in terms of the determinants  $\Phi_J$ 's that are constructed from AOs

$$\Psi = N \sum_J W_J \cdot \Phi_J, \quad (3)$$

$$\Phi_J = |\chi_a(1)\bar{\chi}_r(2)\chi_b(3)\bar{\chi}_s(4)\chi_c(5)\bar{\chi}_t(6)\dots|, \quad (4)$$

where  $\chi$  and  $\bar{\chi}$  are used for  $\alpha$  and  $\beta$  spin AOs, respectively. Suffix  $J$  denotes a set of AO suffixes ( $a, r, b, s, c, t, \dots$ ) and it runs over all permutations of possible AO suffix sets. Allotting the arrows  $\uparrow$  and  $\downarrow$  to the electrons of  $\alpha$  and  $\beta$  spin AOs, respectively, each  $\Phi_J$  is figured as the spin distribution. One spin distribution of butadiene is shown in Fig. 1. Among the  $\Phi_J$ 's, some terms show the same spin distribution because they are constructed from the same  $\alpha$  spin AOs and the same  $\beta$  AOs. Therefore, we can make the determinants of the same spin distribution coincide with that of the representative term  $W_0^T \cdot \Phi_0^T$  by suitably permuting their columns. Here  $W_0^T \cdot \Phi_0^T$  is given as (with omission of the normalization constant  $N$  for simplicity)

$$\begin{aligned} W_0^T &= (C_{1a} \cdot C_{2b} \cdot C_{3c} \dots) \cdot (C_{1r} \cdot C_{2s} \cdot C_{3t} \dots), \\ \Phi_0^T &= |\chi_a(1)\bar{\chi}_r(2)\chi_b(3)\bar{\chi}_s(4)\chi_c(5)\bar{\chi}_t(6)\dots|, \end{aligned} \quad (5)$$

where AO suffixes are placed in ascending order for both  $\alpha$  and  $\beta$  spin AOs. Furthermore, the coefficients of other terms equivalent to  $W_0^T \cdot \Phi_0^T$  are obtained by applying the permutation operator to the representative term. Consequently, all terms that belong to the same spin distribution  $T$  can be collected [13] to

$$SD(T) = Z(T) \cdot \Phi_0^T, \quad (6)$$

$$Z(T) = \sum (-1)^A \cdot A(C_{1a} \cdot C_{2b} \cdot C_{3c} \dots) (-1)^B \cdot B(C_{1r} \cdot C_{2s} \cdot C_{3t} \dots), \quad (7)$$

where  $A$  and  $B$  are the respective permutation operators for  $\alpha$  and  $\beta$  spin AO suffixes. When the permutation  $A$  is even,  $(-1)^A$  is  $+1$ , and otherwise is  $-1$ . Similar comments apply for the permutation  $B$ .

Rewriting Eq. (7) into the following determinantal form, and exchanging columns and rows in the first determinant,

$$Z(T) = \begin{vmatrix} C_{1a} & C_{2a} & C_{3a} & \dots \\ C_{1b} & C_{2b} & C_{3b} & \dots \\ C_{1c} & C_{2c} & C_{3c} & \dots \\ \dots & \dots & \dots & \dots \end{vmatrix} \cdot \begin{vmatrix} C_{1r} & C_{1s} & C_{1t} & \dots \\ C_{2r} & C_{2s} & C_{2t} & \dots \\ C_{3r} & C_{3s} & C_{3t} & \dots \\ \dots & \dots & \dots & \dots \end{vmatrix} \quad (8)$$

and employing the density matrix,

$$Q_{ar} = \sum_i^{occ} C_{ia} \cdot C_{ir}, \quad (9)$$

we obtain the simple determinantal expression

$$Z(T) = \begin{vmatrix} Q_{ar} & Q_{as} & Q_{at} & \dots \\ Q_{br} & Q_{bs} & Q_{bt} & \dots \\ Q_{cr} & Q_{cs} & Q_{ct} & \dots \\ \dots & \dots & \dots & \dots \end{vmatrix} \quad (10)$$

where  $Q_{ar}$  is half of the usual bond order  $P_{ar}$ . Eq. (10) may also be written as

$$Z(T) = \sum (-1)^B \cdot \mathbf{B}(Q_{ar} \cdot Q_{bs} \cdot Q_{ct}, \dots), \quad (11)$$

where  $\mathbf{B}$  is the same operator shown in Eq. (7) active only on the  $\beta$  AO suffixes ( $r, s, t, \dots$ ). Eqs. (10) and (11) are widely valid for all of spin distributions even including ionic sites. These expressions are generally applicable to a determinantal wave function constructed from the doubly occupied MOs. Using Eq. (11), we can directly calculate the coefficients of spin distributions concealed in the LCAO MO scheme.

## 2.2 The spin distribution and the geminal expression

As the coefficients of the spin distributions are calculated by Eq. (11), the total wave function  $\Psi$  can be expanded in terms of a linear combination of spin distributions. The VB structure corresponding to the molecular structural formula might be written as the products of ethylenic bonds or ionic sites. In order to construct the VB structure, spin distributions are expanded in terms of the products of  $2 \times 2$  determinants. As an example, the collected terms of the spin distribution  $T$  given by Eq. (5) are considered. Using Eq. (11),  $SD(T)$  in Eq. (6) is expanded as follows.

$$SD(T) = \sum_{\mathbf{B}} (-1)^B Q_{a\mathbf{B}(r)} \cdot Q_{b\mathbf{B}(s)} \cdot Q_{c\mathbf{B}(t)} \cdots \times \Phi_0^T. \quad (12)$$

Exchanging the columns of each  $\Phi_0^T$  so that the order of the AO suffixes may coincide with that of coefficient suffixes, we can make the signs of all terms be  $+1$ .

$$SD(T) = \sum_{\mathbf{B}} Q_{a\mathbf{B}(r)} \cdot Q_{b\mathbf{B}(s)} \cdot Q_{c\mathbf{B}(t)} \cdots \\ \times |\chi_a(1)\bar{\chi}_{\mathbf{B}(r)}(2)\chi_b(3)\bar{\chi}_{\mathbf{B}(s)}(4)\chi_c(5)\bar{\chi}_{\mathbf{B}(t)}(6)\cdots|, \quad (13)$$

where  $\mathbf{B}(x)$  is the label to which the permutation  $\mathbf{B}$  sends  $x$ . Next, we apply the Laplace expansion to each determinant in Eq. (13). Where we notice that the rows and columns correspond to the electron coordinates and AO suffixes, respectively. When the Laplace expansion is performed for the columns (1, 2) of the determinant  $\Phi_0^T$  in Eq. (5),  ${}_{2n}C_2$  terms written as the product of  $(2 \times 2)$  and  $(2n-2) \times (2n-2)$  determinants are obtained as follows.

$$\Phi_0^T = \sum_{1 < i < j < 2n} (-1)^{i+j+1} |\chi_a(i)\bar{\chi}_r(j)| \cdot |\chi_b(k)\bar{\chi}_s(1)\chi_c(u)\bar{\chi}_l(v), \dots|.$$

When  $i+j$  is odd, the sign becomes  $+1$ , otherwise it is  $-1$ . In the latter case, we exchange the rows ( $i, j$ ) of the  $2 \times 2$  determinant so that the sign becomes  $+1$ . When the same procedure is repeated for the first two columns of the remaining  $(2n-2) \times (2n-2)$  determinant and so on, we can obtain  ${}_{2n}C_2 \times {}_{2n-2}C_2 \times \cdots \times {}_4C_2$  terms written as the products of  $2 \times 2$  determinants as

$$\begin{aligned}
\Phi_0^T = & |\chi_a(1)\bar{\chi}_r(2)| \cdot |\chi_b(3)\bar{\chi}_s(4)| \cdot |\chi_c(5)\bar{\chi}_t(6)| \dots \\
& + |\chi_a(3)\bar{\chi}_r(1)| \cdot |\chi_b(2)\bar{\chi}_s(4)| \cdot |\chi_c(5)\bar{\chi}_t(6)| \dots \\
& + |\chi_a(1)\bar{\chi}_r(4)| \cdot |\chi_b(2)\bar{\chi}_s(3)| \cdot |\chi_c(5)\bar{\chi}_t(6)| \dots \\
& + \dots
\end{aligned} \tag{14}$$

In Eq. (14), all terms are the same for AO suffixes and are different in the electron coordinates from each other in their arrangements. Taking out only the electron labels from each term and placing them in a row, we can obtain the electron-label sequences  $E$ 's, which are written as

$$E = (i, j, k, l, \dots)$$

Among  $E$ 's, there is the standard set  $(1, 2, 3, \dots, 2n)$ , where the suffixes are placed in ascending order. Noticing from the discussion given above, all  $E$ 's are sequences of electron labels that are obtained through even permutation of the standard electron set. Thus,  $\Phi_0^T$  can be written by using  $E$  as

$$\Phi_0^T = \sum_E |\chi_a(i)\bar{\chi}_r(j)| \cdot |\chi_b(k)\bar{\chi}_s(l)| \cdot |\chi_c(u)\bar{\chi}_t(v)| \dots \tag{15}$$

Eq. (15) is recognized as a geminal expression of the spin distribution. Applying the same procedure to every determinant in Eq. (13), the following expression is obtained.

$$\begin{aligned}
SD(T) = & \sum_{\mathbf{B}} Q_{a\mathbf{B}(r)} \cdot Q_{b\mathbf{B}(s)} \cdot Q_{c\mathbf{B}(t)} \dots \\
& \times \sum_E |\chi_a(i)\bar{\chi}_{\mathbf{B}(r)}(j)| |\chi_b(k)\bar{\chi}_{\mathbf{B}(s)}(l)| |\chi_c(u)\bar{\chi}_{\mathbf{B}(t)}(v)| \dots
\end{aligned} \tag{16}$$

As shown above, a certain spin distribution has been divided into various kinds of geminal expressions. Each coefficient is written as a product of density matrices.

### 2.3 The geminal expression and the VB structure

When the total wave function  $\Psi$  is expanded in terms of geminal expressions [Eq. (16)], many terms with the same coefficient arise from different spin distributions. We consider a certain geminal expression obtained from another spin distribution

$$\sum_E (Q_{ra} \cdot Q_{bs} \cdot Q_{ct} \dots) \{ |\chi_r(i)\bar{\chi}_a(j)| \cdot |\chi_b(k)\bar{\chi}_s(1)| \cdot |\chi_c(u)\bar{\chi}_t(v)| \dots \},$$

where AO suffixes  $a$  and  $r$  is exchanged compared to that of Eq. (15). As  $Q_{ar} = Q_{ra}$ , the coefficients gives the same value as that of Eq. (15). When the same argument is applied to the other AO suffix pairs in the remaining  $2 \times 2$  determinants, all terms that have the same coefficient are collected as follows.

$$\begin{aligned}
& (Q_{ar} \cdot Q_{bs} \cdot Q_{ct}, \dots) \\
& \times \sum_E \sum_I \{ |\chi_a(i)\bar{\chi}_r(j)| \cdot |\chi_b(k)\bar{\chi}_s(l)| \cdot |\chi_c(u)\bar{\chi}_t(v)| \dots \},
\end{aligned} \tag{17}$$

where  $I$  is the inversion operator between two bonded AO suffixes in each  $2 \times 2$  determinant. Utilizing Eq. (17), the VB structure is directly constructed and the coefficient is simply given as a product of the density matrices.

Supposing all suffixes ( $a, b, c, r, s, t \dots$ ) are different from each other, the covalent terms are written as

$$\text{covalent terms} = \sum_i k_i (\text{VB})_i, \quad (18)$$

$$k_i = Q_{ar} \cdot Q_{bs} \cdot Q_{ct} \dots, \quad (19)$$

$$(\text{VB})_i = \sum_E (\text{BOND})_{ar} \cdot (\text{BOND})_{bs} \cdot (\text{BOND})_{ct} \dots,$$

$$(\text{BOND})_{ar} = \{|\chi_a(i)\bar{\chi}_r(j)| + |\chi_r(i)\bar{\chi}_a(j)|\}/\sqrt{2}, \quad (20)$$

where  $(\text{VB})_i$  represents a given VB structure  $i$ . Since  $(\text{BOND})_{ar}$  is a representation of an ethylenic bond, we call it ‘‘bond geminal’’. The coefficient of the covalent VB structure is simply written as the product of the density matrices related to each VB structure. Eqs. (18) and (19) give the relation between a single determinant of MOs and VB structures derived from it. The expressions do not depend on whether orthogonal AOs are used in the calculational scheme. As shown in the following section, they are also useful for decomposing ionic VB structures.

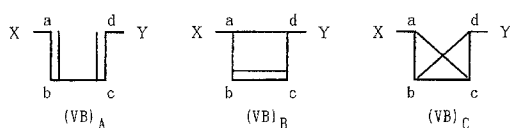
#### 2.4 Independent VB structures

According to the VB theory, the number of independent singlet covalent VB structures must be  $(2n)!/\{n! \cdot (n+1)!\}$ , this also being the number of  $S^2 = 0$  eigenfunctions in spin space [33]. When Eq. (18) is applied to the  $2n$  electrons system,  $(2n)!/(2^n \cdot n!)$  VB structures are obtained. This discrepancy indicates that our method includes the excess terms and they must be written as a linear combination of the independent terms. Although the selection of the independent terms is arbitrary, the magnitude of the absolute value of coefficients may be used as a criterion for this selection. Namely, the  $(2n)!/\{n! \cdot (n+1)!\}$  VB structures that have the larger coefficients are taken as the candidates for the independent VB structures. The dependence must be inspected for the candidates one by one. When a dependent term is found, it must be omitted and another term is brought from the remainders. Once the independent VB structures are selected, the others can be written as a linear combination of selected ones in the following manner. Each VB structure  $(\text{VB})_i$  can be rewritten in terms of related  $\Phi_0^T$ 's as follows.

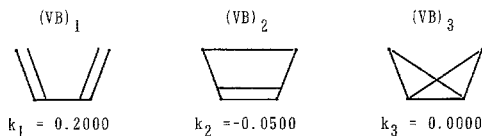
$$(\text{VB})_i = \sum_{T \in i} M \cdot \Phi_0^T, \quad (21)$$

where  $M$  is to be  $+1$  or  $-1$ . Comparing  $\Phi_0^T$ 's in each  $(\text{VB})_i$ , we can recognize how the dependent VB structures are constructed from the selected ones. Particularly, there is the following standard relation among the three specific VB structures shown in Fig. 2. They have almost the same structures and different only for two bonds that are made from the same four AO sites.

$$(\text{VB})_A + (\text{VB})_B + (\text{VB})_C = 0. \quad (22)$$



**Fig. 2.** Specific VB structures related to Eq. (22). *X* and *Y* represent remaining parts of a molecule. Two bonds associated with four AO sites *a*, *b*, *c*, *d* are different from each other



**Fig. 3.** Covalent VB structures and coefficients for butadiene

For butadiene, the covalent VB structures and coefficients are shown in Fig. 3. The covalent terms can be written as follows.

$$\text{Covalent terms} = k_1 \cdot (\text{VB})_1 + k_2 \cdot (\text{VB})_2 + k_3 \cdot (\text{VB})_3 .$$

Since three VB structures have the same relation with that in Fig. 2,

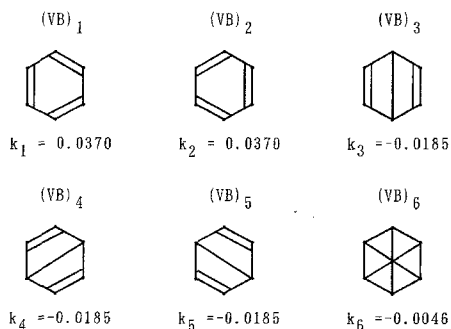
$$(\text{VB})_1 + (\text{VB})_2 + (\text{VB})_3 = 0 ,$$

the following expression is obtained.

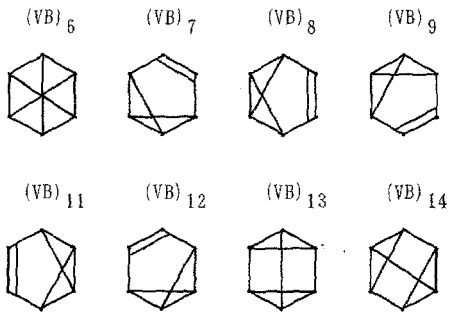
$$\text{Covalent terms} = (k_1 - k_3) \cdot (\text{VB})_1 + (k_2 - k_3) \cdot (\text{VB})_2 ,$$

where  $(\text{VB})_1$  and  $(\text{VB})_2$  are selected as the independent VB structures referring to the magnitude of their coefficients, namely  $|k_1| > |k_2| > |k_3|$ . In the case of the Hückel calculation for butadiene,  $(\text{VB})_3$  does not have an effect on the independent VB structures because  $k_3 = 0$  [Eq. (19)].  $(\text{VB})_3$  will become important in a four electron system that contains hetero-atoms. The above expression will be also necessary for VB analysis in the case that configuration interactions are included.

For benzene, the VB structures of non-zero coefficient are collected in Fig. 4, and ten dependent VB structures are shown in Fig. 5. In these figures, we can find the specific VB structures that have the same relation with that in Fig. 2. For example, We can find the relation among  $\{(\text{VB})_1, (\text{VB})_3, (\text{VB})_{11}\}$ ,  $\{(\text{VB})_3, (\text{VB})_6, (\text{VB})_{13}\}$ ... and so on. Using these relations repeatedly, ten dependent VB structures are written in terms of the selected five independent ones (Table 1).



**Fig. 4.** Covalent VB structures of benzene, whose coefficients are not zero



**Fig. 5.** Ten dependent VB structures of benzene

**Table 1.** Benzene VB structures expanded in terms of two Kekulé and three Dewar structures

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$$\begin{aligned}
 (\text{VB})_6 &= -(\text{VB})_1 - (\text{VB})_2 - (\text{VB})_3 - (\text{VB})_4 - (\text{VB})_5 \\
 (\text{VB})_7 &= -(\text{VB})_1 - (\text{VB})_5 \\
 (\text{VB})_8 &= -(\text{VB})_2 - (\text{VB})_3 \\
 (\text{VB})_9 &= -(\text{VB})_1 - (\text{VB})_4 \\
 (\text{VB})_{10} &= -(\text{VB})_2 - (\text{VB})_5 \\
 (\text{VB})_{11} &= -(\text{VB})_1 - (\text{VB})_3 \\
 (\text{VB})_{12} &= -(\text{VB})_2 - (\text{VB})_4 \\
 (\text{VB})_{13} &= +(\text{VB})_1 + (\text{VB})_2 + (\text{VB})_4 + (\text{VB})_5 \\
 (\text{VB})_{14} &= +(\text{VB})_1 + (\text{VB})_2 + (\text{VB})_3 + (\text{VB})_4 \\
 (\text{VB})_{15} &= +(\text{VB})_1 + (\text{VB})_2 + (\text{VB})_3 + (\text{VB})_5
 \end{aligned}$$


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Next, the singly polar (ionic) term is considered for a four electrons system. The spin distributions composed of an ionic site  $r$  and two open sites  $a$  and  $b$  are collected as the singly polar terms as follows.

$$\text{Singly polar terms} = Q_{ab} \cdot Q_{rr}(\text{VB})_{abbr} + Q_{ar} \cdot Q_{rb}(\text{VB})_{arrb},$$

$$(\text{VB})_{abbr} = \{|\chi_a(1)\bar{\chi}_b(2)| + |\chi_b(1)\bar{\chi}_a(2)|\} \cdot |\chi_r(3)\bar{\chi}_r(4)|/2,$$

$$(\text{VB})_{arrb} = \{|\chi_a(1)\bar{\chi}_r(2)| \cdot |\chi_r(3)\bar{\chi}_b(4)| + |\chi_r(1)\bar{\chi}_a(2)| \cdot |\chi_b(3)\bar{\chi}_r(4)|\}/2,$$

where  $(\text{VB})_{abbr}$  includes the covalent bond  $a-b$  and the ionic site  $r$ .  $(\text{VB})_{arrb}$  is constructed from four electrons which delocalize over three atoms, so we call it "delocalized ionic structure". Since two ionic VB structures are not independent with each other and have the following relation:

$$(\text{VB})_{abbr} + (\text{VB})_{arrb} = 0,$$

one of these must be selected as the independent VB structure referring to the magnitude of their coefficients. In the case of  $Q_{ab} \cdot Q_{rr} > Q_{ar} \cdot Q_{rb}$ ,  $(\text{VB})_{abbr}$  is chosen as the independent ionic structure.

$$\{Q_{ab} \cdot Q_{rr} - Q_{ar} \cdot Q_{rb}\}(\text{VB})_{abbr}.$$

In the other case of  $Q_{ar} \cdot Q_{rb} > Q_{ab} \cdot Q_{rr}$ , we adopt  $(\text{VB})_{arrb}$ .

$$\{Q_{ar} \cdot Q_{rb} - Q_{ab} \cdot Q_{rr}\}(\text{VB})_{arrb}.$$

The dotted line is used for the figures of the delocalized ionic structures. Examples are shown in Table 2 (structures 7 and 8).



**Table 2.** Coefficients of VB structures and structural weights for butadiene<sup>a</sup>

VB structures	Coefficients	Degeneracy	Weights (Ref. [15])
1	0.2000	1	0.1800 (0.1839)
2	-0.0500	1	0.0300 (0.0278)
3	0.2236	2	0.2000 (0.2010)
4	0.2236	2	0.2000 (0.2044)
5	0.1118	2	0.0500 (0.0474)
6	-0.1118	2	0.0500 (0.0474)
7	0.1000	2	0.0400 (-----)
8	-0.1000	2	0.0400 (-----)
9	0.2500	2	0.1250 (0.1250)
10	0.2000	1	0.0400 (0.0418)
11	0.2000	1	0.0400 (0.0404)
12	0.0500	2	0.0050 (-----)

<sup>a</sup> Results of the ab initio calculation (Ref. [15]) are indicated in parentheses. A hypothetical geometry with all C-C bond lengths fixed to 1.4 Å is used

According to the expansion method of Hiberty et al. [13], the independent VB structures are fixed at the beginning of the calculations. In our analysis, the independent VB structures are selected by means of the magnitude of the coefficient of the VB structure. Therefore, we consider that our method will be able to pick up the chemically important VB structures from the MO results.

### 3 Results and discussion

In Table 2, the calculated results for butadiene are summarized. The coefficients of two covalent terms are to be 0.2000 and -0.0500, respectively. In terms of density matrices, they are written as  $Q_{12} \cdot Q_{34}$  and  $Q_{23} \cdot Q_{14}$  [Eq. (19)], respectively. There are relations  $Q_{12} = Q_{34}$  and  $Q_{23} = -Q_{14}$  among them, so the coefficients  $Q_{12} \cdot Q_{34}$  and  $Q_{14} \cdot Q_{23}$  can be rewritten as  $(Q_{12})^2$  and  $-(Q_{14})^2$ , respectively. This fact shows that the coefficients of the covalent VB structures are closely related to the bond index  $(WB)_{ab}$  [20] which is given by the square of the density matrix as follows.

$$(WB)_{ab} = (2 \times Q_{ab})^2$$

Table 3. Structural weights of benzene<sup>a</sup>

Structures	Degeneracy	Weights (Ref. [14])	Structures	Degeneracy	Weights (Ref. [14])
	2	0.0486 (0.0486)		6	0.0370 (0.0370)
	3	0.0208 (0.0208)		6	0.0208 (0.0208)
	12	0.1852 (0.1852)		6	0.0370 (0.0370)
	12	0.0741 (0.0741)		6	0.0023 (-----)
	6	0.0648 (0.0486)		12	0.0185 (-----)
	6	---0.0046 (-----)		6	0.0370 (-----)
	12	0.0556 (-----)		12	0.0185 (-----)
	12	0.0556 (-----)		6	0.0370 (-----)
	12	0.0185 (0.0185)		6	0.0012 (0.0012)
	6	0.0370 (0.0370)		12	0.0370 (0.0370)
	12	0.1667 (0.1667)		2	0.0313 (0.0312)

<sup>a</sup> Results of the ab initio calculation (Ref. [14]) are indicated in parentheses

Employing the bond index, the ground state VB structures of some molecules have been discussed by Trindle [21]. The excited state of butadiene has also been analyzed by Whangbo and Lee [22].

According to the previous study [13], the following definition can be used for the weight,  $R_i$ , of a given VB structure  $(\text{VB})_i$ .

$$R_i = \sum_j \langle k_i(\text{VB})_i | k_j(\text{VB})_j \rangle. \quad (23)$$

The calculation of the weight is easy in the Hückel approximation because there is the following unique relationship between two spin distributions.

$$\langle \Phi_0^i | \Phi_0^j \rangle = \delta_{ij}.$$

The calculated weights of VB structures for butadiene show a good agreement with those of ab initio calculation.

For benzene, two Kekulé and three Dewar structures are selected as the independent VB structures. Using the results given in Table 1, the covalent terms of benzene are written by the independent five VB structures as

$$\begin{aligned} \text{covalent terms} &= \sum_{i=1}^{15} k_i \cdot (\text{VB})_i \\ &= (k_1 - k_6 - k_7 - k_9 - k_{11} + k_{13} + k_{14} + k_{15}) \cdot (\text{VB})_1 \\ &\quad + (k_2 - k_6 - k_8 - k_{10} - k_{12} + k_{13} + k_{14} + k_{15}) \cdot (\text{VB})_2 \\ &\quad + (k_3 - k_6 - k_8 - k_{11} + k_{14} + k_{15}) \cdot (\text{VB})_3 \\ &\quad + (k_4 - k_6 - k_9 - k_{12} + k_{13} + k_{14}) \cdot (\text{VB})_4 \\ &\quad + (k_5 - k_6 - k_7 - k_{10} + k_{13} + k_{15}) \cdot (\text{VB})_5 \end{aligned}$$

the coefficients of the covalent terms are calculated as follows.

$$\text{Covalent terms} = 0.04167 \cdot \{(\text{VB})_1 + (\text{VB})_2\} - 0.01389 \cdot \{(\text{VB})_3 + (\text{VB})_4 + (\text{VB})_5\}.$$

The simplest way to calculate the weight of a given VB structure  $i$  is to take the square of the coefficient. Using this definition, the ratio of the Kekulé structure to the Dewar one is estimated to be 6.000 : 1.000.

The calculated weights using Eq. (23) are given in Table 3. Our results completely agree with those of Hiberty et al. [14], except only **17**. Disagreement seen at **17** may be due to the different selection of the independent VB structures. The weights of Kekulé and Dewar structures are calculated to be 0.0486 and 0.0208, respectively. These values show that the Hückel MO calculation includes Kekulé and Dewar structures in the ratio of 7.000 : 3.000. The same ratio has been obtained from the VB analysis for the ab initio SCF level calculation [14] and it becomes 6.687 : 3.313 in the case of the full CI calculation [15]. The corresponding ratios obtained from the Mixed VB method [1] and Spin-coupled VB method [2] are 7.760 : 2.240 and 8.056 : 1.944, respectively.

In Table 4, the calculated weights of the independent VB structures are summarized for hexatriene. The weight of the normal molecular structural formula **35** is calculated to be 0.0596, and that for butadiene to be 0.1800. Those for Kekulé structures of benzene are calculated to be  $0.0243 \times 2 = 0.0486$ . These results show that the normal molecular structural formula is the dominant among the covalent type VB structures.

Table 4. Structural weights of hexatriene<sup>a</sup>

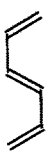



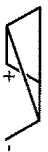

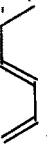


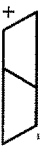


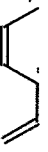






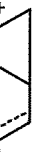

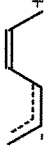
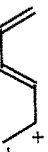



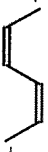
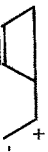


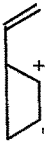
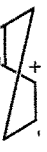
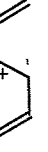
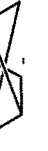


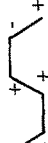


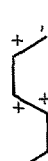
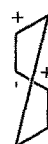
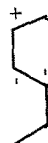
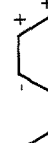
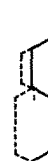

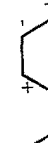
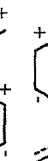
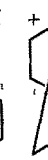
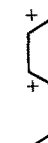

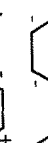
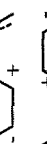

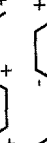
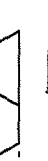
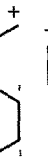
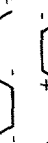
Structures	Weights	Structures	Weights	Structures	Weights
Covalent terms					
	0.0596 (1)		0.0173 (2)		0.0213 (2)
<b>35</b>			0.0057 (2)		-0.0007 (2)
	0.0201 (2)		0.0664 (2)		0.0048 (2)
<b>36</b>			0.0124 (2)		0.0006 (2)
	0.0041 (1)		0.0138 (2)		0.0213 (2)
<b>37</b>			0.0039 (2)		-0.0007 (2)
	0.0004 (1)		0.0170 (2)		0.0055 (2)
<b>38</b>			-0.0008 (2)		0.0013 (2)
Singly polar terms			0.0151 (2)		0.0053 (2)
	0.0664 (2)		0.0011 (2)		0.0016 (2)
<b>39</b>			0.0138 (2)		0.0078 (2)
	0.0124 (2)		0.0039 (2)		0.0016 (2)
<b>40</b>					
	0.0173 (2)				
<b>41</b>					
	0.0057 (2)				
<b>42</b>					
	0.0732 (2)				
<b>43</b>					
	0.0013 (2)				
<b>44</b>					

Table 4. Continued

Structures	Weights	Structures	Weights	Structures	Weights
Doubly polar terms					
	0.0022 (2)		0.0001(2)		0.0146 (2)
	0.0009 (2)		0.0292 (2)		0.0071 (2)
	0.0013 (2)		0.0111 (2)		0.0071 (2)
	0.0001 (2)		0.0090 (2)		0.0180 (1)
	0.0001 (2)		0.0043 (2)		0.0007 (1)
	0.0000 (2)		0.0035 (2)		0.0292 (2)
	0.0474 (2)		0.0013 (2)		0.0058 (2)
	0.0111 (2)		0.0058 (2)		0.0071 (2)
	0.0146 (2)		0.0094 (2)		0.0003 (2)
	0.0004 (2)		0.0385 (2)		0.0004 (2)
	0.0005 (2)		0.0022 (2)		0.0001 (2)
			0.0090 (2)		0.0474 (2)

Table 4. Continued

Structures	Weights	Structures	Weights	Structures	Weights
	0.0094 (2)		0.0017 (1)		0.0017 (2)
	0.0071 (2)		0.0022 (2)		0.0007 (2)
	0.0057 (2)		0.0022 (2)		0.0017 (2)
	0.0043 (2)		0.0007 (1)		0.0313 (2)
	0.0009 (2)		0.0017 (1)		0.0180 (2)
	0.0111 (2)	Triply polar terms			0.0119 (2)
	0.0111 (2)		0.0000 (2)		0.0007 (2)
	0.0180 (1)		0.0003 (2)		0.0180 (2)

<sup>a</sup> Degeneracy is indicated in parentheses

**Table 5.** Comparison of structural weights for various types of polar structures

Molecules	Covalent terms	Singly polar terms	Doubly polar terms	Triply polar terms
Butadiene	0.2100	0.5800	0.2100	(---)
Benzene	0.0694	0.4306	0.4306	0.0694
Hexatriene	0.0842	0.4158	0.4158	0.0842

In Table 5, the calculated weights of butadiene, benzene and hexatriene are summarized for various types of polar terms. As seen from this table, the structural weights of covalent terms are surprisingly small. This fact tells us that the excess ionic terms are included in the LCAO MO calculations. This problem will be discussed using the calculated results for butadiene. As shown in Table 2, the coefficients of the covalent terms are small compared with the ionic ones. Here, we consider two structures **1** and **4** in Table 2, whose coefficients are calculated as follows:

$$0.2000(\mathbf{1}) = Q_{12} \cdot Q_{34} = 0.4472 \times 0.4472,$$

$$0.2236(\mathbf{4}) = Q_{11} \cdot Q_{34} = 0.5000 \times 0.4472.$$

Comparing these expressions, it is found that the excess ionic term is originated in the large value of  $Q_{11}$  and the relation  $Q_{11} > Q_{12}$ .

It is known that the overestimation of ionic terms is improved by taking into account the correlation effect. As our theory is directly applicable to the calculations including pair excited configurations, the effect of the pair excitation on VB structures may be discussed using the density matrix.

#### 4 Concluding remarks

An analytical method for resolving an LCAO MO wavefunction into VB structures is proposed. The coefficient of a VB structure is directly calculated as a product of density matrices. Referring to the magnitude of calculated coefficients, the chemically important VB structures are selected as the independent VB structures. The dependent VB structures are written in terms of the independent ones by comparing their structural formula graphically. Our theory is widely applicable to the analysis of VB structures in LCAO MO results. The method may be also useful to analyze the resonance energy or aromaticity discussed by chemical graph theory. Our method is not restricted to the Hückel MO scheme, and it is easily enlarged to other  $\pi$ -electron theories. In PPP calculations, our theory will be effective in describing the characteristics of the excited states. The VB structures of excited molecules will be discussed in the following paper.

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