

# On the pairing of the natural orbitals for projected broken symmetry states

**Esper Dalgaard**

Department of Chemistry, University of Aarhus, DK-8000 Aarhus C., Denmark

A pairing scheme for the natural orbitals of projected broken symmetry states, which can be expressed as a superposition of two generally non-orthogonal Slater determinants, is presented. The results obtained here are generalizations of a pairing scheme representation of natural orbitals derived recently by Hendeković within the complex molecular orbital method. As a simple example the Kekulé structure of benzene is discussed.

**Key words:** Natural orbitals—Broken symmetry—Complex molecular orbital method.

## 1. Introduction

Simple models for the electronic structure of molecules have retained their importance in spite of the impressive advances in unitary group *ab initio* configuration interaction methods [1]. In particular we may mention the growing interest in valence bond theory and related geminal methods. Symmetry breaking in Hartree–Fock calculations indicates strong correlation effects. A systematic method for an approximate handling of such correlation effects is offered by Löwdin's extended Hartree–Fock theory [2].

The simplest applications of the extended Hartree–Fock method lead to ground state representatives, which can be expressed as a linear combination of two generally non-orthogonal Slater determinants, e.g. when gerade or ungerade states are projected out from a single determinant of symmetry broken orbitals [3] for a molecule having inversion symmetry. Another case in which a superposition of two states becomes relevant as a starting point arises, when a molecule has two equivalent classical resonance structures, e.g. the Kekulé structures of benzene.

It is the purpose of this brief communication to discuss a pairing scheme for the natural orbitals, which are derived from a state vector of this simple form. The results presented here are generalizations of a pairing representation of the natural orbitals, which have been discovered recently by Hendeković and Pavlović [4] for the so-called complex molecular orbital method [5]. In this method the ground state is expressed as the real part of a single determinant  $|\phi\rangle$ , i.e.

$$|\text{CMO}\rangle = \text{Re} |\phi\rangle = \frac{1}{2}(|\phi\rangle + |\phi^*\rangle). \quad (1)$$

The complex molecular orbital method is therefore a form of projected Hartree-Fock theory [6] corresponding to time-reversal symmetry.

## 2. The natural orbital pairing scheme

We proceed now to analyze the one-particle density matrix for a reference state, which can be expressed as

$$|0\rangle = |\phi_1\rangle + |\phi_2\rangle\kappa = a_1^+ \cdots a_n^+ |vac\rangle + b_1^+ \cdots b_n^+ |vac\rangle\kappa \quad (2)$$

in unnormalized form.  $\kappa$  is an expansion coefficient, which takes into account that the two states need not have the same weight for the pairing theorem to hold. Creation operators for the two sets of  $n$  molecular spin orbitals,

$$\{u_l(\xi)|l=1, \dots, n\} \quad \text{and} \quad \{v_l(\xi)|l=1, \dots, n\} \quad (3)$$

which are occupied in  $|\phi_1\rangle$  and  $|\phi_2\rangle$ , respectively, are denoted by  $\{a_l^+\}$  and  $\{b_l^+\}$ . No symmetry labels for the molecular orbitals will be introduced here, because the results which we shall obtain are not related to symmetry. Block diagonalizations due to either spin or point group symmetry can always be added at the end [4].

There is no loss of generality in assuming that each of the sets  $\{u_l\}$  and  $\{v_l\}$  are orthonormal so that

$$[a_b, a_{l'}^+]_+ = [b_b, b_{l'}^+]_+ = \delta_{ll'} \quad (4)$$

while keeping the overlap matrix between the two sets completely general:

$$\Delta_{ll'} = \int d\xi u_l(\xi)^* v_{l'}(\xi). \quad (5)$$

Correspondingly, we have the following anticommutation relations between the two sets of creation operators [7],

$$[a_b, b_{l'}^+]_+ = \Delta_{ll'}; \quad [a_b, b_{l'}]_+ = 0. \quad (6)$$

Our first observation concerning the one-particle density matrix is that at most  $2n$  natural orbital occupation numbers,  $\nu_s$ , can be non-vanishing, since the state  $|0\rangle$  is constructed from  $2n$  spin orbitals. Any natural orbital for which  $\nu_s \neq 0$  must be of the form

$$\Theta_s(\xi) = \sum_1^n (u_l(\xi)X_{ls} + v_l(\xi)Z_{ls}) \quad (7)$$

and the coefficients  $X_{ls}$  and  $Z_{ls}$  can be derived from the eigenvalue equation [2, 7]:

$$\int d\xi' \langle \psi^+(\xi') \psi(\xi) \rangle \Theta_s(\xi') = \Theta_s(\xi) \nu_s \quad (8)$$

where  $\psi(\xi)$  is the electronic field operator [7] and  $\langle \cdot \cdot \cdot \rangle$  denotes the expectation value in the state  $|0\rangle$ . From the identities

$$a_l \equiv \int d\xi u_l^*(\xi) \psi(\xi) \quad \text{and} \quad b_l \equiv \int d\xi v_l^*(\xi) \psi(\xi) \quad (9)$$

and Eqs. (5), (7) and (8) we obtain the equation system

$$\begin{Bmatrix} \langle a^+ a \rangle & \langle a^+ b \rangle \\ \langle b^+ a \rangle & \langle b^+ b \rangle \end{Bmatrix} \begin{Bmatrix} X^* \\ Z^* \end{Bmatrix} = \begin{Bmatrix} 1 & \Delta^* \\ \tilde{\Delta} & 1 \end{Bmatrix} \begin{Bmatrix} X^* \\ Z^* \end{Bmatrix} \begin{Bmatrix} \nu_1 & \dots & 0 \\ 0 & \dots & \nu_{2n} \end{Bmatrix} \quad (10)$$

where the symbol “ $\sim$ ” is used for matrix transposition. The next step is to invoke the polar decomposition [8] for the matrices  $\tilde{\Delta}$  and  $\Delta^*$ :

$$\tilde{\Delta} = VSU^+ \quad \text{or} \quad \Delta^* = US^*V^+ \quad (11)$$

where  $U$  and  $V$  are unitary  $n \times n$  matrices and  $S$  is a diagonal matrix. A detailed account on the polar decomposition of matrices can be found in the text by Gantmacher [8]. The polar decomposition was introduced in molecular orbital theory by Amos and Hall [9] and applied by Martin [10] in a study of symmetry breaking. The matrices  $U$ ,  $V$  and  $S$  are not completely unique since the columns of  $V$  and  $U$  may be multiplied by arbitrary phase factors if the inverse phase factors are absorbed in  $S$ . We choose phase factors such that  $|U| = |V| = 1$ . For this reason we allow for the possibility that the elements of  $S$  are complex numbers.

Eq. (10) can now be written as

$$\begin{Bmatrix} \langle \alpha^+ \alpha \rangle & \langle \alpha^+ \beta \rangle \\ \langle \beta^+ \alpha \rangle & \langle \beta^+ \beta \rangle \end{Bmatrix} \begin{Bmatrix} K^* \\ L^* \end{Bmatrix} = \begin{Bmatrix} 1 & S^* \\ S & 1 \end{Bmatrix} \begin{Bmatrix} K^* \\ L^* \end{Bmatrix} \begin{Bmatrix} \nu_1 & \dots & 0 \\ 0 & \dots & \nu_{2n} \end{Bmatrix} \quad (12)$$

where  $K^* = U^+ X^*$  and  $L^* = V^+ Z^*$ . New annihilation operators are defined as

$$\alpha_j = \sum a_l U_{lj}; \quad \beta_j = \sum b_l V_{lj}. \quad (13)$$

Each of the sets  $\{\alpha_j, \alpha_j^+\}$  and  $\{\beta_j, \beta_j^+\}$  satisfy ordinary anticommutation relations, while

$$[\alpha_j, \beta_j^+]_+ = (V^+ \tilde{\Delta} U)_{jj} = \delta_{jj} S_j \quad (14)$$

Unitary transformations, with determinant one, among occupied orbitals do not change a Slater determinant so that

$$|\phi_1\rangle = \alpha_1^+ \dots \alpha_n^+ |vac\rangle; \quad |\phi_2\rangle = \beta_1^+ \dots \beta_n^+ |vac\rangle. \quad (15)$$

Then Eq. (14) shows that

$$\alpha_j |\phi_2\rangle = (-1)^{j-1} \beta_1^+ \beta_2^+ \dots \beta_{j-1}^+ [\alpha_j, \beta_j^+]_+ \beta_{j+1}^+ \dots \beta_n^+ |vac\rangle = \beta_j |\phi_2\rangle S_j \quad (16)$$

and similarly  $\beta_j |\phi_1\rangle = \alpha_j |\phi_1\rangle S_j^*$ .

The matrix elements occurring in the left hand side of Eq. (12) are obtained from Eqs. (2), (15) and (16) as

$$\langle 0 | \alpha_j^+ \alpha_j | 0 \rangle = \delta_{jj'} \{ 1 + |\kappa|^2 |S_j|^2 + 2 \operatorname{Re}(\kappa P) \} \quad (17)$$

$$\langle 0 | \beta_j^+ \beta_j | 0 \rangle = \delta_{jj'} \{ |S_j|^2 + |\kappa|^2 + 2 \operatorname{Re}(\kappa P) \} \quad (18)$$

$$\langle 0 | \alpha_j^+ \beta_j | 0 \rangle = \delta_{jj'} \{ S_j^* + |\kappa|^2 S_j^* + \kappa P / S_j + \kappa^* S_j^* P^* \} \quad (19)$$

$$\langle 0 | 0 \rangle = 1 + |\kappa|^2 + 2 \operatorname{Re}(\kappa P) \quad (20)$$

where

$$P = \langle \phi_1 | \phi_2 \rangle = S_1 S_2 \cdots S_n \quad (21)$$

Eq. (12) can now be rearranged as  $n$  independent ( $2 \times 2$ ) equations of the form

$$\begin{Bmatrix} a_j & b_j \\ b_j^* & c_j \end{Bmatrix} \begin{Bmatrix} K_{j\mu} \\ L_{j\mu} \end{Bmatrix} = \begin{Bmatrix} 1 & S_j \\ S_j^* & 1 \end{Bmatrix} \begin{Bmatrix} K_{j\mu} \\ L_{j\mu} \end{Bmatrix} \nu_{j\mu} \quad \mu = 1, 2 \quad (22)$$

where the paired natural orbitals are labelled  $j\mu$ ;  $\mu = 1, 2$ , and

$$a_j = \langle \alpha_j^+ \alpha_j \rangle; \quad b_j = \langle \beta_j^+ \alpha_j \rangle; \quad c_j = \langle \beta_j^+ \beta_j \rangle; \quad j = 1, 2, \dots, n. \quad (23)$$

Thus we find that the paired natural orbital occupation numbers are given by the roots of the determinant

$$\begin{vmatrix} (a_j - \nu) & (b_j - \nu S_j) \\ (b_j^* - \nu S_j^*) & (c_j - \nu) \end{vmatrix} = 0. \quad (24)$$

The sum of the two roots is

$$\nu_{j_1} + \nu_{j_2} = [a_j + c_j - 2 \operatorname{Re}(b_j^* S_j)] / (1 - |S_j|^2) = 1. \quad (25)$$

In terms of the original basis sets  $\{u_i\}$  and  $\{v_i\}$  the natural orbitals can be written

$$\Theta_{j\mu} = \tilde{u}_j K_{j\mu} + \tilde{v}_j L_{j\mu} \quad (26)$$

where

$$\tilde{u}_j(\xi) = \sum u_i(\xi) U_{ij}^*; \quad \tilde{v}_j(\xi) = \sum v_i(\xi) V_{ij}^*. \quad (27)$$

Similarly, creation operators corresponding to the natural orbitals are given by

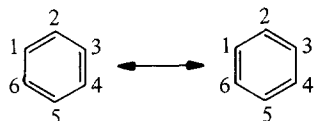
$$a_{j\mu}^+ = \alpha_j^+ K_{j\mu} + \beta_j^+ L_{j\mu}. \quad (28)$$

Hendeković and Pablović [11] have already demonstrated how such operators may be used to simplify configuration interaction calculations based on the state |CMO) in Eq. (1) as the point of departure.

### 3. Application to $\pi$ -bonds in benzene

We close this communication by giving a brief discussion of the Kekulé structures of benzene as an example of applications of the pairing representation in elementary molecular orbital theory. The localized  $\pi$ -bonds are described in terms of

the six atomic  $\pi$ -orbitals as



$$\begin{aligned}
 u_1 &= (p_1 + p_2)/\sqrt{2} & v_1 &= (p_2 + p_3)/\sqrt{2} \\
 u_2 &= (p_3 + p_4)/\sqrt{2} & v_2 &= (p_4 + p_5)/\sqrt{2} \\
 u_3 &= (p_5 + p_6)/\sqrt{2} & v_3 &= (p_6 + p_1)/\sqrt{2}
 \end{aligned} \tag{29}$$

where we have assumed that the atomic  $\pi$ -orbitals,  $p_i$ , are orthonormal. The Kekulé ground state representative is  $|0\rangle = |\phi_1\rangle + |\phi_2\rangle$ , with the definition

$$|\phi_1\rangle = a_{1\alpha}^+ \cdots a_{3\beta}^+ |vac\rangle; \quad |\phi_2\rangle = b_{1\alpha}^+ \cdots b_{3\beta}^+ |vac\rangle. \tag{30}$$

The state  $|0\rangle$  has the correct symmetry,  ${}^1A_{1g}$ , in  $D_{6h}$  so that the natural orbitals are identical to the delocalized Hückel molecular orbitals. The various matrix transformations outlined in the previous section can therefore easily be written down using symmetry. Thus, we obtain the overlap matrix for the spatial orbitals  $\{u_i\}$  and  $\{v_i\}$  and its polar decomposition as

$$\begin{aligned}
 \Delta &= \begin{pmatrix} \frac{1}{2} & 0 & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} & 0 \\ 0 & \frac{1}{2} & \frac{1}{2} \end{pmatrix} = US\tilde{V} \\
 &= \begin{pmatrix} 1/\sqrt{3} & 2/\sqrt{6} & 0 \\ 1/\sqrt{3} & -1/\sqrt{6} & 1/\sqrt{2} \\ 1/\sqrt{3} & -1/\sqrt{6} & -1/\sqrt{2} \end{pmatrix} \begin{Bmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & 0 \\ 0 & 0 & -\frac{1}{2} \end{Bmatrix} \begin{pmatrix} 1/\sqrt{3} & 1/\sqrt{3} & 1/\sqrt{3} \\ -1/\sqrt{6} & 2/\sqrt{6} & -1/\sqrt{6} \\ -1/\sqrt{2} & 0 & 1/\sqrt{2} \end{pmatrix}.
 \end{aligned} \tag{31}$$

We have made sure here that  $|U| = |V| = 1$ . Paired orbitals are now, according to Eq. (27), given as

$$\begin{aligned}
 \tilde{u}_1 &= (u_1 + u_2 + u_3)/\sqrt{3}; & \tilde{v}_1 &= (v_1 + v_2 + v_3)/\sqrt{3} \\
 \tilde{u}_2 &= (2u_1 - u_2 - u_3)/\sqrt{6}; & \tilde{v}_2 &= (-v_1 + 2v_2 - v_3)/\sqrt{6} \\
 \tilde{u}_3 &= (u_2 - u_3)/\sqrt{2}; & \tilde{v}_3 &= (-v_1 + v_3)/\sqrt{2}.
 \end{aligned} \tag{32}$$

Obviously,  $\tilde{u}_1 = \tilde{v}_1$  is the totally symmetric natural orbital, which therefore attains a total occupancy of 2. The remaining pairs  $(\tilde{u}_2, \tilde{v}_2)$  and  $(\tilde{u}_3, \tilde{v}_3)$  are degenerate so that Eq. (22) has to be solved only once. The various terms in Eq. (22) are

$$\begin{aligned}
 P &= S_{1\alpha} S_{1\beta} \cdots S_{3\beta} = 1/16; & \langle 0|0\rangle &= 17/8 \\
 a_2 &= a_3 = c_2 = c_3 = 11/17; & b_2 &= b_3 = -37/68.
 \end{aligned} \tag{33}$$

The results are given in Table 1, which also includes results for a realistic  $\pi$ - $\pi$  overlap of 0.25.

A quantity of some interest when comparing the Kekulé ground state and the Hückel molecular orbital ground state representative,  $|\text{MO}\rangle$ , built from the first

**Table 1**

Natural orbital	Occupation numbers	
	$\langle p_j   p_{j+1} \rangle = 0$	$\langle p_j   p_{j+1} \rangle = 0.25$
$a_{2u}$	2	2
$e_{1g}$	$\frac{54}{17} = 3.18$	3.61
$e_{2u}$	$\frac{14}{17} = 0.82$	0.39
$b_{2g}$	0	0

three natural orbitals in Table 1, is the overlap integral

$$\langle \text{MO} | \text{Kekulé} \rangle = (\langle \text{MO} | \phi_1 \rangle + \langle \text{MO} | \phi_2 \rangle) / \langle 0 | 0 \rangle^{1/2}. \quad (34)$$

We find that

$$\langle \text{MO} | \text{Kekulé} \rangle = \begin{cases} \frac{9}{4} \sqrt{\frac{2}{17}} = 0.7717 & \text{for } \langle p_j | p_{j+1} \rangle = 0 \\ 0.8974 & \text{for } \langle p_j | p_{j+1} \rangle = 0.25. \end{cases} \quad (35)$$

Thus we see that the two ground state representatives become more similar when  $\pi$ - $\pi$  overlap is taken into account. Likewise, the rather unrealistic promotion of electrons into antibonding orbitals in the Kekulé model is significantly reduced when  $\pi$ - $\pi$  overlap is included. Similar consequences of overlap is found in comparisons of the molecular orbital and valence bond descriptions of the hydrogen molecule [12].

## References

1. See e.g. Methods of electronic structure theory (ed. H. F. Schaefer III) vol. III. New York: Plenum Press 1977
2. Löwdin, P.-O.: Phys. Rev. **97**, 1474, 1490, 1509 (1955)
3. Broer-Braam, H. B.: Localized orbitals and broken symmetry in molecules. Thesis, The University of Groningen, 1981
4. Hendeković, J., Pavlović, M.: Chem. Phys. Letters **73**, 381 (1980); Hendeković, J.: J. Chem. Phys. Lett. **76**, 593 (1980)
5. Hendeković, J.: Int. J. Quantum Chem. **8**, 799 (1974) and references therein
6. Löwdin, P.-O.: In: Quantum theory of atoms, molecules and solid state p. 601, Löwdin, P.-O., (ed.), New York: Academic Press 1966
7. See e.g. Linderberg, J. & Öhrn, Y.: Propagators in quantum chemistry, chapters 4 and 9 New York: Academic Press 1973
8. Gantmacher, F. R.: The theory of matrices, p. 276 Chelsea 1959
9. Amos, A. T. & Hall, G. G.: Proc. R. Soc. **A263**, 483 (1961)
10. Martin, R. L.: In: Recent developments and applications of multiconfigurational Hartree-Fock methods, p. 154. NRCC Proceedings no. 10 (1981)
11. Pavlović, M. & Hendeković, J.: Chem. Phys. Letters **77**, 377 (1981)
12. Linderberg, J.: (private communication)

Received February 28/August 2, 1983