The Splitting Theorem and Properties of Alternant Systems

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The notion of alternant systems, as defined in various semi-empirical theories of alternant hydrocabrons, is generalised to arbitrary symmetric Hamiltonians. Alternant operators are shown to be linear combinations of the so called reduced alternant operators, and a simple construction of an arbitrary (symmetric) alternant Hamiltonian is presented. A simple test to decide whether a given symmetric Hamiltonian is alternant or not is given as well. A configuration interaction space X_n generated by n electrons moving over $2n$ orthonormalised orbitals is considered. Eigenstates $\Psi \in X_n$ of alternant Hamiltonians are shown to be contained in complementary spaces X_n^+ and X_n^-, subspaces of the space X_n. Each state $\Psi^\pm \in X_n^\pm$ has characteristic properties of eigenstates associated with neutral alternant hydrocarbon systems, a uniform charge density distribution and vanishing bond orders between vertices of the same parity. In addition to these properties of one-particle density matrices, some general properties of two-particle density matrices associated with states $\Psi^\pm \in X_n^\pm$ are also derived.

1. INTRODUCTION

This paper discusses the splitting theorem and some of its consequences. In particular, the so-called »alternant« systems are considered and various properties of density matrices associated with these systems are derived. The splitting theorem is formulated in the configuration interaction (CI) space X_n.[1,2] This space is generated by n fermions (electrons) moving over $2n$ ortho-normalised orbitals. The theorem was originally derived for one-particle operators[1] in connection with the molecular orbital resonance theory (MORT)[3,4] approach, and then generalised to two-particle operators as well[2]. The present formulation essentially follows Ref. 2, with the proviso that the second quantisation formalism is used more consistently.

In the second section a short account of the splitting theorem is given. In brief, this theorem states that the space X_n can be partitioned into two complementary subspaces X_n^+ and X_n^- such that each state $\Psi \in X_n^+$ as well as each state $\Psi \in X_n^-$ is »alternant-like« in the sense that it has all the essential properties of eigenstates of neutral alternant hydrocarbon (AH) systems. The theorem is formulated for the symmetrical one- and two-particle operators, but it can be generalised to arbitrary operators.[5] Besides, most operators of interest in quantum chemistry are symmetric one- and two-particle (or their

linear combination) operators. In particular, each velocity independent Hamiltonian is such an operator.

In order to formulate the theorem, the so called »reduced« operators are defined. These operators are of two kinds, »alternant« and »antialternant«. Alternant reduced operators are block diagonalised in the space X_n into subspaces X_n^+ and X_n^-, i. e. they have vanishing matrix elements between all the states $\Psi^+ \in X_n^+$ and $\Psi^- \in X_n^-$ contained in different subspaces. On the other hand, antialternant reduced operators have vanishing matrix elements between all the states contained in the same subspace, either in X_n^+ or in X_n^-. The set of all reduced operators is »complete« in the sense that each symmetric operator can be represented as a linear combination of these operators. Each linear combination of reduced alternant operators is further defined to be an alternant operator, while each linear combination of reduced antialternant operators is defined to be an antialternant operator.

In the third section it is shown how an arbitrary symmetric operator can be represented as a linear combination of an alternant and an antialternant operator. Alternant hermitian operators have the complete set of alternant-like eigenstates, and in the fourth section necessary and sufficient conditions for an arbitrary symmetric Hamiltonian to possess the complete set of alternant--like eigenstates are given (corollary 1). This presents the most general definition of alternant systems and alternant Hamiltonians, as long as symmetric operators are considered. This definition is constructive in the sense that each alternant Hamiltonian can be represented as a linear combination of reduced alternant operators and, in addition, each linear combination (with real coefficients) of reduced alternant operators is such a Hamiltonian.

In the fifth section various properties of one- and two-particle density matrices of alternant-like states are derived. These properties are generalisations of the well known properties of neutral AH systems, the uniform charge density distribution and vanishing bond orders between all atoms of the same parity. The generalisation is twofold: firstly, it is shown that the above properties are valid within entire spaces X_n^+ and X_n^-, and not only for particular eigenstates associated with neutral AH systems, and secondly, some novel properties involving one-particle as well as two-particle density matrices are derived.

2. REDUCED OPERATORS AND THE SPLITTING THEOREM

Let us first define reduced operators which play a crucial role in the following analysis. These operators serve as building blocks of alternant and antialternant operators, and they induce the splitting of the n-particle space X_n into complementary subspaces X_n^+ and X_n^-. The proof of different properties of reduced operators, spaces X_n^+ and X_n^- etc. can be found elsewhere.[1,2] However, an attempt is made in the present approach to formulate these results within the framework of the second quantisation formalism. There are, hence, some minor differences in various definitions as given here and in the previous papers. These differences are mainly formal, and the careful reader may easily establish the correspondence between these approaches.

Let η_i^+ and η_i be creation and annihilation operators, respectively, satisfying anticommutation relations

$$[\eta_i^+, \eta_j^+]_+ = [\eta_i, \eta_j]_+ = 0 \qquad\qquad [\eta_i^+, \eta_j]_+ = \delta_{ij} \qquad\qquad (1)$$

Let further $|0\rangle$ be a vacuum state

$$\eta_i |0\rangle = 0 \tag{2}$$

Reduced operators $\hat{R}_{ij}$ and $\hat{R}_{ij,\,kl}$ are now defined as:[2]

$$\hat{R}_{ij} = \hat{A}_{ij} - \delta_{ij} \tag{3a}$$

$$\hat{R}_{ij,\,kl} = \hat{A}_{ij,\,kl} \qquad (i \neq j \neq k \neq l)$$

$$\hat{R}_{ik,\,jk} = -\hat{R}_{ik,\,kj} = 2\,\hat{A}_{ik,\,jk} + \hat{A}_{ij} \qquad (k \neq i \neq j) \tag{3b}$$

$$\hat{R}_{ij,\,ij} = -\hat{R}_{ij,\,ji} = 2\,\hat{A}_{ij,\,ij} + \hat{A}_{ii} + \hat{A}_{jj} - 1 \qquad (i \neq j)$$

where

$$\hat{A}_{ij} = \eta_i^+ \eta_j + \eta_j^+ \eta_i$$

$$\hat{A}_{ij,\,kl} = \eta_i^+ \eta_j^+ \eta_k \eta_l + \eta_l^+ \eta_k^+ \eta_j \eta_i \tag{3c}$$

A unit operator is defined to be a reduced operator as well. For the sake of reference, and as suggested by the graphical representation of the above operators, we use the following terminology: operators $\hat{A}_{ii}$ are vertex operators, operators $\hat{A}_{ij}$ $(i \neq j)$ are bond operators, operators $\hat{A}_{ij,\,ij} = -\hat{A}_{ij,\,ji}$ $(i \neq j)$ are vertex-vertex operators, operators $\hat{A}_{ik,\,jk} = -\hat{A}_{ik,\,kj}$ $(i \neq j \neq k)$ are bond-vertex operators, while operators $\hat{A}_{ij,\,kl}$ $(i \neq j \neq k \neq l)$ are bond-bond operators. Analogous terminology is used to denote reduced operators. Accordingly, indices (i), (j), (k) and (l) are referred to as vertices[1,2] (Figure 1).
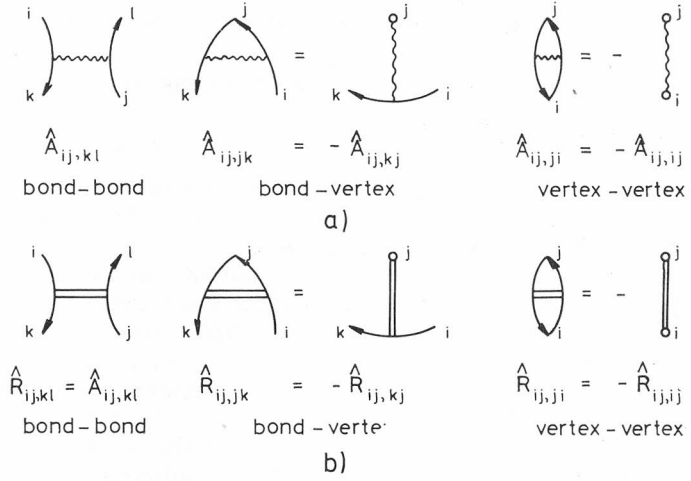

Figure 1. Graphical representation of bond-bond, bond-vertex and vertex-vertex operators. Bond and vertex operators[2] are represented in a similar way.

a) Graphical representation of operators $\hat{A}_{ij,\,kl}$

b) Graphical representation of reduced operators $\hat{R}_{ij,\,kl}$

Operators $\hat{A}_{ij}$ and $\hat{A}_{ij,\,kl}$ are symmetric, *i. e.* they satisfy

$$\langle \Psi_1 \,|\, \hat{A}_{ij} \,|\, \Psi_2 \rangle = \langle \Psi_2 \,|\, \hat{A}_{ij} \,|\, \Psi_1 \rangle$$

$$\langle \Psi_1 \,|\, \hat{A}_{ij,\,kl} \,|\, \Psi_2 \rangle = \langle \Psi_2 \,|\, \hat{A}_{ij,\,kl} \,|\, \Psi_1 \rangle \tag{4}$$

whenever states Ψ_1 and Ψ_2 are real. These operators are also hermitian, *i. e.*

$$\hat{A}_{ij}{}^+ = \hat{A}_{ij} \qquad \hat{A}^+_{ij,\,kl} = \hat{A}_{ij,\,kl} \tag{5}$$

Relations (3) imply that reduced operators are hermitian and symmetric as well. In addition, operators $\hat{A}_{ij}$ and $\hat{A}_{ij,\,kl}$ satisfy symmetry relations

$$\hat{A}_{ij} = \hat{A}_{ji} \qquad \hat{A}_{ij,\,kl} = -\,\hat{A}_{ji,\,kl} = \hat{A}_{kl,\,ij} \tag{6a}$$

and hence

$$\hat{R}_{ij} = \hat{R}_{ji} \qquad \hat{R}_{ij,\,kl} = -\,\hat{R}_{ji,\,kl} = \hat{R}_{kl,\,ij} \tag{6b}$$

One can easily show that each symmetric one- and two-particle operator can be represented as a linear combination of operators $\hat{A}_{ij}$ and $\hat{A}_{ij,\,kl}$. Moreover, this representation is unique up to the symmetry relations (6a) (*i. e.* provided operators $\hat{A}_{ij}$ and $\hat{A}_{ji}$ are considered to be one and the same operator, *etc.*). Inverse relations to relations (3) are

$$\hat{A}_{ij} = \hat{R}_{ij} + \delta_{ij} \quad \text{(bond and vertex operators)} \tag{7a}$$

$$\hat{A}_{ij,\,kl} = \hat{R}_{ij,\,kl} \quad \text{(bond-bond operators)}$$

$$\hat{A}_{ik,\,jk} = (\hat{R}_{ik,\,jk} - \hat{R}_{ij})/2 \quad \text{(bond-vertex operators)} \tag{7b}$$

$$\hat{A}_{ij,\,ij} = (\hat{R}_{ij,\,ij} - \hat{R}_{ii} - \hat{R}_{jj} - 1)/2 \quad \text{(vertex-vertex operators)}$$

and hence each symmetric one- and two-particle operator can be represented as a linear combination of reduced operators as well. This representation is also unique up to the symmetry relations (6b).

Let there now be $2n$ (an even number) creation and $2n$ annihilation operators, and partition the set $B = \{i\}$ of $2n$ indices (vertices) $i = 1, \ldots, 2n$ into subsets B° and B^* containing n vertices each. Apart from the condition that subsets B° and B^* should contain the same number of vertices, this partition is arbitrary. We refer to the vertex (i), creation operator η_i^+, annihilation operator η_i, and one-particle state (orbital) $|\, i \,\rangle = |\, \chi_i \,\rangle = \eta_i^+ |\, 0 \,\rangle$ as »source« if $(i) \in B^\circ$, and as »sink« if $(i) \in B^{*6}$. The partition of the set B into two subsets induces the partition of all reduced operators into »alternant« and »antialternant«.[1,2] Reduced operator $\hat{R}_{ij}$ is »alternant« if vertices (i) and (j) are of the opposite parity, *i. e.* if one of these vertices is source while the other is sink. It is antialternant if vertices (i) and (j) are of the same parity, *i. e.* if they are either both source or both sink.[1,2]. Similarly, a reduced operator $\hat{R}_{ij,\,kl}$ is

»alternant« if an even number among four vertices (i), (j), (k) and (l) is source, and antialternant otherwise.[2] A unit operator is an alternant operator as well. A notion of »alternant« and »antialternant« reduced operators is relative to the partition of the set B into source and sink subsets. A given reduced operator can be »alternant« with respect to one partition, and »antialternant« with respect to another. However, whatever this partition, vertex operators $\hat{R}_{ii}$ are always antialternant, while vertex-vertex operators $\hat{R}_{ij, ij}$ and a unit operator are always alternant. Generalising the notion of reduced alternant and antialternant operators, we call each symmetric operator »alternant« if it can be expressed as a linear combination of reduced alternant operators, and »antialternant« if it can be expressed as a linear combination of reduced antialternant operators. If a symmetric operator is neither alternant nor antialternant we call it »nonalternant« (see Table I).

TABLE I

Type	Reduced operators*	
	Alternant	Antialternant
Unit operator	I	
Bond	$\hat{R}_{12}\ \hat{R}_{14}\ \hat{R}_{23}\ \hat{R}_{34}$	$\hat{R}_{13}\ \hat{R}_{24}$
Vertex		$\hat{R}_{11}\ \hat{R}_{22}\ \hat{R}_{33}\ \hat{R}_{44}$
Bond-bond	$\hat{R}_{12, 34}\ \hat{R}_{13, 24}\ \hat{R}_{14, 23}$	
Bond-vertex	$\hat{R}_{12, 14}\ \hat{R}_{23, 34}$ $\hat{R}_{12, 23}\ \hat{R}_{14, 34}$	$\hat{R}_{12, 13}\ \hat{R}_{13, 14}\ \hat{R}_{12, 24}\ \hat{R}_{23, 24}$ $\hat{R}_{13, 23}\ \hat{R}_{13, 34}\ \hat{R}_{14, 24}\ \hat{R}_{24, 34}$
Vertex-vertex	$\hat{R}_{12, 12}\ \hat{R}_{13, 13}\ \hat{R}_{14, 14}$ $\hat{R}_{23, 23}\ \hat{R}_{24, 24}\ \hat{R}_{34, 34}$	

* Reduced operators in the case $n = 2$. There are $2n = 4$ vertices, and vertices (1) and (3) are chosen to be source, while vertices (2) and (4) are chosen to be sink. Each linear combination of reduced alternant operators is an alternant operator, while each linear combination of reduced antialternant operators is an antialternant operator. Operators like $\hat{R}_{12} + \hat{R}_{13}$ which are neither alternant nor antialternant are nonalternant. An arbitrary one- and two-particle symmetric operator constructed out of four creation and annihilation operators η_i^+ and η_i $(i = 1, \ldots, 4)$ can be represented as a linear combination of the above reduced operators.

Now let X_n be the n-particle space spanned by all n-particle states $| \Delta_\nu \rangle$[7]

$$| \Delta_\nu \rangle = \eta_{i1}^+ \eta_{i2}^+ \ldots \eta_{in}^+ | 0 \rangle = | i_1, i_2, \ldots, i_n \rangle \tag{8}$$

In the notation of Refs. 1 and 2 $| \Delta_\nu \rangle$ is the n-particle Slater determinant

$$\Delta_\nu = | \chi_{i1}, \chi_{i2}, \ldots, \chi_{in} | \tag{9}$$

where χ_{ir} are one-particle orbitals (in particular spin-orbitals), and the space X_n is usually called the configuration interaction (CI) space.

The partition of the set B into two subsets induces now the partition of the space X_n into subspaces X_n^+ and X_n^-. These subspaces are mutually complementary, *i. e.* the space X_n^- contains all the vectors orthogonal to the space X_n^+, and *vice versa*. Each state $\Psi \in X_n$ can be hence written in a unique way as a sum

$$\Psi = \Psi^+ + \Psi^- \tag{10}$$

where $\Psi^+ \in X_n^+$ and $\Psi^- \in X_n^-$. In addition, subspaces X_n^+ and X_n^- can be shown to be of the same dimension.[5] Of course, one can partition the space X_n into two complementary subspaces in many different ways, but the above partition is not arbitrary, and it is determined by the partition $B \rightarrow \{B^0, B^*\}$. The construction of spaces X_n^+ and X_n^- is shown in the Appendix, and it can be found with more details elsewhere.[1,2] The importance and the justification of this particular partition lies in the fact that spaces X_n^+ and X_n^- have very special properties in connection with alternant and antialternant operators as defined above. This connection is expressed by the following theorem[1,2]:

The Splitting Theorem

a) Let $\hat{O}_{al}$ be an alternant operator and let $\Psi^+ \in X_n^+$ and $\Psi^- \in X_n^-$. Then

$$\langle \Psi^+ | \hat{O}_{al} | \Psi^- \rangle = \langle \Psi^- | \hat{O}_{al} | \Psi^+ \rangle = 0 \tag{11a}$$

b) Let $\hat{O}_{nal}$ be an antialternant operator and let either $\Psi_1, \Psi_2 \in X_n^+$ or $\Psi_1, \Psi_2 \in X_n^-$. Then

$$\langle \Psi_1 | \hat{O}_{nal} | \Psi_2 \rangle = 0 \tag{11b}$$

In other words, alternant operators can have nonvanishing matrix elements only between the states in the same subspace, while antialternant operators can have nonvanishing matrix elements only between the states in different subspaces. In particular, this holds true for reduced alternant and antialternant operators, respectively. This theorem *a posteriori* justifies the definition of reduced alternant and antialternant operators, as well as the splitting of the space X_n into subspaces X_n^+ and X_n^-. Note that the partition $B \rightarrow \{B^0, B^*\}$ determines both, the partition of the set of all reduced operators into alternant and antialternant operators as well as the splitting $X_n \rightarrow \{X_n^+, X_n^-\}$ which defines complementary spaces X_n^+ and X_n^-. Once the partition $B \rightarrow \{B^0, B^*\}$ is fixed, the splitting theorem establishes the connection between alternant and antialternant operators with complementary spaces X_n^+ and X_n^-. Anticipating the results of the following sections, we call each state $\Psi = \Psi^+ \in X_n^+$ as well as each state $\Psi = \Psi^- \in X_n^-$ »alternant-like«.[1,2]

One further point should be emphasized here. Reduced operators $\hat{R}_{ij}$, $\hat{R}_{ij, kl}$ and I (a unit operator) are linearly independent provided the whole space Y_n generated by the creation operators η_i^+ from the vacuum state $|0\rangle$ is considered. This space contains the vacuum state, all the one-particle states, all the two-particle states *etc.* The n-particle space X_n is the subspace of the space Y_n, and reduced operators are not linearly independent of X_n alone. This

can be easily seen since the number of particles operator $\hat{N} = \Sigma_i \eta_i^+ \eta_i$ is constant over X_n, i. e.

$$\hat{N}\,\Psi = n\,\Psi \tag{12a}$$

for each state $\Psi \in X_n$. Hence the antialternant operator $\hat{O}_{\mathrm{nal}} = \hat{N} - n = (\Sigma_i \hat{R}_{ii})/2$ vanishes over X_n. Similarly the operator

$$\hat{O} = \alpha\,(\hat{N} - n) + \beta\,(N - n)^2 = (n\,\beta + \alpha\,\Sigma_i R_{ii} + \beta \sum_{i<j} \hat{R}_{ij,\,ji})/2 \tag{12b}$$

with arbitrary coefficients α and β vanishes over X_n as well. This is not the most general operator with such a property. For example the operator

$$\hat{O} = \alpha\,(\hat{N} - \hat{n}_1 - n) + \beta\,(\hat{N} - \hat{n}_1 - n)^2 + (\alpha - \beta)\,\hat{n}_1 \tag{13}$$

where $\hat{n}_1 = \eta_1^+ \eta_1$, also vanishes over X_n. Namely, $\hat{n}_1$ commutes with $\hat{N}$, $(\hat{n}_1)^2 = \hat{n}_1$, and $\hat{N}$ equals n over X_n, i. e. $\hat{O}\,\Psi = [-\alpha\,\hat{n}_1 + \beta\,(\hat{n}_1)^2 + (\alpha - \beta)\,\hat{n}_1]\,\Psi = 0$ whenever $\Psi \in X_n$. In the Appendix we derive

Lemma 1:

Each symmetric operator $\hat{O}$ which vanishes over X_n is of a form

$$\hat{O} = \lambda + C \sum_i \hat{R}_{ii} + \sum_{i<j} \lambda_{ij} \hat{R}_{ij,\,ji} + \sum_{i<j} C_{ij} \sum_k \hat{R}_{ik,\,kj} =$$

$$\lambda + \sum_{i<j} \lambda_{ij} \hat{R}_{ij,\,ji} + [2\,C + \sum_{i \neq j} C_{ij} \overset{\vee}{\hat{A}}_{ij}]\,(\hat{N} - n) \tag{14a}$$

where C and C_{ij} are arbitrary coefficients, while coefficients λ and λ_{ij} satisfy some additional conditions which will be considered elsewhere.[5]

If in addition operator $\hat{O}$ is an antialternant operator, then only reduced antialternant operators in (14a) remain, and one obtains:

Lemma 2:

The necessary and sufficient condition for an antialternant operator $\hat{O}_{\mathrm{nal}}$ to vanish over X_n is that it is of the form

$$\hat{O}_{\mathrm{nal}} = C \sum_i \hat{R}_{ii} + \sideset{}{^-}\sum_{i<j} C_{ij} \sum_k \hat{R}_{ik,\,kj} = [2\,C + \sideset{}{^-}\sum_{ij} C_{ij}\,\hat{A}_{ij}]\,(\hat{N} - n) \tag{14b}$$

where C and C_{ij} are arbitrary coefficients, and the summation Σ^- is performed over vertices (i) and (j) of the opposite parity. Since $\hat{A}_{ij} = \hat{A}_{ji}$ one can without loss of generality assume $C_{ij} = C_{ji}$.[9]

The vanishing of the operator $\hat{O}_{\mathrm{nal}}$ over X_n is obvious from the second form of this operator in (14b). Namely, if $\Psi \in X_n$ then one has $(\hat{N} - n)\,\Psi = 0$ and

hence $\hat{O}_{\text{nal}}\, \Psi = 0$. According to lemma 2 operator (14b) is at the same time the most general operator with such a property.[9]

3. REPRESENTATION OF AN ARBITRARY SYMMETRIC OPERATOR AS A SUM OF AN ALTERNANT AND ANTIALTERNANT OPERATOR

An arbitrary symmetric operator can be written in the form

$$\hat{O} = \lambda + \sum_{ij} \lambda_{ij}\, \eta_i^+ \eta_j + \sum_{i<j} \sum_{k<l} \lambda_{ij,\,kl}\, \eta_i^+ \eta_j^+ \eta_l \eta_k \tag{15a}$$

where the coefficients λ_{ij} and $\lambda_{ij,\,kl}$ satisfy

$$\lambda_{ij} = \lambda_{ji} \qquad \lambda_{ij,\,kl} = \lambda_{kl,\,ij} \tag{15b}$$

Moreover, $\eta_i^+ \eta_j^+ = -\eta_j^+ \eta_i^+$ and $\eta_i \eta_j = -\eta_j \eta_i$ implies

$$\lambda_{ij,\,kl} = -\lambda_{ij,\,lk} \tag{15c}$$

Hence one obtains

$$\hat{O} = \lambda + [\sum_{i,\,j} \lambda_{ij}\, \hat{A}_{ij} + \sum_{i<j} \sum_{k<l} \lambda_{ij,\,kl}\, \hat{A}_{ij,\,lk}]/2 \tag{16}$$

Using relations (7) one can express operator $\hat{O}$ as a linear combination of reduced operators

$$\hat{O} = \lambda + \{\sum_i [\lambda_{ii} + 1/4 \sum_j \lambda_{ij,\,ij}] + \sum_i [\lambda_{ii} + 1/2 \sum_j \lambda_{ij,\,ij}]\, \hat{R}_{ii} +$$

$$+ \sum_{i \neq j} [\lambda_{ij} + 1/2 \sum_l \lambda_{il,\,jl}]\, \hat{R}_{ij} + 1/2 \sum_{i<j} \lambda_{ij,\,ij}\, \hat{R}_{ij,\,ji} +$$

$$+ 1/2 \sum_l \sum_{i \neq j} \lambda_{il,\,jl}\, \hat{R}_{il,\,lj} + \sum_{i<j} \sum_{k<l} \lambda_{ij,\,kl}\, \hat{R}_{ij,\,lk}\}/2 \tag{17}$$

where the last summation is performed over mutually disjunct vertices (i), (j), (k) and (l), i. e. only over bond-bond operators. Operator $\hat{O}$ can be now written in the form

$$\hat{O} = \hat{O}_{\text{al}} + \hat{O}_{\text{nal}} \tag{18a}$$

where $\hat{O}_{\text{al}}$ contains only alternant, while $\hat{O}_{\text{nal}}$ contains only antialternant reduced operators

$$\hat{O}_{\text{al}} = \lambda + \{\sum_i [\lambda_{ii} + 1/4 \sum_j \lambda_{ij,\,ij}] + \sum_{ij}^- [\lambda_{ij} + 1/2 \sum_l \lambda_{il,\,jl}]\, \hat{R}_{ij} +$$

$$+ 1/2 \sum_{i<j} \lambda_{ij,\,ij}\, \hat{R}_{ij,\,ji} + 1/2 \sum_l \sum_{i \neq j}^+ \lambda_{il,\,jl}\, \hat{R}_{il,\,lj} + \sum_{i<j,\,k<l}^+ \lambda_{ij,\,kl}\, \hat{R}_{ij,\,lk}\}/2 \tag{18b}$$

$$\hat{O}_{\text{nal}} = \{\sum_i [\lambda_{ii} + 1/2 \sum_j \lambda_{ij,\,ij}]\, \hat{R}_{ii} + \sum_{i \neq j}^+ [\lambda_{ij} + 1/2 \sum_l \lambda_{il,\,jl}]\, \hat{R}_{ij} +$$

$$+ 1/2 \sum_l \sum_{ij}^- \lambda_{il,\,jl}\, \hat{R}_{il,\,lj} + \sum_{i<j,\,k<l}^- \lambda_{ij,\,kl}\, \hat{R}_{ij,\,lk}\}/2 \tag{18c}$$

In Eq. (18) the following convention concerning different summations is used: double summations Σ_{ij}^+ and Σ_{ij}^- are performed over vertices (i) and (j) of the same and of the opposite parity, respectively. Quadruple summations Σ_{ijkl}^+ and Σ_{ijkl}^- are performed over mutually distinct vertices (i), (j), (k) and (l), i. e. over bond-bond operators. In the former case (Σ^+) an even number of these vertices is source, while in the latter case (Σ^-) an odd number of these vertices is source.

Eqs. (18) can be used to split an arbitrary symmetric operator (15) into its alternant and antialternant part. These relations particularly simplify if $\hat{O}$ is either a one-particle or a proper two-particle operator.

4. ALTERNANT HAMILTONIANS

A special case of a symmetric operator is a symmetric Hamiltonian operator. According to Eqs. (15), an arbitrary symmetric Hamiltonian can be written in the form

$$H = \lambda + \sum_{ij} \lambda_{ij} \eta_i^+ \eta_j + \sum_{i<j} \sum_{k<l} \lambda_{ij,\,kl} \eta_i^+ \eta_j^+ \eta_l \eta_k = H_{\text{al}} + H_{\text{nal}} \tag{19}$$

where H_{al} is a linear combination of reduced alternant operators, while H_{nal} is a linear combination of reduced antialternant operators. Since H is hermitian, coefficients λ, λ_{ij} and $\lambda_{ij,\,kl}$ are real. From the splitting theorem it follows that each alternant Hamiltonian $H = H_{\text{al}}$ has a complete set of alternant-like eigenstates. However, this is not the most general symmetric Hamiltonian with such a property. According to lemma 2, to each operator acting in the space X_n one can add the antialternant operator (14b) without altering eigenvalues and eigenstates. Moreover, this is the most general antialternant operator with such a property, and hence one obtains

Corollary 1:

The neccessary and sufficient condition for an arbitrary symmetric Hamiltonian (19) to possess the complete set of alternant-like eigenstates is

$$H_{\text{nal}} = C \sum_i \hat{R}_{ii} + \sum_{i<j} C_{ij} \sum_k \hat{R}_{ik,\,kj} = [2\,C + \sum_{ij} C_{ij}\, \hat{A}_{ij}]\,(\hat{N} - n) \tag{20a}$$

where C and C_{ij} are arbitrary real coefficients.[9] Since $\hat{A}_{ij} = \hat{A}_{ji}$ one can without loss of generality assume $C_{ij} = C_{ji}$.

Since antialternant reduced operators are linearly independent on Y_n, corollary 1 in conjunction with the relation (18c) implies

1. $\lambda_{ii} + 1/2 \sum_j \lambda_{ij,\,ij} = \text{const.}$

2. $\lambda_{ij} + 1/2 \sum_l \lambda_{il,\,jl} = 0$ i and j are of the same parity, $i \neq j$

3. $\lambda_{il,\,jl} = C_{ij}$ i and j are of the opposite parity, $l \neq i, j$ (20b)

4. $\lambda_{ij,\,kl} = 0$ odd number of source vertices, $i \neq j \neq k \neq l$

Relations (20b) are neccessary and sufficient conditions for an arbitrary symmetric Hamiltonian (19) to possess the complete set of alternant-like eigenstates. Note that in Ref. 2 only sufficient conditions were obtained, since the third condition in (20b) was erroneously derived to read $\lambda_{il,jl} = 0$ instead of $\lambda_{il,jl} = C_{ij}$ with $C_{ij} = C_{ji}$ arbitrary.

Corollary 1 implies that each symmetric Hamiltonian possessing the complete set of alternant-like eigenstates can be written as a linear combination of reduced alternant operators. We will show in the following sections that alternant-like states $\Psi^{\pm}$ have all the properties traditionally associated with the π-electron ground state of neutral alternant hydrocarbon systems. We have hence obtained the most general definition of alternant Hamiltonians and alternant systems, as long as only symmetric Hamiltonians are considered.

One further point should be emphasised. Degenerate eigenstates of an alternant Hamiltonian are not neccessarily alternant-like. Namely, if $\Psi^{+} \in X_n^{+}$ and $\Psi^{-} \in X_n^{-}$ are two degenerate eigenstates of some alternant Hamiltonian H, then their linear combination $\Psi = \alpha \Psi^{+} + \beta \Psi^{-}$ is an eigenstate of H which is not alternant-like. However, if some eigenstates of an alternant Hamiltonian are not alternant-like, they are necessarily degenerate, and one can always perform a linear combination of these eigenstates in order to obtain an equivalent set of alternant-like eigenstates. In this sense spaces X_n^{+} and X_n^{-} can be considered to contain all possible eigenstates of alternant Hamiltonians.

In connection with the pairing properties various authors have discussed different alternant systems.[10-16] Pairing properties refer to the eigenstates of AH Hamiltonians constructed by different semiempirical methods. These properties were originally derived within the Hückel approach[10-11], then generalised to the LCAO-SCF method using the Pariser-Parr-Pople (PPP) type approximation[12], to the unrestricted PPP approach[13], and finally generalised to some symmetric two-particle Hamiltonians as well[14]. It can be shown that alternant Hamiltonians as defined here include all Hamiltonians considered to be alternant by these authors[1,2,5]. Moreover, alternant-like states as defined here satisfy the properties implied by the pairing theorem[1,5]. It should be noted that a rather general definition of alternant Hamiltonians as given by Koutecký[14] is implicit, i. e. it does not permit an easy construction of such Hamiltonians, and it is not easy to decide whether a given Hamiltonian is alternant or not. In the present approach each alternant Hamiltonian can be easily constructed as a linear combination of reduced alternant operators, and relations (20b) represent an easy test to decide whether a given Hamiltonian is alternant or not.[2]

5. DENSITY MATRICES OF ALTERNANT SYSTEMS

There are some interesting consequences of the splitting theorem concerning the properties of alternant-like states. Thus, for example, since $\hat{R}_{ii} = 2\eta_i^{+}\eta_i - 1$ is an antialternant operator, it follows that the diagonal elements γ_{ii} satisfy[1,2]

$$\gamma_{ii} = \langle \Psi \mid \eta_i^{+}\eta_i \mid \Psi \rangle = 1/2 \qquad (i = 1, \ldots, 2n) \qquad (21a)$$

whenever either $\Psi = \Psi^{+} \in X_n^{+}$ or $\Psi = \Psi^{-} \in X_n^{-}$. In other words, each alternant-like state $\Psi^{\pm}$ has a uniform charge density distribution of 1/2 over all orbitals χ_i. Charge polarisation is hence the result of the interference between

spaces X_n^+ and X_n^-, i. e. only the state $\Psi \in X_n$ with nontrivial components in both subspaces X_n^+ and X_n^- can be polarised.[1,2] Analogously one finds

$$\gamma_{ij}(\Psi\pm) = \langle\, \Psi\pm \,|\, \hat{A}_{ij} \,|\, \Psi\pm \,\rangle/2 = 0 \qquad (i \neq j) \tag{21b}$$

whenever vertices (i) and (j) are of the same parity. These properties are essentially the properties of one-particle density matrices associated with neutral AH systems. Alternant-like states beside properties (21) satisfy

$$\langle\, \Psi\pm \,|\, \hat{R}_{il,\,jl} \,|\, \Psi\pm \,\rangle = 0 \qquad i \text{ and } j \text{ are of the opposite parity} \tag{22a}$$

$$\langle\, \Psi\pm \,|\, \hat{A}_{ij,\,kl} \,|\, \Psi\pm \,\rangle = 0 \qquad \text{odd number of source vertices } (i \neq j \neq k \neq l) \tag{22b}$$

The above relations directly follow from the splitting theorem. In terms of the two-particle density matrix $\mathbf{\Gamma}$ (see Appendix) these relations are equivalent to

$$\Gamma_{il,\,jl}(\Psi\pm) = \gamma_{ij}(\Psi\pm)/4 \qquad i \text{ and } j \text{ are of the opposite parity } (l \neq i, j) \tag{23a}$$

$$\Gamma_{ij,\,kl}(\Psi\pm) = 0 \qquad \text{odd number of source vertices } (i \neq j \neq k \neq l) \tag{23b}$$

According to the relation (23a) matrix elements $\Gamma_{il,\,jl}$ (i and j are of the opposite parity, $i \neq j \neq l$) of the two-particle density matrix $\mathbf{\Gamma}$ are completely determined by the matrix elements γ_{ij} of the one-particle density matrix. In particular, (23a) implies that $\Gamma_{il,\,jl}$ does not depend on l, provided $l \neq i, j$ and i and j are of the opposite parity. Unlike the relation (23a), the relation (23b) contains only matrix elements of a two-particle density matrix, analogous to the relation (21b) which contains only matrix elements of the one-particle density matrix. Note the twofold role of matrix elements γ_{ij} of a one-particle density matrix: if i and j are of the same parity, these matrix elements either vanish ($i \neq j$), or they are uniformly constant ($i = j$). On the other hand, if i and j are of the opposite parity, these matrix elements are in general different from zero, but then they determine matrix elements $\Gamma_{il,\,jl}$ of the two-particle density matrix.

Note finally that in the case when $\Psi \in X_n$ is a one-determinental function, a two-particle density matrix $\mathbf{\Gamma}$ satisfies[17-19]

$$\Gamma_{ij,\,kl} = 1/2\,(\gamma_{ik}\,\gamma_{jl} - \gamma_{il}\,\gamma_{jk}) \tag{24}$$

i e. it is completely determined by the one-particle density matrix γ. In this case relations (23) follow from relations (21), i. e. they are not independent. Namely, if $\Gamma_{ij,\,kl}$ contains an odd number of source vertices, then either vertices (i) and (k), or vertices (j) and (l) are of the same parity. If these vertices are mutually distinct, then (21b) implies $\gamma_{ik}\,\gamma_{jl} = 0$, i. e. the first term in the expression (24) vanishes. Similarly one finds $\gamma_{il}\,\gamma_{jk} = 0$, which proves relation (23b). Consider now matrix element $\Gamma_{il,\,jl} = (\gamma_{ij}\,\gamma_{ll} - \gamma_{il}\,\gamma_{jl})/2$. If vertices (i) and (j) are of the opposite parity and if, in addition, $l \neq i, j$, then (21b) implies $\gamma_{il}\,\gamma_{jl} = 0$. Further, according to (21a) $\gamma_{ll} = 1/2$ and hence $\Gamma_{il,\,jl} = \gamma_{ij}/4$, in accord with the relation (23a). This shows that, in the case of the one-determinental functions, relations (23) are the consequence of relations (21). However, relations (23) are valid generally for an arbitrary alternant-like state $\Psi\pm \in X_n^\pm$. In the general case a two-particle density matrix $\mathbf{\Gamma}$ does not satisfy relation (24) or any similar relation, and relations (23) are idenpendent of relations (21).

In order to get a closer physical picture of the significance of the above relations, let us specify our consideration. Creation and annihilation operators η_i^+ and η_i usually refer to spin-orbitals. In most cases one assumes that there are n spin-α orbitals $\chi_i = w_i\,\alpha$ and n spin-β orbitals $\overline{\chi_i} = w_i\,\beta$, where w_i are orthonormalised atomic orbitals, while α and β are spin-α and spin-β states, respectively. In this picture there is one electron per atomic orbital, *i. e.* this is essentially the minimum basic set assumption provided only valence electrons are considered, but it exceeds the minimum basic set if inner non-valence electrons are also included. Source and sink vertices can now be defined in such a way that if χ_i is source, then $\overline{\chi_i}$ is sink, and *vice versa*. In other words, the two spin-orbitals associated with the same atomic orbital w_i are of the opposite parity. By convention, the parity of the atomic orbital w_i and of the vertex (i) is chosen to coincide with the parity of the corresponding spin-α orbital χ_i. We refer to this picture as model A.[1,2]

Annihilation operators η_i $(i = 1, \ldots, 2n)$ can now be rewritten in the form

$$a_i = \eta_i$$
$$b_i = \eta_{n+i} \qquad\qquad (i = 1, \ldots, n) \qquad\qquad (25)$$

where a_i are spin-α annihilation operators associated with spin-α orbitals χ_i, while b_i are spin-β annihilation operators associated with spin-β orbitals $\overline{\chi_i}$. The corresponding creation operators η_i^+ are rewritten in a similar way. In terms of these operators one can now define charge density and bond-order operators

$$\hat{q}_i{}^\alpha = a_i^+ a_i \qquad \hat{q}_i{}^\beta = b_i^+ b_i \qquad \hat{q}_i = \hat{q}_i{}^\alpha + \hat{q}_i{}^\beta$$

$$\hat{p}_{ij}{}^\alpha = (a_i^+ a_j + a_j^+ a_i)/2 \qquad \hat{p}_{ij}{}^\beta = (b_i^+ b_j + b_j^+ b_i)/2 \qquad (i \ne j)$$

$$\hat{p}_{ij}{}^{\alpha\beta} = (a_i^+ b_j + b_i^+ a_i)/2 \qquad \hat{p}_{ij} = \hat{p}_{ij}{}^\alpha + \hat{p}_{ij}{}^\beta \qquad\qquad (26)$$

where $\hat{q}_i{}^\alpha$ are spin-α charge density operators, $\hat{q}_i{}^\beta$ are spin-β charge density operators, $\hat{q}_i$ are total charge density operators *etc.* Operators $\hat{p}_{ij}{}^{\alpha\beta}$ are »cross« bond-order operators connecting spin-α and spin-β orbitals. Relation (21a) now reads

$$Q_i{}^\alpha\,(\Psi\pm) = Q_i{}^\beta\,(\Psi\pm) = 1/2 \qquad (i = 1, \ldots, n) \qquad\qquad (27a)$$

and hence

$$Q_i\,(\Psi\pm) = 1 \qquad (i = 1, \ldots, n) \qquad\qquad (27b)$$

where $Q_i{}^\alpha$, $Q_i{}^\beta$ and Q_i are spin-α, spin-β and total densities, respectively (see Appendix). Similarly, relation (21b) becomes

$$\gamma_{ij}{}^\alpha\,(\Psi\pm) = \gamma_{ij}{}^\beta\,(\Psi\pm) = 0 \qquad i \text{ and } j \text{ are of the same parity, } i \ne j \qquad (27c)$$

and

$$\gamma_{ij}{}^{\alpha\beta}\,(\Psi\pm) = 0 \qquad i \text{ and } j \text{ are of the opposite parity} \qquad (27d)$$

where $\gamma_{ij}{}^\alpha$, $\gamma_{ij}{}^\beta$ and $\gamma_{ij}{}^{\alpha\beta}$ are spin-α, spin-β and »cross« bond-orders, respectively. Hence

$$P_{ij}\,(\Psi\pm) = 0 \qquad i \text{ and } j \text{ are of the same parity, } i \ne j \qquad (27e)$$

i. e. total bond orders between vertices of the same parity vanish. In particular, if an AH is considered, and if orbitals w_i are $2p_z$ atomic orbitals situated at carbon atoms, then the partition on sink and source vertices can be chosen to coincide with the partition on starred and nonstarred atoms, respectively.[1,2] Relation (27e) now implies the vanishing of bond-orders between all atoms of the same parity, while relation (27b) implies that the total charge density at all carbon atoms is uniformly one. These are well-known properties of eigenstates of neutral AH systems, and hence by an obvious generalisation we call each state $\Psi^\pm \in X_n^\pm$ »alternant-like«. Special properties of eigenstates of neutral AH systems are thus shown to be shared by all alternant-like states, *i. e.* to be properties of the entire spaces X_n^+ and X_n^-. Concerning two-particle density matrices, one finds that two-particle spin-α ($\Gamma_{ij,kl}^{\alpha\alpha}$), spin-$\beta$ ($\Gamma_{ij,kl}^{\beta\beta}$) and cross ($\Gamma_{ij,kl}^{\alpha\beta}$) and ($\Gamma_{ij,kl}^{\beta\alpha}$) density matrices satisfy relations (23). For example

$$\Gamma_{il,jl}^{\alpha\alpha}(\Psi\pm) = \gamma_{ij}^{\alpha}(\Psi\pm)/4 \qquad i \text{ and } j \text{ are of the opposite parity, } (l \neq i,j) \qquad (28)$$

etc. From these relations it follows that the spin-independent density matrix $\mathbf{P}$ satisfies

$$P_{il,jl}(\Psi\pm) = \varrho_{ij}(\Psi\pm)/2 \qquad i \text{ and } j \text{ are of the opposite parity, } (l \neq i,j) \qquad (29a)$$

and

$$P_{ij,kl}(\Psi\pm) = 0 \qquad \text{odd number of sink vertices } (i \neq j \neq k \neq l) \qquad (29b)$$

All the above relations follow from the splitting theorem, and they ultimately express properties of reduced operators.

Note that the space X_n is in general allowed to be an arbitrary CI space spanned by n electrons moving over $2n$ orbitals χ_i, and it does not necessarily describe the π-electron system. In this way rather complex σ-electron systems can be described. For example, if only valence electrons are considered, a benzene molecule can be described by $n = 6 \cdot (1 + 4) = 30$ electrons moving over $2n = 60$ spin-orbitals, and the corresponding CI space is of the type discussed above. If, however, all electrons are considered, then there are $6 \cdot (1 + 6) = 42$ electrons moving over 72 spin-orbitals. In this case one can add 12 »dummy« spin-orbitals (*e. g.* some higher carbon orbitals) in order to satisfy the condition of $n = 42$ electrons moving over $2n = 84$ orbitals, which again leads to the CI space of the above type. It is also not necessary that orbitals χ_i be chosen according to the model A. For example, spin-α and spin-β CI spaces ${}^{\alpha}X_n$ and ${}^{\beta}X_n$ can be built upon n electrons moving over $2n$ spin-α orbitals and upon n electrons moving over $2n$ spin-β orbitals, respectively.[1] This is in accord with the spin-separation assumption that each state Ψ can be written in the form

$$\Psi = |\,\Phi_\alpha\,\overline{\Phi_\beta}\,\rangle \qquad (30)$$

where $\Phi_\alpha \in {}^{\alpha}X_n$ and $\overline{\Phi_\beta} \in {}^{\beta}X_n$ are spin-α and spin-β substates, respectively.[1] Relations (21)—(23) now hold true in each space ${}^{\alpha}X_n$ and ${}^{\beta}X_n$ separately, *etc.* In conclusion, the notion of alternant-like states as defined here is a very substantial generalisation of the characteristic properties of π-electron eigenstates of neutral AH systems.

6. DISCUSSION

It was shown by various authors that within a range of models π-electron eigenstates of neutral alternant hydrocarbon (AH) systems have uniform charge density distribution over all carbon atoms and vanishing bond orders between atoms of the same parity.[10-16] These properties follow from the so called pairing theorem, and they are not shared by nonalternant systems. Hence one can consider these properties as characteristic of neutral AH systems, and this suggests two quite natural questions: first, which Hamiltonians are »alternant« in the sense that they possess eigenstates with the above properties, and second, which states are »alternant-like«, *i. e.* such that they possess these properties.

The first question was treated by many authors.[10-16]. The most general *explicit* solution was given by McLachlan.[13] He has shown that eigenstates of the PPP Hamiltonian associated with an AH system satisfy the pairing theorem, and hence the above properties follow in the case of neutral AH systems. Koutecký demonstrated that there are some even more general (symmetric) alternant Hamiltonians.[14] However, his approach is rather implicit, and it does not permit an easy construction of an alternant Hamiltonian, nor does it present any simple test to decide whether a given Hamiltonian is alternant or not.

In the present paper an explicit, and as far as symmetric Hamiltonians are considered, a complete answer to this question is given. The following results are obtained:

1. Each alternant operator can be written as a linear combination of the complete set of some elementary (called »reduced«) alternant operators. In addition, each linear combination of these elementary operators is an alternant operator. This result is neither trivial nor obvious, and hence the definition of alternant operators as a linear combination of reduced alternant operators is implicitly a theorem: it implies that all alternant Hamiltonians, and only these Hamiltonians (with the proviso of corollary 1) possess the complete set of alternant-like eigenstates.

2. Reduced alternant operators are explicitly constructed and it is found that they are very simple (see section 2). Hence one can very easily construct alternant (symmetric) Hamiltonians, *i. e.* such that have the complete set of alternant-like eigenstates.

3. A simple test is obtained to decide whether a given operator is alternant or not. Applying this test to an arbitrary Hamiltonian, one can very easily decide wheather its eigenstates are alternant-like or not, *i. e.* whether the system will have a uniform charge density distribution, vanishing bond orders between vertices of the same parity, *etc.*

The above points completely answer the first question, construction and identification of alternant Hamiltonians and operators. However, in the process of answering this question, some additional results were obtained:

4. Each symmetric operator can be uniquely written as a sum of an alternant and an »antialternant« operator. It is shown that similarly to the case of the alternant operators, each antialternant operator can also be written as a linear combination of the complete set of some elementary (called reduced) antialternant operators.

5. Reduced antialternant operators are explicitly constructed (see section 2), and it is found that they are also very simple.

6. The set of all reduced (alternant and antialternant) operators is complete in the sense that each symmetric operator can be represented as their linear combination. This set is also linearly independent over the total space X. It is however not linearly independent over the n-particle subspace X_n of the space X, as demonstrated by lemmas 1 and 2.

Reduced alternant and antialternant operators are thus shown to be natural building blocks of alternant and antialternant operators, respectively. Each symmetric operator can be analysed in terms of these operators, and in particular in terms of the splitting in the alternant and antialternant part.

Let us now consider another question raised above: the identification of the alternant-like states. Are these states only some »accidental« eigenstates of alternant Hamiltonians, or does the set of all alternant-like states exhibit some regularity and order? This question was not treated by other authors, and the results obtained here are also quite interesting:

It is found that alternant-like states form complete spaces X_n^+ and X_n^-. These spaces are subspaces of the CI space X_n, they are mutually orthogonal, and their sum is the space X_n itself. In other words, each state $\Psi \in X_n$ can be uniquely written in the form $\Psi = \Psi^+ + \Psi^-$ where $\Psi^+ \in X_n^+$ and $\Psi^- \in X_n$ are alternant-like states. This is quite a surprising result, and it is by no means obvious. As a consequence, each nonalternant state (with nonuniform charge density distribution *etc.*) necessarily has non-vanishing components in both subspaces X_n^+ and X_n^-. The entire spaces X_n^+ and X_n^- should hence be considered as alternant-like.

One further point should be emphasized here. We defined each state $\Psi^\pm \in X_n^\pm$ to be alternant-like, and we have shown that all these states satisfy relations (21), *i. e.* that they possess some characteristic properties of π-electron eigenstates of neutral AH systems. However, the inverse is not necessarily true: an arbitrary state $\Psi \in X_n$ satisfying relations (21) is not necessarily alternant-like, *i. e.* it is possible for this state to have nonvanishing components in both subspaces, X_n^+ and X_n^-. In spite of that, spaces X_n^+ and X_n^- are for all practical purposes large enough. Firstly, each nondegenerate eigenstate of an alternant Hamiltonian is alternant-like, *i. e.* it is contained either in X_n^+ or in X_n^-. Secondly, each alternant Hamiltonian possesses the complete set of alternant-like states. In other words, if some eigenstates of an alternant Hamiltonian are not alternant-like, they are necessarily degenerate, and one can always perform a linear combination of these eigenstates in order to obtain alternant-like eigenstates. In this sense spaces X_n^+ and X_n^- contain all the eigenstates of alternant Hamiltonians.

This completes the answer to the second question. However, here again we have some additional results. It is found that the uniform charge density distribution and vanishing bond orders between vertices of the same parity are not the only general properties of alternant-like states. Beside these properties, which in fact express regularities of one-particle density matrices associated with alternant systems, there are some properties of two-particle density matrices which are common to all alternant-like states. These properties either refer to the matrix elements of the two-particle density matrix

alone (*e. g.* relation 23b), or they express the connection between some matrix elements of the two-particle and one-particle density matrix (*e. g.* relation 23a).

The results presented here are some far reaching generalisations of the characteristic properties of neutral AH systems and they are not restricted to π-electron systems alone. The definition of reduced operators is completely general, since any one- and two-particle operator can be split into its alternant and antialternant part as long as it is symmetric. Even this last restriction is not essential and one can generalise the notion of reduced operators to completely arbitrary systems.[5] Concerning the space of states, we are restricted in this paper to the CI space X_n which is generated by n electrons moving over $2n$ orbitals. This is not the most general CI space. However, besides π-electron systems, it is flexible enough to describe rather complicated σ-electron systems. In addition, all the results obtained here can be generalised to arbitrary CI spaces.[5] Hence these results express rather general properties of fermion systems.

<div align="center">APPENDIX</div>

A1. *The Space* X_n *and its Subspaces* X_n^+ *and* X_n^-

Let η_i^+ and η_i ($i = 1, \ldots, 2n$) be $2n$ creation and $2n$ annihilation operators satisfying anticommutation relations (1). Consider the space X spanned by all vectors $|\Delta_\nu\rangle$[7,8]

$$|\Delta_\nu\rangle = \eta_{i1}^+ \eta_{12}^+ \ldots \eta_{ik}^+ |0\rangle = |i_1, i_2, \ldots, i_k\rangle \quad (k = 0, 1, \ldots, 2n) \tag{A1}$$

where $|0\rangle$ is a vacuum state

$$\eta_i |0\rangle = 0 \quad (i = 1, \ldots, 2n) \tag{A2}$$

The state $|\Delta_\nu\rangle = |i_1, \ldots, i_k\rangle$ is antisymmetric with respect to the permutation of any two indeces

$$|\ldots i \ldots j \ldots\rangle = -|\ldots j \ldots i \ldots\rangle \tag{A3}$$

and from the anticommutation relations (1) it follows

$$\eta_i^+ |\Delta_\nu\rangle = \begin{cases} 0 & \text{if} \quad (i) \in \{\nu\} = \{i_1, i_2, \ldots, i_k\} \\ |i, i_1, i_2, \ldots, i_k\rangle & \text{if} \quad (i) \notin \{\nu\} \end{cases} \tag{A4}$$

$$\eta_{ir} |\Delta_\nu\rangle = \begin{cases} 0 & \text{if} \quad i_r \notin \{\nu\} \\ (-1)^{r+1} |i_1, \ldots, i_{r-1}, i_{r+1}, \ldots, i_k\rangle & \text{if} \quad i_r \in \{\nu\} \end{cases} \tag{A5}$$

The space X_n is the n-particle subspace of the space Y_n, *i. e.* it contains all the vectors of the form $|\Delta_\nu\rangle = |i_1, i_2, \ldots, i_n\rangle$.

a) *Regular resonance structures.* — Partition the set $B = \{i\}$ of $2n$ vertices (*i*) into subsets B° and B^* containing n vertices each.[6] Call creation operator η_i^+, annihilation operator η_i, one-particle state (orbital) $\eta_i^+ |0\rangle$ and vertex (*i*) »source« if (*i*) $\in B^\circ$ and »sink« if (*i*) $\in B^*$. Form excited and nonexcited bond-orbital(annihilation)operators (BOO)

$$E_s = E_{ij} = \frac{1}{\sqrt{2}} (\eta_i - \eta_j) \qquad \text{excited BOO}$$

$$\tag{A6}$$

$$N_s = N_{ij} = \frac{1}{\sqrt{2}} (\eta_i + \eta_j) \qquad \text{nonexcited BOO}$$

where vertices (i) and (j) satisfy

$$(i) \in B^\circ \quad \text{and} \quad (j) \in B^* \tag{A7}$$

Similarly, creation BOO-s E_s^+ and N_s^+ are constructed. These operators acting on the vacuum state $|0\rangle$ create excited and nonexcited bond orbitals (BO) $|\varphi_s^*\rangle = |s^*\rangle$ and $|\varphi_s\rangle = |s\rangle$, respectively

$$E_s^+|O\rangle = |s^*\rangle \qquad N_s^+|0\rangle = |s\rangle \tag{A8}$$

Consider the set $\mathscr{F}(n)$ of all n-particle states $|S\rangle$

$$|S\rangle = N_{s1}^+ \ldots N_{sn}^+|0\rangle = |s_1, s_2, \ldots, s_n\rangle$$
$$|S\rangle = E_{s1}^+ \ldots E_{sn}^+|0\rangle = |s_1^*, s_2^*, \ldots, s_n^*\rangle \tag{A9}$$

where $s_1 = (i_1, j_1)$, $s_2 = (i_2, j_2), \ldots, s_n = (i_n, j_n)$ are all possible sets of n mutually disjunct bonds (*i. e.* such which have no vertex in common) satisfying (A7).[1,2] States (A9) are normalized and they span the space X_n. In the notation of Ref. 1 each state (A9) is a Slater determinant containing n mutually disjunct excited and/or nonexcited bond orbitals, and these states are called regular resonance structures (RRS).[1,2] Without loss of generality one can assume sink indices to be even and source indices to be odd. Structures (A9) can now be written in the form

$$\vdots$$
$$N_{1, j1}^+ N_{3, j2}^+ E_{5, j3}^+ N_{7, j4}^+ \ldots |0\rangle = |j_1, 0; j_2, 0; j_3, 1; j_4, 0; \ldots\rangle \tag{A10}$$
$$\vdots$$

where $j_1, \ldots, j_n$ denote sink vertices connected with source vertices $1, 3, 5, \ldots, 2n-1$, respectively, while zeroes and ones denote whether the corresponding BO is excited (1) or not (0). Notation (A10) automatically fixes the relative phase between different RRS-s, and this fixation is equivalent to the normal phase convention as defined in Ref. 2. Matrix elements of one- and two-particle operators between RRS-s (A10) are evaluated elsewhere[2,3] and will not be given here.

(b) *Positive and negative structures and positive and negative spaces* X_n^+ *and* X_n^-. — Each ordered set $\{j_1, \ldots, j_n\}$ of n annihilation indices $(j) \in B^*$ is a permutation P_j of the ordered set $\{2, 4, \ldots, 2n\}$. Let N_e denote the number of excited BO-s contained in the RRS $S \in \mathscr{F}(n)$, *i. e.* let N_e be the number of »ones« in the notation (A10). Define:

Definition 1:

The parity $P(S)$ of the structure $S \in \mathscr{F}(n)$ is

$$P(S) = (-1)^{P_j + N_e} \tag{A11}$$

In other words, the parity $P(S)$ of the RRS $S \in \mathscr{F}(n)$ equals the parity of the permutation P_j of sink vertices if the number N_e of excited BO-s is even, and it equals $-P_j$ if this number is odd. For example

$P(S) = 1$ \qquad if \qquad $S = |2,0; 4,0; 6,0\rangle$

$P(S) = -1$ \qquad if \qquad $S = |2,0; 4,1; 6,0\rangle$

$P(S) = 1$ \qquad if \qquad $S = |4,0; 2,0; 6,1\rangle$

etc. The above definition of the parity of RRS-s is in accord with the superposition criteria using the notion of »active« and »passive« cycles, as done elsewhere.[1,2] This definition partions the set $\mathscr{F}(n)$ of all RRS-s into subsets $\mathscr{F}^+(n)$ and $\mathscr{F}^-(n)$ containing »positive« (even) and »negative« (odd) structures, respectively. It can be shown that the space X_n^+ spanned by all positive structures $S \in \mathscr{F}^+(n)$ is orthogonal to the space X_n^- spanned by all negative structures $S \in \mathscr{F}^-(n)$.[1,2] Spaces X_n^+ and X_n^- are complementary, they are of the same dimension and they are uniquely (up to the exchange $X_n^+ \leftrightarrow X_n^-$) determined by the splitting $B \to \{B^\circ, B^*\}$. Hence each state $\Psi \in X_n$ can be uniquely written as a sum $\Psi = \Psi^+ + \Psi^-$, where $\Psi^+ \in X_n^+$ and $\Psi^- \in X_n^-$.[1,2]

A2. *Proof of Lemmas 1 and 2 and Corollary 1*

(a) *Proof of lemmas 1 and 2.* — Each symmetric operator $\hat{O}$ can be written as a linear combination of reduced operators $\hat{I}$, $\hat{R}_{ij}$ and $\hat{R}_{ij,\,kl}$

$$\hat{O} = a + \sum_{ij} a_{ij} \hat{R}_{ij} + \sum_{i<j,\,k<l} a_{ij,\,kl} \hat{R}_{ij,\,lk} \tag{A12}$$

Operator $\hat{O}$ contains a unit operator, vertex operators, bond operators, vertex-vertex operators, bond-vertex operators and bond-bond operators. Assume now that the operator $\hat{O}$ vanishes over the space X_n, and consider the action of the bond-bond operator $\hat{R}_{ij,\,kl} = \hat{A}_{ij,\,kl}$ on the state $|\Delta_\nu\rangle = |i_1, i_2, \ldots, i_n\rangle \in X_n$. Without loss of generality one can assume $i, j \in \{\nu\} = \{i_1, i_2 \ldots, i_n\}$ and $k, l \notin \{\nu\}$. Using relations (A4) and (A5) one finds that operator $\hat{A}_{ij,\,kl}$ acting on the state $|\Delta_\nu\rangle$ creates two particles in orbitals χ_k and χ_l, and annihilates two particles in orbitals χ_i and χ_j. In other words it transforms the state $|\Delta_\nu\rangle = |\ldots, i, \ldots, j, \ldots\rangle$ into the state $|\Delta_{\nu'}\rangle = |\ldots, k, \ldots, l, \ldots\rangle$. None of other operators contained in the expression (A12) creates the state $|\Delta_{\nu'}\rangle$ from the state $|\Delta_\nu\rangle$. Since vectors (A1) are linearly independent, $\hat{O}|\Delta_\nu\rangle = 0$ implies $a_{ij,\,kl} = 0$ whenever $i \neq j \neq k \neq l$. Hence the operator $\hat{O}$ does not contain any bond-bond operator in the linear combination (A12). Consider now the action of the bond-vertex operator $\hat{R}_{ik,\,kj}$ contained in (A12) on the state $|\Delta_\nu\rangle$. Notice first that in the case of bond-vertex operators

$$\hat{R}_{ik,\,kj} = \hat{A}_{ij} \hat{R}_{kk} = \hat{A}_{ij} (2n_k - 1) \tag{A13}$$

where $\hat{n}_k$ is the operator of the number of particles in the orbital χ_k, i. e. $\hat{n}_k |\Delta_\nu\rangle = 0$ if $k \notin \{\nu\}$ and $\hat{n}_k |\Delta_\nu\rangle = |\Delta_\nu\rangle$ if $k \in \{\nu\}$. Hence

$$\hat{R}_{kk} |\Delta_\nu\rangle = \begin{cases} |\Delta_\nu\rangle & \text{if} \quad k \in \{\nu\} \\ -|\Delta_\nu\rangle & \text{if} \quad k \notin \{\nu\} \end{cases} \tag{A14}$$

If further $i \in \{\nu\}$ and $j \notin \{\nu\}$ then (A3)—(A5) imply

$$\hat{A}_{ij} |\ldots, i, \ldots\rangle = |\ldots, j, \ldots\rangle = |\Delta_{i \to j}\rangle \tag{A15}$$

i. e. operator $\hat{A}_{ij}$ acting on the state $|\Delta_\nu\rangle$ creates one particle in the orbital χ_j and annihilates one particle in the orbital χ_i. Hence each of the bond-vertex operators

$\hat{R}_{ik, kj}$ $(k \neq i, j)$ as well as the operator $\hat{A}_{ij}$ acting on the state $|\Delta_v\rangle$ creates the state $|\Delta_{i \to j}\rangle$ from the state $|\Delta_v\rangle$. Combining the above relations one finds that $\hat{O} |\Delta_v\rangle = 0$ implies

$$a_{ij} + \sum_{k \in \{v\}} a_{ik, jk} - \sum_{k \notin \{v\}} a_{ik, jk} = 0 \qquad \text{(A16a)}$$

Replace now the state $|\Delta_v\rangle$ with the state $|\Delta_\mu\rangle$ satisfying $i \in \{\mu\}$ and $j \notin \{\mu\}$ as well. This leads to

$$a_{ij} + \sum_{k \in \{\mu\}} a_{ik, jk} - \sum_{k \notin \{\mu\}} a_{ik, jk} = 0 \qquad \text{(A16b)}$$

With an appropriate choice of the states $|\Delta_v\rangle$ and $|\Delta_\mu\rangle$ relations (A16) imply $a_{ij} = 0$ and $a_{ik, jk} = C_{ij}$. In other words, operator $\hat{O}$ does not contain any bond operator, while all reduced bond-vertex operators $\hat{R}_{ik, kj}$ enter operator $\hat{O}$ with coefficients independent on k, but otherwise arbitrary. Operator $\hat{O}$ is hence necessarily of the form (14a) where coefficients λ and λ_{ij} satisfy some additional conditions which will be discussed elsewhere.[5,9] This proves lemma 1. If in addition operator $\hat{O}$ is anti-alternant, then all coefficients in front of reduced alternant operators in (14a) should be set zero. This leads to lemma 2, *i. e.* to the expression (14b).

(b) *Proof of corollary 1.* — Let $H = H_{al} + H_{nal}$ be a symmetric Hamiltonian operator. If H_{nal} is of the form (20a), then according to lemma 2 it is identically zero over X_n, and hence the splitting theorem implies $\langle \Psi^+ | H | \Psi^- \rangle = 0$ whenever $\Psi^+ \in X_n^+$ and $\Psi^- \in X_n^-$. Hamiltonian H hence has the complete set of alternant-like eigenstates. This proves that the condition (20a) is sufficient. We will prove that this condition is also necessary by a reduction *ad absurdum*. Assume namely that H has the complete set of alternant-like eigenstates Ψ_i, while H_{nal} is not of the form (20a). Then according to lemma 2 H_{nal} does not vanish over X_n, and hence there is $\Psi \in X_n$ such that $\langle \Psi | H_{nal} | \Psi \rangle \neq 0$. However, $\Psi = \Psi^+ + \Psi^-$ and hence one obtains $\langle \Psi^- | H | \Psi^+ \rangle \neq 0$. But the state $\Psi^+ \in X_n^+$ can be written as a linear combination of eigenstates $\Psi_i = \Psi_i^+ \in X_n^+$ of the Hamiltonian H, and hence $H \Psi^+ = H \sum_i \lambda_i \Psi_i^+ = \sum_i \lambda_i E_i \Psi_i^+ \in X_n^+$, in contradiction with $\langle \Psi^- | H | \Psi^+ \rangle \neq 0$. This proves that the condition (20a) is also necessary.[9]

A3. *Density Matrices*

There is some ambiguity in the literature concerning the definition of density matrices.[17-19] Density matrices as defined here are real. This is in accord with the assumption that only symmetric operators are considered, since eigenstates of hermitian symmetric operators are necessarily real, unless there is some accidental degeneracy. In any case, relations (A17), (A21) *etc.* defining density matrices can simply be considered as definitions and all conclusions obtained in this paper are then valid for arbitrary real as well as complex alternant-like states.

(a) *One-particle density matrices.* — One-particle density matrix γ_{ij} is

where the state Ψ is assumed normalised, while η_i^+ and η_i are creation and annihilation fermion operators, respectively. In particular, spin-α density matrix $\gamma_{ij}{}^\alpha$, spin-β density matrix $\gamma_{ij}{}^\beta$ and »cross« density matrix $\gamma_{ij}{}^{\alpha\beta}$ are

$$\gamma_{ij}{}^\alpha (\Psi) = \langle\, \Psi \,|\, (a_i^+ a_j + a_j^+ a_i)/2 \,|\, \Psi \,\rangle$$

$$\gamma_{ij}{}^\beta (\Psi) = \langle\, \Psi \,|\, (b_i^+ b_j + b_j^+ b_i)/2 \,|\, \Psi \,\rangle \qquad\qquad \text{(A18)}$$

$$\gamma_{ij}{}^{\alpha\beta} (\Psi) = \langle\, \Psi \,|\, (a_i^+ b_j + b_j^+ a_i)/2 \,|\, \Psi \,\rangle$$

where a_i^+ and b_i^+ are spin-α and spin-β creation operators, respectively. In order to stress that diagonal matrix elements of the spin-α density matrix represent spin-α charges, while diagonal matrix elements of the spin-β density matrix represent spin-β charges, we use the notation $Q_i{}^\alpha = \gamma_{ii}{}^\alpha$ and $Q_i{}^\beta = \gamma_{ii}{}^\beta$ for spin-α and spin-β charges, respectively.

Spin independent density matrix ϱ_{ij} is defined as a sum

$$\varrho_{ij} = \gamma_{ij}{}^\alpha + \gamma_{ij}{}^\beta \qquad\qquad \text{(A19)}$$

Diagonal matrix elements ϱ_{ii} of this matrix represent total charges, while off-diagonal matrix elements ϱ_{ij} $(i \neq j)$ represent bond-orders. Hence we sometimes use the notation $Q_i = \varrho_{ii}$ and $P_{ij} = \varrho_{ij}$ $(i \neq j)$ for total charges and total bond orders, respectively. Relation (A19) is now equivalent to

$$Q_i = Q_i{}^\alpha + Q_i{}^\beta \qquad\qquad P_{ij} = \gamma_{ij}{}^\alpha + \gamma_{ij}{}^\beta \qquad (i \neq j) \qquad\qquad \text{(A20)}$$

(b) *Two particle density matrices.* — Two-particle density matrix $\Gamma_{ij,\,kl}$ is

$$\Gamma_{ij,\,kl} \langle\, \Psi \,|\, (\eta_i^+ \eta_j^+ \eta_l \eta_k + \text{C. C.})/4 \,|\, \Psi \,\rangle = \langle\, \Psi \,|\, \hat{A}_{ij,\,lk} \,|\, \Psi \,\rangle/4 \qquad\qquad \text{(A21)}$$

where C. C. stands for the complex conjugate.

Spin independent density matrix $P_{ij,\,kl}$ is defined as a sum

$$P_{ij,\,kl} = \Gamma_{ij,\,kl}^{\alpha\alpha} + \Gamma_{ij,\,kl}^{\alpha\beta} + \Gamma_{ij,\,kl}^{\beta\alpha} + \Gamma_{ij,\,kl}^{\beta\beta} \qquad\qquad \text{(A22)}$$

where

$$\Gamma_{ij,\,kl}^{\alpha\alpha} = \langle\, \Psi \,|\, (a_i^+ a_j^+ a_l a_k + \text{C. C.})/4 \,|\, \Psi \,\rangle$$

$$\Gamma_{ij,\,kl}^{\alpha\beta} = \langle\, \Psi \,|\, (a_i^+ b_j^+ b_l a_k + \text{C. C.})/4 \,|\, \Psi \,\rangle$$

$$\Gamma_{ij,\,kl}^{\beta\alpha} = \langle\, \Psi \,|\, (b_i^+ a_j^+ a_l b_k + \text{C. C.})/4 \,|\, \Psi \,\rangle \qquad\qquad \text{(A23)}$$

$$\Gamma_{ij,\,kl}^{\beta\beta} = \langle\, \Psi \,|\, (b_i^+ b_j^+ b_l b_k + \text{C. C})/4 \,|\, \Psi \,\rangle$$

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6. In Refs. 1 and 2 the set of all one-particle states $|\chi_i> = |i> = \eta_i^+|0>$ (called »orbitals«) was partitioned into source and sink subsets. The present approach is equivalent, and it offers some formal advantages.

7. In the second quantisation formalism the state $|\Delta_v>$ is usually written in the form $|\Delta_v> = |\nu_1, \nu_2, \nu_3, \ldots>$ where $\nu_i = 1$ if orbital χ_i is occupied, and $\nu_i = 0$ otherwise.[8] The procent notation is equivalent, and it offers some advantages in the case of the space X_n, i. e. when only n-particle states are considered.

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SAŽETAK

Teorem cijepanja i svojstva alternantnih sistema

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Pojam alternantnih sistema, definiran u raznim poluiskustvenim teorijama alternantnih ugljikovodika, poopćen je na proizvoljne simetrične hamiltonijane. Pokazano je da su alternantni operatori linearne kombinacije tako zvanih reduciranih alternantnih operatora, i dana je jednostavna konstrukcija proizvoljnih (simetričnih) alternantnih hamiltonijana. Također je izveden jednostavan test kojim se može odrediti je li neki hamiltonijan alternantan ili nije. Promatran je konfiguracijsko--interakcijski prostor X_n što ga tvori n elektrona nad $2n$ ortonormiranih orbitala. Pokazano je da su vlastite funkcije $\Psi \in X_n$ alternantnih hamiltonijana sadržane u komplementarnim prostorima X_n^+ i X_n^-, potprostorima prostora X_n. Svako stanje $\Psi\pm \in X_n\pm$ ima karakteristična svojstva vlastitih stanja neutralnih alternantnih ugljikovodika, kao što su na primjer jednolika raspodjela naboja i iščezavanje reda veze među atomima iste parnosti. Uz ta svojstva jednočestičnih matrica gustoće, izvedena su i neka svojstva dvočestičnih matrica gustoće pridruženih stanjima $\Psi\pm \in X_n\pm$.