

Spin Eigenstates and Spin-Independent Alternant Systems

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The configuration interaction space X_n , built upon n electrons moving over n spin- α orbitals $X_i = w_i \alpha$ and n spin- β orbitals $\bar{X}_i = w_i \beta$, w_i being orthonormalized atomic orbitals, is considered. Spin-independent alternant systems are defined in terms of the corresponding Hamiltonians. Each Hamiltonian \mathbf{H} describing such a system is a linear combination of a spin-independent alternant operator \mathbf{O}_{alt} and operator \mathbf{Z} vanishing over X_n . The space of all spin-independent alternant operators is a linear space and it is spanned by »reduced« spin-independent alternant operators, which are explicitly obtained. Similarly, the space of all operators vanishing over X_n is spanned by some basis operators, which are also explicitly given. Hence, each Hamiltonian describing a spin-independent alternant system can easily be constructed and identified. All such Hamiltonians have a complete set of semi-alternantlike (SAL) eigenstates. These states have many properties which generalize the well known properties of π -electron eigenstates of neutral alternant hydrocarbons. In particular, each SAL state $\Psi \in X_n$ has a uniform total charge density distribution over all vertices (i), vanishing total bond orders between vertices of the same parity, etc. The complete set of spin-independent properties common to all SAL states is obtained. Standard representations $\{\mathbf{S}^2, \mathbf{S}_z\}$ are also considered. These representations are defined by basis vectors $\Psi_{s,m,\tau}^z \in X_n$, common eigenstates to operators \mathbf{S}^2 and \mathbf{S}_z with eigenvalues $s(s+1)$ and m , respectively. It is shown that among all such representations there are some with a special property that each space $\varepsilon_{s,\tau}$ spanned by $(2s+1)$ vectors $\Psi_{s,m,\tau}^z$ (variable m) contains only SAL states. In particular, all basis vectors $\Psi_{s,m,\tau}^z$ are SAL states. Such representations are called »alternantlike« (AL). A similar result is obtained for the standard representations $\{\mathbf{S}^2, \mathbf{S}_x\}$, and the connection between AL representations $\{\mathbf{S}^2, \mathbf{S}_z\}$ and $\{\mathbf{S}^2, \mathbf{S}_x\}$ is established. It is shown that common eigenstates to the Hamiltonian \mathbf{H} describing a spin-independent alternant system and operators \mathbf{S}^2 and \mathbf{S}_z (or \mathbf{S}_x) can be chosen to be SAL states. In addition, if beside spin multiplicity there is no other degeneracy, all eigenstates common to operators \mathbf{H} , \mathbf{S}^2 and \mathbf{S}_z (or \mathbf{S}_x) are SAL states.

1. INTRODUCTION

It is well known that conjugated hydrocarbons can be partitioned into two classes, alternant and non-alternant.¹⁻² Unlike alternant hydrocarbons, non-alternant hydrocarbons contain at least one ring composed of an odd number of unsaturated carbon atoms.² In the case of an alternant hydrocarbon

it is possible to divide the unsaturated carbon atoms into two sets, called »starred« and »unstarred«, in such a way that no two atoms of the same set are joined by a bond.² Alternant hydrocarbons possess some remarkable properties which distinguish them from non-alternant systems.¹⁻⁶ For example, azulene, $C_{10}H_8$, which is an unsaturated non-alternant hydrocarbon, has very different properties from those of its alternant isomer, naphthalene: it has a blue colour, it is a good triplet quencher, and it has quite a large dipole moment for a hydrocarbon, 1 D according to Wheland and Mann.⁷ Naphthalene, which is an alternant hydrocarbon, has none of these properties. There have been many attempts to find a theoretical explanation for these differences.¹⁻⁵ Coulson and Rushbrooke have shown that within the Hückel theory the π -electron charge of every carbon atom of a neutral alternant hydrocarbon equals unity, and hence there is no permanent dipole moment.² In addition, in the case of neutral alternant hydrocarbons, π -electron bond orders vanish between carbon atoms of the same parity, being either both starred or both unstarred.² The Hückel theory is a relatively crude approximation, and Pople et al. have shown that the above conclusions can be obtained within the more sophisticated SCF Pariser-Parr-Pople (PPP) approximation.³ McLachlan was able to extend these conclusions to the unrestricted PPP method, i. e. to show that they remain valid if one considers the complete configuration interaction (CI) space in conjunction with the PPP Hamiltonian.⁴ Using mainly the same formalism as McLachlan, Koutecký obtained some general conditions which symmetric Hamiltonians should satisfy in order to describe alternant systems.⁵ His definition of alternant systems is rather implicit, and it is given in terms of commutation and anticommutation relations of the Hamiltonian with certain operators.⁵ All these results were obtained within the framework of the molecular orbital (MO) theory, and they follow from the so called pairing theorem.¹⁻⁵ In general, this theorem relates different properties of positive and negative ions derived from the same parent conjugated hydrocarbon.¹⁻⁵ In particular, in the case of neutral molecules one obtains a uniform charge density distribution and vanishing bond orders between pairs of atoms in the same set (starred or unstarred).¹⁻⁵

There are a few questions that can be raised in relation to the above conclusions: firstly, do neutral alternant hydrocarbons have beside a uniform charge density distribution and vanishing bond orders between atoms of the same parity any other common properties? Secondly, how general are these properties, i. e. do they apply to all eigenstates of neutral alternant hydrocarbons, and if not, to which not? Finally, once all⁸ properties common to neutral alternant hydrocarbons are identified, which is the most general form of the Hamiltonian having eigenstates with such properties, i. e. how far can one generalize the notion of alternant systems? All these questions can be efficiently treated using the formalism of the Molecular Orbital Resonance Theory (MORT)⁹⁻¹³ In this approach one considers the so called regular resonance structures (RRS) which are n -particle states and which span the configuration interaction (CI) space X_n determined by n electrons moving over $2n$ spin-orbitals.^{10,11} Formally, RRS-s span just another basis in X_n . However, the choice of this basis is highly advantageous. The set of all RRS-s is a natural way splits into two subsets containing »positive« and »negative« structures. These subsets span complementary spaces X_n^+ and X_n^- . Each state

$\psi \in X_n^+$, as well as each state $\psi \in X_n^-$, is »alternantlike« in the sense that it has the above properties of π -electron eigenstates of neutral alternant hydrocarbons.¹⁰ Besides these properties, a set of all⁸ properties of alternantlike states can be identified.¹² Further, the set of all Hamiltonians having a complete set of alternantlike eigenstates can be easily constructed.¹² Among these is also the well known PPP Hamiltonian discussed by McLachlan.^{10,13} Within the MORT approach one thus obtains general answers to the above questions, and one can extend the notion of alternancy to arbitrary systems. Originally, this notion was defined only for unsaturated hydrocarbons in conjunction with their π -electron eigenstates,^{2,4} though Koutecký implicitly extended this notion to some other systems.⁵ The confinement to hydrocarbons is due to the fact that carbon atoms are partitioned into »starred« and »unstarred« ones. The alternancy is defined in terms of the connection between carbon atoms, i.e. in topological terms. In the MORT approach the partition of the set of all carbon atoms in two classes is replaced by the partition of the set of all spin-orbitals into two classes called »source« and »sink«. This latter partition determines the set of all RRS-s, the splitting of the space X_n into complementary subspaces X_n^+ and X_n^- , and the splitting of each operator into its »alternant« and »antialternant« component.⁹⁻¹³ Alternancy is thus defined in purely algebraic terms, and one can legitimately ask whether an arbitrary Hamiltonian describes an alternant system. This approach can be successfully applied also to nonalternant systems, since each Hamiltonian can be easily written as a sum of an alternant and an antialternant operator.^{12,13} An arbitrary system can hence be considered as a perturbed alternant system.¹³

In this paper we will not consider arbitrary Hamiltonians, but rather only those Hamiltonians which describe spin-independent systems. Such systems are quite numerous, and in particular the PPP Hamiltonian describes a spin-independent system. We also intend to find the connection between spin eigenstates in X_n and complementary spaces X_n^+ and X_n^- . Spin-independent systems have some special properties which are not explicitly treated in the general MORT approach to alternant and nonalternant systems. For example, each alternant Hamiltonian has the complete set of alternantlike eigenstates,^{12,13} but this does not yet imply that each eigenstate of such a Hamiltonian is alternantlike.¹⁰⁻¹³ Whenever there is a degeneracy, the corresponding eigenstates are not necessarily alternantlike, and one is hence not sure of the uniform charge density distribution, vanishing bond orders between spin-orbitals of the same parity, etc.¹⁰⁻¹³ However, an eigenstate of a spin-independent Hamiltonian is degenerate unless it is a singlet state, and hence it is not guaranteed to be alternantlike. Hence the question about the properties of the common eigenstates to the spin-independent alternant Hamiltonian \mathbf{H} , and spin operators \mathbf{S}^2 and \mathbf{S}_z remains to be answered.

The plan of the presentation in this paper is as follows: in the second section some previous results of the MORT approach, which are needed later on in the paper, are given. The crucial role is played, on the one hand, by the alternant and antialternant operators which span arbitrary operators, and, on the other hand, by complementary spaces X_n^+ and X_n^- whose direct sum in the n -particle CI space X_n . These operators and spaces can easily be constructed,¹⁰⁻¹³ and their mutual connection is explicitly given by the splitting

theorem.^{10,12} In particular, all states $\psi^\pm \in X_n^\pm$ are alternantlike (AL) in the sense that they generalize characteristic properties of π -electron eigenstates associated with neutral alternant hydrocarbons. In order to be able to treat spin properties along the same general lines, one has to specify the nature of spin orbitals X_i which build up the CI space X_n . This is done in the third section and the parity of the corresponding spin- α and spin- β orbitals is defined in accord with the so called normal convention. In the fourth section spin operators in the normal space X_n are considered. The set of all reduced spin-independent operators is constructed, and reduced alternant, as well as reduced antialternant, operators are identified. Using these operators one can explicitly construct and identify an arbitrary spin-independent alternant, as well as an arbitrary spin-independent antialternant operator. In the fifth section, the so called semi-alternantlike (SAL) states are defined. These states are more general than AL states, and this generalization is necessary if one wants to treat all spin eigenstates on equal footing. All characteristic spin-independent properties of SAL states are explicitly found, and they are expressed in terms of matrix elements of one- and two-particle density matrix. In the sixth section, spin eigenstates in X_n are considered and it is shown that these eigenstates can easily be analyzed in terms of SAL states. The seventh section discusses some algebraic relations connecting various spin eigenstates. In the eighth section, spin-independent systems are considered and the connection between eigenstates of the corresponding Hamiltonians and SAL states is obtained. In the ninth section, some examples of spin-independent systems are given, and the tenth section contains a summary and main conclusions reached in the paper.

The results obtained apply explicitly to the normal CI space X_n , and to the one- and two-particle operators. Accordingly, »the complete set of eigenstates« refers to the space X_n , and not to some larger spaces. Similarly, »all operators« means »all zero (unity), one- and two-particle operators and all linear combinations of such operators«, etc. There is also a frequent reference to all properties of different sets of states in X_n . What we mean are all linear one- and two-particle properties. These properties can be expressed as the vanishing of the expectation values of different operators, as considered in a previous paper.¹²

2. ALTERNANT AND ANTIALTERNANT OPERATORS

Let us give a brief account of some results of the MORT approach which will be needed in this paper. We consider the configuration interaction space X_n generated by n electrons moving over $2n$ orthonormalized orbitals. The space X_n is spanned by all vectors $|\Delta_v\rangle$ of the form

$$|\Delta_v\rangle = \eta_{i_1}^+ \eta_{i_2}^+ \dots \eta_{i_n}^+ |0\rangle; \quad i_s = 1, 2, \dots, 2n \quad (1a)$$

where η_i^+ and η_i ($i = 1, \dots, 2n$) are fermion creation and annihilation operators, respectively, while $|0\rangle$ is the vacuum state

$$\eta_i |0\rangle = 0; \quad i = 1, \dots, 2n \quad (1b)$$

Note that the $2n$ creation operators η_i^+ acting on the vacuum state $|0\rangle$ generate the space Y_n which is larger than the space X_n . The space Y_n is spanned by all vectors $|\Delta_v\rangle$ of the form

$$|\Delta_v\rangle = \eta_{i_1}^+ \eta_{i_2}^+ \dots \eta_{i_k}^+ |0\rangle; \quad k = 0, 1, \dots, 2n \quad (1c)$$

and it contains the vacuum state ($k = 0$), all the one-particle states ($k = 1$), all the two-particle states ($k = 2$), etc. The n -particle space X_n is the non-trivial subspace of the space Y_n . Unless otherwise specified, we will consider here only the space X_n .

Each operator¹⁴ acting in the space Y_n can be written as a linear combination of the reduced operators **I**, **R**_{ij}, **P**_{ij}, **R**_{ij,kl} and **P**_{ij,kl}¹⁵:

I, a unit operator

$$\mathbf{R}_{ij} = \mathbf{A}_{ij} - \delta_{ij}$$

$$\mathbf{P}_{ij} = \mathbf{B}_{ij}$$

$$\mathbf{R}_{ij,kl} = \mathbf{A}_{ij,kl}; \quad i \neq j \neq k \neq l$$

$$\mathbf{P}_{ij,kl} = \mathbf{B}_{ij,kl}; \quad i \neq j \neq k \neq l$$

$$\mathbf{R}_{ik,jk} = \mathbf{A}_{ik,jk} + \mathbf{A}_{ij}/2; \quad i \neq j \neq k$$

$$\mathbf{P}_{ik,jk} = \mathbf{B}_{ik,jk} + \mathbf{B}_{ij}/2; \quad i \neq j \neq k$$

$$\mathbf{R}_{ij,ij} = \mathbf{A}_{ij,ij} + (\mathbf{A}_{ii} + \mathbf{A}_{jj})/2; \quad i \neq j \quad (2a)$$

where

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

$$\mathbf{B}_{ij} = \sqrt{-1} (\eta_i^+ \eta_j - \eta_j^+ \eta_i)$$

$$\mathbf{A}_{ij,kl} = \eta_i^+ \eta_j^+ \eta_k \eta_l + \eta_l^+ \eta_k^+ \eta_j \eta_i$$

$$\mathbf{B}_{ij,kl} = \sqrt{-1} (\eta_i^+ \eta_j^+ \eta_k \eta_l - \eta_l^+ \eta_k^+ \eta_j \eta_i) \quad (2b)$$

The usefulness of reduced operators will become apparent later in connection with the splitting theorem. It is convenient to extend the definition of these operators to arbitrary indices i, j, k and l , and to write operators **R**_{ij,kl} and **P**_{ij,kl} in the compact form

$$\mathbf{R}_{ij,kl} = \mathbf{A}_{ij,kl} + (\delta_{ik} \mathbf{A}_{jl} + \delta_{jl} \mathbf{A}_{ik} - \delta_{il} \mathbf{A}_{jk} - \delta_{jk} \mathbf{A}_{il})/2$$

$$\mathbf{P}_{ij,kl} = \mathbf{B}_{ij,kl} + (\delta_{ik} \mathbf{B}_{jl} + \delta_{jl} \mathbf{B}_{ik} - \delta_{il} \mathbf{B}_{jk} - \delta_{jk} \mathbf{B}_{il})/2 \quad (2c)$$

All reduced operators are hermitian and they satisfy symmetry relations

$$\begin{aligned} \mathbf{R}_{ij} &= \mathbf{R}_{ji}, & \mathbf{R}_{ij,kl} &= -\mathbf{R}_{ji,kl} = \mathbf{R}_{kl,ij} \\ \mathbf{P}_{ij} &= -\mathbf{P}_{ji}, & \mathbf{P}_{ij,kl} &= -\mathbf{P}_{ji,kl} = -\mathbf{P}_{kl,ij} \end{aligned} \quad (3)$$

In addition, operators **I**, **R**_{ij} and **R**_{ij,kl} are real and symmetric while operators **P**_{ij} and **P**_{ij,kl} are imaginary and antisymmetric.¹² In other words, in the base (1c) these operators satisfy

$$\begin{aligned} \langle \Delta_v | \mathbf{R} | \Delta_\mu \rangle &= \langle \Delta_\mu | \mathbf{R} | \Delta_v \rangle = \langle \Delta_v | \mathbf{R} | \Delta_\mu \rangle^* \\ \langle \Delta_v | \mathbf{P} | \Delta_\mu \rangle &= -\langle \Delta_\mu | \mathbf{P} | \Delta_v \rangle = -\langle \Delta_v | \mathbf{P} | \Delta_\mu \rangle^* \end{aligned} \quad (4)$$

where **R** stands for real reduced operators **I**, **R**_{ij} and **R**_{ij,kl}, while **P** stands for imaginary reduced operators **P**_{ij} and **P**_{ij,kl}. Each operator¹⁴ can be represented

as a linear combination of the reduced operators. This representation is unique up to the symmetry relations (3) (i. e. provided operators \mathbf{R}_{ij} and \mathbf{R}_{ji} are considered to be one and the same operator, etc.) For the sake of reference, as suggested by the graphical representation of the above operators, we use the following terminology: operators \mathbf{R}_{ii} are vertex operators, \mathbf{R}_{ij} and \mathbf{P}_{ij} ($i \neq j$) are bond operators, $\mathbf{R}_{ij,ij} = -\mathbf{R}_{ij,ji}$ ($i \neq j$) are vertex-vertex operators $\mathbf{R}_{ik,jk} = -\mathbf{R}_{ik,kj}$ and $\mathbf{P}_{ik,jk} = -\mathbf{P}_{ik,kj}$ ($i \neq j \neq k$) are bond-vertex operators, while $\mathbf{R}_{ij,kl}$ and $\mathbf{P}_{ij,kl}$ ($i \neq j \neq k \neq l$) are bond-bond operators.¹⁰⁻¹² Accordingly, indices (i), (j), (k) and (l) are referred to as vertices.¹⁰⁻¹³ Vertex (i) is associated with the one-particle state (orbital) $X_i = \eta_i^+ |0\rangle$, and there are $2n$ such vertices. Partition now the set $B = \{i\}$ containing $2n$ vertices ($i = (1), \dots, (2n)$) into subsets B° and B^* containing n vertices each. We refer to the set B° as »source« and to the set B^* as »sink«. ¹⁰⁻¹³ The partition $B \rightarrow \{B^\circ, B^*\}$ uniquely defines the partition of the set of all reduced operators into »alternant« and »antialternant« operators. The reduced alternant operators are:

I, a unit operator

$$\begin{aligned} \mathbf{R}_{ij}; & \quad \mathcal{P}(i, j) = -1 \\ \mathbf{P}_{ij}; & \quad \mathcal{P}(i, j) = 1 \\ \mathbf{R}_{ij,kl}; & \quad \mathcal{P}(i, j, k, l) = 1 \\ \mathbf{P}_{ij,kl}; & \quad \mathcal{P}(i, j, k, l) = -1 \end{aligned} \quad (5a)$$

while the reduced antialternant operators are¹²:

$$\begin{aligned} \mathbf{R}_{ij}; & \quad \mathcal{P}(i, j) = 1 \\ \mathbf{P}_{ij}; & \quad \mathcal{P}(i, j) = -1 \\ \mathbf{R}_{ij,kl}; & \quad \mathcal{P}(i, j, k, l) = -1 \\ \mathbf{P}_{ij,kl}; & \quad \mathcal{P}(i, j, k, l) = 1 \end{aligned} \quad (5b)$$

where \mathcal{P} is the parity function defined in the following way: $\mathcal{P}(i, j) = 1$ if vertices (i) and (j) are of the same parity (either both source or both sink), and $\mathcal{P}(i, j) = -1$ otherwise. Further, $\mathcal{P}(i, j, k, l)$ is defined to satisfy

$$\mathcal{P}(i, j, k, l) = \mathcal{P}(i, j) \mathcal{P}(k, l) \quad (5c)$$

and one easily finds that $\mathcal{P}(i, j, k, l) = 1$ if an even number among four vertices (i), (j), (k) and (l) is source, and $\mathcal{P}(i, j, k, l) = -1$ otherwise. The parity function \mathcal{P} is invariant with respect to the permutation of any two indices, i. e. $\mathcal{P}(i, j) = \mathcal{P}(j, i)$, $\mathcal{P}(i, j, k, l) = \mathcal{P}(j, i, k, l) = \mathcal{P}(k, j, i, l) = \dots$, etc. Each linear combination of reduced alternant operators (5a) is now defined to be an alternant operator, while each linear combination of reduced antialternant operators (5b) is defined to be an antialternant operator. Accordingly, the set of all alternant operators forms a linear space, a subspace of the space of all operators. Similarly, the set of all antialternant operators forms a linear space, a subspace of the space of all operators. An arbitrary operator¹⁴ can be uniquely split into its alternant and antialternant component.^{12,13}

Linear independence of operators \mathbf{I} , \mathbf{R} and \mathbf{P} is here considered in the algebraic sense, i. e. these operators are linearly independent over the space Y_n which is the largest space that can be generated by a repeated application of the creation operators η_i^+ on the vacuum state $|0\rangle$. However, these operators are not linearly independent over the n -particle subspace X_n . To each operator \mathbf{O} one can add an arbitrary operator vanishing over X_n without altering the matrix elements of the operator \mathbf{O} in X_n . Since we are concerned here with the space X_n , it is important to know the general form of operators vanishing over X_n . Each¹⁴ »vanishing« operator \mathbf{Z} , i. e. each operator \mathbf{Z} satisfying

$$\langle \psi_1 | \mathbf{Z} | \psi_2 \rangle = 0 \quad (6)$$

for arbitrary states $\psi_1, \psi_2 \in X_n$, is a linear combination of the following basis operators

$$\begin{aligned} \mathbf{Z}^s &= \sum_i \mathbf{R}_{ii} \\ \mathbf{Z}_{ij}^s &= \sum_k \mathbf{R}_{ik,kj} + \delta_{ij} n \mathbf{I} \\ \mathbf{Z}_{ij}^a &= \sum_k \mathbf{P}_{ik,kj} \end{aligned} \quad (7)$$

The set of all vanishing operators forms a linear space, subspace of the space of all operators. The above basis is particularly suitable, since each of the above operators is either alternant or antialternant: operators \mathbf{Z}_{ij}^s ($\mathcal{P}(i, j) = 1$) and \mathbf{Z}_{ij}^a ($\mathcal{P}(i, j) = -1$) are alternant, while operators \mathbf{Z}^s , \mathbf{Z}_{ij}^s ($\mathcal{P} = 1$) and \mathbf{Z}_{ij}^s ($\mathcal{P}(i, j) = -1$) and \mathbf{Z}_{ij}^a ($\mathcal{P}(i, j) = 1$) are antialternant. In addition, operators \mathbf{Z}^s and \mathbf{Z}_{ij}^s are symmetric, while operators \mathbf{Z}_{ij}^a are antisymmetric. The above operators were in part, obtained elsewhere.^{12,13}

In the MORT approach the state $\psi \in X_n$ is expanded in terms of the regular resonance structures (RRS), and not in terms of basis vectors (1a). Each RRS is an n -particle state containing n mutually disjunct excited and/or nonexcited bond orbitals.^{10,11} Each of these bond orbitals should contain one source and one sink spin-orbital, i. e. bond orbitals connecting either two source or two sink spin-orbitals are not allowed.^{10,11} The set of all such structures spans the space X_n . This set splits into two subsets containing »positive« and »negative« structures, and given any two RRS-s one can easily decide whether they are of the same or of opposite parity.^{10,11} Structures of opposite parity are mutually orthogonal, and spaces X_n^+ and X_n^- spanned by positive and negative structures, respectively, are hence orthogonal as well. Thus, each partition $B \rightarrow \{B^\circ, B^*\}$ induces the splitting of the CI space X_n into complementary subspaces X_n^+ and X_n^- . Once the partition $B \rightarrow \{B^\circ, B^*\}$ is fixed, this splitting is unique up to the exchange $X_n^+ \leftrightarrow X_n^-$.¹⁰ Each state $\psi^+ \in X_n^+$, as well as each state $\psi^- \in X_n^-$, is called alternantlike (AL) state.¹⁰ In particular, each RRS is an AL state. Spaces X_n^+ and X_n^- are of the same dimension, and each state $\psi \in X_n$ can be uniquely represented as a linear combination of two AL states of opposite parity, $\psi = \psi^+ + \psi^-$, where $\psi^+ \in X_n^+$ and $\psi^- \in X_n^-$. These spaces are related to alternant and antialternant operators as defined above in the following way¹⁰⁻¹³:

Theorem 1 (The Splitting Theorem)

a) Let \mathbf{O}_{al} be an alternant operator, and let $\psi^+ \in X_n^+$ and $\psi^- \in X_n^-$ be two AL of the same parity, i. e. either $\psi_1, \psi_2 \in X_n^+$, or $\psi_1, \psi_2 \in X_n^-$. Then

$$\langle \psi^+ | \mathbf{O}_{al} | \psi^- \rangle = \langle \psi^- | \mathbf{O}_{al} | \psi^+ \rangle = 0 \quad (8a)$$

b) Let \mathbf{O}_{nal} be an antialternant operator, and let ψ_1 and ψ_2 be two AL states of the parity, i. e. either $\psi_1, \psi_2 \in X_n^+$, or $\psi_1, \psi_2 \in X_n^-$. Then

$$\langle \psi_1 | \mathbf{O}_{nal} | \psi_2 \rangle = 0 \quad (8b)$$

One can add any linear combination of vanishing operators (7) to each alternant operator \mathbf{O}_{al} and to each antialternant operator \mathbf{O}_{nal} without changing properties (8a) and (8b), respectively. One finds that each¹⁴ operator \mathbf{O}_{al}' satisfying (8a) for arbitrary AL states of opposite parity is of the form^{12,13}

$$\mathbf{O}_{al}' = \mathbf{O}_{al} + \mathbf{Z}_{nal} \quad (9a)$$

i. e. it is a linear combination of an alternant operator (\mathbf{O}_{al}) and an antialternant vanishing operator (\mathbf{Z}_{nal}). The former operator is a linear combination of reduced alternant operators (5a), while the latter is a linear combination of vanishing antialternant operators $\mathbf{Z}^s, \mathbf{Z}_{ij}^s$ ($\mathcal{P}(i, j) = -1$) and \mathbf{Z}_{ij}^a ($\mathcal{P}(i, j) = 1$). Similarly, each¹⁴ operator \mathbf{O}_{nal}' satisfying (8b) for arbitrary AL states of the same parity is of the form^{12,13}

$$\mathbf{O}_{nal}' = \mathbf{O}_{nal} + \mathbf{Z}_{al} \quad (9b)$$

i. e. it is a linear combination of an antialternant operator (\mathbf{O}_{nal}) and an alternant vanishing operator (\mathbf{Z}_{al}). Operators \mathbf{O}_{al}' and \mathbf{O}_{nal}' satisfying the above properties are called »weakly«-alternant and »weakly«-antialternant, respectively¹².

The splitting theorem implies:

Corollary 1

Let \mathbf{O}_{nal} be an antialternant operator. Then

$$\langle \psi^\pm | \mathbf{O}_{nal} | \psi^\pm \rangle = 0 \quad (10)$$

where $\psi^\pm \in X_n^\pm$ is an arbitrary AL state.

According to the above corollary, with each antialternant operator \mathbf{O}_{nal} a property common to all AL states is associated. In order to obtain the complete set of these properties, one should consider the complete set of antialternant operators. A natural choice is to consider reduced antialternant operators (5b). In terms of one- and two-particle density matrices γ and Γ

$$\begin{aligned} \gamma_{ij}(\psi) &= \langle \psi | \eta_i^+ \eta_j^- | \psi \rangle \\ \Gamma_{ij,kl}(\psi) &= \langle \psi | \eta_i^+ \eta_j^+ \eta_l^- \eta_k^- | \psi \rangle / 2 \end{aligned} \quad (11)$$

these properties can be expressed in the following way:

- a) $\gamma_{ii}(\psi^\pm) = 1/2$
 b) $\gamma_{ij}^r(\psi^\pm) = 0; \quad \mathcal{P}(i, j) = 1$
 c) $\gamma_{ij}^c(\psi^\pm) = 0; \quad \mathcal{P}(i, j) = -1$
 e) $\Gamma_{ik,jk}^r(\psi^\pm) = \gamma_{ij}^r(\psi^\pm)/4; \quad \mathcal{P}(i, j) = -1$
 d) $\Gamma_{ik,jk}^c(\psi^\pm) = \gamma_{ij}^c(\psi^\pm)/4; \quad \mathcal{P}(i, j) = 1$
 f) $\Gamma_{ij,kl}^r(\psi^\pm) = 0; \quad \mathcal{P}(i, j, k, l) = -1$
 g) $\Gamma_{ij,kl}^c(\psi^\pm) = 0; \quad \mathcal{P}(i, j, k, l) = 1$ (12)

In the above relations superscripts r and c refer to real and imaginary components, respectively, of matrices Y and Γ :

$$\begin{aligned} \gamma_{ij}^r &\equiv (\gamma_{ij} + \gamma_{ij}^*)/2 = \langle \psi | \mathbf{A}_{ij} | \psi \rangle / 2 \\ \gamma_{ij}^c &\equiv (\gamma_{ij} - \gamma_{ij}^*)/2 = \sqrt{-1} \langle \psi | \mathbf{B}_{ji} | \psi \rangle / 2 \\ \Gamma_{ij,kl}^r &\equiv (\Gamma_{ij,kl} + \Gamma_{ij,kl}^*)/2 = \langle \psi | \mathbf{A}_{ij,kl} | \psi \rangle / 4 \\ \Gamma_{ij,kl}^c &\equiv (\Gamma_{ij,kl} - \Gamma_{ij,kl}^*)/2 = \sqrt{-1} \langle \psi | \mathbf{B}_{ij,kl} | \psi \rangle / 4 \end{aligned} \quad (13a)$$

and

$$\gamma_{ij} \equiv \gamma_{ij}^r + \gamma_{ij}^c; \quad \Gamma_{ij,kl} \equiv \Gamma_{ij,kl}^r + \Gamma_{ij,kl}^c \quad (13b)$$

In addition, all indices in relations (12) are assumed to be mutually different, e. g. in (12b) it is assumed $i \neq j$, etc. Since matrices Y and Γ are hermitian

$$\gamma_{ij} = \gamma_{ji}^* \quad \Gamma_{ij,kl} = \Gamma_{kl,ij}^* \quad (13c)$$

real and imaginary components coincide with symmetric and antisymmetric components, respectively.¹² The physical significance of relations (12) is straightforward. Thus, the operator $\mathbf{Q}_i = \eta_i^+ \eta_i$ is a charge density operator, and hence relation (12a), i. e. $\langle \psi^\pm | \mathbf{Q}_i | \psi^\pm \rangle = 1/2$, implies a uniform charge density of 1/2 over all $2n$ vertices (i). Similarly, relation (12b) expresses the vanishing of bond orders between vertices of the same parity, etc. These properties resemble the characteristic properties of eigenstates associated with neutral alternant hydrocarbons, and this justifies the notion »alternantlike« for the states $\psi^\pm \in X_n^\pm$. Relations (12) contain the complete set of characteristic one- and two-particle linear properties of AL states.¹² Besides properties expressed by these relations, there are some other one- and two-particle properties which are common to all states $\psi \in X_n$. The latter properties can be derived from the relation

$$\langle \psi | \mathbf{Z} | \psi \rangle = 0 \quad (14)$$

satisfied by all states $\psi \in X_n$, in an analogous way to properties (12) being derived from the relation (10) satisfied by all states $\psi^\pm \in X_n^\pm$.¹² However, the properties thus obtained are not characteristic properties of AL states, and hence they will not be considered here.

Beside Corollary 1, the splitting theorem implies few additional corollaries which will be needed in the paper:

Corollary 2

- a) The product of two alternant operators, as well as the product of two antialternant operators, is an alternant operator.
- b) The product of an alternant and an antialternant operator is an antialternant operator.

This corollary is a straightforward consequence of the splitting theorem and the fact that in X_n one can always choose a base of AL states. Namely, this implies $\mathbf{O}_{al} \psi^+ \in X_n^+$ and $\mathbf{O}_{nal} \psi^+ \in X_n^-$, and hence $\langle \psi^- | \mathbf{O}_{al} \mathbf{O}_{al}' | \psi^+ \rangle = 0$, etc. Corollary 2 contains an implicit definition of three-particle, four-particle, etc. alternant and antialternant operators. Thus, if \mathbf{O}_{al} and \mathbf{O}_{al}' are two-particle alternant operators, operator $\mathbf{O} = \mathbf{O}_{al} \mathbf{O}_{al}'$ is a four-particle alternant operator, etc. The explicit construction of all alternant and antialternant operators based on this corollary will be given elsewhere,¹⁶ and it is not so important in relation to the problems discussed in this paper. What matters is that higher particle alternant and antialternant operators thus constructed satisfy relations (8a) and (8b), respectively. They are, however, not expressible as linear combinations of reduced operators (2a).

Corollary 3

Each hermitian weakly-antialternant operator has the complete set of AL eigenstates. The inverse is also true:

Corollary 3'

Each hermitian operator having the complete set of AL eigenstates is a weakly-alternant operator.

Corollary 4

Let \mathbf{O}_{nal}' be a hermitian weakly-alternant operator and let $\psi \in X_n$ be a normalized eigenstate of \mathbf{O}_{nal}' with the eigenvalue λ . Then

- a) If $\lambda \neq 0$ the state ψ is of the form

$$\psi = \frac{1}{\sqrt{2}}(\psi^+ + \psi^-) \quad (15a)$$

where $\psi^+ \in X_n^+$ and $\psi^- \in X_n^-$ are normalized AL states of opposite parity, and in addition the state ψ'

$$\psi' = \frac{1}{\sqrt{2}}(\psi^+ - \psi^-) \quad (15b)$$

is an eigenstate of \mathbf{O}_{nal}' with the eigenvalue $\lambda' = -\lambda$.

- b) If $\lambda = 0$, the state ψ can be both alternantlike and non-alternantlike. If, however, ψ is not an AL state, i. e. if it is of the form

$$\psi = \psi^+ + \psi^-, \quad \psi^+, \psi^- \neq 0 \quad (15c)$$

then it is degenerate, and AL states ψ^+ and ψ^- are both eigenstates of \mathbf{O}'_{nal} with the eigenvalue $\lambda = 0$.

According to this corollary, eigenstates of weakly-antialternant operator \mathbf{O}'_{nal} cannot be alternantlike, unless the corresponding eigenvalue λ equals zero.

Corollaries 3 and 4 can be easily derived from the splitting theorem. In the derivation of point a) of corollary 4 one should use the fact that eigenstates ψ and ψ' belonging to different eigenvalues of \mathbf{O}'_{nal} are orthogonal, i. e. that $\langle \psi | \psi' \rangle = (\langle \psi^+ | \psi^+ \rangle - \langle \psi^- | \psi^- \rangle) / 2 = 0$.

The splitting theorem thus implies that all weakly-alternant Hamiltonians have the complete set of AL eigenstates, i. e. those which satisfy relations (12). Each weakly-alternant operator is a linear combination of reduced alternant operators (5a) and vanishing antialternant operators (7).

Since these latter operators vanish over X_n , each alternant system can be represented by an alternant Hamiltonian. This leads to an efficient and exhaustive definition of alternant systems.^{12,13} Due to these results, the definition (2) of reduced operators, the partition (5) of these operators on alternant and antialternant operators, as well as the partition $X_n \rightarrow \{X_n^+, X_n^-\}$ of the space X_n on complementary subspaces X_n^+ and X_n^- is natural and well justified.

3. NORMAL MODEL OF THE SPACE X_n

In connection with the above formalism, there are a few related questions of considerable interest: firstly, one may ask, what are spin eigenstates in the CI space X_n ? In particular, how are the eigenstates of the spin operators \mathbf{S}^2 and \mathbf{S}_z related to subspaces X_n^+ and X_n^- ? Further, AL states are shown to possess linear properties expressed by relations (12). However, all these properties are in general spin dependent. For example, if X_i are spin orbitals, then relation (12a) expresses the uniform spin density of 1/2 over all vertices (i). This may be either spin- α or spin- β density, depending on the nature of the orbital X_i . However, in many cases one is interested only in spin-independent properties, such as total charges, total bond orders, etc.

The above questions are not properly formulated, unless one specifies the spin nature of orbitals X_i . We shall now formulate the so called »normal« model of the space X_n . In this model the $2n$ orbitals X_i ($i = 1, \dots, 2n$) are specified to consist of n spin- α orbitals $X_i = w_i \alpha$ and n spin- β orbitals $\bar{X}_i = w_i \beta$, where w_i ($i = 1, \dots, n$) are orthonormalized atomic orbitals, while α and β are spin- α and spin- α states, respectively. Annihilation operators η_i ($i = 1, \dots, 2n$) are accordingly rewritten as spin- α and spin- β annihilation operators $\eta_{i\alpha}$ and $\eta_{i\beta}$ ($i = 1, \dots, n$), respectively, and analogously for the corresponding creation operators. The latter operators satisfy

$$\begin{aligned} \eta_{i\alpha}^+ | 0 \rangle &= X_i \\ \eta_{i\beta}^+ | 0 \rangle &= \bar{X}_i \end{aligned} \quad (16)$$

In addition, the parity of different vertices is defined in accord with the »normal« parity convention: for each (i), spin vertices ($i\alpha$) and ($i\beta$) associated with spin-orbitals X_i and \bar{X}_i , respectively, are of opposite parity. In other words, if ($i\alpha$) is source, then ($i\beta$) is sink, and vice versa. We also define the parity of the atomic orbitals w_i and associated spin-independent vertices (i). By definition, the parity of the atomic orbital w_i and of the vertex (i) coincides with the parity of the spin- α orbital X_i , i. e. with the parity of the

spin-vertex ($i\alpha$). According to this convention, the parity of atomic orbitals w_i can be considered arbitrary, and once it is fixed, it uniquely defines the parity of spin-orbitals X_i and \bar{X}_i .

The normal model is general enough to illustrate the most important features of the spin treatment within the MORT approach. Some preliminary discussion of the normal model, though not under the same name, can be found elsewhere.^{12,13} The essential assumption of this model is the above specification of $2n$ orbitals X_i in such a way that they consist of n spin- α and n spin- β orbitals. This is the usual way of forming one-particle orbitals within the molecular orbital (MO) or within the valence bond (VB) approach, and hence it is not a serious restriction to the generality. The normal parity convention is introduced in order to simplify mathematical manipulations. This convention is not irrelevant since most subsequent results depend on it. However, what matters is that one can always partition the $2n$ spin-orbitals into source and sink in accord with this convention, and hence it does not impose any restriction to the generality.

All relations (1)–(15) can be now applied to the normal model. One has only to replace everywhere vertex (i) with vertices ($i\alpha$) and ($i\beta$), and one has to observe the above parity convention concerning these vertices. For example, relation (12a) becomes

$$\gamma_{i\alpha,i\alpha}(\psi^\pm) = 1/2, \quad \gamma_{i\beta,i\beta}(\psi^\pm) = 1/2; \quad i = 1, \dots, n \quad (17a)$$

i. e. spin- α and spin- β density of AL states equals 1/2 at each vertex (i), and hence the total density $\rho_i(\psi) = \gamma_{i\alpha,i\alpha}(\psi) + \gamma_{i\beta,i\beta}(\psi)$ satisfies

$$\rho_i(\psi^\pm) = 1; \quad i = 1, \dots, n \quad (17b)$$

Similarly, the total bond order $\mathbf{P}_{ij}(\psi) = \gamma_{i\alpha,j\alpha}(\psi) + \gamma_{i\beta,j\beta}(\psi)$, ($i \neq j$) is in the case of AL states found to vanish between vertices of the same parity

$$\mathbf{P}_{ij}(\psi^\pm) = 0; \quad \mathcal{P}(i, j) = 1, \quad i \neq j \quad (17c)$$

etc. Relations (17b) and (17c) express spin-independent properties, and in a similar way many other spin-independent properties of AL states can be derived.¹² The normal model is hence suitable enough to answer the two questions formulated at the beginning of this section. We shall now proceed to treat in a systematic way spin-independent properties of different states in the space X_n . Unless otherwise specified, a normal model of the space X_n will be assumed.

4. SPIN INDEPENDENT OPERATORS

In the second quantization formalism components of the total spin operator $\mathbf{S} \equiv (\mathbf{S}_x, \mathbf{S}_y, \mathbf{S}_z)$ are given by¹⁷

$$\begin{aligned} \mathbf{S}_x &= 1/2 \sum_{i=1}^n (\eta_{i\alpha}^+ \eta_{i\beta} + \eta_{i\beta}^+ \eta_{i\alpha}) \\ \mathbf{S}_y &= \sqrt{-1} 1/2 \sum_{i=1}^n (\eta_{i\beta}^+ \eta_{i\alpha} - \eta_{i\alpha}^+ \eta_{i\beta}) \\ \mathbf{S}_z &= 1/2 \sum_{i=1}^n (\eta_{i\alpha}^+ \eta_{i\alpha} - \eta_{i\beta}^+ \eta_{i\beta}) \end{aligned} \quad (18)$$

and they satisfy commutation relations

$$[\mathbf{S}_x, \mathbf{S}_y] = i \mathbf{S}_z, [\mathbf{S}_y, \mathbf{S}_z] = i \mathbf{S}_x, [\mathbf{S}_z, \mathbf{S}_x] = i \mathbf{S}_y \quad (19)$$

characteristic of vector operators¹⁸. Relations (18) can be derived using Pauli matrices¹⁸ $\sigma \equiv (\sigma_x, \sigma_y, \sigma_z)$

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (20)$$

and they depend on the particular representation (20). One can express relations (18) in terms of reduced operators (2a)

$$\begin{aligned} \mathbf{S}_x &= 1/2 \sum_{i=1}^n \mathbf{R}_{i\alpha, i\beta} \\ \mathbf{S}_y &= 1/2 \sum_{i=1}^n \mathbf{P}_{i\beta, i\alpha} \\ \mathbf{S}_z &= 1/4 \sum_{i=1}^n (\mathbf{R}_{i\alpha, i\alpha} - \mathbf{R}_{i\beta, i\beta}) \end{aligned} \quad (21)$$

According to the partition (5) and the normal parity convention, each operator $\mathbf{R}_{i\alpha, i\beta}$ is an alternant operator since vertices $(i\alpha)$ and $(i\beta)$ are of opposite parity. Similarly, operators $\mathbf{P}_{i\beta, i\alpha}$, $\mathbf{R}_{i\alpha, i\alpha}$ and $\mathbf{R}_{i\beta, i\beta}$ are found to be antialternant operators. We, thus, obtain the important result that the x -component \mathbf{S}_x of the total spin operator \mathbf{S} is an alternant operator, while y - and z -components \mathbf{S}_y and \mathbf{S}_z of the total spin operator \mathbf{S} are antialternant operators. Note that this result depends on the convention that, given (i) , vertices $(i\alpha)$ and $(i\beta)$ are of opposite parity. Namely, if $(i\alpha)$ and $(i\beta)$ (fixed i) were chosen to be of the same parity, then \mathbf{S}_x would be an antialternant operator, while \mathbf{S}_y would be an alternant operator. Other possible partitions into source and sink vertices lead to \mathbf{S}_x and \mathbf{S}_y , which are neither alternant nor antialternant. However, whatever the partition, z -component, \mathbf{S}_z , is always an antialternant operator. It is a considerable advantage if the partition $B \rightarrow \{B^\circ, B^*\}$ is done in such a way that each component of the total spin operator \mathbf{S} is either alternant or antialternant. This is a partial justification of the otherwise arbitrary convention that vertices $(i\alpha)$ and $(i\beta)$ (fixed i) should be of opposite parity.

According to Corollary 2 the square of the total spin operator

$$\mathbf{S}^2 = \mathbf{S}_x^2 + \mathbf{S}_y^2 + \mathbf{S}_z^2 \quad (22)$$

is an alternant operator as well.

As an immediate consequence, operator \mathbf{S}^2 can be diagonalized in the base of AL states (Corollary 3). Moreover, since \mathbf{S}_x is also an alternant operator, and since it commutes with \mathbf{S}^2 , operators \mathbf{S}^2 and \mathbf{S}_x can be simultaneously diagonalized in the base of AL states. However, this is not possible with the operators \mathbf{S}^2 and \mathbf{S}_z .

Let us now consider spin-independent operators. It is natural to define each operator \mathbf{O}^0 satisfying

$$[\mathbf{O}^0, \mathbf{S}_x] = [\mathbf{O}^0, \mathbf{S}_y] = [\mathbf{O}^0, \mathbf{S}_z] = 0 \quad (23)$$

i. e. commuting with the components of the total spin operator \mathbf{S} , as a spin-independent operator. This definition is analogous to the definition of scalar operators which are required to commute with components of the total angular momentum operator $\mathbf{J} = \mathbf{L} + \mathbf{S}$.¹⁸ Note that, according to this definition, the square \mathbf{S}^2 of the total spin operator \mathbf{S} is a spin-independent operator, while components \mathbf{S}_x , \mathbf{S}_y and \mathbf{S}_z are not. For the sake of notation, we shall mark spin-independent operators with superscript (o), as this is done above. We would like to find all spin-independent alternant and all spin-independent antialternant operators.¹⁴ Consider the following set of operators

$$\begin{aligned} \mathbf{I}, & \text{ a unit operator} \\ \mathbf{A}_{ij}^o &= \mathbf{A}_{i\alpha, j\alpha} + \mathbf{A}_{i\beta, j\beta} \\ \mathbf{B}_{ij}^o &= \mathbf{B}_{i\alpha, j\alpha} + \mathbf{B}_{i\beta, j\beta} \\ \mathbf{A}_{ij,kl}^o &= \mathbf{A}_{i\alpha j\alpha, k\alpha l\alpha} + \mathbf{A}_{i\beta j\beta, k\beta l\beta} + \mathbf{A}_{i\alpha j\beta, k\beta l\alpha} + \mathbf{A}_{i\beta j\alpha, k\alpha l\beta} \\ \mathbf{B}_{ij,kl}^o &= \mathbf{B}_{i\alpha j\alpha, k\alpha l\alpha} + \mathbf{B}_{i\beta j\beta, k\beta l\beta} + \mathbf{B}_{i\alpha j\beta, k\beta l\alpha} + \mathbf{B}_{i\beta j\alpha, k\alpha l\beta} \end{aligned} \quad (24a)$$

where

$$\begin{aligned} \mathbf{A}_{i\alpha j\alpha} &= \eta_{i\alpha}^+ \eta_{j\alpha} + \eta_{j\alpha}^+ \eta_{i\alpha} \\ \mathbf{A}_{i\alpha, j\beta, k\beta, l\alpha} &= \eta_{i\alpha}^+ \eta_{j\beta}^+ \eta_{k\beta} \eta_{l\alpha} + \eta_{l\alpha}^+ \eta_{k\beta} \eta_{j\beta} \eta_{i\alpha} \end{aligned} \quad (24b)$$

etc. as inferred from relations (2b). Using anticommutation relations of fermion operators $\eta_{i\alpha}^+$, $\eta_{i\beta}^+$, $\eta_{i\alpha}$ and $\eta_{i\beta}$ one can show that all operators (24a) satisfy relations (23), i. e. that they are spin-independent operators. It is somewhat more difficult to show that each¹⁴ spin-independent operator can be represented as a linear combination of operators (24a). The proof is quite space consuming and it will be omitted here. Hence, operators (24a) form the base in the space of all¹⁴ spin-independent operators. Operators (24a) are hermitian. In addition, operators \mathbf{I} and \mathbf{A}^o are real and symmetric, while operators \mathbf{B}^o are imaginary and antisymmetric.

Consider now another set of operators

$$\begin{aligned} \mathbf{I}, & \text{ a unit operator} \\ \mathbf{R}_{ij}^o &= \mathbf{R}_{i\alpha, j\alpha} + \mathbf{R}_{i\beta, j\beta} \\ \mathbf{P}_{ij}^o &= \mathbf{P}_{i\alpha, j\alpha} + \mathbf{P}_{i\beta, j\beta} \\ \mathbf{R}_{ij,kl}^o &= \mathbf{R}_{i\alpha j\alpha, k\alpha l\alpha} + \mathbf{R}_{i\beta j\beta, k\beta l\beta} + \mathbf{R}_{i\alpha j\beta, k\beta l\alpha} + \mathbf{R}_{i\beta j\alpha, k\alpha l\beta} \\ \mathbf{P}_{ij,kl}^o &= \mathbf{P}_{i\alpha j\alpha, k\alpha l\alpha} + \mathbf{P}_{i\beta j\beta, k\beta l\beta} + \mathbf{P}_{i\alpha j\beta, k\beta l\alpha} + \mathbf{P}_{i\beta j\alpha, k\alpha l\beta} \end{aligned} \quad (25)$$

Symmetry relations (3) imply

$$\begin{aligned} \mathbf{R}_{ij}^o &= \mathbf{R}_{ji}^o, & \mathbf{P}_{ij}^o &= -\mathbf{P}_{ji}^o \\ \mathbf{R}_{ij,kl}^o &= \mathbf{R}_{ji,lk}^o = \mathbf{R}_{kl,ij}^o, & \mathbf{P}_{ij,kl}^o &= \mathbf{P}_{ji,lk}^o = -\mathbf{P}_{kl,ij}^o \end{aligned} \quad (25)$$

Each of the above operators is expressed as a linear combination of reduced operators. Moreover, all reduced operators entering in a particular linear combination are of the same kind, i. e. they are either all alternant or all antialternant. Thus, according to the parity convention $\mathscr{P}(i\alpha, j\alpha) = \mathscr{P}(i\beta, j\beta)$,

and \mathcal{P} hence, operators \mathbf{R}_{ij}° and \mathbf{P}_{ij}° have definite symmetry properties. Analogously, the normal parity convention implies $\mathcal{P}(i\alpha, j\alpha, k\alpha, l\alpha) = \mathcal{P}(i\beta, j\beta, k\beta, l\beta) = \mathcal{P}(i\alpha, j\beta, k\beta, l\alpha) = \mathcal{P}(i\beta, j\alpha, k\alpha, l\alpha)$, and hence operators $\mathbf{R}_{ij,kl}^{\circ}$ and $\mathbf{P}_{ij,kl}^{\circ}$ have also definite symmetry properties. Each of the operators (25) is hence either alternant or antialternant. Alternant operators are found to be

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$$\begin{aligned} \mathbf{R}_{ij}^{\circ}; & \quad \mathcal{P}(ij) = -1 \\ \mathbf{P}_{ij}^{\circ}; & \quad \mathcal{P}(ij) = 1 \\ \mathbf{R}_{ij,kl}^{\circ}; & \quad \mathcal{P}(ij, kl) = 1 \\ \mathbf{P}_{ij,kl}^{\circ}; & \quad \mathcal{P}(ij, kl) = -1 \end{aligned} \quad (27a)$$

while antialternant operators are

$$\begin{aligned} \mathbf{R}_{ij}^{\circ}; & \quad \mathcal{P}(ij) = 1 \\ \mathbf{P}_{ij}^{\circ}; & \quad \mathcal{P}(ij) = -1 \\ \mathbf{R}_{ij,kl}^{\circ}; & \quad \mathcal{P}(ij, kl) = -1 \\ \mathbf{P}_{ij,kl}^{\circ}; & \quad \mathcal{P}(ij, kl) = 1 \end{aligned} \quad (27b)$$

where the function \mathcal{P} now refers to the parity of atomic orbitals w_i . The partition (27) of operators (25) into alternant and antialternant parallels the partition (5) of reduced operators (2a) into alternant and antialternant. Using relations (2) and (24) one finds that operators (25) can be expressed in the form

$$\begin{aligned} \mathbf{R}_{ij}^{\circ} &= \mathbf{A}_{ij}^{\circ} - 2\delta_{ij} \\ \mathbf{P}_{ij}^{\circ} &= \mathbf{B}_{ij}^{\circ} \\ \mathbf{R}_{ij,kl}^{\circ} &= \mathbf{A}_{ij,kl}^{\circ} + (\delta_{ik}\mathbf{A}_{jl}^{\circ} + \delta_{jl}\mathbf{A}_{ik}^{\circ})/2 - \delta_{il}\mathbf{A}_{jk}^{\circ} - \delta_{jk}\mathbf{A}_{il}^{\circ} \\ \mathbf{P}_{ij,kl}^{\circ} &= \mathbf{B}_{ij,kl}^{\circ} + (\delta_{ik}\mathbf{B}_{jl}^{\circ} + \delta_{jl}\mathbf{B}_{ik}^{\circ})/2 - \delta_{il}\mathbf{B}_{jk}^{\circ} - \delta_{jk}\mathbf{B}_{il}^{\circ} \end{aligned} \quad (28a)$$

i. e. all these operators are linear combinations of spin-independent operators (24a), and hence they are spin-independent operators as well. One can also express spin-independent operators (24a) in terms of operators (25)

$$\begin{aligned} \mathbf{A}_{ij}^{\circ} &= \mathbf{R}_{ij}^{\circ} + 2\delta_{ij}, & \mathbf{B}_{ij}^{\circ} &= \mathbf{P}_{ij}^{\circ} \\ \mathbf{A}_{ij,kl}^{\circ} &= \mathbf{R}_{ij,kl}^{\circ} + \delta_{il}\mathbf{R}_{jk}^{\circ} + \delta_{jk}\mathbf{R}_{il}^{\circ} + 4\delta_{il}\delta_{jk} - (\delta_{ik}\mathbf{R}_{jl}^{\circ} + \delta_{jl}\mathbf{R}_{ik}^{\circ})/2 - 2\delta_{ik}\delta_{jl} \\ \mathbf{B}_{ij,kl}^{\circ} &= \mathbf{P}_{ij,kl}^{\circ} + \delta_{il}\mathbf{P}_{jk}^{\circ} + \delta_{jk}\mathbf{P}_{il}^{\circ} - (\delta_{ik}\mathbf{P}_{jl}^{\circ} + \delta_{jl}\mathbf{P}_{ik}^{\circ})/2 \end{aligned} \quad (28b)$$

implying that operators (25) form the basis in the space of all spin-independent operators. Operators (25) are hence well chosen: each of these operators is either a spin-independent alternant or a spin-independent antialternant operator. The corresponding partition (27) of these operators into alternant and antialternant is analogous to the partition (5) of reduced operators (2a) into alternant and antialternant. Further, these operators form the complete set in the space of all¹⁴ spin-independent operators, i. e. each spin-independent operator can be represented as their linear combination. In addition, one can

show that this representation is unique up to symmetry relations (26) (i. e. provided operators $\mathbf{R}^{o_{ij}}$ and $\mathbf{R}^{o_{ji}}$ are considered to be one and the same operator, etc.). Due to all these properties it is proper to consider operators (25) as »reduced« spin-independent operators. Each linear combination of reduced spin-independent alternant operators (27a) is a spin-independent alternant operator. Similarly, each linear combination of reduced spin-independent anti-alternant operators (27b) is a spin-independent anti-alternant operator. One can easily show that an arbitrary spin-independent operator \mathbf{O}^o can be represented as a linear combination of a spin-independent alternant operator $\mathbf{O}^{o_{al}}$ and a spin-independent anti-alternant operator $\mathbf{O}^{o_{nal}}$, $\mathbf{O}^o = \mathbf{O}^{o_{al}} + \mathbf{O}^{o_{nal}}$. This representation is unique.

5. SPIN INDEPENDENT PROPERTIES AND SEMI-ALTERNANTLIKE STATES

We have defined spin-independent operators (25) in order to be able to treat spin-independent properties of various states in the space X_n . In analogy to the relation (10) each spin-independent anti-alternant operator $\mathbf{O}^{o_{nal}}$ satisfies

$$\langle \psi^\pm | \mathbf{O}^{o_{nal}} | \psi^\pm \rangle = 0 \quad (29)$$

and hence it is associated with a particular spin-independent property of AL states ψ^\pm . Relation (29) thus generates a set of relations analogous to relations (12). However, in order to analyze spin eigenstates in terms of spin-independent properties the set of all AL states is not sufficient. This can easily be shown by an example: let $\psi_{1,1}$ and $\psi_{1,0}$ be triplet states with the projections on the z -axis $m = 1$ and $m = 0$, respectively,

$$\begin{aligned} \mathbf{S}^2 \psi_{1,1} &= 2 \psi_{1,1}, & \mathbf{S}^2 \psi_{1,0} &= 2 \psi_{1,0}, \\ \mathbf{S}_z \psi_{1,1} &= \psi_{1,1}, & \mathbf{S}_z \psi_{1,0} &= 0 \end{aligned} \quad (30)$$

and let, in addition, these states be degenerate eigenstates of an alternant Hamiltonian \mathbf{H} . Corollaries 3 and 4 imply that, unless there is some additional degeneracy, the state $\psi_{1,0}$ is an AL state. Hence, this state possesses all the properties (12), and in particular all the spin-independent properties such as uniform total charge, etc. which can be inferred from the relation (29). Since the state $\psi_{1,1}$ is degenerate with the state $\psi_{1,0}$, one would expect the state $\psi_{1,1}$ to possess, if not all properties (12), then at least some spin-independent properties common with the state $\psi_{1,0}$. However, according to Corollary 4, the state $\psi_{1,1}$ is not an AL state. It is, hence, not obvious whether the state $\psi_{1,1}$ has any of the properties (12) and, a posteriori, any of the spin-independent properties in common with the state $\psi_{1,0}$. In order to be able to analyze this and similar situations, one has to introduce the notion of the so called »semi«-alternantlike (SAL) states:

Definition 1

Let $\psi^\pm \in X_n^\pm$ be an AL state and let $\mathbf{U} = f(\mathbf{S})$ be a unitary operator which is otherwise an arbitrary function of spin operators \mathbf{S}_x , \mathbf{S}_y and \mathbf{S}_z .²⁰ Then the state

$$\psi = \mathbf{U} \psi^\pm \quad (31)$$

is a semi-alternantlike (SAL) state. The trivial choice $\mathbf{U} = \mathbf{I}$ demonstrates that each AL state is also a SAL state. The inverse is not true. The set of all SAL states is significantly larger than the set of all AL states. Moreover, this set does not form a linear space, i. e. if ψ_a and ψ_b are SAL states then their linear combination is not necessarily a SAL state.

We shall now show that SAL states satisfy all the spin-independent properties common to AL states and that, in addition, the set of all SAL states is large enough to treat the problems such as the above one and similar.

Due to the relations (23) each spin independent operator \mathbf{O}^0 commutes with the unitary operator $\mathbf{U} = f(\mathbf{S})$, and hence the splitting theorem implies

Lemma 1

Let ψ_1 and ψ_2 be AL states and let $\mathbf{U} = f(\mathbf{S})$ be a unitary operator, function of spin operators \mathbf{S}_x , \mathbf{S}_y and \mathbf{S}_z .²⁰ Consider SAL states $\psi_a = \mathbf{U}\psi_1$ and $\psi_b = \mathbf{U}\psi_2$

a) If ψ_1 and ψ_2 are AL states of the same parity, then

$$\langle \psi_a | \mathbf{O}_{\text{nal}}^0 | \psi_b \rangle = 0 \quad (32a)$$

for each spin-independent antialternant operator $\mathbf{O}_{\text{nal}}^0$.

b) If ψ_1 and ψ_2 are AL states of opposite parity, then

$$\langle \psi_a | \mathbf{O}_{\text{al}}^0 | \psi_b \rangle = 0 \quad (32b)$$

for each spin-independent alternant operator \mathbf{O}_{al}^0 . In particular, the above lemma implies:

Corollary 5

Let $\psi = \mathbf{U}\psi^\pm$ be a SAL state, and let $\mathbf{O}_{\text{nal}}^0$ be a spin-independent anti-alternant operator. Then

$$\langle \psi | \mathbf{O}_{\text{nal}}^0 | \psi \rangle = 0 \quad (33)$$

Relation (33) involving SAL states is analogous to the relation (10) involving AL states. According to this relation, a particular property common to all SAL states is associated with each spin-independent antialternant operator $\mathbf{O}_{\text{nal}}^0$. In order to obtain a complete set of these properties, one should consider the complete set of spin-independent antialternant operators. A natural choice is to consider reduced spin-independent antialternant operators (27b). In terms of one- and two-particle spin-independent density matrices ρ and \mathbf{P}

$$\begin{aligned} Q_{ij}(\psi) &= \gamma_{i\alpha, j\alpha}(\psi) + \gamma_{i\beta, j\beta}(\psi) \\ \mathbf{P}_{ij,kl}(\psi) &= \Gamma_{i\alpha j\alpha, k\alpha l\alpha}(\psi) + \Gamma_{i\beta j\beta, k\beta l\beta}(\psi) + \\ &+ \Gamma_{i\alpha j\beta, k\alpha l\beta}(\psi) + \Gamma_{i\beta j\alpha, k\beta l\alpha}(\psi) \end{aligned} \quad (34)$$

these properties can be expressed in the following way

- a) $Q_{ii}(\psi) = 1$
 b) $Q_{ij}^r(\psi) = 0; \quad \rho(i, j) = 1$
 c) $Q_{ij}^c(\psi) = 0; \quad \rho(i, j) = -1$
 d) $\mathbf{P}_{ik,jk}^r(\psi) = -2\mathbf{P}_{ik,kj}^r(\psi) = Q_{ij}^r(\psi)/2; \quad \rho(i, j) = -1$
 e) $\mathbf{P}_{ik,jk}^c(\psi) = -2\mathbf{P}_{ik,kj}^c(\psi) = Q_{ij}^c(\psi)/2; \quad \rho(i, j) = 1$
 f) $\mathbf{P}_{ii,kj}^r(\psi) = 0; \quad \rho(k, j) = -1$
 g) $\mathbf{P}_{ii,kj}^c(\psi) = 0; \quad \rho(k, j) = 1$
 h) $\mathbf{P}_{ii,ji}^r(\psi) = Q_{ij}^r(\psi)/4; \quad \rho(i, j) = -1$
 i) $\mathbf{P}_{ii,ji}^c(\psi) = Q_{ij}^c(\psi)/4; \quad \rho(i, j) = 1$
 j) $\mathbf{P}_{ij,kl}^r(\psi) = 0; \quad \rho(ij, kl) = -1$
 k) $\mathbf{P}_{ij,kl}^c(\psi) = 0; \quad \rho(ij, kl) = 1$
 l) $\mathbf{P}_{ii,jj}^c(\psi) = 0$ (35)

In the above relations ψ is a SAL state, while superscripts r and c refer to real and imaginary components, respectively, of matrices ρ and P :

$$\begin{aligned}
 Q_{ij}^r &\equiv (Q_{ij} + Q_{ij}^*)/2 = \langle \psi | \mathbf{A}_{ij}^0 | \psi \rangle / 2 \\
 Q_{ij}^c &\equiv (Q_{ij} - Q_{ij}^*)/2 = \sqrt{-1} \langle \psi | \mathbf{B}_{ji}^0 | \psi \rangle / 2 \\
 \mathbf{P}_{ij,kl}^r &\equiv (\mathbf{P}_{ij,kl} + \mathbf{P}_{ij,kl}^*)/2 = \langle \psi | \mathbf{A}_{ij,kl}^0 | \psi \rangle / 4 \\
 \mathbf{P}_{ij,kl}^c &\equiv (\mathbf{P}_{ij,kl} - \mathbf{P}_{ij,kl}^*)/2 = \sqrt{-1} \langle \psi | \mathbf{B}_{kl,ij}^0 | \psi \rangle / 4
 \end{aligned} \tag{36a}$$

and

$$Q_{ij} \equiv Q_{ij}^r + Q_{ij}^c, \quad \mathbf{P}_{ij,kl} \equiv \mathbf{P}_{ij,kl}^r + \mathbf{P}_{ij,kl}^c \tag{36b}$$

In addition, all indices in relations (35) are assumed to be mutually different. For example, in (35b) it is assumed $i \neq j$, etc. Since matrices ρ and P are hermitian

$$Q_{ij} = Q_{ji}^*, \quad \mathbf{P}_{ij,kl} = \mathbf{P}_{kl,ij}^* \tag{36c}$$

their real and imaginary components coincide with symmetric and antisymmetric components, respectively.

Relations (35) contain the same amount of information as Corollary 5; we have only written different conditions explicitly and in a particular basis of spin-independent operators. These relations express spin-independent properties of SAL states, and they are analogous to relations (12) expressing properties of AL states. In particular, according to (35a) all SAL states have uniform total charge density distribution over atomic orbitals w_i , while according to (35b) these states have vanishing total bond orders between atomic orbitals of the same parity. McLachlan has shown that the same properties are satisfied by some π -electron eigenstates of neutral alternant hydrocarbons within the PPP approach.⁴ These eigenstates are, hence, good candidates to be SAL states, and in the following sections we will show that this is really so. The list of properties (35) is, however, much longer than

the one found by McLachlan and others²⁻⁵ in their treatment of neutral alternant systems.

In connection with Corollary 5 and a fortiori to relations (35), a few points should be emphasized:

a) Relations (35) contain all⁸ characteristic spin-independent properties of SAL states. Namely, each spin-independent property common to SAL states can be written in the form $\langle \psi | \mathbf{O}^o | \psi \rangle = 0$, where \mathbf{O}^o is a spin-independent operator which is in general a linear combination of zero-, one- and two-particle operators, while ψ is an arbitrary SAL state. Further, each spin-independent operator \mathbf{O}^o is of the form $\mathbf{O}^o = \mathbf{O}^o_{al} + \mathbf{O}^o_{nal}$. Assume now that ψ is an AL state, $\psi \equiv \psi^\pm \in X_n^\pm$. Then $\langle \psi | \mathbf{O}^o | \psi \rangle = 0$ implies $\langle \psi^\pm | \mathbf{O}^o_{al} | \psi^\pm \rangle = 0$ and $\langle \psi^\pm | \mathbf{O}^o_{nal} | \psi^\pm \rangle = 0$. The second relation leads to conditions (35). Independent conditions, if any, should be hence contained in the first relation. However, if this relation is to be satisfied for all AL states ψ^\pm , then \mathbf{O}^o_{al} vanishes over X_n , i. e. it is a \mathbf{Z} operator. The corresponding property is hence a common property to all states $\psi \in X_n$, and it is neither characteristic of AL nor of SAL states.

b) Properties (35) contain also all characteristic spin-independent properties of AL states. In other words, though the set of all AL states is a proper subset of the set of all SAL states, there is no spin-independent property common to AL states which is not at the same time common to SAL states. This can be shown in an analogous way as point a) above.

c) If ψ is a singly-determinantal SAL state, properties (35) d) through l) involving two-particle density matrix \mathbf{P} follow from properties (35) a) through c) involving only one-particle density matrix ρ . This is the consequence of the factorization of the two-particle density matrix \mathbf{P} in terms of the one-particle density matrix ρ (see ref. 13.) However, if ψ is not a singly-determinantal function, there is no such a direct connection between properties involving a two-particle density matrix and properties involving only a one-particle density matrix.

d) If ψ is real, properties c), e), g), i), k) and l) involving imaginary components of density matrices ρ and \mathbf{P} are automatically satisfied since these components vanish. However, in the case of complex ψ , these properties are nontrivial.

In conclusion, relations (35) contain all characteristic spin-independent properties of SAL states, and also all characteristic spin-independent properties of AL states.⁸ These relations are simplified in some special cases such as singly-determinantal and/or real functions. It should be noted that in the case of AL states relations (35) were partly derived elsewhere.¹⁰⁻¹³

6. SPIN EIGENSTATES IN X_n

Since \mathbf{S}^2 commutes with each of the components of \mathbf{S} , one can form a complete set of common eigenstates of \mathbf{S}^2 and one of its components.¹⁸ Let $\psi_{s,m,\tau}^z$ be an eigenstates of \mathbf{S}^2 and \mathbf{S}_z corresponding to the eigenvalues $s(s+1)$ and m , respectively,

$$\begin{aligned} \mathbf{S}^2 \psi_{s,m,\tau}^z &= s(s+1) \psi_{s,m,\tau}^z \\ \mathbf{S}_z \psi_{s,m,\tau}^z &= m \psi_{s,m,\tau}^z \end{aligned} \quad (37)$$

We use the superscript z in order to emphasize that the z -axis is chosen as the quantization axis. Since S^2 and S_z do not usually form a complete set of commuting observables, there will be many systems of basis vectors common to these two operators.¹⁸ This is anticipated by the quantum number τ in the above relations. Among the representations with \mathbf{S}^2 and \mathbf{S}_z diagonal, there are certain in which manipulations of the spin operator are particularly simple. They are called standard representations $\{\mathbf{S}^2, \mathbf{S}_z\}$.¹⁸ In these representations basis vectors corresponding to a specific value of the quantum number s can be grouped in one or several series of $(2s + 1)$ vectors connected by the relations

$$\begin{aligned} \mathbf{S}_+^z \psi_{s,m,\tau}^z &= \sqrt{s(s+1) - m(m+1)} \psi_{s,m+1,\tau}^z \\ \mathbf{S}_-^z \psi_{s,m,\tau}^z &= \sqrt{s(s+1) - m(m-1)} \psi_{s,m-1,\tau}^z \end{aligned} \quad (38a)$$

where

$$\mathbf{S}_+^z = \mathbf{S}_x + i\mathbf{S}_y, \quad \mathbf{S}_-^z = \mathbf{S}_x - i\mathbf{S}_y \quad (38b)$$

are two hermitian conjugate operators.^{17,18} The $(2s + 1)$ vectors

$$\psi_{s,s,\tau}^z, \psi_{s,s-1,\tau}^z, \dots, \psi_{s,-s,\tau}^z \quad (39)$$

span $(2s + 1)$ -dimensional space $\varepsilon_{s,\tau}$, a subspace of the space X_n . This subspace is invariant with respect to operators \mathbf{S}_x , \mathbf{S}_y and \mathbf{S}_z , i. e. each function $f(\mathbf{S})$ of the components of the operator \mathbf{S} transforms vectors in $\varepsilon_{s,\tau}$ one into another.¹⁸ The same is true of the subspace $\varepsilon_s = \bigoplus_{\tau} \varepsilon_{s,\tau}$, which is a direct sum of subspaces $\varepsilon_{s,\tau}$, and which contains all the vectors with quantum number s fixed. In general, quantum number s assumes integer and half integer values. However, which of the integer and half integer numbers actually make up the spectrum of s , and how many series of $(2s + 1)$ linearly independent vectors correspond to each of these values of s , depends on the problem considered.¹⁸ We will now specify and apply the above general considerations to the normal CI space X_n .

Notice first that the dimension $d(n)$ of the space X_n equals¹⁰

$$d(n) = (2n)!/(n!)^2 \quad (40)$$

Further, since the space X_n contains n -particle states, spin quantum number $s \geq 0$ assumes values $s = n/2, n/2 - 1, n/2 - 2, \dots$ etc. One can now ask the following question: how many of these $d(n)$ states have the projection m along the z -axis? Obviously, there is only one state $\psi_{n/2,n/2,\tau}^z$ with the spin projection $m = n/2$, since this state should contain all n particles in the spin- α orbitals, and this can be accomplished in only one way:

$$\psi_{n/2,n/2,\tau}^z = \eta_{1\alpha}^+ \eta_{2\alpha}^+ \dots \eta_{n\alpha}^+ |0\rangle \quad (41)$$

It can be shown¹⁰ that the number $Z_n(m)$ of linearly independent states having the projection m along the z -axes equals

$$\begin{aligned} Z_n(m) &= \binom{n}{n/2-m}^2 = [n!/((n/2-m)!(n/2+m)!)]^2; \\ m &= n/2, n/2 - 1, \dots, -n/2 \end{aligned} \quad (42)$$

Hence, the number $S_n(s)$ of spin multiplets with the total spin quantum number s equals¹⁰

$$S_n(n/2) = 1$$

$$S_n(s) = \binom{n}{n/2-s}^2 - \binom{n}{n/2-s-1}^2; \quad s = n/2 - 1, n/2 - 2, \dots \quad (43)$$

For example, the space X_4 contains $S_4(0) = 20$ singlets, $S_4(1) = 15$ triplets and $S_4(2) = 1$ quintet. There are, hence, $20 \cdot 1 + 15 \cdot 3 + 1 \cdot 5 = 70$ linearly independent states in X_4 . This equals $d(4)$, as it should be, etc.

Let us now see how eigenstates $\psi_{s,m,\tau}^z$ are related to spaces X_n^+ and X_n^- . Since S_z is an antialternant operator, Corollary 4 implies.

Corollary 6

a) Let $\psi_m \in X_n$ be a normalized eigenstate of S_z with the eigenvalue $m \neq 0$:

$$S_z \psi_m = m \psi_m \quad (44a)$$

Then ψ_m is of the form

$$\psi_m = 1/\sqrt{2} (\psi_{|m|}^+ + \psi_{|m|}^-) \quad (44b)$$

where $\psi_{|m|}^+ \in X_n^+$ and $\psi_{|m|}^- \in X_n^-$ are normalized AL states of opposite parity. In addition, the state $\psi_{-m} = (\psi_{|m|}^+ - \psi_{|m|}^-)/\sqrt{2}$ is an eigenstate of S_z with the eigenvalue $-m$:

$$S_z \psi_{-m} = -m \psi_{-m} \quad (44c)$$

b) Let $\psi_0 \in X_n$ be an eigenstate of S_z with the eigenvalue $m = 0$. In this case the state ψ_0 can be both, alternantlike and non-alternantlike. If, however, ψ_0 is not an AL state, i. e. if it is of the form $\psi_0 = \psi_0^+ + \psi_0^-$, where $\psi_0^+ \neq 0$ and $\psi_0^- \neq 0$, then it is degenerate, and ψ_0^+ and ψ_0^- are both eigenstates of S_z with the eigenvalue $m = 0$.

In the above relations $|m|$ is the absolute value of the quantum number m . Note that $\psi_{|m|}^+$ and $\psi_{|m|}^-$ are not eigenstates of the spin operator S_z . They are only some normalized AL states which are of opposite parity and which depend on the absolute value of the quantum number m .

We will now show that standard representation $\{S^z, S_z\}$ can be chosen in such a way that all basis vectors $\psi_{s,m,\tau}^z$ satisfy properties expressed by the above corollary. Note first that the relations (38) imply

$$\psi_{s,m,\tau}^z = f(s, m) ((S_+^z)^m \psi_{s,0,\tau}^z)$$

$$\psi_{s,-m,\tau}^z = f(s, m) (S_-^z)^m \psi_{s,0,\tau}^z \quad (45a)$$

where $f(s, m)$ is a function of s and m . Further

$$(S_+^z)^m \equiv (S_x + i S_y)^m = \sum_{k=0}^m i^k \binom{m}{k} \{S_x^{m-k} S_y^k\}_{pr}$$

$$(S_-^z)^m \equiv (S_x - i S_y)^m = \sum_{k=0}^m (-i)^k \binom{m}{k} \{S_x^{m-k} S_y^k\}_{pr} \quad (45b)$$

where $\{ \dots \}_{pr}$ indicates that in the evaluation of the product of $(m - k)$ operators S_x with k operators S_y one has to observe the exact ordering of these operators, since they do not commute with one another. One now finds

$$(S_+^s)^m = O_{al} + O_{nal}, \quad (S_-^s)^m = O_{al} - O_{nal} \tag{46a}$$

where

$$O_{al} = \sum_{k=0} (-1)^k \binom{m}{2k} \{ S_x^{m-2k} S_y^{2k} \}_{pr}$$

$$O_{nal} = i \sum_{k=0} (-1)^k \binom{m}{1+2k} \{ S_x^{m-2k-1} S_y^{2k+1} \}_{pr} \tag{46b}$$

Hence

$$\psi_{s,m,\tau}^s = \psi_1 + \psi_2$$

$$\psi_{s,-m,\tau}^s = \psi_1 - \psi_2 \tag{47a}$$

where

$$\psi_1 = f(s, m) O_{al} \psi_{s,o,\tau}$$

$$\psi_2 = f(s, m) O_{nal} \psi_{s,o,\tau} \tag{47b}$$

The operator $\{ S_x^{m-2k} S_y^{2k} \}_{pr}$ is a product of $(m - 2k)$ alternant operators S_x and $2k$ antialternant operators S_y . According to Corollary 2 it is an alternant operator, irrespective of the order in which particular operator S_x and S_y enter this product. The operator O_{al} is, hence, an alternant operator as well. Operator O_{nal} is similarly found to be an antialternant operator. Further, according to Corollary 6, the state $\psi_{s,o,\tau}^s$ can be chosen to be an AL state. Assuming such a choice, ψ_1 and ψ_2 become AL states of opposite parity, and the above relations are found to imply.

Lemma 2

Standard representation $\{ S^2, S_z \}$ can be chosen in such a way that all basis vectors $\psi_{s,o,\tau}^z$ are AL states, while basis vectors $\psi_{s,m,\tau}^z$ and $\psi_{s,-m,\tau}^z$ ($m \neq 0$) are related to each other according to

$$\psi_{s,m,\tau}^z = 1/\sqrt{2} (\psi_{s,|m|,\tau}^+ + \psi_{s,|m|,\tau}^-)$$

$$\psi_{s,-m,\tau}^z = 1/\sqrt{2} (\psi_{s,|m|,\tau}^+ - \psi_{s,|m|,\tau}^-) \tag{48}$$

where $\psi_{s,|m|,\tau}^+ \in X_n^+$ and $\psi_{s,|m|,\tau}^- \in X_n^-$ are normalized AL states of opposite parity.

Note that basis vectors $\psi_{s,m,\tau}^z$ ($m \neq 0$) are not AL states. However, linear combinations $\psi_{s,m,\tau}^z \pm \psi_{s,-m,\tau}^z$ are AL states. We will later show that though base vectors $\psi_{s,m,\tau}^z$ are generally not AL states, they are SAL states, hence, they satisfy properties (35). We call each standard representation $\{ S^2, S_z \}$ satisfying properties expressed by the above Lemma »alternantlike« (AL). Lemma 2, thus, states that in X_n there exists at least one AL representation $\{ S^2, S_z \}$.

Instead of quantizing along the z -axis, we could have equally well quantized along any other axis, for example along the x -axis. This leads to the basis vectors $\psi_{s,m,\tau}^x$, common eigenstates of the operator \mathbf{S}^2 and \mathbf{S}_x :

$$\begin{aligned}\mathbf{S}^2 \psi_{s,m,\tau}^x &= s(s+1) \psi_{s,m,\tau}^x \\ \mathbf{S}_x \psi_{s,m,\tau}^x &= m \psi_{s,m,\tau}^x\end{aligned}\quad (49)$$

In analogy to the standard representation $\{\mathbf{S}^2, \mathbf{S}_z\}$, one can form a standard representation $\{\mathbf{S}^2, \mathbf{S}_x\}$ in which basis vectors $\psi_{s,m,\tau}^x$ corresponding to a specific value of the quantum number s can be grouped in one or several series of $(2s+1)$ vectors connected by relations

$$\begin{aligned}\mathbf{S}_+^x \psi_{s,m,\tau}^x &= \sqrt{s(s+1) - m(m+1)} \psi_{s,m-1,\tau}^x \\ \mathbf{S}_-^x \psi_{s,m,\tau}^x &= \sqrt{s(s+1) - m(m-1)} \psi_{s,m+1,\tau}^x\end{aligned}\quad (50a)$$

where

$$\mathbf{S}_+^x = \mathbf{S}_y + i \mathbf{S}_z, \quad \mathbf{S}_-^x = \mathbf{S}_y - i \mathbf{S}_z \quad (50b)$$

The $(2s+1)$ vectors

$$\psi_{s,s,\tau}^x, \psi_{s,s-1,\tau}^x, \dots, \psi_{s,-s,\tau}^x \quad (51)$$

span the space $\varepsilon'_{s,\tau}$, invariant subspace of the space X_n . Since \mathbf{S}^2 and \mathbf{S}_x are alternant, basis vectors $\psi_{s,m,\tau}^x$ of the standard representation $\{\mathbf{S}^2, \mathbf{S}_x\}$ can be chosen to be AL states, i. e. each $\psi_{s,m,\tau}^x$ satisfies either $\psi_{s,m,\tau}^x \equiv \psi_{s,m,\tau}^+ \in X_n^+$ or $\psi_{s,m,\tau}^x \equiv \psi_{s,m,\tau}^- \in X_n^-$. This is in accord with relations (50), since operators \mathbf{S}_+^x and \mathbf{S}_-^x are antialternant, and, hence, they transform each AL state of a positive parity into an AL state of a negative parity, and vice versa. One thus derives:

Lemma 3

Standard representation $\{\mathbf{S}^2, \mathbf{S}_x\}$ can be chosen in such a way that basic vectors $\psi_{s,m,\tau}^x$ are AL states. In the case of such a choice, $\psi_{s,m,\tau}^x \in X_n^+$ implies $\psi_{s,m\pm 1,\tau}^x \in X_n^-$, and vice versa.

We call each standard representation $\{\mathbf{S}^2, \mathbf{S}_x\}$ satisfying the above properties »alternantlike«. Lemma 3 thus states that in X_n there exists at least one AL representation $\{\mathbf{S}^2, \mathbf{S}_x\}$. Note that the AL representation $\{\mathbf{S}^2, \mathbf{S}_x\}$ is defined in a different way from the AL representation $\{\mathbf{S}^2, \mathbf{S}_z\}$ (see Lemma 2). Lemma 3 implies:

Corollary 7

Let $\varepsilon'_{s,\tau}$ be an invariant subspace spanned by $(2s+1)$ vectors (51) set up in accord with the above lemma: Then:

a) If s is half integer, then the states $\psi_{s,m,\tau}^x$ and $\psi_{s,-m,\tau}^x$ are AL states of opposite parity, i. e. $\psi_{s,m,\tau}^x \in X_n^+$ implies $\psi_{s,-m,\tau}^x \in X_n^-$, and vice versa.

b) If s is integer, then the states $\psi_{s,m,\tau}^x$ and $\psi_{s,-m,\tau}^x$ are AL states of the same parity, i. e. either $\psi_{s,m,\tau}^x, \psi_{s,-m,\tau}^x \in X_n^+$ or $\psi_{s,m,\tau}^x, \psi_{s,-m,\tau}^x \in X_n^-$.

In particular, in the case of half integer s , basis vectors of the AL representation $\{\mathbf{S}^2, \mathbf{S}_x\}$ spanning the space $\varepsilon'_{s,\tau}$ are symmetrically distributed among spaces X_n^+ and X_n^- : the space $\varepsilon'_{s,\tau}$ contains $(2s+1)/2$ basis vectors of

positive parity, and $(2s + 1)/2$ basis vectors of negative parity. However, in the case of integer s , there is a basis vector $\psi_{s,0,\tau}^x \in \varepsilon'_{s,\tau}$ which introduces asymmetry into this distribution. Hence in, the case of integer s one can introduce the notion of the »parity« of the space $\varepsilon'_{s,\tau}$: if $\psi_{s,0,\tau}^x \in X_n^+$ then $\varepsilon'_{s,\tau}$ is »positive«, and if $\psi_{s,0,\tau}^x \in X_n^-$ then $\varepsilon'_{s,\tau}$ is »negative«.

Let us now establish the connection between subspaces $\varepsilon_{s,\tau}$ and $\varepsilon'_{s,\tau}$. Since these subspaces are invariant with respect to the components of the total spin operator \mathbf{S} , and due to relations (38) and (50), the space $\varepsilon_{s,\tau}$ is either identical to the space $\varepsilon'_{s,\tau}$, or the two spaces have no vector in common (except nulvector). Hence and from the results obtained so far one can now derive.

Theorem 2

Standard representations $\{\mathbf{S}^2, \mathbf{S}_z\}$ and $\{\mathbf{S}^2, \mathbf{S}_x\}$ can be set up in such a way that they satisfy Lemma 3 and 4, respectively, and that in addition the $(2s + 1)$ vectors (39) connected to each other according to (38), and the $(2s + 1)$ vectors (51) connected to each other according to (50), span the same space $\varepsilon_{s,\tau}$.

In other words, AL representations $\{\mathbf{S}^2, \mathbf{S}_z\}$ and $\{\mathbf{S}^2, \mathbf{S}_x\}$ can be chosen to be in accord with each other, i. e. to generate the same set of subspace $\varepsilon_{s,\tau}$. Such representations will be called »complementary«. Theorem 2 thus states that in X_n there exists at least one pair of complementary AL representations $\{\mathbf{S}^2, \mathbf{S}_z\}$ and $\{\mathbf{S}^2, \mathbf{S}_x\}$. Each space $\varepsilon_{s,\tau}$ corresponding to a particular spin multiplet is spanned by $(2s + 1)$ vectors (39), and also by $(2s + 1)$ basis vectors (51). All basis vectors (51) are AL states, and they alternate in parity as the quantum number m gradually increases from $m = -s$ to $m = s$. Basis vectors (39) are not AL states and they satisfy relations (48), except for the basis vector $\psi_{s,0,\tau}^z$ which is an AL state. There are two cases which should be distinguished: the case with s halfinteger and the case with s integer. In the former case (s is halfinteger), base vectors (51) spanning the space $\varepsilon_{s,\tau}$ are symmetrically distributed among spaces X_n^+ and X_n^- . This symmetry is also revealed by basis vectors (39), since in this case there is no state $\psi_{s,0,\tau}^z$, while relations (48) clearly demonstrate that components of the base vectors $\psi_{s,m,\tau}^z$ are symmetrically distributed among spaces X_n^+ and X_n^- . In the latter case (s is integer), this distribution is not symmetrical, and one can define the parity of the space $\varepsilon_{s,\tau}$. The space $\varepsilon_{s,\tau}$ is defined to be »positive« if $\psi_{s,0,\tau}^z \in X_n^+$, and negative otherwise. Note that the space X_n contains the states with halfinteger s if n is odd, and it contains the states with integer s if n is even. For example, the space X_2 (n even) contains three singlets and one triplet. From Theorem 2 it follows that two singlets and one triplet component have one parity, while the third singlet and the two remaining triplet components have another parity. The distribution of singlet and triplet components among subspaces X_n^+ and X_n^- is not symmetric. In the case of the space X_3 (n odd), there are eight doublets and one quartet. In the AL representation each doublet contains one component in X_3^+ and another component in X_3^- . Similarly, a quartet contains two components in X_3^+ and another two in X_3^- .

The partition of these spin components among subspaces X_3^+ and X_3^- is hence symmetric, etc.

We have shown above that basis vectors $\psi_{s,m,\tau}^x$ of the AL representation $\{\mathbf{S}^2, \mathbf{S}_x\}$ are AL states. Hence, all these vectors satisfy relations (12) which express characteristic properties of AL states. Basis vectors $\psi_{s,m,\tau}^z$ of the AL representation $\{\mathbf{S}^2, \mathbf{S}_z\}$ are not AL states, except for vectors $\psi_{s,m,\tau}^z$ with $m = 0$, and hence these vectors in general do not satisfy relations (12). On the other hand, the quantization axis is arbitrary, and one can equally well quantize along the x -axis, as well as along the z -axis. Hence, the above asymmetry in the properties of the two sets of basis vectors is to some extent surprising. However, a closer examination reveals that we have lifted the symmetry between AL representations $\{\mathbf{S}^2, \mathbf{S}_z\}$ and $\{\mathbf{S}^2, \mathbf{S}_x\}$ by choosing the particular representation (20) of Pauli matrices and by fixing source and sink vertices according to the normal parity convention. Hence, one should not be surprised that one obtains some asymmetry with respect to the two AL representations. We will now show that this asymmetry does not involve spin-independent properties (35), but rather only more detailed properties (12).

Consider the unitary operator $\mathbf{U} = f(\mathbf{S})$, function of spin operators $\mathbf{S}_x, \mathbf{S}_y$ and \mathbf{S}_z .²⁰ Definition 1 implies that if ψ is a SAL state, then $\psi' = \mathbf{U}\psi$ is a SAL state as well. Further, since \mathbf{U} is a function of spin operators alone, it leaves invariant the space $\varepsilon_{s,\tau}$. Consider now two normalized vectors ψ_1 and ψ_2 contained in the space $\varepsilon_{s,\tau}$. It can be shown that, given $\psi_1, \psi_2 \in \varepsilon_{s,\tau}$, there is a unitary operator $\mathbf{U} = f(\mathbf{S})$ such that $\psi_2 = \mathbf{U}\psi_1$. This follows from the relations (38) which imply that an arbitrary vector $\psi \in \varepsilon_{s,\tau}$ can be obtained from any of the $(2s + 1)$ basis vectors $\psi_{s,m,\tau}^z \in \varepsilon_{s,\tau}$ through the repeated application of operators \mathbf{S}_{+z} and \mathbf{S}_{-z} , which are themselves functions of operators \mathbf{S}_x and \mathbf{S}_y . Hence, if $\psi \in \varepsilon_{s,\tau}$ is a SAL state then any other vector $\psi' \in \varepsilon_{s,\tau}$ is a SAL state as well, and vice versa. There follows

Lemma 4

a) Let $\varepsilon_{s,\tau}$ be a $(2s + 1)$ dimensional space spanned by $(2s + 1)$ basis vectors (39) connected to each other according to relations (38). Then, either all states in $\varepsilon_{s,\tau}$ are SAL states, or no state in $\varepsilon_{s,\tau}$ (except nulvector) is a SAL state.

b) Let $\varepsilon'_{s,\tau}$ be a $(2s + 1)$ dimensional space spanned by $(2s + 1)$ vectors (51) connected to each other according to relations (50). Then, either all states in $\varepsilon'_{s,\tau}$ are SAL states, or no state in $\varepsilon'_{s,\tau}$ (except nulvector) is a SAL state.

Since basis vectors $\psi_{s,m,\tau}^x$ of the AL representation $\{\mathbf{S}^2, \mathbf{S}_x\}$ as well as basis vectors $\psi_{s,0,\tau}^z$ of the AL representation $\{\mathbf{S}^2, \mathbf{S}_z\}$, are AL and hence SAL states, Lemma 4 implies:

Corollary 8

Let $\{\mathbf{S}^2, \mathbf{S}_z\}$ and $\{\mathbf{S}^2, \mathbf{S}_x\}$ be AL representations in X_n . Then, each subspace $\varepsilon_{s,\tau}$, as well as each subspace $\varepsilon'_{s,\tau}$, contains only SAL states.

Corollary 8 contains in the condensed form the main result of this section: in the space X_n there exists at least one pair of complementary AL representations $\{\mathbf{S}^z, \mathbf{S}_z\}$ and $\{\mathbf{S}^z, \mathbf{S}_x\}$. All subspaces $\varepsilon_{s,\tau}$ generated by these representations contain only SAL states. These states satisfy spin-independent properties (35). In particular, all basic vectors $\psi_{s,m,\tau}^z$ of the AL representation $\{\mathbf{S}^z, \mathbf{S}_z\}$ are SAL states. This is now an a posteriori justification of Definition 1 of SAL states. The set of all SAL states is thus shown to be sufficiently large to discuss spin eigenstates and their relation to spin-independent properties.

7. CONNECTION BETWEEN COMPLEMENTARY REPRESENTATIONS $\{\mathbf{S}^z, \mathbf{S}_z\}$ AND $\{\mathbf{S}^z, \mathbf{S}_x\}$

One can establish a more intimate connection between basis vectors $\psi_{s,m,\tau}^z$ and $\psi_{s,m,\tau}^x$ of complementary representations $\{\mathbf{S}^z, \mathbf{S}_z\}$ and $\{\mathbf{S}^z, \mathbf{S}_x\}$, respectively. Operator $\mathbf{U} = f(\mathbf{S})$ can be chosen to be

$$\mathbf{U}_u(\varphi) = \exp(-i\varphi \mathbf{S}_u) \quad (52a)$$

where

$$\mathbf{S}_u = \mathbf{S}_x u_x + \mathbf{S}_y u_y + \mathbf{S}_z u_z \quad (52b)$$

is a scalar product between the spin operator \mathbf{S} and a unit vector $u \equiv (u_x, u_y, u_z)$. Operator (52) represents the rotation of spin states about the u -axis for the angle ψ .¹⁸ In particular, the operator

$$\mathbf{U}(\pi/2) = \exp(-i\pi \mathbf{S}_y/2) = \cos(\mathbf{S}_y \pi/2) - i \sin(\mathbf{S}_y \pi/2) = \mathbf{C} - i \mathbf{D} \quad (53)$$

rotates spin states about y -axis for the angle $\varphi = \pi/2$. Hence, it transforms eigenstates of \mathbf{S}_z into eigenstates of \mathbf{S}_x . Since the subspace $\varepsilon_{s,\tau}$ is invariant with respect to the operator $\mathbf{U}(\pi/2)$, this operator transforms basis vectors $\psi_{s,m,\tau}^z$ of the AL representation $\{\mathbf{S}^z, \mathbf{S}_z\}$ into basis vectors $\psi_{s,m,\tau}^x$ of the AL representation $\{\mathbf{S}^z, \mathbf{S}_x\}$:

$$\mathbf{U}(\pi/2) \psi_{s,m,\tau}^z = \psi_{s,m,\tau}^x \quad (54a)$$

The inverse transformation reads

$$\mathbf{U}^{-1}(\pi/2) \psi_{s,m,\tau}^x = \psi_{s,m,\tau}^z \quad \mathbf{U}^{-1}(\pi/2) = \mathbf{U}(-\pi/2) = \mathbf{C} + i \mathbf{D} \quad (54b)$$

while operators \mathbf{C} and \mathbf{D} satisfy the identity relation

$$\mathbf{C}^2 + \mathbf{D}^2 \equiv \mathbf{I} \quad (55)$$

Let us now concentrate on the particular space $\varepsilon_{s,\tau}$. For the sake of simplicity we will suppress quantum numbers s and τ in denoting basis vectors (39) and (51), all vectors being tacitly assumed to be contained in the space $\varepsilon_{s,\tau}$. Using (48), relations (54) can be now written in the form:

$$\begin{aligned} (\mathbf{C} + i \mathbf{D}) \psi_m^x &= 1/\sqrt{2} (\psi_{|m|^+} + \psi_{|m|^-}) & m \neq 0 \\ (\mathbf{C} + i \mathbf{D}) \psi_{-m}^x &= 1/\sqrt{2} (\psi_{|m|^+} - \psi_{|m|^-}) \end{aligned} \quad (56a)$$

and

$$\begin{aligned} (\mathbf{C} - i \mathbf{D}) 1/\sqrt{2} (\psi_{|m|^+} + \psi_{|m|^-}) &= \psi_m^x \\ (\mathbf{C} - i \mathbf{D}) 1/\sqrt{2} (\psi_{|m|^+} - \psi_{|m|^-}) &= \psi_{-m}^x \end{aligned} \quad m \neq 0 \quad (56b)$$

Consider now operator $\mathbf{C} = \cos(\pi\mathbf{S}_y/2)$. This operator is a linear combination of even powers of the antialternant operator \mathbf{S}_y , and according to Corollary 2 it is an alternant operator.²¹ Similarly, operator $\mathbf{D} = \sin(\pi\mathbf{S}_y/2)$ is a linear combination of odd powers of the antialternant operator \mathbf{S}_y , and hence it is an antialternant operator.²¹ Further, all vectors ψ_m^x are AL states. Hence, in the above relations one can separate components contained in the space X_n^+ from the components contained in the space X_n^- . Two cases can be considered, depending on whether s is integer or half integer:

a) *Quantum Number s is Half Integer*

Spin quantum number s is half integer in the case of spaces X_n with n odd, i. e. describing an odd number of particles. According to Corollary 7, basis vectors ψ_m^x and ψ_{-m}^x are in this case AL states of opposite parity. Let us assume $\psi_m^x \in X_n^+$ and $\psi_{-m}^x \in X_n^-$. Relations (56a) now imply:

$$\begin{aligned} \psi_{|m|}^+ &= \sqrt{2} \mathbf{C} \psi_m^x, & \psi_{|m|}^- &= i \sqrt{2} \mathbf{D} \psi_m^x \\ \psi_{|m|}^+ &= i \sqrt{2} \mathbf{D} \psi_{-m}^x, & \psi_{|m|}^- &= -\sqrt{2} \mathbf{C} \psi_{-m}^x \end{aligned} \quad (57a)$$

while relations (56b) imply:

$$\begin{aligned} \psi_m^x &= 1/\sqrt{2} (\mathbf{C} \psi_{|m|}^+ - i \mathbf{D} \psi_{|m|}^-), & \mathbf{C} \psi_{|m|}^- &= i \mathbf{D} \psi_{|m|}^+ \\ \psi_{-m}^x &= -1/\sqrt{2} (\mathbf{C} \psi_{|m|}^- + i \mathbf{D} \psi_{|m|}^+), & \mathbf{C} \psi_{|m|}^+ &= -i \mathbf{D} \psi_{|m|}^- \end{aligned} \quad (57b)$$

and hence

$$\begin{aligned} \psi_m^x &= \sqrt{2} \mathbf{C} \psi_{|m|}^+ = -i \sqrt{2} \mathbf{D} \psi_{|m|}^- \\ \psi_{-m}^x &= \sqrt{2} \mathbf{C} \psi_{|m|}^- = -i \sqrt{2} \mathbf{D} \psi_{|m|}^+ \end{aligned} \quad (58)$$

Analogous relations are obtained in the case $\psi_m^x \in X_n^-$, $\psi_{-m}^x \in X_n^+$. Note that according to Lemma 3, $\psi_m^x \in X_n^+$ implies $\psi_{m\pm 1}^x \in X_n^-$, etc. From relations (57) and (58) it follows that basis vectors $\psi_{s,m,\tau}^x \equiv \psi_m^x$ and $\psi_{s,m,\tau}^z \equiv \psi_m^z$ of AL representations $\{\mathbf{S}^2, \mathbf{S}_x\}$ and $\{\mathbf{S}^2, \mathbf{S}_z\}$, respectively, satisfy:

$$\begin{aligned} (\mathbf{C}^2 - 1/2) \psi_{s,m,\tau}^x &= (\mathbf{D}^2 - 1/2) \psi_{s,m,\tau}^x = 0 \\ (\mathbf{C}^2 - 1/2) \psi_{s,m,\tau}^z &= (\mathbf{D}^2 - 1/2) \psi_{s,m,\tau}^z = 0 \end{aligned} \quad (59)$$

Using identity (55) the first pair of relations in (59) can be derived from the second pair, and vice versa.

b) *Quantum Number s is Integer*

Spin quantum number s is integer in the case of spaces X_n with n even, i. e. those describing an even number of particles. This case can be analyzed analogously to the half integer case starting from relations (56). However, the case with $m = 0$ should be treated separately. Corollary 7 states that basis vectors ψ_m^z and ψ_{-m}^z of the AL representation $\{\mathbf{S}^2, \mathbf{S}_x\}$ are of the same parity, and there is now a vector ψ_0^x having the projection $m = 0$ on the x -axis and defining the parity of the subspace $\epsilon_{s,\tau}$. Without loss of generality, one can assume that the parity of the space $\epsilon_{s,\tau}$ is positive. Assume further that $\psi_0^x \in X_n^+$. In this case one obtains:

Basis vectors ψ_o^x and ψ_o^z satisfy:

$$\mathbf{C} \psi_o^x = \psi_o^z, \quad \mathbf{C} \psi_o^z = \psi_o^x, \quad \mathbf{D} \psi_o^x = \mathbf{D} \psi_o^z = 0 \quad (60a)$$

Vectors with m even ($m \neq 0$) satisfy

$$\begin{aligned} \psi|_m|^+ &= \sqrt{2} \mathbf{C} \psi_m^x = \sqrt{2} \mathbf{C} \psi_{-m}^x \\ \psi|_m|^- &= i \sqrt{2} \mathbf{D} \psi_m^x = -i \sqrt{2} \mathbf{D} \psi_{-m}^x \\ \mathbf{C} \psi|_m|^- &= \mathbf{D} \psi|_m|^+ = 0 \\ 1/\sqrt{2} (\psi_m^x + \psi_{-m}^x) &= \mathbf{C} \psi|_m|^+ \\ 1/\sqrt{2} (\psi_m^x - \psi_{-m}^x) &= -i \mathbf{D} \psi|_m|^- \end{aligned} \quad (60b)$$

Similar relations can be derived for vectors with m odd.

8. SPIN EIGENSTATES AND SPIN-INDEPENDENT ALTERNANT AND NONALTERNANT SYSTEMS

Let us now consider spin-independent systems. Intuitively, these systems are expected to have a complete set of eigenstates which are simultaneously common eigenstates to spin operators \mathbf{S}^2 and \mathbf{S}_z . We will now define spin-independent alternant and spin-independent nonalternant (arbitrary) systems in terms of the corresponding Hamiltonians, and we will show that these systems can be efficiently analyzed using the complementary AL representations $\{\mathbf{S}^2, \mathbf{S}_z\}$ and $\{\mathbf{S}^2, \mathbf{S}_x\}$.

a) Spin-independent Alternant Systems

Consider the Hamiltonian operator

$$\mathbf{H} = \mathbf{H}_{al}^0 + \mathbf{Z} \quad (61)$$

where \mathbf{H}_{al}^0 is a spin-independent alternant operator, while \mathbf{Z} is a vanishing operator. In other words, \mathbf{H}_{al}^0 is a linear combination of reduced spin-independent alternant operators (27a) while \mathbf{Z} is a linear combination of vanishing operators (7). Since \mathbf{H}_{al}^0 is spin-independent, operators \mathbf{H}_{al}^0 , \mathbf{S}^2 and \mathbf{S}_x commute with one another, and hence they can be simultaneously diagonalized. Due to the vanishing of \mathbf{Z} over X_n , it follows that in X_n there is a complete set of common eigenstates to operator \mathbf{H} , \mathbf{S}^2 and \mathbf{S}_x . Since further operators \mathbf{H} , \mathbf{S}^2 and \mathbf{S}_x are weakly-alternant, all these eigenstates can be chosen to be alternantlike. Hence, there always exists a complete set of AL eigenstates common to operators \mathbf{H} , \mathbf{S}^2 and \mathbf{S}_x . Moreover, unless there is some additional degeneracy which is not due to the spin multiplicity, this set is unique. All these eigenstates satisfy properties (12) characteristic of AL states. Note that eigenstates to the operator \mathbf{H} alone are not necessarily AL states. The form (61) guarantees only the existence of the complete set of AL eigenstates, which does not yet imply that each eigenstate of \mathbf{H} is an AL state. Namely, if \mathbf{H} contains some degenerate eigenstates, non-AL eigenstates may exist. This is actually the case, since common eigenstates to \mathbf{H} and \mathbf{S}^2 other than singlet states are degenerate. The same conclusion can be reached in a slightly different way. The three operators \mathbf{H}_{al}^0 , \mathbf{S}^2 and \mathbf{S}_z also commute with one another.

Hence, there is a complete set of common eigenstates to operators \mathbf{H} , \mathbf{S}^2 and \mathbf{S}_z , as well. However, \mathbf{S}_z is an antialternant operator, and hence according to Corollary 4, its eigenstates are not AL states, unless the corresponding eigenvalue m vanishes. Accordingly, an eigenstate common to \mathbf{H} , \mathbf{S}^2 and \mathbf{S}_z is not an AL state, unless $m = 0$. Using the results obtained in the preceding sections one can show that common eigenstates to \mathbf{H} , \mathbf{S}^2 and \mathbf{S}_z can be chosen to be SAL states, and moreover, that there always exists complete set of common eigenstates to \mathbf{H} , \mathbf{S}^2 and \mathbf{S}_z which is in accord with Theorem 2. In other words, one can derive

Theorem 3

Let $\mathbf{H} = \mathbf{H}_{\text{al}}^0 + \mathbf{Z}$ be a Hamiltonian operator where \mathbf{H}_{al}^0 is a spin-independent alternant operator, while \mathbf{Z} is a vanishing operator. Then, there are complementary AL representations $\{\mathbf{S}^2, \mathbf{S}_z\}$ and $\{\mathbf{S}^2, \mathbf{S}_x\}$ such that basis vectors $\psi_{s,m,\tau}^z$ of the AL representation $\{\mathbf{S}^2, \mathbf{S}_z\}$, as well as basis vectors $\psi_{s,m,\tau}^x$ of the AL representation $\{\mathbf{S}^2, \mathbf{S}_x\}$, are eigenstates of the Hamiltonian operator \mathbf{H} :

$$\begin{aligned}\mathbf{H} \psi_{s,m,\tau}^z &= E_{s,\tau} \psi_{s,m,\tau}^z \\ \mathbf{H} \psi_{s,m,\tau}^x &= E_{s,\tau} \psi_{s,m,\tau}^x\end{aligned}\tag{62b}$$

According to the above theorem, all properties and relations derived in the preceding sections for the vectors contained in the space $\varepsilon_{s,\tau}$ apply to the above eigenstates of the Hamiltonian operator \mathbf{H} . In particular, each space $\varepsilon_{s,\tau}$ spanned by $(2s + 1)$ vectors (39), or equivalently by $(2s + 1)$ vectors (51), contains only SAL states. All these states are degenerate (unless $s = 0$) eigenstates of the Hamiltonian operator \mathbf{H} , and they all satisfy spin-independent properties (35). Moreover, states $\psi_{s,m,\tau}^x$ which are common eigenstates to operators \mathbf{H} , \mathbf{S}^2 and \mathbf{S}_x , are AL states and hence they satisfy, besides spin-independent properties (35), also more demanding properties (12). The parity of these states alternates as one gradually increases m from $m = -s$ to $m = s$ (s and τ being fixed), etc. Due to all these properties, it is proper to consider each Hamiltonian of the type (61) as describing some spin-independent alternant system. We will also consider that Hamiltonians of the type (61) describe all such systems, i. e. we will consider operator form (61) as the defining property of spin-independent systems.

Theorem 3 guarantees the existence of the representations $\{\mathbf{S}^2, \mathbf{S}_z\}$ and $\{\mathbf{S}^2, \mathbf{S}_x\}$ with the said properties. It does not yet imply that each eigenstate of the Hamiltonian operator \mathbf{H} is a SAL state. For example, if $\psi_{s,m,\tau}^z$ and $\psi_{s,m,\nu}^z$ are degenerate eigenstates of \mathbf{H} with the common eigenvalue $E_{s,\tau} = E_{s,\nu}$, then each linear combination of these two states is also an eigenstate of \mathbf{H} , but it is not necessarily a SAL state. However, if besides spin multiplicity there is no additional degeneracy, such cases cannot arise and hence

Corollary 9

Let eigenstates of the Hamiltonian operator (61) have no degeneracy other than spin multiplicity. Then,

- a) There is one and only one AL representation $\{\mathbf{S}^2, \mathbf{S}_z\}$, such that all basis vectors $\psi_{s,m,\tau}^z$ of this representation are eigenstates of \mathbf{H} .
- b) There is one and only one AL representation $\{\mathbf{S}^2, \mathbf{S}_z\}$, such that all basis vectors $\psi_{s,m,\tau}^x$ of this representation are eigenstates of \mathbf{H} .
- c) Representations $\{\mathbf{S}^2, \mathbf{S}_z\}$ and $\{\mathbf{S}^2, \mathbf{S}_x\}$ are complementary and each eigenstate of \mathbf{H} is contained in some subspace $\varepsilon_{s,\tau}$.

In particular, this corollary implies:

Corollary 10

If besides spin multiplicity there is no additional degeneracy, each eigenstate of the Hamiltonian operator (61) is a SAL state.

Hence, all eigenstates of such an operator satisfy spin-independent properties (35).

b) Spin-independent Nonalternant Systems

Let us now consider arbitrary spin-independent systems which are described by Hamiltonian operators of the general type

$$\mathbf{H} = \mathbf{H}^0 + \mathbf{Z} \quad (63)$$

where $\mathbf{H}^0 = \mathbf{H}_{\text{al}}^0 + \mathbf{H}_{\text{nal}}^0$ is an arbitrary spin-independent operator, while \mathbf{Z} is an operator vanishing over X_n . Since \mathbf{H}^0 , \mathbf{S}^2 and \mathbf{S}_x , as well as \mathbf{H}^0 , \mathbf{S}^2 and \mathbf{S}_z , are mutually commuting operators, there exists a complete set of common eigenstates to operators \mathbf{H} , \mathbf{S}^2 and \mathbf{S}_z , as well as a complete set of common eigenstates to operators \mathbf{H} , \mathbf{S}^2 and \mathbf{S}_x . However, unless $\mathbf{H}_{\text{nal}}^0$ vanishes over X_n , an operator \mathbf{H} is not a weakly-alternant operator, and hence its eigenstates are not guaranteed to possess either properties (35) or properties (12). In fact, one can show that if $\mathbf{H}_{\text{nal}}^0$ does not vanish over X_n , a Hamiltonian (63) cannot have the complete set of AL eigenstates.^{12,13} Hence, if $\{\mathbf{S}^2, \mathbf{S}_z\}$ is an AL representation, eigenstates $\psi_{s,m,\mu}$ common to operators \mathbf{H} , \mathbf{S}^2 and \mathbf{S}_z are generally not contained in spaces $\varepsilon_{s,\tau}$ but rather have nonvanishing components in several such spaces, i. e. they are of the form

$$\psi_{s,m,\mu} = \sum_{\tau} C_{s,m,\tau}^{\mu} \psi_{s,m,\tau}^z \quad (64)$$

Though each state $\psi_{s,m,\tau}^z$ is a SAL state, the state $\psi_{s,m,\mu}$ is not necessarily such a state, and it usually does not satisfy properties (35). There is one interesting exception. According to relation (43) there is only one spin multiplet with the total spin number $s = n/2$. In other words, there is only one space $\varepsilon_{n/2,\tau}$ (τ assumes only one value) and hence

Corollary 11

Let $\mathbf{H} = \mathbf{H}^0 + \mathbf{Z}$ be a Hamiltonian operator describing some spin-independent system. Each vector in the space $\varepsilon_{n/2,\tau}$ (τ assumes only one value) is a common eigenstate of operators \mathbf{H} and \mathbf{S}^2 . All these states are SAL states satisfying properties (35). In particular, the $(n+1)$ vectors $\psi_{n/2,m,\tau}^x$ spanning the space $\varepsilon_{n/2,\tau}$ are common eigenstates to \mathbf{H} , \mathbf{S}^2 and \mathbf{S}_x and they are AL states satisfying relations (12).

Thus, despite the fact that the operator (63) in general describes nonalternant systems, there are always $(n + 1)$ linearly independent AL states which are degenerate eigenstates of \mathbf{H} and which correspond to the highest spin multiplet $s = n/2$. For example, in the case $n = 2$ there is only one triplet, and hence all triplet eigenstates of the Hamiltonian (63) are SAL states, irrespective of the nature of the spin-independent operator \mathbf{H}^0 .

9. SOME EXAMPLES OF SPIN-INDEPENDENT ALTERNANT AND NONALTERNANT SYSTEMS

In order to illustrate the applicability of the results obtained in the preceding sections, let us give some examples of the spin-independent alternant and nonalternant systems.

a) In the second quantization formalism the Pariser-Parr-Pople (PPP) Hamiltonian of a conjugated hydrocarbon system can be written in the form

$$\mathbf{H}_p = K \sum_i \mathbf{p}_i + \sum_{i,j} \beta_{ij} \mathbf{p}_{ij} + \sum_{i < j} \gamma_{ij} (\mathbf{q}_i - 1) (\mathbf{q}_j - 1) + \sum_i \gamma_{ii} (\mathbf{q}_i^\alpha - 1/2) (\mathbf{q}_i^\beta - 1/2) \quad (65a)$$

where \mathbf{q}_i^α and \mathbf{q}_i^β are spin- α and spin- β charge operators, respectively, while \mathbf{q}_i and \mathbf{p}_{ij} are total charge and total bond order operators:

$$\begin{aligned} \mathbf{q}_i^\alpha &= \eta_{i\alpha}^+ \eta_{i\alpha}, \quad \mathbf{q}_i^\beta = \eta_{i\beta}^+ \eta_{i\beta}, \quad \mathbf{q}_i = \mathbf{q}_i^\alpha + \mathbf{q}_i^\beta \\ \mathbf{p}_{ij} &= \mathbf{p}_{ij}^\alpha + \mathbf{p}_{ij}^\beta = (\eta_{i\alpha}^+ \eta_{j\alpha} + \eta_{j\alpha}^+ \eta_{i\alpha} + \eta_{i\beta}^+ \eta_{j\beta} + \eta_{j\beta}^+ \eta_{i\beta})/2; \quad i \neq j \end{aligned} \quad (65b)$$

In addition, $\beta_{ij} = \beta_{ji}$ are resonance integrals, K is the effective potential energy of a π -electron which is the same on each carbon atom (i), and $\gamma_{ij} = \gamma_{ji}$ are electron repulsion integrals

$$\gamma_{ij} = \int w_i(1) w_i(1) 1/r_{12} w_j(2) w_j(2) d1 d2 \quad (66)$$

Up to the constant, the Hamiltonian (65) is identical to the PPP Hamiltonian as defined by McLachlan.⁴ The form (65) is, however, more suitable for our purpose here. In the case of alternant hydrocarbons, resonance integrals β_{ij} vanish if atoms (i) and (j) are of the same parity. Using reduced spin-independent operators (25) one finds

$$\begin{aligned} \Sigma \mathbf{q}_i &= 1/2 \Sigma \mathbf{R}_{ii}^0 + n \mathbf{I} \\ \mathbf{p}_{ij} &= 1/2 \mathbf{R}_{ij}^0 \\ (\mathbf{q}_i - 1) (\mathbf{q}_j - 1) &= 1/2 \mathbf{R}_{ij,ji}^0 + 1 \\ (\mathbf{q}_i^\alpha - 1/2) (\mathbf{q}_i^\beta - 1/2) &= 1/4 (\mathbf{R}_{ii,ii}^0 + 1) \end{aligned} \quad (67)$$

Since $\mathbf{R}_{ii}^0 = \mathbf{R}_{i\alpha,i\alpha} + \mathbf{R}_{i\beta,i\beta}$, relations (7) imply $\Sigma_i \mathbf{R}_{ii}^0 = \mathbf{Z}^s$ and hence $\Sigma_i \mathbf{R}_{ii}^0/2$ vanishes over X_n . The operator $\Sigma_i \mathbf{q}_i$ is thus a linear combination of a spin-independent alternant operator $n\mathbf{I}$, and a vanishing operator \mathbf{Z}^s . Consider now bond order operator \mathbf{p}_{ij} . These operators are spin-independent alternant operators whenever vertices (i) and (j) are of opposite parity. In the case of alternant hydrocarbons, the partition of vertices (i) on source and sink can be chosen so that it coincides with the partition of carbon atoms on starred and nonstarred ones.^{10,12} This being assumed, all bond operators \mathbf{p}_{ij} contained in the expression $\mathbf{O}_2 = \sum_{i,j} \beta_{ij} \mathbf{p}_{ij}$ are alternant operators, and hence \mathbf{O}_2 is an

alternant operator as well. Further, operators $\mathbf{R}_{ij,ji}^0$ and $\mathbf{R}_{ii,ii}^0$ are alternant operators irrespective of the parity of indices (i) and (j). The PPP Hamiltonian (65) is hence a linear combination of a spin-independent alternant operator and an operator vanishing over X_n , i. e. it is of the form (61) and hence it describes a spin-independent alternant system. This proves that in the case of neutral alternant hydrocarbons the eigenstates of the PPP Hamiltonian \mathbf{H}_p have all the properties discussed in the preceding section. In particular, these eigenstates satisfy spin-independent properties (35), etc.

In the treatment of the eigenstates of the PPP Hamiltonian (65) associated with neutral alternant hydrocarbons, McLachlan has shown that »even« and »odd« eigenstates of this Hamiltonian have a uniform charge density distribution over all carbon atoms and vanishing bond orders between carbon atoms of the same parity,⁴ i. e. he has derived properties (35a) and (35b) for such eigenstates. Even and odd functions were originally introduced by Pariser in connection with the classification of the SCF π -electron eigenstates of neutral alternant hydrocarbons.²² He classified singly-excited states into plus and minus types, and McLachlan generalized this notion to the corresponding CI space. Plus states as defined by Pariser are odd states as defined by McLachlan.⁴ It can be shown that even and odd eigenstates of the PPP Hamiltonian (65a) are SAL states.¹⁶ On the one hand, eigenstates of this Hamiltonian are either even or odd.⁴ On the other hand, we have shown here that, unless there is some additional degeneracy, all eigenstates $\psi \in X_n$ of the Hamiltonian (65a) are SAL states. Hence, each even and each odd eigenstate $\psi \in X_n$ of this Hamiltonian should be a SAL state. However, these states are not necessarily AL states.¹⁶ This establishes the connection between the MO approach which is based on the pairing theorem and our approach here which is based on the splitting theorem.

The PPP Hamiltonian for a nonalternant hydrocarbon system is identical to the PPP Hamiltonian for the alternant system, except that resonance integrals β_{ij} are now allowed to be arbitrary. Hence, it contains spin-independent antialternant operators \mathbf{p}_{ij} with (i) and (j) of the same parity, i. e. it is of a general form (63). Similarly, if the PPP Hamiltonian describes a conjugated heterocompound with the heteroatom at the vertex (s), effective potential energy K_s of a π -electron situated at this heteroatom differs from the effective potential energy K , and to the operator (65) one has to add the perturbation

$$\delta K_{q_s} = 1/2 \delta K \mathbf{R}_{ss}^0 + \delta K \mathbf{I} = \mathbf{O}_{\text{nal}}^0 + \mathbf{O}_{\text{al}}^0 \quad (63)$$

where $\delta K = K_s - K$. There is also a change in the resonance integrals β_{si} and in the Coulomb integrals γ_{ss} and γ_{si} . However, these integrals are associated with spin-independent alternant operators. Hence, the PPP Hamiltonian is again of the general form (63), since it contains a spin-independent antialternant operator $1/2 \delta K \mathbf{R}_{ss}^0$ which does not vanish over X_n . In both cases, as in numerous others of the type (63), eigenstates of the PPP Hamiltonian are in general not SAL states. Hence, they usually do not satisfy spin-independent properties (35), but they can be represented in the form (64).

b) Consider the Hamiltonian operator

$$\mathbf{H}_h = \sum f_{ij} \mathbf{S}_i \mathbf{S}_j \quad (69)$$

where $f_{ij} = f_{ji}^*$ are coefficients forming a hermitian matrix, while $\mathbf{S}_i \equiv (\mathbf{S}_{ix}, \mathbf{S}_{iy}, \mathbf{S}_{iz})$ is a spin operator associated with the vertex (i):

$$\begin{aligned}\mathbf{S}_{ix} &= 1/2 (\eta_{i\alpha}^+ \eta_{i\beta} + \eta_{i\beta}^+ \eta_{i\alpha}) \\ \mathbf{S}_{iy} &= \sqrt{-1} 1/2 (\eta_{i\beta}^+ \eta_{i\alpha} - \eta_{i\alpha}^+ \eta_{i\beta}) \\ \mathbf{S}_{iz} &= 1/2 (\eta_{i\alpha}^+ \eta_{i\alpha} - \eta_{i\beta}^+ \eta_{i\beta})\end{aligned}\quad (70)$$

Besides magnetic dipole interaction between two spin-1/2 particles, the term $\mathbf{S}_i \mathbf{S}_j$ in (69) can also describe the exchange interaction between these particles.²³ Such an interaction is due to the Pauli exclusion principle; it is much larger than the magnetic dipole interaction, and it does not depend explicitly on spin.²³ In physics, the Hamiltonian (69) is known as the Heisenberg spin model, and it describes ferromagnetic and antiferromagnetic systems.^{23,24} In chemistry, the same Hamiltonian describes neutral conjugated hydrocarbons within the simple valence bond (VB) theory.²⁵ In this latter case $f_{ij} \neq 0$ for directly bonded carbon atoms, and $f_{ij} = 0$ otherwise.²⁵ The usual treatment of the Hamiltonian (69) is to assume that at each vertex (i) there is a particle which is either in the spin- α or in the spin- β state.²³ Accordingly, eigenstates of the operator (69) are expanded in terms of the basis vectors

$$\begin{aligned}\eta_{1\alpha}^+ \eta_{2\alpha}^+ \cdots \eta_{n\alpha}^+ |0\rangle \\ \eta_{1\beta}^+ \eta_{2\alpha}^+ \cdots \eta_{n\alpha}^+ |0\rangle \\ \eta_{1\beta}^+ \eta_{2\beta}^+ \cdots \eta_{n\beta}^+ |0\rangle\end{aligned}\quad (71a)$$

containing no pair $\{\eta_{i\alpha}^+, \eta_{i\beta}^+\}$ of creation operators associated with the same vertex (i). Formally, vectors (71a) span some linear subspace of the space X_n . Besides these vectors, the space X_n contains vectors such as

$$\eta_{1\alpha}^+ \eta_{1\beta}^+ \cdots |0\rangle\quad (71b)$$

etc. containing two electrons of the opposite spin situated at the same vertex. We will treat the Hamiltonian \mathbf{H}_h from this more general point of view, i. e. we will consider the whole space X_n , and not only its subspace spanned by vectors (71a). The restriction of the space X_n to the subspace spanned by vectors (71a) may be partly justified on the grounds that for the usual choices of the coefficients f_{ij} , basis vectors of the type (71b) are energetically less favourable than basis vectors (71a), and that, in addition, there is no interaction between basis vectors (71a) and other vectors in the space X_n . Hence, the energetically lowest eigenstates of the Hamiltonian \mathbf{H}_h can be expanded in terms of basis vectors (71a). However, we would like to treat a Hamiltonian (69) for an arbitrary selection of coefficients f_{ij} and not only for those rendering basis vectors of the type (71b) less favourable. Even more important is that a Hamiltonian (69) may be considered as an approximation to a more realistic Hamiltonian containing terms which couple basis vectors (71a) with other basis vectors in X_n . In general, no eigenstate of such a perturbed Hamiltonian lies entirely in the space spanned by vectors (71a), but rather contains nonvanishing components of the type (71b).

Let us now consider eigenstates of \mathbf{H}_h in X_n . Operators \mathbf{n}_i

$$\mathbf{n}_i = \eta_{i\alpha}^+ \eta_{i\alpha} + \eta_{i\beta}^+ \eta_{i\beta}\quad (72)$$

which describe the total number of particles at the vertex (i) commute with \mathbf{H}_h , \mathbf{S}^2 and \mathbf{S}_z . Hence, there is a basis in X_n which simultaneously diagonalizes \mathbf{H}_h , \mathbf{S}^2 , \mathbf{S}_z and \mathbf{n}_i ($i = 1$ to n). Each operator \mathbf{n}_i has eigenvalues $n_i = 0, 1, 2$. Basis vectors (71a) are eigenstates of operators \mathbf{n}_i with the eigenvalues $n_i = 1$ ($i = 1$ to n). Hence, the eigenstates of \mathbf{H}_h spanned by these basis vectors correspond to eigenvalues $n_i = 1$ ($i = 1$ to n) of operators \mathbf{n}_i . One easily selects in X_n all basis vectors corresponding to the particular set $\{n_1, n_2, \dots, n_n\}$ ($\sum n_i = n$) of eigenvalues of operators \mathbf{n}_i . These basis vectors span a subspace in X_n , and one can diagonalize \mathbf{H}_h in this subspace in the same way as \mathbf{H}_h is usually diagonalized in the subspace spanned by vectors (71a). One finds that all doubly occupied vertices, i. e. such which are associated with the eigenvalue $n_i = 2$, do not interact with other vertices. Hamiltonian \mathbf{H}_h is effective only between vertices occupied by one electron, i. e. those which correspond to the eigenvalue $n_i = 1$. Note that among the above eigenstates of \mathbf{H}_h , only those spanned by vectors (71a) have a uniform charge over all vertices (i). In the case of all other simultaneous eigenstates of \mathbf{H}_h and operators \mathbf{n}_i there is at least one vertex where the charge equals two, and at least one vertex where the charge vanishes. Since each SAL state satisfies (35), such eigenstates of H_h are not SAL states.

Let us now treat the Hamiltonian \mathbf{H}_h from the points of view of the general method developed in this paper. Using relations (2) spin operators $\mathbf{S}_i \equiv (\mathbf{S}_{ix}, \mathbf{S}_{iy}, \mathbf{S}_{iz})$ can be expressed in terms of the reduced operators

$$\begin{aligned} \mathbf{S}_{ix} &= 1/2 \mathbf{R}_{i\alpha, i\beta} \\ \mathbf{S}_{iy} &= -1/2 \mathbf{P}_{i\alpha, i\beta} \\ \mathbf{S}_{iz} &= 1/4 (\mathbf{R}_{i\alpha, i\alpha} - \mathbf{R}_{i\beta, i\beta}) \end{aligned} \quad (73)$$

and according to (5) operators \mathbf{S}_{iy} and \mathbf{S}_{iz} are antialternant, while operators \mathbf{S}_{ix} are alternant. It follows from Corollary 2 that each operator $\mathbf{S}_i \mathbf{S}_j$ is an alternant operator. In addition, using the anticommutation algebra of creation and annihilation operators η^+ and η one finds that $\mathbf{S}_i \mathbf{S}_j$ commutes with the components of the total spin operator \mathbf{S} , i. e. that it is a spin-independent operator. The same conclusion can be drawn explicitly since relations (25) imply

$$\mathbf{S}_i \mathbf{S}_j = -1/8 (2 \mathbf{R}_{ij, ij}^o + \mathbf{R}_{ij, ji}) \quad (74)$$

i. e. $\mathbf{S}_i \mathbf{S}_j$ is a linear combination of spin-independent alternant operators. The Hamiltonian H_h is hence a spin-independent alternant operator and it describes a spin-independent alternant system.²⁷ All conclusions derived in the preceding section about spin-independent alternant operators are hence valid in the case of the operator \mathbf{H}_h as well. For example, there exists a complete set of common eigenstates to \mathbf{H}_h , \mathbf{S}^2 and \mathbf{S}_x satisfying relations (12), as well as a complete set of common eigenstates to \mathbf{H}_h , \mathbf{S}^2 and \mathbf{S}_z satisfying spin-independent properties (35), etc. In addition, in the particular case of the operator \mathbf{H}_h one can draw some other interesting conclusions. Common eigenstates to \mathbf{H}_h , \mathbf{S}^2 and \mathbf{S}_z satisfying relations (35) are SAL states, but we have shown above that \mathbf{H}_h contains many eigenstates which are not SAL states. These states are, hence, linear combinations of SAL states, and it follows that, irrespective of

the numerical values of the coefficients f_{ij} , eigenstates of the Hamiltonian operator (69) have degeneracy which is not due to the spin multiplicity. One can express SAL states which are common eigenstates to \mathbf{H}_h , \mathbf{S}^2 and \mathbf{S}_z in terms of the common eigenstates to \mathbf{H}_h , \mathbf{S}^2 , \mathbf{S}_z and \mathbf{n}_i ($i = 1$ to n).¹⁶ It should also be noted that using (74) the square $\mathbf{S}^2 = \sum_{ij} \mathbf{S}_i \mathbf{S}_j$ of the total spin operator \mathbf{S} can be explicitly written as a linear combination of spin-independent alternant operators. The operator \mathbf{S}^2 is hence a spin-independent alternant operator, which we have already independently concluded in the fourth section.

It is instructive to compare the PPP Hamiltonian \mathbf{H}_p formulated within the MO theory with the Hamiltonian \mathbf{H}_h which can be considered to be a simple VB Hamiltonian. The former Hamiltonian is alternant, provided resonance integrals β_{ij} vanish between carbon atoms of the same parity, i. e. provided it describes an alternant hydrocarbon system. The latter Hamiltonian is alternant irrespective of the hydrocarbon system it describes, i. e. it is an alternant operator even if it describes nonalternant hydrocarbons. Hence, the PPP Hamiltonian \mathbf{H}_p clearly distinguishes between alternant and nonalternant hydrocarbons, and in particular it predicts charge polarization in the case of nonalternant hydrocarbons, while the simple VB Hamiltonian \mathbf{H}_h is unable to predict this charge polarization. This also explains why the pairing theorem,²⁻⁵ or any of its equivalents, was originally formulated within the MO and not within the VB approach.

c) The PPP Hamiltonian (65) was very successful in describing π -electron eigenstates of conjugated alternant hydrocarbons. However, this Hamiltonian explicitly neglects all two-particle interactions, except for Coulomb interactions. Thus, the operator $(\mathbf{q}_i - 1)(\mathbf{q}_j - 1)$ contained in the third term of the Hamiltonian (65a) corresponds to the Coulomb interaction between effective charges on atoms (i) and (j), while the operator $(\mathbf{q}_i^\alpha - 1/2)(\mathbf{q}_i^\beta - 1/2)$ contained in the last term of this Hamiltonian describes the Coulomb interaction between two electrons with opposite spins situated at the same atom (i). One can add to the Hamiltonian (65), as well as to the Hamiltonian (69), any linear combination of spin-independent alternant operators (27a) without altering the general properties of the corresponding eigenstates, as expressed by Theorem 3. In particular, one can consider the Hamiltonian

$$\mathbf{H} = \mathbf{H}_p + \mathbf{H}_h \quad (75)$$

where \mathbf{H}_p is alternant. This Hamiltonian again describes a spin-independent alternant system. One can look upon the Hamiltonian (75) as the refinement of the PPP Hamiltonian \mathbf{H}_p with the inclusion of the spin-spin interactions and/or exchange interactions. Alternatively, one can consider this Hamiltonian as a more realistic Heisenberg (simple VB) Hamiltonian \mathbf{H}_h which includes resonance integrals β_{ij} , Coulomb integrals γ_{ij} , etc.

We could now give many other examples of operators describing spin-independent alternant systems. All these operators can be written in the general form (61). Once the operator is shown to be of this type, its eigenstates possess all the properties derived in the preceding sections.

10. SUMMARY AND CONCLUSION

We have considered the CI space X_n generated by n electrons moving over n spin- α orbitals $X_i = w_i \alpha$ and n spin- β orbitals $X_i = w_i \beta$, w_i being orthonormalized atomic orbitals. The space X_n is a direct sum of complementary subspaces X_n^+ and X_n^- containing alternantlike (AL) states.¹⁰ These states satisfy properties (12) which are not shared by arbitrary states $\psi \in X_n$.¹² In order to derive these properties one has to define reduced alternant and reduced antialternant operators which span the space of all alternant and the space of all antialternant operators, respectively.¹² These results were obtained elsewhere,¹⁰⁻¹³ and using a similar approach we have investigated here spin-independent operators and spin-independent properties. Such an analysis is highly interesting, since many Hamiltonians describing actual physical systems are spin-independent operators. The following results were obtained:

a) A set of all¹⁴ reduced spin-independent alternant and spin-independent antialternant operators is obtained (eqs. 25 to 27). Each spin-independent alternant operator is a linear combination of reduced spin-independent alternant operators, and each spin-independent antialternant operator is a linear combination of reduced spin-independent antialternant operators. An arbitrary spin-independent operator can be represented as a linear combination of a spin-independent alternant and a spin-independent antialternant operator. This representation is unique. Reduced spin-independent operators thus serve as »building blocks« of spin-independent alternant and spin-independent antialternant operators.

b) Semi-alternantlike (SAL) states are defined. These states generalize the notion of AL states, and this generalization is necessary in order to investigate spin-independent properties of spin eigenstates. Each SAL state is of the form $\psi = \mathbf{U} \psi^\pm$, where \mathbf{U} is a unitary operator, a function of spin operators \mathbf{S}_x , \mathbf{S}_y and \mathbf{S}_z ,²⁰ while $\psi^\pm \in X_n^\pm$ is an alternantlike state. A complete set of all one- and two-particle spin-independent linear properties of SAL states is obtained. This set is the same as the complete set of all one- and two-particle spin-independent linear properties of AL states. In other words, there is no spin-independent linear property common to AL states which is not at the same time common to SAL states as well. In particular, it is shown that SAL states have a uniform total charge density distribution over atomic orbitals w_i , vanishing total bond orders between atomic orbitals of the same parity, etc. These properties are natural generalizations of the properties of π -electron eigenstates associated with neutral alternant hydrocarbons.

c) Standard representations $\{\mathbf{S}^2, \mathbf{S}_z\}$ and $\{\mathbf{S}^2, \mathbf{S}_x\}$ in X_n are considered. Each orthonormalized set $\{\psi_{s,m,\tau}^z\}$ of common eigenstates of operators \mathbf{S}^2 and \mathbf{S}_z defines a representation with \mathbf{S}^2 and \mathbf{S}_z diagonal. Standard representation $\{\mathbf{S}^2, \mathbf{S}_z\}$ is such a representation in which the basic vectors corresponding to a specified value of the quantum number s can be grouped into one or several series of $(2s + 1)$ vectors connected to each other via operators $\mathbf{S}_+^z = \mathbf{S}_x + i\mathbf{S}_y$ and $\mathbf{S}_-^z = \mathbf{S}_x - i\mathbf{S}_y$.¹⁸ An analogous property is satisfied by standard representations $\{\mathbf{S}^2, \mathbf{S}_x\}$. It is shown that standard representations $\{\mathbf{S}^2, \mathbf{S}_z\}$

and $\{\mathbf{S}^2, \mathbf{S}_x\}$ can be chosen in such a way as to satisfy the following additional properties:

1) The $(2s + 1)$ vectors $\psi^z_{s,m,\tau}$ (variable m) and the $(2s + 1)$ vectors $\psi^x_{s,m,\tau}$ (variable m) span the same space $\varepsilon_{s,\tau}$. The space X_n is a direct sum of subspaces $\varepsilon_{s,\tau}$.

2) Each space $\varepsilon_{s,\tau}$ contains only SAL states. Some of these SAL states can also be AL states.

3) Each basis vector $\psi^x_{s,m,\tau}$, common eigenstate to operators \mathbf{S}^2 and \mathbf{S}_x , is an AL state. In addition, if $\psi^x_{s,m,\tau} \in X_n^+$, then $\psi^x_{s,m\pm 1,\tau} \in X_n^-$, and vice versa.

4) Basis vectors $\psi^z_{s,o,\tau}$ are AL states. In particular, all singlet states $\psi^z_{o,o,\tau}$ are AL states.

5) Basis vectors $\psi^z_{s,m,\tau}$ ($m \neq 0$) satisfy relations (48) where $\psi^+ \in X_n^+$ and $\psi^- \in X_n^-$ are AL states. In particular, these vectors are SAL states, but they are not AL states. However, linear combinations $\psi^z_{s,m,\tau} \pm \psi^z_{s,-m,\tau}$ are AL states.

6) Many additional properties of basis vectors $\psi^z_{s,m,\tau}$ and basis vectors $\psi^x_{s,m,\tau}$ are also obtained in the paper.

7) If the standard representation $\{\mathbf{S}^2, \mathbf{S}_z\}$ satisfies property 4), then there is a standard representation $\{\mathbf{S}^2, \mathbf{S}_x\}$, so that these two standard representations satisfy properties 1) through 6). Similarly, if the standard representation $\{\mathbf{S}^2, \mathbf{S}_x\}$ satisfies property 3), then there is a standard representation $\{\mathbf{S}^2, \mathbf{S}_z\}$, so that these two standard representations satisfy properties 1) through 6). In the former case we say that the representation $\{\mathbf{S}^2, \mathbf{S}_z\}$ is »alternantlike« (AL), while in the latter case we say that AL is the representation $\{\mathbf{S}^2, \mathbf{S}_x\}$. If standard representations $\{\mathbf{S}^2, \mathbf{S}_z\}$ and $\{\mathbf{S}^2, \mathbf{S}_x\}$ are AL, and if in addition they are in accord with each other, i. e. if they satisfy the point 1) above, then we say that they are »complementary«.

d) Let $\mathbf{H} = \mathbf{H}^0_{al} + \mathbf{Z}$ be a Hamiltonian operator where \mathbf{H}^0_{al} is a spin-independent alternant operator, while \mathbf{Z} is an operator vanishing over X_n . Eigenstates of \mathbf{H} can be chosen to be in accord with complementary AL representations $\{\mathbf{S}^2, \mathbf{S}_z\}$ and $\{\mathbf{S}^2, \mathbf{S}_x\}$, i. e. with properties c) above. If besides the spin multiplicity there is no other degeneracy, this choice is unique. In particular, common eigenstates to \mathbf{H} , \mathbf{S}^2 and \mathbf{S}^z are SAL states $\psi^z_{s,m,\tau}$, common eigenstates to \mathbf{H} , \mathbf{S}^2 and \mathbf{S}_x are AL states $\psi^x_{s,m,\tau}$, etc. All these eigenstates satisfy spin-independent properties (35). In addition, those eigenstates which are AL states (e. g. eigenstates $\psi^x_{s,m,\tau}$) satisfy more demanding properties (12). Hamiltonian operators of the form $\mathbf{H} = \mathbf{H}^0_{al} + \mathbf{Z}$ are hence considered to describe spin-independent alternant systems, and this operator form is taken as a definition of such systems.

Using the results obtained in this paper one can get an exhaustive insight into the scope of spin-independent properties associated with alternant systems. All spin-independent alternant systems can easily be constructed and identified. The corresponding eigenstates possess remarkable properties (35). Arbitrary spin-independent systems can also be analyzed using the same formalism. In this case the corresponding eigenstates are not necessarily SAL states and they do not satisfy spin-independent properties (35). However, each eigenstate can still be represented as a linear combination of SAL states.

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15. Reduced operators $\mathbf{R}_{ik,jk}$, $\mathbf{P}_{ik,jk}$ and $\mathbf{R}_{ij,ij}$ ($i \neq j \neq k$), as defined in (2a), differ from the same operators as defined previously.¹¹⁻¹³ Previous definition of these operators was: $\mathbf{R}_{ik,jk} = 2\mathbf{A}_{ik,jk} + \mathbf{A}_{ij}$,¹¹⁻¹³ $\mathbf{P}_{ik,jk} = 2\mathbf{B}_{ik,jk} + \mathbf{B}_{ij}$ ¹² and $\mathbf{R}_{ij,ij} = 2\mathbf{A}_{ij,ij} + \mathbf{A}_{ii} + \mathbf{A}_{jj} - \mathbf{I}$.¹¹⁻¹³ In the case of operators $\mathbf{R}_{ik,jk}$ and $\mathbf{P}_{ik,jk}$ we have changed the normalization constant, while in the case of the operators $\mathbf{R}_{ij,ij}$ we have in addition deleted the unit operator \mathbf{I} . One easily finds that the new definition does not effect the splitting theorem or any of its consequences. Operators $\mathbf{R}_{ij,ij}$ are alternant as defined in the old or in the new way, and similarly, operators $\mathbf{R}_{k,jk}$ and $\mathbf{P}_{k,jk}$ retain their symmetry properties. The present definition is chosen in order to express all reduced operators $\mathbf{R}_{ij,kl}$ and $\mathbf{P}_{ij,kl}$ in the compact form (2c).
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SAŽETAK

Spinska vlastita stanja i alternantni sustavi

T. Živković

Razmatran je konfiguracijsko-interakcijski prostor X_n koji je izgrađen od $2n$ spinskih orbitala w_i, σ gdje w_i ($i = 1$ to n) određuje prostorni $a \sigma$ ($\sigma = \alpha, \beta$) spinski dio valne funkcije w_i, σ . Spinski neovisni alternantni sustavi definirani su s pomoću odgovarajućih hamiltonijana. Svaki od tih hamiltonijana je linearna kombinacija spinski-neovisnog alternatnog operatora O_{a1} i operatora Z koji se poništava preko prostora X_n . Prostor svih spinski-neovisnih alternantnih operatora jest linearni prostor razapet »reduciranim« spinsko-neovisnim alternirajućim operatorima koji su eksplicitno dani. Slično, prostor svih poništavajućih operatora Z razapet je nekim osnovnim operatorima koji su također jasno definirani. Slijedi da se svaki hamiltonijan spinsko-neovisnih alternantnih sustava može lako konstruirati i identificirati. Vlastita stanja tih hamiltonijana imaju niz interesantnih svojstava koja su u stvari generalizacija dobro poznatih svojstava neutralnih alternantnih ugljikovodika.