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Splitting of the Configuration Interaction Space X_n into Two Complementary Subspaces

T. P. Živković

Rudjer Bošković Institute, POB 1016, 41001 Zagreb, Yugoslavia

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The configuration interaction space X_n generated by n particles moving over $2n$ orbitals is considered. The formalism of the molecular orbital resonance theory (MORT) approach is used. It is shown that the space X_n can be split into subspaces X_n^+ *and* X_n^- so that »elementary« one-particle operators connect either the states contained in the same subspace, or they connect the states contained in different subspaces. In particular, each state $\Psi^+ \in X_n^+$ and each state $\Psi^- \in X_n^-$ has a uniform charge density distribution over all $2n$ orbitals, and vanishing bond orders between orbitals of the same parity. As a simple consequence the pairing theorem results. To be »alternant-like« is thus shown to be the property of whole spaces X_n^+ and X_n^-, rather than the property of particular eigenstates. The connection with the pairing theorem as derived by other authors is discussed.

INTRODUCTION

A new approach to the treatment of quantum chemical problems was recently proposed.[1–4] This aproach, called the Molecular Orbital Resonance Theory (MORT) retains the concept of the resonance from the VB method, but it treats each particular bond in the MO sense. Accordingly, a MORT resonance structure is a determinant containing bond orbitals. Many quantum chemical problems can be expressed in a very simple form using these structures. For example, a very primitive model retaining only Kekulé structure in conjunction with the Hückel Hamiltonian satisfactorily reproduces the heats of atomisation of conjugated hydrocarbons as well as of conjugated heterocompounds.[1] The Hückel (4m+2) rule can be generalised to arbitrary conjugated hydrocarbons not only within the Hückel,[2] but also within the more sophisticated Pople approximation.[3] Charge polarisation and bond length fixation can also be explained in a very simple way.[4] These results suggest that the MORT approach is quite natural in representing a certain class of quantum chemical problems. In the present paper we will further develop this method. In particular, the well known pairing theorem will be derived within this approach.

In the first section the configurationo interaction (*CI*) space X_n is considered and MORT resonance structures spanning this space are defined. In the second section it is shown how the space X_n can be split into subspaces X_n^+ and X_n^- spanned by »positive« and »negative« structures, respectively. In the third section the so called splitting theorem is derived. According to this theorem there are two kinds of »elementary« one-particle operators. These operators connect either the states in the same subspace (X_n^+ or X_n^-), or they connect the states in different subspaces. As a simple consequence of this theorem, each state $\Psi^+ \in X_n^+$, as well as each state $\Psi^- \in X_n^-$, is »alternant-like«. In other words $\Psi^\pm$ is the state with uniform charge density distribution over all vertices (atoms), and with vanishing bond orders between vertices (atoms) of the same parity. This is discussed in the fourth section. In the fifth section the pairing theorem is derived for a variety of quantum chemical models. The theorem follows from the fact that eigenstates of the Hamiltonian corresponding to an alternant system lie in subspaces X_n^+ and X_n^-. This theorem is thus a simple consequence of the special properties of spaces X_n^+ and X_n^-, as expressed by the more general splitting theorem. In the sixth section a comparison with the derivation of the pairing theorem by other authors is given. In particular, it is shown that resonance structures as defined in the MORT approach are eigenstates of the pairing operator C defined by Koutecký. These structures hence form the most natural base in the CI space X_n in which to express the pairing theorem.

1. Configuration Interaction Space X_n and MORT Resonance Structures

Let us first define the configuration interaction (*CI*) space X_n to be treated here. This space is determined by n particles moving over $2n$ orthonormalised orbitals χ_i. Orbitals χ_i can be spin-orbitals, atomic orbitals, molecular orbitals etc.. For the sake of reference and unless otherwise specified, we will call orbitals χ_i primitive orbitals (PO). The set of all normalised determinants containing n primitive orbitals forms an orthonormalised base in the space X_n. Accordingly, the dimension of the space X_n equals

$$d(n) = (2n)!/(n!)^2 \tag{1}$$

One can now construct different MORT resonance structures in X_n. Normal resonance structures (NRS) are defined to be normalised determinants containing n mutually disjunct bond orbitals (BO) constructed out of PO-s χ_i (see Appendix). The set $\mathbf{N}$ (n) of all NRS-s spans the space X_n and hence all quantum chemical problems defined in X_n can be expressed in terms of NRS-s. This set is however overcomplete, and one can restrict consideration to the so called regular resonance structures (RRS) alone. The set $\mathbf{R}$ (n) of all RRS-s is a subset of the set $\mathbf{N}$ (n). The definition of this set depends on the partition of the set B of all $2n$ PO-s χ_i into subsets B^o and B^x containing n PO-s each. For the sake of reference orbitals $\chi_i \in B^o$ are called source, while orbitals $\chi_j \in B^x$ are called sink. Only these BO-s are considered which contain one source and one sink PO. Each NRS containing only such BO-s is by definition a RRS. In the Appendix it is proved that the set $\mathbf{R}$ (n) of all RRS-s spans the *CI* space X_n. This set however, is still overcomplete. On can show that the set $\mathbf{R}$ (n) can be further reduced by taking into account only nonexcited and singly excited structures.[5] We will not here further elaborate on the linear dependence of RRS-a and this question will be treated elsewhere[5]. For our purpose here it is enough to say that the set $\mathbf{R}(n)$ spans the space X_n.

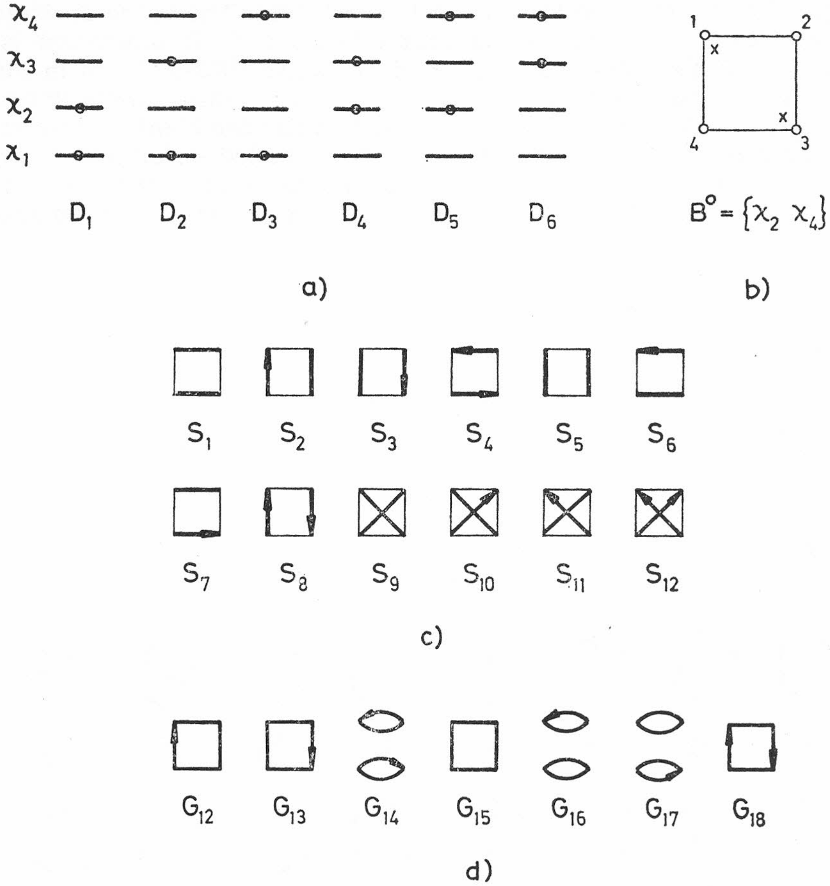

Figure 1. Normal and regular resonance structures in the case $n = 2$.

a) The space X_2 is spanned by six determinants D_1 to D_6. Each of these determinants represents one possible distribution of two particles over four orbitals χ_i.

b) Partition of the set $B = \{\chi_1, \chi_2, \chi_3, \chi_4\}$ on subsets B^o and B^x. Orbitals χ_2 and χ_4 (2 and 4) are defined to be source, while orbitals χ_1 and χ_3) (1 and 3) are sink.

c) Normal resonance structures. Nonoriented bonds represent nonexcited bond orbitals, while oriented bonds represent excited bond-orbitals. With respect to the partition $B^o = \{\chi_2, \chi_4\}$ structures S_1 to S_8 are regular resonance structures.

d) Superpositions G_{12} to G_{14} contain an even number of passive cycles, while superpositions G_{15} to G_{18} contain an odd number (in this case one) of passive cycles. Structures S_1 to S_4 span the space X_2^+, while structures S_5 to S_8 span the space X_2^-.

Note that the definition of the set $\mathbf{R}(n)$ depends on the partition of the set B on subsets B° and $B^{\times}$. There is a one- to -one correspondence between different sets $\mathbf{R}(n)$ and different partitions of the set B on subsets B° and $B^{\times}$ (up to the exchange $B^{\circ} \longleftrightarrow B^{\times}$). Hence there are $N(n) = (1/2)\ (2n!)/(n!)^2 = d(n)/2$ different sets $\mathbf{R}(n)$ corresponding to the same set $N(n)$. In Figure 1 the case $n = 2$ is considered. The space X_2 is generated by two particles occupying four orbitals and its dimension is six (Figure 1a). The same space is spanned by twelve NRS-s shown in Figure 1c. One way to partition the set $B = \{\chi_1, \chi_2, \chi_3, \chi_4\}$ into subsets B° and $B^{\times}$ is $B^{\circ} = \{\chi_2\ \chi_4\}$, $B^{\times} = \{\chi_1, \chi_3\}$ (Figure 1b). In this case eight structures (S_1 to S_8) are contained in the set $\mathbf{R}(2)$. Double exacited structures S_4 and S_8 can be eliminated as they are linear combinations of structures S_1 to S_3 and S_5 to S_7, respectively[5]. A different partition of the set B into subsets

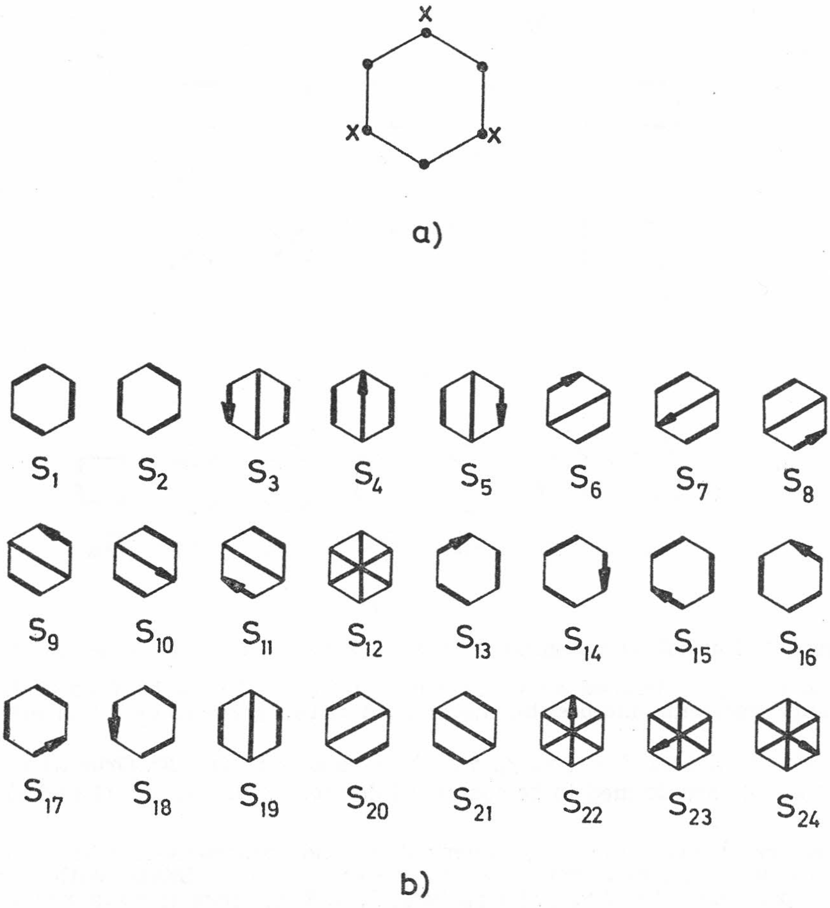

Figure 2. Regular resonance structures in the case $n = 3$.

a) Partition on sink and source orbitals.

b) Nonexcited and single excited RRS-s. Structures S_1 to S_{12} span the space X_3^{+}, while structures S_{13} to S_{24} span the space X_3^{-}.

B^o and B^x would select a different subset of eight structures from the set **N**(2) to form the set **R**(2). Two more such partitions defined by $B^o = \{\chi_1, \chi_2\}$ and $B^o = \{\chi_1, \chi_4\}$, respectively, are possible. In Figure 2 the case $n = 3$ is shown. Only nonexcited and singly excited RRS-s are drawn, since they alone span the space X_3. Since $d(3) = 20$ this set is still overcomplete by four structures.

2. *Splitting of the Space X_n into Spaces X_n^+ and X_n^-*

Consider the set **R** (n) of all n-particle RRS-s. In the Appendix it is shown that one can partition this set into subsets $\mathbf{R}^+(n)$ and $\mathbf{R}^-(n)$ in the following way:

Definition 1

Let S_a, $S_b \in \mathbf{R}(n)$. Form the superposition $G_{ab} = S_a + S_b$.[2] If this superposition contains an even number of passive cycles, then these two structures are contained in the same subset, either in $\mathbf{R}^+(n)$ or in $\mathbf{R}^-(n)$. Otherwise they are contained in different subsets.

The above partition of RRS-s on positive and negative structures resembles on the similar-partition of VB structures on positive and negative structures.[6] In fact, the notion of passive cycle reduces to the notion of 4m-cycle if the two RRS-a in question are nonexcited. The two sets of structures have however completely different meaning, and the analogy is mainly graphical.[2] According to the Definition 1, only the partition of the set $\mathbf{R}(n)$ on subsets $\mathbf{R}^+(n)$ and $\mathbf{R}^-(n)$ is fixed. Which subset is called $\mathbf{R}^+(n)$ and which $\mathbf{R}^-(n)$ is arbitrary. The consistency of the superposition criteria is proved in the Appendix. This consistency is not trivial. It can be shown that the set $\mathbf{I}(n) \subseteq \mathbf{N}(n)$ can be consistently partitioned on positive and negative structures if and only if there is some set $\mathbf{R}(n) \subseteq \mathbf{N}(n)$ of RRS-s such that $\mathbf{I}(n) \subseteq \mathbf{R}(n)$. In other words, only subsets of different sets of RRS-s can be partitioned on positive and negative structures[5]. For example, the three NRS-s shown in Figure 3a form a set **I**(2) which is contained in no set **R**(2). All the three superpositions G_{15}, G_{19} and G_{59} contain a single passive cycle (Figure 3b). If we were to satisfy the su-

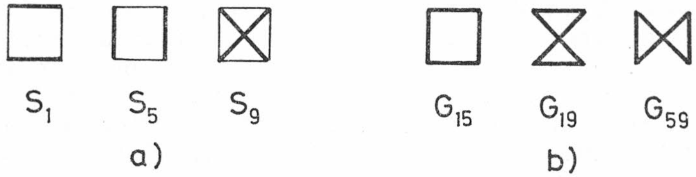

Figure 3. Only subsets of different sets of RRS-s can be consistently partitioned on positive and negative structures.

a) The set **I** (2) = $\{S_1, S_5, S_9\}$ is contained in no set **R**(2) of RRS-s.

b) Each of the superpositions G_{15}, G_{19} and G_{59} contains a single passive cycle. Partition of the set **I** (2) on positive and negative structures is not possible.

perposition criteria, all the three structures should be contained in different subsets. This however can not be done with just two subsets, $\mathbf{R}^+(2)$ and $\mathbf{R}^-(2)$, i.e. the set $\mathbf{I}(2)$ can not be partitioned on positive and negative structures alone. On the other hand, using the superposition criteria one easily finds that structures S_1 to S_4 in Figure 1 form $\mathbf{R}^+(2)$, while structures S_5 to S_8 form $\mathbf{R}^-(2)$. Similarly, in Figure 3 structures S_1 to S_{12} form $\mathbf{R}^+(3)$, while structures S_{13} to S_{24} form $\mathbf{R}^-(3)$.

It can be shown that the overlap S_{ab} between RRS-s S_{a} and S_{b} equals[2].

$$S_{\mathrm{ab}} = \begin{cases} 2^{\rho-n} & \text{if } G_{\mathrm{ab}} \text{ contains no passive cycle} \\ 0 & \text{otherwise} \end{cases} \tag{2}$$

where ρ is the number of cycles contained in the superposition G_{ab} of these two structures. From this equation and the definition 1 it follows

Lema 1

Let $S_{\mathrm{a}}, S_{\mathrm{b}} \in \mathbf{R}(n)$. If $S_{\mathrm{a}} \in \mathbf{R}^+(n)$ *and* $S_{\mathrm{b}} \in \mathbf{R}^-(n)$ then the overlap S_{ab} vanishes:

$$S_{\mathrm{a}} \in \mathbf{R}^+(n),\ S_{\mathrm{b}} \in \mathbf{R}^-(n) \longrightarrow S_{\mathrm{ab}} = 0 \tag{3}$$

The space X_{n}^+ spanned by the subset $\mathbf{R}^+(n)$ is hence orthogonal to the space X_{n}^- spanned by the subset $\mathbf{R}^-(\mathrm{n})$, i.e. these two spaces have no vector in common (except nulvector). Since the set $\mathbf{R}(\mathrm{n})$ spans the whole *CI* space X_{n}, it follows that each state $\Psi \in X_{\mathrm{n}}$ can be represented as a linear combination of some states $\Psi^+ \in X_{\mathrm{n}}^+$ and $\Psi^- \in X_{\mathrm{n}}^-$.

$$\Psi \in X_{\mathrm{n}} \ \rightarrow\ \Psi = \Psi^+ + \Psi^- \text{ where } \Psi^+ \in X_{\mathrm{n}}^+,\ \Psi^- \in X_{\mathrm{n}}^- \tag{4}$$

Given spaces X_{n}^+ and X_{n}^-, this representation is unique. Furthermore, each choice of a particular set B° (or B^{x}) uniquely fixes the partition of the space X_{n} on subspaces X_{n}^+ and X_{n}^-, and hence there are $d(n)/2$ such partitions (up to the exchange $X_{\mathrm{n}}^+ \longleftrightarrow X_{\mathrm{n}}^-$ which forms no new partition). Moreover, one can show that spaces X_{n}^+ and X_{n}^- have the same dimension which hence equals $d(n)/2$.[5] For example, in Figure 1b structures S_1 to S_4 span the subspace X_2^+, while structures S_5 to S_8 span the subspace X_2^-. Both, X_2^+ and X_2^- are three-dimensional. One can show that any three of four structures $S_1, \ldots, S_4$ span X_2^+, whereas any three of four structures $S_5, \ldots, S_8$ span X_2^-.[5] Similarly, in Figure 2 structures S_1 to S_{12} span the space X_3^+, whereas structures S_{13} to S_{24} span the space X_3^-. Since $d(3) = 20$ spaces X_3^+ and X_3^- are ten-dimensional. Sets $\{S_1, \ldots, S_{12}\}$ and $\{S_{13}, \ldots, S_{24}\}$ are hence both overcomplete by two structures.

For reasons which will be apparent in the subsequent sections, we will call each state $\Psi \in X_{\mathrm{n}}^+$ and each state $\Psi \in X_{\mathrm{n}}^-$ an alternant-like state. In conclusion, given spaces X_{n}^+ and X_{n}^- an arbitrary state $\Psi \in X_{\mathrm{n}}$ can be represented in a unique way as a linear combination of two alternant-like states.

3. *The Splitting Theorem*

Each one-particle operator defined in the space X_n can be represented as a linear combination of elementary one-particle operators A^{kl} and B^{kl} such that[2]

$$<\chi_i | A^{kl} | \chi_j> = \delta_{ik}\,\delta_{jl} + \delta_{jk}\,\delta_{il}, \quad <\chi_i | B^{kl} | \chi_j> = \sqrt{-1}\,(\delta_{ik}\,\delta_{jl} - \delta_{il}\,\delta_{jk}) \tag{5a}$$

In terms of creation and annihilation operators one can write

$$\begin{aligned} A^{kl} &= a^{+}_{k}\, a_{l} + a^{+}_{l}\, a_{k} \\ B^{kl} &= \sqrt{-1}\ (a^{+}_{k}\, a_{l} - a^{+}_{l}\, a_{k}) \end{aligned} \tag{5b}$$

where a^{+}_{i} and a_i are creation and annihilation operators associated with the orbital χ_i. Operators A^{kl} are real, while operators B^{kl} are imaginary. Both, A^{kl} and B^{kl} are hermitean operators.

In ref. 2. matrix elements of elementary operators between NRS-s were derived. Analysing these matrix elements one can prove the following

Theorem 1

1. Let the states Ψ_a and Ψ_b be contained in the same subspace, either X_n^{+} or X_n^{-}. Then

a) Matrix element $A^{k}_{ab} = <\Psi_a|A^{k}|\Psi_b>$ of each vertex operator $A^{k} = A^{kk}$ equals overlap S_{ab}.

b) Matrix element $A^{s}_{ab} = <\Psi_a|A^{s}|\Psi_b>$ of each trans-bridge operator $A^{s} = A^{kl}$ vanishes.

c) Matrix element $B^{s}_{ab} = <\Psi_a|B^{s}|\Psi_b>$ of each cis-bridge operator $B^{s} = B^{kl}$ vanishes.

2. Let the states Ψ_a and Ψ_b be contained in different subspaces, one in the subspace X_n^{+} and another in the subspace X_n^{-}. Then

a) Matrix element A^{s}_{ab} of each cis-bridge operator A^{s} vanishes.

b) Matrix element B^{s}_{ab} of each trans-bridge operator B^{s} vanishes.

In other words:

$$\Psi_a, \Psi_b \in X_n^{+} \ \text{or} \ \Psi_a, \Psi_b \in X_n^{-} \rightarrow A^{k}_{ab} = S_{ab},\ A^{s}_{ab} = 0 \ \text{if} \ A^{s} \ \text{is trans-bridge},\ B^{s}_{ab} = 0 \ \text{if} \ B^{s} \ \text{is cis-bridge} \tag{6a}$$

and

$$\begin{aligned} &\Psi_a \in X_n^{+},\ \Psi_b \in X_n^{-} \ \text{or} \ \Psi_a \in X_n^{-},\ \Psi_b \in X_n^{+} \rightarrow \\ &\qquad A^{s}_{ab} = 0 \ \text{if} \ A^{s} \ \text{is cis-bridge} \\ &\qquad B^{s}_{ab} = 0 \ \text{if} \ B^{s} \ \text{is trans-bridge} \end{aligned} \tag{6b}$$

The various terms, cis-bridge, trans-bridge etc. are explained in the Appendix. We refer to the above theorem as a splitting theorem. All elementary one-particle operators are shown to be of two kinds. They either connect states contained in the same subspace, or they do connect states contained in different subspaces. This is explicitly true for all bond operators, either of the cis-bridge or of the trans-bridge type. Concerning vertex operators A^{k}, they effectively connect only the states in different subspaces, since (6a) implies $<\Psi_a|A^{k} - I|\Psi_b> = 0$ whenever either $\Psi_a, \Psi_b \in X_n^{+}$ or $\Psi_a, \Psi_b \in X_n^{-}$.

4. *Charge Densities and Bond Orders*

There are some very simple and important consequences of the splitting theorem. Consider for example a conjugated π-electron system. Assume that the π electrons move over n orthonormalised $2p_z$ orbitals w_i, one orbital from each atom participating in the conjugation. Using these orbitals one can now construct various CI spaces:

1. Let the set B contain 2n spin-orbitals χ_i

$$\chi_i = w_i\,\alpha \qquad (i = 1, \ldots, n) \tag{7}$$
$$\chi_{n+i} = \overline{\chi}_i = w_i\,\beta$$

where α and β are spin-α and spin-β states, respectively. This set uniquely defines the *CI* space X_n. Let a^+_i be creation and a_i annihilation operators of the spin-α orbital $\chi_i = w_i\,\alpha$, and let b^+_i be creation and b_i annihilation operators of the spin-β orbital $\chi_i = w_i\,\beta$. Define operators for electron densities (Q_i) and bond orders (P_{ij}) for electrons of α and β spins

$$q^{\alpha}_{i} = a_i^+\,a_i \qquad q^{\beta}_{i} = b_i^+\,b_i$$

$$p^{\alpha}_{ij} = (a_i^+\,a_j + a_j^+\,a_i)/2 \qquad p^{\beta}_{ij} = (b_i^+\,b_j + b_j^+\,b_i)/2 \tag{8a}$$

and for total bond orders and electron densities

$$q_i = q^{\alpha}_{i} + q^{\beta}_{i} \qquad p_{ij} = p^{\alpha}_{ij} + p^{\beta}_{ij} \tag{8b}$$

Similarly, »cross« bond orders can be defined

$$p^{\alpha\beta}_{ij} = (a_i^+\,b_j + b_j^+\,a_i)/2 \tag{8c}$$

Partition now the set *B* into subsets B^0 and B^x and form corresponding subspaces X_n^+ and X_n^-. Then according to the splitting theorem

$$Q^{\alpha}_{i} = \langle \Psi^{\pm} | \, q^{\alpha}_{i} \, | \Psi^{\pm} \rangle = Q^{\beta}_{i} = \langle \Psi^{\pm} | \, q^{\beta}_{i} \, | \Psi^{\pm} \rangle = 1/2 \tag{9a}$$

$$Q_i = \langle \Psi^{\pm} | \, q_i \, | \Psi^{\pm} \rangle = 1$$

for each normalised state $\Psi^+ \in X_n^+$ and $\Psi^- \in X_n^-$. The subspaces X_n^+ and X_n^- have a special property that each alternant-like state $\Psi^{\pm} \in X_n^{\pm}$ has a uniform spin-α and a uniform spin-β density of 1/2 over all conjugated atoms (*i*) ($i = 1, \ldots, n$). The spin-α and spin-β charge polarisation, and hence the total charge polarisation results from the mixing of states Ψ^+ and Ψ^- in respective subspaces X_n^+ and X_n^-. In other words, the charge polarisation is due to the interference between the two subspaces. Further, if $\Psi^{\pm}$ is an alternant-like state then

$$P^{\alpha}_{ij} = \langle \Psi^{\pm} | \, p^{\alpha}_{ij} \, | \Psi^{\pm} \rangle = 0 \tag{9b}$$

whenever spin orbitals χ_i and χ_j are of the same parity. Similarly $P^{\beta}_{ij} = < \Psi^{\pm} \mid p^{\beta}_{ij} \mid \Psi^{\pm} > = 0$ whenever spin orbitals $\bar{\chi}_i$ and $\bar{\chi}_j$ are of the same parity, and analogously for cross bond orders $P^{\alpha\beta}_{ij}$. Since the choice of n spin orbitals contained in B^{o} (or in B^{x}) is arbitrary, spin orbitals χ_i and $\bar{\chi}_i$ associated with the same conjugated atom (i), are not necessarily of the same parity. In particular consider the following choices

1a) Let spin orbitals χ_i and $\bar{\chi}_i$ ($i = 1, \ldots, n$) be of the same parity. Such a choice requires n begin even, since otherwise subsets B^{o} and B^{x} can not contain the same number of spin orbitals. In this case one obtains

$$< \Psi^{\pm} \mid p^{\alpha}_{ij} \mid \Psi^{\pm} > = < \Psi^{\pm} \mid p^{\beta}_{ij} \mid \Psi^{\pm} > = < \Psi^{\pm} \mid p^{\alpha\beta}_{ij} \mid \Psi^{\pm} > = 0$$

and hence (10)

$$P_{ij} = < \Psi^{\pm} \mid p_{ij} \mid \Psi^{\pm} > = 0$$

whenever atoms (i) and (j) are of the same parity. For example, the *CI* space X_4 corresponding to the cyclobutadiene π-electron system is constructed out of eight spin orbitals (Figure 4a). Carbon atoms 2 and 4

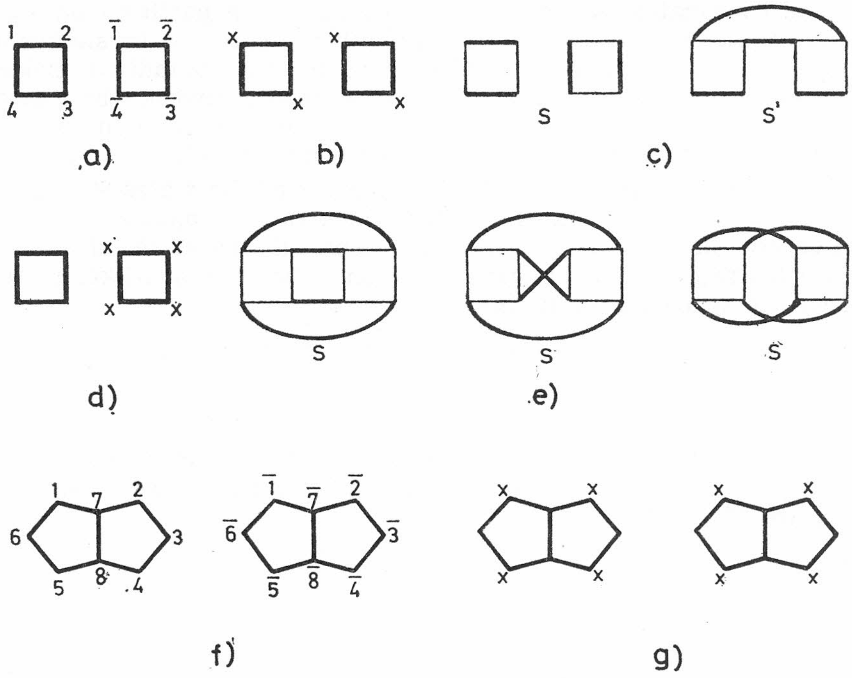

Figure 4. Illustration of the discussion on charge densities and bond orders. For details see text.

a) Spin orbitals forming cyclobutadiene π-electron system.
b) Spin orbitals χ_i and $\bar{\chi}_i$ are chosen to be of the same parity.
c) Some RRS-s consistent with the partition in b).
d) Spin orbitals χ_i are chosen to be source, while spin orbitals $\bar{\chi}_i$ are sink.
e) Some RRS-s consistent with the partition in d).
f) Spin orbitals forming pentalene π-electron system.
g) Spin orbitals χ_i and $\bar{\chi}_i$ are chosen to be of the same parity.

can be chosen to be the source, and carbon atoms 1 and 3 to be the sink (Figure 4b). Each state $\Psi^{\pm} \in X_4^{\pm}$ has uniform spin densities $Q_i^{\alpha} = Q_i^{\beta} = 1/2$ over all carbon atoms (i). In addition, it has vanishing bond orders P_{ij}^{α}, P_{ij}^{β}, $P_{ij}^{\alpha\beta}$ and P_{ij} between all atoms of the same parity (1 and 3 or 2 and 4). Similarly, in the case of the pentalene molecule carbon atoms $(i) = (3, 8, 6, 7)$ can be chosen to be the source, and carbon atoms $(i) = (1, 2, 4, 5)$ to be the sink (Figure 4g). Each state $\Psi^{\pm} \in X_8^{\pm}$ has uniform electron densities $Q_i^{\alpha} = Q_i^{\beta} = 1/2$ and $Q_i = 1$ over all eight carbon atoms. In addition, it has vanishing bond orders P_{ij}^{α}, P_{ij}^{β}, $P_{ij}^{\alpha\beta}$ and P_{ij} between all atoms of the same parity. In particular, $< \Psi^{\pm} \mid p_{78} \mid \Psi^{\mp} > = 0$, i.e. bond order P_{78} across a »nonalternant« central bond (78) vanishes if either $\Psi = \Psi^{+} \in X_8^{+}$ or $\Psi = \Psi^{-} \in X_8^{-}$. Since pentalene is a nonalternant molecule the eigenstates of the corresponding Hamiltonian are polarised. Hence these eigenstates are neither in the subspace X_8^{+} nor in the subspace X_8^{-} but should contain components of both.

If the conjugated system is even alternant, the partition on source and sink atoms can be made to coincide with the partition on starred and unstarred atoms, as we did in the case of the cyclobutadiene molecule (Figure 4b). The eigenstates of neutral alternant hydrocarbon system possess a specific property that they have uniform charge density distribution over all carbon atoms and vanishing bond orders between all atoms of the same parity. This is exactly the property of the states $\Psi^{\pm} \in X_n^{\pm}$, and hence we call such states alternant-like. In the following section it will be shown that, under certain assumptions, all eigenstates of a neutral alternant hydrocarbon system can be chosen to be alternant-like, i.e. to lie either in the space X_n^{+} or in the space X_n^{-}.

1b) Consider now the following partition of the set B on subsets B^{o} and B^{x}:

$$\chi_i \in B^{o} \qquad \overline{\chi_i} \in B^{x} \qquad (i = 1, \ldots, n) \tag{11}$$

Each RRS contains now only those BO-s which connect one spin-α and one spin-β orbital. All spin-α orbitals are of one parity, while all spin-β orbitals are of another. Hence

$$< \Psi^{\pm} \mid p_{ij}^{\alpha} \mid \Psi^{\pm} > = < \Psi^{\pm} \mid p_{ij}^{\beta} \mid \Psi^{\pm} > = 0$$

and (12)

$$P_{ij} = < \Psi^{\pm} \mid p_{ij} \mid \Psi^{\pm} > = 0$$

for all atoms (i) and (j) $(i \neq j)$. In this representation bond orders P_{ij} are nonvanishing only between the states Ψ^{+} and Ψ^{-} contained in different subspaces. Only cross bond orders $P_{ij}^{\alpha\beta}$ can connect the states within the same subspace (see Figure 4d) and 4e)). Partitions (1a) and (1b) are two extreme examples. Many other partitions of the set B on subsets B^{o} and B^{x} are possible. Each of these partitions redefines the notion of the alternant-like state. As illustrated by relations (10) and (12), this leads to the vanishing of different sets of bond orders of alternant-like states.

2. In a spin-separation approximation the state Ψ is assumed to be an antisymmetrised product of a spin-α and a spin-β states $\Phi_\alpha$and $\overline{\Phi}_\beta$ respectively[1]

$$\Psi = | \Phi_\alpha \overline{\Phi}_\beta > \tag{13}$$

In particular, the ground state of a conjugated system containing an even number of electrons is usually well represented in the form (13) where $\Phi_\alpha = \Phi_\beta = \Phi$ is an n-particle state[11]. Hence we will consider the space Y_n which is the smallest space containing all spin separated states (13) such that substates Φ_α and Φ_β contain n particles each. This space is a nonlinear subspace of the complete *CI* space X_{2n}. The state (13) is however more general than one-determinental states assumed in various SCF approaches. As far as corresponding spaces are conserned, the spin--separation assumption is intermediate between the SCF approach and the complete *CI* treatment. Let ${}^{\alpha}X_n$ and ${}^{\beta}X_n$ be CI spaces associated with sets ${}^{\alpha}B = \{\chi_i \,|\, i, \dots, 2n\}$ and ${}^{\beta}B = \{\overline{\chi}_i \,|\, i = 1, \dots, 2n\}$, respectively. Partition the set ${}^{\alpha}B$ on subsets ${}^{\alpha}B^{o}$ and ${}^{\alpha}B^{x}$. This partition determines spaces ${}^{\alpha}X_n{}^{+}$ and ${}^{\alpha}X_n{}^{-}$, subspaces of the spin-α space ${}^{\alpha}X_n$. One finds

$$Q_i^{\alpha} = < \Phi^{\pm} | q_i^{\alpha} | \Phi^{\pm} > = 1/2 \qquad (i = 1, \dots, 2n) \tag{14a}$$

for each normalised state $\Phi^{\pm} \in {}^{\alpha}X_n{}^{\pm}$. Also

$$P_{ij}^{\alpha} = < \Phi^{\pm} | p_{ij}^{\alpha} | \Phi^{\pm} > = 0 \tag{14b}$$

whenever orbitals χ_i and χ_j are of the same parity. Similarly, spaces ${}^{\beta}X_n{}^{+}$ and ${}^{\beta}X_n{}^{-}$ can be constructed. Hence

$$Q_i = < \Psi | q_i | \Psi > = < \Phi_\alpha \overline{\Phi}_\beta | q_i | \Phi_\alpha \overline{\Phi}_\beta > = 1 \tag{14c}$$

whenever Φ_α and $\overline{\Phi}_\beta$ are alternant-like, i.e. $\Phi_\alpha \in {}^{\alpha}X_n{}^{\pm}$ and $\overline{\Phi}_\beta \in {}^{\beta}X_n{}^{\pm}$ (Φ_α and Φ_β are normalised). If the partition is such that $\chi_i \in {}^{\alpha}B^{o}$ implies $\overline{\chi}_i \in {}^{\beta}B^{o}$, then for alternant-like Φ_α and $\overline{\Phi}_\beta$

$$< \Psi | p_{ij} | \Psi > = < \Phi_\alpha \overline{\Phi}_\beta | p_{ij} | \Phi_\alpha \overline{\Phi}_\beta > = 0 \tag{15}$$

whenever atoms (i) and (j) are of the same parity. In conclusion, each alternant-like spin-α state $\Phi_\alpha \in {}^{\alpha}X_n$ has a uniform spin-α density of 1/2 over all atoms (i), and vanishing bond orders P_{ij}^{α} between all atoms of the same parity. Analogous relations hold for each alternant-like spin-β state $\Phi_\beta \in {}^{\beta}X_n$ and hence for each state $\Psi = | \Phi_\alpha \overline{\Phi}_\beta > \in \overline{Y}_n$ constructed out of alternant-like states Φ_α and $\overline{\Phi}_\beta$. For example, RRS-s in Figure 2 can be considered to span the *CI* space ${}^{\alpha}X_3$ (or the *CI* space ${}^{\beta}X_3$) associated with the benzene molecule. Structures S_1 to S_{12} now span the subspace ${}^{\alpha}X_3{}^{+}$, while structures S_{13} to S_{24} span the subspace ${}^{\alpha}X_3{}^{-}$. Each linear combination of structures S_1 to S_{12}, i.e. each state $\Phi \in {}^{\alpha}X_3{}^{+}$, has a uniform spin-$\alpha$ density of 1/2 over all six carbon atoms and vanishing spin-α bond orders P_{ij}^{α} between all atoms of the same parity. Similarly for each state $\Phi \in {}^{\alpha}X_3{}^{-}$ which is a linear combination of structures S_{13} to S_{24}. Charge polarisation is again due to the interference between subspaces ${}^{a}X_3^{+}$ and ${}^{a}X_3^{-}$. In the spin separation approximation the ground state of the π-electron benzene system is of the form $\Psi = |\Phi\overline{\Phi}>$ where Φ is alternant-like, i.e. $\Phi \in {}^{a}X_3^{\pm}$. Moreover, $\Phi \in {}^{a}X_3^{+}$ since the subspace ${}^{a}X_3^{+}$ contains Kekulé structures S_1 and S_2 which are most stable.

3. The above approach can be generalised to include σ-electrons as well. Let w_i $(i = 1, \ldots, n)$ be orthonormalised atomic orbitals including now orbitals forming σ bonds as well. Define the set B to contain $2n$ spin orbitals $\chi_i = w_i\,\alpha$ and $\overline{\chi}_i = w_i\,\beta$, in analogy with (7). Define operators for electron densities on atom (μ) and bond orders between atoms (μ) and (υ):

$$q^{\alpha}_{\mu} = \sum_{i\in\mu} a^{+}_{i}\, a_{i} \qquad\qquad q^{\beta}_{\mu} = \sum_{i\in\mu} b^{+}_{i}\, b_{i}$$

$$p^{\mu\upsilon}_{\alpha} = \sum_{i\in\mu,\, j\in\nu} (a^{+}_{i}\, a_{j} + a^{+}_{j}\, a_{i})/2 \tag{16a}$$

$$p^{\beta}_{\mu\nu} = \sum_{i\in\mu,\, j\in\nu} (b^{+}_{i}\, b_{j} + b^{+}_{j}\, b_{i})/2$$

for spin-α and spin-β electron densities and bond orders. The symbol $i\in\mu$ means that the i-th spin orbital is localised on the atom (μ) and the summation is performed accordingly. Similarly cross bond orders

$$p^{\alpha\beta}_{\mu\nu} = \sum_{i\in\mu,\, j\in\nu} (a^{+}_{i}\, b_{j} + b^{+}_{j}\, a_{i})/2 \tag{16b}$$

and total bond orders and electron densities

$$q_{\mu} = q^{\alpha}_{\mu} + q^{\beta}_{\mu} \qquad\qquad p_{\mu\nu} = p^{\alpha}_{\mu\nu} + p^{\beta}_{\mu\nu} \tag{16c}$$

can be defined. The set B determines the corresponding *CI* space X_n. For an arbitrary partition of B on subsets B° and B^{x} one finds

$$\begin{aligned} &< \Psi^{\pm} | q^{\alpha}_{\mu} | \Psi^{\pm} > = < \Psi^{\pm} | q^{\beta}_{\mu} | \Psi^{\pm} > = n_{\mu}/2 \\ &< \Psi^{\pm} | q_{\mu} | \Psi^{\pm} > = n_{\mu} \end{aligned} \tag{17a}$$

where n_{μ} is the number of AO-s w_i localised on the atom (μ), and the states $\Psi^{\pm} \in X_n^{\pm}$ are normalised. If the partition of the set B on subsets B° and B^{x} is such that all spin orbitals localised on a particular atom (μ) are of the same parity, then

$$\begin{aligned} &< \Psi^{\pm} | p^{\alpha}_{\mu\nu} | \Psi^{\pm} > = < \Psi^{\pm} | p^{\beta}_{\mu\nu} | \Psi^{\pm} > = \\ &< \Psi^{\pm} | p^{\alpha\beta}_{\mu\nu} | \Psi^{\pm} > = < \Psi^{\pm} | p_{\mu\nu} | \Psi^{\pm} > = 0 \end{aligned} \tag{17b}$$

whenever atoms (μ) and (ν) are of the same parity. Relations (17) are generalisations of relations (9a) and (10).

5. *The Pairing Theorem*

In the context of the Hückel or Pariser-Parr-Pople approximation, molecular orbitals nad orbital energies of alternant hydrocarbons have »pairing properties«. These properties were first deduced by Coulson and Rushbrooke[7] using Hückel theory, while Pople[8] did the same for the SCF theory. Mc Lachlan[9] extended the treatment to the complete *CI* space, while Koutecký[10] deduced rather general conditions for the occurance of pairing properties. He formulated these conditions in terms of the system of equations to be satisfied by one- and two-particle parts of the Hamiltonian operator.[10] In the case of neutral alternant hydrocarbons, the most important consequence of pairing properties is uniform π-electron charge density and vanishing bond orders between all carbon atoms of the same parity (starred or nonstarred). We will refer here to these properties as a pairing theorem. This theorem will be derived here for a variety of approximations using the MORT approach.

(1) In the second quantisation formalism the PPP Hamiltonian of an alternant hydrocarbon system can be written in the form

$$\mathbf{H} = K \sum_{i} q_i + \sum_{i,j} p_{ij}\,\beta_{ij} + \sum_{i<j} \gamma_{ij}\,(q_i - 1)\,(q_j - 1) + \\ + \sum_{i} \gamma_{ii}\,(q^{\alpha}_{i} - 1/2)\,(q^{\beta}_{i} - 1/2) \tag{18}$$

where the resonance integrals $\beta_{ij} = \beta_{ji}$ vanish unless atoms (i) and (j) are of different parity, $K = E_i + \gamma_{ii}/2$ is the effective potential energy of a π electron which is the same on each carbon atom, and γ_{ij} are electron repulsion integrals

$$\gamma_{ij} = \int w_i\,(1)\, w_i\,(1)\; 1/r_{12}\, w_j\,(2)\, w_j\,(2)\; d1\, d2 \tag{19}$$

Up to the constant the Hamiltonian (18) is identical to the PPP Hamiltonian as defined by McLachlan in ref. (9). Consider now the *CI* space X_n defined in the paragraph (1) and subspaces X_n^+ and X_n^- as defined in the paragraph (1a) of section 4. Define projection operators P^+ and P^- which project a state $\Psi \in X_n$ onto subspaces X_n^+ and X_n^-, respectively

$$P^+ X_n = X_n^+ \qquad\qquad P^- X_n = X_n^- \tag{20a}$$

These operators satisfy

$$P^+ + P^- = \mathrm{I} \quad \text{and} \quad P^+ P^- = 0 \tag{20b}$$

Since the operator $\mathbf{N} = \sum q_i$ is the operator of the total number of electrons it follows

$$[N, P^+] = [N, P^-] = 0 \tag{21a}$$

i.e., the first term in the Hamiltonian (18) commutes with both, P^+ and P^-. Furthermore, according to the splitting theorem $< \Psi^+ \,|\, p_{ij} \,|\, \Psi^- > = 0$ whenever vertices (i) and (j) are of different parity. Hence

$$[p_{ij}, P^{\pm}] = 0 \tag{21b}$$

if (i) and (j) are of different parity, and thus the second term in the Hamiltonian (18) commutes with $P^{\pm}$ as well. Consider now the commutator $[(q_i^{\alpha} - 1/2)(q_j^{\beta} - 1/2), P^{+}]$ and observe the action of this commutator on the state $\Psi^{+} \in X_n^{+}$. Relations (9) imply $(\hat{q}_j^{\beta} - 1/2) P^{+} \Psi^{+} = (q_j^{\beta} - 1/2) \Psi^{+} = \Psi' \in X_n^{-}$, and further $(q_i^{\alpha} - 1/2) \Psi' = \Psi'' \in X_n^{+}$. Analogously, $P^{+} (q_i^{\alpha} - 1/2)(q_j^{\beta} - 1/2) \Psi^{+} = P^{+} (q_i^{\alpha} - 1/2) \Psi' = P^{+} \Psi'' = \Psi''$. Hence $[\ldots] \Psi^{+} = 0$. One can similarly show that $[\ldots] \Psi^{-} = 0$ where $\Psi^{-} \in X_n^{-}$. Hence the commutator $[\ldots]$ vanishes. In the same way the following relations can be derived:

$$[(q_i^{\alpha} - 1/2)(q_j^{\alpha} - 1/2), P^{\pm}] = 0 \qquad [(q_i^{\alpha} - 1/2)(q_j^{\beta} - 1/2), P^{\pm}] = 0$$

$$[(q_i^{\beta} - 1/2)(q_j^{\beta} - 1/2), P^{\pm}] = 0 \qquad [(q_i - 1)(q_j - 1), P^{\pm}] = 0 \tag{21c}$$

Relations (21) imply that the Hamiltonian **H** is blockdiagonalised in spaces X_n^{+} and X_n^{-}. This proves the pairing theorem since each state $\Psi^{\pm} \in X_n^{\pm}$ has a uniform electron density $Q_i = 1$ over all atoms (i), and vanishing bond orders $P_{ij} = 0$ between all atoms of the same parity.

(2) In addition to the property $Q_i = 1$ alternant-like states $\Psi^{\pm}$ satisfy $Q_i^{\alpha} = 1/2$ and $Q_i^{\beta} = 1/2$. Similarly, not only total bond orders P_{ij}, but also spin bond orders P_{ij}^{α} and P_{ij}^{β}, as well as cross bond orders $P_{ij}^{\alpha\beta}$ vanish between atoms of the same parity. This is a stronger assertion than the one implied by the pairing theorem as stated above. In connection with it note that

$$< \Psi^{\pm} | S_z | \Psi^{\pm} > = 0 \quad \text{where} \quad S_z = \Sigma_i (q^{\alpha} - q^{\beta})/2 \tag{22}$$

is the operator of the spin projection. This operator is however an integral of the motion, i.e. $[S_z, \mathbf{H}] = 0$. It implies that triplet and higher multiplet states must be pairwise degenerate in spaces X_n^{+} and X_n^{-}. Namely, if Ψ satisfies

$$\mathbf{H}\,\Psi = E\Psi \quad \text{and} \quad S_z \Psi = (m/2)\Psi \quad m \neq 0 \tag{23a}$$

then it must be of the form $\Psi = \Psi^{+} + \Psi^{-}$ where $\Psi^{\pm} \neq 0$ (23b)

since otherwise $< \Psi | S_z | \Psi > = 0$, contrary to (23a). Since however **H** is block-diagonalised in X_n^{+} and X_n^{-}, states Ψ^{+} and Ψ^{-} are degenerate eigenstates of the Hamiltonian **H** with the eigenvalue E. Furthermore, if the state $\Psi = \Psi^{+} + \Psi^{-}$ is an eigenstate of the operator S_z with the eigenvalue $(m/2)$, then the state $\Psi' = \Psi^{+} - \Psi^{-}$ is an eigenstate of the same operator with the eigenvalue $(-m/2)$. Eigenstates Ψ and Ψ' (and Ψ^{+} and Ψ^{-}) of the Hamiltonian operator **H** thus appear in pairs. If however $m = 0$ then either $\Psi = \Psi^{+}$ or $\Psi = \Psi^{-}$, unless there is an accidental degeneracy. In particular, unless there is an accidental degeneracy each singlet eigenstate is contained either in X_n^{+} or in X_n^{-}.

(3) A pairing theorem derived in (1) follows from the commutation relations (21). According to the splitting theorem and the results obtained so far, all the following operators commute with projection operators P^+ and P^-:

$$\begin{array}{ll}
p^{\alpha}_{ij}\,,\ p^{\beta}_{ij}\,,\ p^{\alpha\beta}_{ij} & (i) \text{ and } (j) \text{ are of different parity} \\
\left.\begin{array}{l}
B^{ij}{}_{\alpha} = \sqrt{-1}\,(a^{+}{}_{i}\,a_{j} - a^{+}{}_{j}\,a_{i}) \\
B^{ij}{}_{\alpha\beta} = \sqrt{-1}\,(a^{+}{}_{i}\,b_{j} - b^{+}{}_{j}\,a_{i}) \\
B^{ij}{}_{\beta} = \sqrt{-1}\,(b^{+}{}_{i}\,b_{j} - b^{+}{}_{j}\,b_{i})
\end{array}\right\} & (i) \text{ and } (j) \text{ are of the same parity} \\
\left.\begin{array}{l}
(q^{\alpha}_{i} - 1/2)\,(q^{\alpha}_{j} - 1/2) \\
(q^{\beta}_{i} - 1/2)\,(q^{\beta}_{j} - 1/2) \\
(q^{\alpha}_{i} - 1/2)\,(q^{\beta}_{j} - 1/2)
\end{array}\right\} & (i) \text{ and } (j) \text{ are arbitrary} \\
N = \Sigma_{i}\, q_{i} &
\end{array} \qquad (24)$$

Eigenfunctions of any Hamiltonian which is an arbitrary function of the above operators satisfy the pairing theorem. The PPP Hamiltonian (18) is only the special case. Using various operators in (24) one can explicitly construct all such Hamiltonians.

(4) In the SCF formulation of the PPP approach, the eigenstate Ψ is assumed to be a single-determinantal function.[8] In particular, a closed shell singlet state is of the form

$$\begin{array}{l}
\Psi = |\psi_1, \overline{\psi_1}, \psi_2, \overline{\psi_2}, \ldots, \psi_n, \overline{\psi_n}| = (-1)^{n(n-1)/2}\,|\Phi\,\overline{\Phi}> \\
\Phi = |\psi_1, \psi_2, \ldots\, \psi_n|
\end{array} \qquad (25)$$

where ψ_1 are orthonormalised molecular orbitals, linear combinations of $2n$ atomic orbitals w_i[11]. Each state (25) is a spin separated state contained in the space Y_n. An arbitrary single-determinental state $\Psi = |\Phi_\alpha \overline{\Phi}_\beta> \in Y_n$ satisfies

$$<\Psi|\,q^{\alpha}_{i}\;q^{\alpha}_{j}\,|\Psi> = <\Phi_\alpha\,\overline{\Phi_\beta}|\,q^{\alpha}_{i}\;q^{\alpha}_{j}\,|\Phi_\alpha\,\overline{\Phi_\beta}> = Q^{\alpha}_{i}\;Q^{\alpha}_{j} - (P^{\alpha}_{ij})^2 \qquad (26a)$$

$$<\Psi|\,q^{\alpha}_{i}\;q^{\beta}_{j}\,|\Psi> = <\Phi_\alpha|\,q^{\alpha}_{i}\,|\Phi_\alpha><\overline{\Phi_\beta}|\,q^{\beta}_{j}\,|\overline{\Phi_\beta}> = Q^{\alpha}_{i}\;Q^{\beta}_{j}$$

where

$$\begin{array}{l}
Q^{\alpha}_{i} = <\Psi|\,q^{\alpha}_{i}\,|\Psi> = <\Phi_\alpha|\,q^{\alpha}_{i}\,|\Phi_\alpha> \\
P^{\alpha}_{ij} = <\Psi|\,p^{\alpha}_{ij}\,|\Psi> = <\Phi_\alpha|\,p^{\alpha}_{ij}\,|\Phi_\alpha>
\end{array} \qquad (26b)$$

and similarly for β-spins.

Define now a one-particle spin-α Hamiltonian

$$\mathbf{H}_\alpha{}^{P} = \sum_i q_i^\alpha \, [K + 2 \sum_{j \neq i} \gamma_{ij} \, (Q_j^\alpha - 1/2)] + \sum_{i \neq j} p_{ij}^\alpha \, (\beta_{ij} - P_{ij}^\alpha \, \gamma_{ij}) \tag{27}$$

Using (26) one easily finds that

$$2 < \Phi \,|\, \mathbf{H}_\alpha{}^{P} \,|\, \Phi > = \tag{28}$$

$$= K \sum Q_i + 2 \sum_{i<j} P_{ij} \, \beta_{ij} + \sum_{i<j} [(Q_i - 1) \, (Q_j - 1) - (P_{ij})^2/2] \, \gamma_{ij}$$

whenever $\Phi_\alpha = \Phi_\beta = \Phi$. This is in particular true for each state Ψ of the type (25). In this case, however, the expression (28) is equalent to the Pople's expression[8] for the total π-electron energy. Since $\mathbf{H}_a{}^P$ is a one-particle operator, its eigenstates are single-determinantal functions, and hence the iterative diagonalisation of the Hamiltonian $\mathbf{H}_\alpha{}^P$ is equivalent to the People SCF procedure. The pairing theorem now follows by induction. Assume as a first approximation $\Psi_o = | \Phi_o \overline{\Phi_o} >$ and $\Phi_o \in$ $\in {}^\alpha X_n^\pm$. Similarly as above one obtains

$$[\mathbf{H}_\alpha{}^P \, (\Phi_o), \; {}^\alpha P \pm] = 0 \tag{29}$$

where operators ${}^\alpha P^+$ and ${}^\alpha P^-$ project the state $\Phi \in {}^\alpha X_n$ on subspaces ${}^\alpha X_n{}^+$ and ${}^\alpha X^-{}_n$, respectively. Hence $\Phi_1 \in {}^\alpha X_n^\pm$, where $\mathbf{H}_\alpha{}^P \, (\Phi_o) \;\; \Phi_1 = E_1 \;\; \Phi_1$. By induction the SCF limit Φ satisfies $\Phi \in {}^\alpha X_n^\pm$, and hence the state $\Psi =$ $| \Phi \overline{\Phi} >$ satisfies the pairing theorem. Note however that solutions which do not satisfy this theorem may exist. This can happen if $\Phi_o \notin {}^\alpha X_n^\pm$.

(5) An intermediate approach between a full *CI* and one-determinental SCF approach can be formulated. Consider the spin separated states $\Psi \in Y_n$ *and related spaces* ${}^\alpha X_n$ and ${}^\beta X_n$.Define spin-α and spin-β Hamiltonians:

$$\begin{aligned} \mathbf{H}_\alpha \, (\Phi_\beta) &= K \sum_i q_i^\alpha + \sum_{i,j} p_{ij}^\alpha \; \beta_{ij} + \sum_{i<j} \gamma_{ij} \, (q_i^\alpha - 1/2) \, (q_j^\alpha - 1/2) + \\ &+ \sum_{i<j} \gamma_{ij} \, (q_i^\alpha - 1/2) < \overline{\Phi}_\beta \,|\, q_j^\beta - 1/2 \,|\, \overline{\Phi}_\beta > \\ \mathbf{H}_\beta \, (\Phi_\alpha) &= K \sum_i q_i^\beta + \sum_{i,j} p_{ij}^\beta \; \beta_{ij} + \sum_{i<j} \gamma_{ij} \, (q_i^\beta - 1/2) \, (q_j^\beta - 1/2) + \\ &+ \sum_{i<j} \gamma_{ij} \, (q_i^\beta - 1/2) < \Phi_\alpha \,|\, q_j^\alpha - 1/2 \,|\, \Phi_\alpha > \end{aligned} \tag{30}$$

Using relations (26) one finds that each state $\Psi \in Y_n$ satisfies

$$< \Psi \,|\, \mathbf{H} \,|\, \Psi > = < \Phi_\alpha \,|\, \mathbf{H}_\alpha \,|\, \Phi_\alpha > + < \overline{\Phi}_\beta \,|\, \mathbf{H}_\beta \,|\, \overline{\Phi}_\beta > \tag{31}$$

An iterative solution of the eigenvalue equations involving operators $\mathbf{H}_\alpha$ and $\mathbf{H}_\beta$ is thus equivalent to the solution of the single eigenvalue equation involving operator $\mathbf{H}$, as long as one is confined to the spin-separated functions only. If in the first iteration $\Phi^o{}_\alpha \in {}^\alpha X_n^\pm$ and $\Phi^o{}_\beta \in {}^\beta X_n^\pm$, then

$$[\mathbf{H}_\alpha (\Phi^\circ_\beta),\ {}^\alpha P^{\pm}] = [H_\beta (\Phi^\circ_\alpha),\ {}^\beta P^{\pm}] = 0 \qquad (32)$$

which guarantees the pairing theorem for the iterative limit. Similarly as in the SCF one-determinental approach, the solutions which do not satisfy this theorem may exist.

(6) Under the same conditions as above, the pairing theorem can be shown to be true for the following:

a) Each linear subspace of the space X_n in conjuncture with the Hamiltonian (18).

b) Each spin-separated space generated from arbitrary linear subspaces of spaces ${}^\alpha X_n$ and ${}^\beta X_n$ in conjuncture with Hamiltonians (30), etc. For example, let ${}^\alpha\mathbf{K}_n$ and ${}^\beta\mathbf{K}_n$ be the set of all spin-α and spin-β Kekulé structures, respectively. The space ${}^\alpha X^k_n$ spanned by the set ${}^\alpha\mathbf{K}_n$ is a linear subspace of the space ${}^\alpha X_n$, and similarly for the space ${}^\beta X^k_n$ spanned by the set ${}^\beta\mathbf{K}_n$. The pairing theorem now holds for the space Y'_n constaining all the states of the type $\Psi = |\,\Phi_\alpha\ \overline{\Phi}_\beta >$ where $\Phi_\alpha \in {}^\alpha X^k_n$ and $\overline{\Phi}_\beta \in {}^\beta X^k_n$.

6. Comparation with the Other Derivations of the Pairing Theorem

It is interesting to compare the above derivation of the pairing theorem with the results obtained by other authors. Pairing properties are traditionaly derived within the framework of the MO theory.[7–10] In the SCF MO approach the molecular orbitals (MO) ψ_μ are eigenstates of the one-electron Hamiltonian operator H

$$H\,\psi_\mu = \varepsilon_\mu\ \psi_\mu \qquad (33)$$

Each orbital ψ_μ is a linear combination of atomic orbitals w_i which in the case of hydrocarbons are $2p_z$ atomic orbitals localised about each carbon atom. In the case of alternant hydrocarbons one can write

$$\psi_\mu = \sum_i{}^{*}\, c_{\mu i}\, w_i + \sum_j{}^{\circ}\, c_{\mu j}\, w_j \qquad (34a)$$

where summations Σ^* and Σ° are over »starred« and »unstarred« carbon atoms, respectively. For each orbital ψ_μ, there is a paired orbital

$$\psi'_\mu = \sum_i{}^{*} c_{\mu i}\, w_i - \sum_j{}^{\circ}\, c_{\mu j}\, w_j \qquad (34b)$$

the orbital energies being ε_μ and $\varepsilon'_\mu = 2K - \varepsilon_\mu$, respectively. Relations (34) express pairing properties. The pairing theorem is the consequence of these relations. In the Hückel theory the pairing properties follow from the fact that diagonal matrix elements are all equal to a constant K, while off diagonal elements are zero, except between directly bonded atoms, which are of diferent parity.[7] In the SCF PPP approximation, an inductive argument is used.[8] As a zeroth order approximation a set of MO-s is taken which satisfies pairing properties. The effective Hamiltonian constructed out of these orbitals satisfies the condition that diagonal matrix elements are all equal to a constant, while off diagonal elements are zero, except between atoms of different parity. Hence the eigenfunctions of such a Hamiltonian satisfy pairing properties as well. By induction the SCF limit also satisfies these properties.[8] Mc Lachlan extended the above approach to the complete *CI* space.[9] He considers the PPP Hamiltonian which is essentially identical to our Hamiltonian (18). To each configuration Ψ constructed out of molecular orbitals a paired configuration Ψ' constructed out of paired molecular orbitals is associated. Using paired MO-s and paired configurations, Hamiltonian **H'** describing a motion of »paired« holes is constructed. Hamiltonians **H** and **H'** are shown to differ only by a constant, out of which pairing properties of respective eigenfunctions result.[9] Koutecký similarly uses pairing of configurations in order to derive pairing properties.[10] In the process he defines the so-called pairing operator *C*. The pairing properties then result from commutation relations between a pairing operator *C* and respective Hamiltonians. He derived a rather general conditions for a two-particle Hamiltonian to possess pairing properties.[10] There is an interesting connection between the pairing operator *C* as defined by Koutecký and our approach. In the case of the *CI* space X_n this operator can be shown to satisfy[10]

$$C^2 = I \tag{35}$$

and hence its eigenvalues are ± 1. Further, eigenvectors of the Hamiltonian operator of an alternant system are also eigenvectors of *C*, and any vector multiplied by the projection operator

$$S \pm = (I \pm \mathrm{C})/2 \tag{36}$$

is an eigenvector of *C* with eigenvalue $+1$ and -1, respectively. The matrix elements of the Hamiltonian between two vectors, one of which is multiplied by S_+ and another by S_- equals zero.[10] This, however, is exactly the property of projection operators P^+ and P^- defined in the MORT approach. Since this is true for each *PPP* Hamiltonian associated with an alternant system, projection operators $S_{\pm}$ as defined by Koutecký must be the same as projection operators $P^{\pm}$ (or $P^{\mp}$)defined in the MORT approach. It follows that operators $S_{\pm}$ project on spaces $X^{\pm}$ (or $X^{\mp}$). In particular, each RRS is an eigenstate of the projection operators $S_{\pm}$ and hence of the pairing operator *C*. This establishes the connection between MORT structures and the pairing operator.

The difference between the MORT approach and other approaches should be noted. All previous derivations of the pairing theorem are based on some variant of the MO theory and on the pairing of orbitals (34) and its generalisations. The pairing properties and the pairing theorem in particular are then expressed in terms of eigenfunctions of the Hamiltonian operator associated with the alternant system. These eigenfunctions depend on the Hamiltonian and hence they vary from case to case. In the MORT approach the emphasis is on the splitting of the *CI* space X_n *on subspaces* X_n^+ and X_n^-. This splitting has nothing to do with the particular form of the Hamiltonian. All states $\Psi \pm \in X_n{}^{\pm}$ are likely candidates for the eigenfunctions of some Hamiltonian associated with an alternant system. All these states satisfy the pairing theorem. Pairing properties are thus regarded as properties of whole spaces X_n^+ and X_n^-, rather than to be properties of particular eigenfunctions. It turns out that regular resonance structures form the most natural base in which to express the pairing theorem. They already satisfy this theorem, and it is very easy to construct spaces X_n^+ and X_n^- out of these structures.

One further point should be mentioned. The pairing properties as derived by Koutecký, McLachlan and others[7–10] are more general than the pairing theorem derived here in that they apply to ionic alternant systems, odd alternant systems etc.. The derivation presented in the preceeding section can however be generalised to these cases as well.[5] In addition, in some other respects the pairing theorem as derived here is more general. For example, in the paragraph (3) of the preceding section a very general form of Hamiltonians satisfying a pairing theorem is given. The construction of these Hamiltonians is straightforward, and they cover some cases not explicitly considered by other authors. For example Koutecký formulated what was untill now the most general conditions for the occurance of pairing properties. However, he derived these conditions only for symmetrical, i.e. real, Hamiltonians.[10] Hence Hamiltonians containing for example operators B^{ij}_{α}, B^{ij}_{β} and $B^{ij}_{\alpha\beta}$ in (24) are not covered by these conditions.

7. *Summary and Conclusion*

In this paper the *CI* space X_n generated by n particles moving over 2n orbitals is considered. As a base in this space the so called regular resonance structures are used. These structures are defined within the MORT approach, and they are antisymmetrised products of mutually disjunct bond orbitals. The following results are obtained:

1. The space X_n can be split into subspace X_n^+ and X_n^-. »Positive« structures span the space X_n^+, while »negative« structures span the space X_n^-. The simple superposition criteria (Definition 1) determines whether the two structures are contained in the same subspace or not. Each state $\Psi^+ \in X_n^+$ and each state $\Psi^- \in X_n^-$ is defined to be alternant-like.

2. Matrix elements of »elementary« one-particle operators between alternant-like states possess special properties. These operators either connect states contained in the same subspace, or they connect states contained in different subspaces. These properties are summarized in the splitting theorem 1.

3. As a consequence of a splitting theorem each state $\Psi^{\pm} \in X_n{}^{\pm}$ has a uniform charge density distribution over all 2n vertices (orbitals), and a vanishing bond order between vertices (orbitals) of the same parity. This justifies the term »alternant-like« for these states. In brief, to be alternantlike is the property of whole spaces X_n^+ and X_n^-, rather than the property of particular states. From this point of view charge polarisation in nonalternant systems is the result of the interference between spaces X_n^+ and X_n^-. Only states containing nonvanishing components in both subspaces can have a nonuniform charge density distribution.

4. As a further consequence of the splitting theorem eigenstates of Hamiltonians associated with alternant systems are shown to be contained

in subspaces X_n^+ and X_n^-, i.e. they are alternant-like. This then proves the pairing theorem. This theorem is hence a simple consequence of the special properties of spaces X_n^+ and X_n^-. The emphasize here is on these spaces and their properties, which sheds a new light on the structure of the *CI* space X_n.

5. As a by result, an explicite construction of Hamiltonians is given, which possess pairing properties, but which were not till now considered by other authors.

The only restriction to the generality of the above results is that the *CI* space considered should be generated by n particles moving over 2n orbitals. The above results can hence be applied to all systems which can be approximated using the minimum basis set. This approximation follows the physical picture of one electron per atomic orbital, and besides π-electron systems it can be used to describe many σ-electron systems as well. The whole treatment can be however generalised to an arbitrary *CI* space X^N_n generated by n particles moving over N orbitals (n and N arbitrary).[5]

APPENDIX

Let $B = \{\chi_i \,|\, i = 1. \ldots, 2n\}$ be the set of $2n$ orbitals χ_i. Unless otherwise specified orbitals χ_i will be called primitive orbitals (PO), and we will assume the set B to be orthonormalised. Consider now n-particle determinants

$$D = |\chi_{i1}, \chi_{i2}, \ldots, \chi_{in}| = \frac{1}{\sqrt{n!}} \sum_P (-1)^P \chi_{i1}(P1)\, \chi_{i2}(P2) \ldots \chi_{in}(Pn) \qquad (A1)$$

The set of all determinants ($A1$) is orthonormalised and it spans the *CI* space X_n.

Normal Resonance Structures

Normal resonance structures are defined in the following way:

1) Form excited and nonexcited bond orbitals (BO)

$$\begin{aligned} \varphi_s &= \varphi_{ij} = (\chi_i + \chi_j)/\sqrt{2} && \text{nonexcited BO} \\ \varphi^*_s &= \varphi^*_{ij} = (\chi_i - \chi_j)/\sqrt{2} && \text{excited BO} \end{aligned} \qquad (A2)$$

2) Each normalised determinant containing n mutually disjunct BO-s is called normal resonance structure (NRS). By definition, BO-s are mutually disjunct if they have no PO in common.[2] We denote the set of all NRS-s with **N**(n).

Regular Resonance Structures

Regular resonance structures are defined in the following way:

1) Partition the set B containing $2n$ PO-s χ_i into subsets B^o and B^x containing n PO-s each. Call PO χ_i »source« if $\chi_i \in B^o$, and »sink« if $\chi_i \in B^x$. In the case of alternant systems, and if χ_i are spin atomic orbitals, source and sink orbitals can be made to correspond to nonstarred and starred atoms, respectively.

2) Consider only those BO-s φ_{ij} and φ^*_{ij} which satisfy

$$\chi_i \in B^o \quad \text{and} \quad \chi_j \in B^x \qquad (A3)$$

i.e., each BO contains one source and one sink PO.

3) Each normalised determinant containing n mutually disjunct BO-s satisfying the condition (A3) is a regular resonance structure (RRS). The set **R**(n) of all RRS-s is the subset of the set **N**(n).

Kekulé Structures

If all BO-s $|\, s_i) \in S$ contained in the NRS S are nonexcited, and if in addition they correspond to actual bonds, then $S = K$ is a MORT Kekulé structure. Kekulé structures are not neccessarily RRS-s.

Superposition of Structures

Graphically, excited and nonexcited BO-s are represented as oriented and nonoriented bonds, respectively. Superposition of NRS-s S_a and S_b is a graph G_{ab} which is obtained by superimposing graphical representations of these structures, and it consists of disjunct even cycles $c_\mu \in G_{ab}$.[2] Each cycle $c_\mu \in G_{ab}$ is characterised by two numbers, n_μ and m_μ, where $(2n_\mu)$ is the number of bonds in c_μ, while m_μ is the number of oriented bonds in c_μ. Cycle c_μ is »passive« if $(n_\mu + m_\mu)$ is even, and »active« otherwise. A cycle c_μ such that $n_\mu = 1$ is called a γ-cycle.[2]

Different Bond Types

Bond $(s) = (i,j)$ contained in G_{ab} is a normal bond. Bond $(s) = (i,j)$ not contained in G_{ab} is a bridge with respect to G_{ab}, and it is a proper bridge. A normal bond is also considered to be a bridge. If vertices (i) and (j) are contained in the same cycle c_μ, bridge $(s) = (i,j)$ is internal. Otherwise it is external. If vertices (i) and (j) are of the same parity, this bridge is trans-bridge. Otherwise it is cis-bridge. Each cis-bridge internal to the cycle c_μ forms two even cycles over c_μ, while each trans-bridge internal to the cycle c_μ forms two odd cycles over c_μ. Former bridges correspond hence to alternant, while latter correspond to nonalternant bonds with respect to G_{ab}. The notion of cis-bridges and trans-bridges can be consistently extended to the set $\mathbf{R}(n)$ of all RRS-s, but not to the larger set $\mathbf{N}(n)$ of all NRS-s.

Proof of Lemma 1

In order to prove lemma 1 one has to show that each determinant (A1) can be represented as a linear combination of RRS-s. An arbitrary determinant (A1) can be written in the form

$$D = |\, \chi_{i1}, \chi_{i2}, \ldots, \chi_{ir}, \chi_{j(r+1)}, \ldots, \chi_{jn} \,| \tag{A4}$$

where the first r PO-s ($r = 0, \ldots, n$) are source ($\chi_{is} \in B^o$), while last $(n - r)$ PO-s are sink ($\chi_{js} \in B^x$). Using PO-s not contained in D, each PO contained in D can be represented as a linear combination of one excited and one nonexcited BO satisfying (A3). Moreover, since there are n source and n sink PO-s, this can be done in such a way that no two BO-s are adjacent to each other. Expanding D in terms of such BO-s one obtains a linear combination of RRS-s. This proves the lemma 1.

Linear Dependence of the Set $\mathbf{R}$ *(n)*

Consider the set $\mathbf{R}_o(n)$ containing all nonexcited RRS-s i.e. these containing no excited BO. One easily finds that this set contains $R_o(n) = n!$ structures. Each bond in a particular nonexcited RRS can be made to be either excited or nonexcited. Hence each nonexcited RRS $S \in \mathbf{R}_o(n)$ generates 2^n structures $S' \in \mathbf{R}(n)$. It follows that the number $R(n)$ of all RRS-s equals

$$R(n) = 2^n n! \tag{A5}$$

This is larger than the dimension $d(n)$ of the space X_n, unless $n = 1$. The set $\mathbf{R}(n)$ $(n > 1)$ is hence overcomplete.

Consistency of the Definition 1

As shown by Dewar and Longuet-Higgins[6] the set of all VB structures can be partitioned into »positive« and »negative« structures. If the superposition of the two VB structures contains an even number of 4m-cycles, these structures are of the same parity, and hence they belong to the same class. Otherwise they are contained in two different classes.[6] Graphically, there is a one-to -one correspondence between 2n-particle VB structures and n-particle nonexcited RRS-s. Hence the set $\mathbf{R}_o(n)$ of all n-particle nonexcited RRS-s can be consistently partitioned into subsets $\mathbf{R}^+_o(n)$ and $\mathbf{R}^-_o(n)$. Since to each excited RRS there correspond uniquely a nonexcited RRS, this partition can be extended to the partition of all r-excied ($r = 1, \ldots, n$) RRS-s into two subsets. In conjunction with the definition of active and passive cycles, this proves the consistency of definition 1.

Proof of the Theorem 1 (Splitting Theorem)

In ref. 2 the following lemma was derived

Lemma 2

Let $A^s = A^{kl}$ be an internal cis-bridge operator. Matrix element $A^s_{ab} = < S_a \mid A^s \mid S_b >$ equals

$$A^s_{ab} = (-1)^{n_s' + m_s'} S_{ab} \tag{A6}$$

where $(2n'_s)$ is the number of bonds in a cycle c'_s formed by a bridge (s) over the superposition G_{ab}, while m'_s is the number of oriented bonds in this cycle. According to this lemma matrix element A^s_{ab} of an internal cis-bridge operator A^s between RRS-s S_a and S_b is proportional to the overlap S_{ab}. In addition, matrix element A^s_{ab} of an external operator vanishes.[2] Hence and from the eq. (3) matrix element of any cis-bridge operator $A^s = A^{kl}$ between resonance structures $S_a \in X_n^+$ and $S_b \in X_n^-$ vanishes. Since structures $S_a \in X_n^+$ span the space X_n^+, while structures $S_b \in X_n^-$ span the space X_n^-, this proves point 2a) of theorem 1. Similarly all other points of this theorem can be derived.

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11. Since the state Ψ is 2n-particle, the number of associated atomic orbitals w_i is 2n as well. The number of spin-orbitals is hence 4n. Compare to the relation (7).

SAŽETAK

Cijepanje konfiguracijsko-interakcijskog prostora X_n na dva komplementarna podprostora

T. P. Živković

Promatran je n-čestični konfiguracijsko interakcijski prostor X_n izgrađen nad 2n orbitala. Korišten je formalizam molekularno orbitalne rezonantne teorije (MORT). Pokazano je da se prostor X_n cijepa na komplementarne podprostore X_n^+ i X_n^- takove da »elementarni« jednočestični operatori vežu bilo samo stanja u istom podprostoru, ili samo stanja u različitim podprostorima. Iz toga slijedi da svako stanje $\Psi^+ \in X_n^+$, kao i svako stanje $\Psi^- \in X_n^-$, ima jednoliku raspodjelu naboja preko svih 2n orbitala, te iščezavajući red veze među orbitalama iste parnosti. To su karakteristična svojstva vlastitih stanja neutralnih alternatnih ugljikovodika, i kao jednostavna posljedica slijedi teorem parnosti. Cijeli komplementarni prostori X_n^+ i X_n^- su stoga »alternantni«, a ne samo pojedina vlastita stanja određenih Hamiltonijana. Diskutirana je veza sa raznim drugim formulacijama teorema parnosti poznatim iz literature.