Antialternant Perturbations of Alternant Systems

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Rayleigh — Schrödinger perturbation expansion is applied to the system where the unperturbed Hamiltonian $H_0$ is chosen to be an alternant operator, while the perturbation $\lambda V$ is chosen to be an antialternant operator. A configuration interaction space $X$ generated by $n$ electrons moving over $2n$ orthonormalised orbitals is considered. This space splits into two mutually complementary subspaces $X_+$ and $X_-$ containing alternant-like states. These states have characteristic properties of the eigenstates associated with neutral alternant hydrocarbon systems. If the eigenstate $\Phi \in X$ of the unperturbed Hamiltonian $H_0$ is nondegenerate, then it is alternant-like, i.e. either $\Phi \in X_+$ or $\Phi \in X_-$, and without loss of generality one can assume $\Phi = \Phi^+ \in X_+$. In this case the eigenstate $\Psi(\lambda)$ of the total Hamiltonian $H = H_0 + \lambda V$, as expanded in the power series of the expansion parameter $\lambda$, is of the form $\Psi(\lambda) = \Phi^+ + \lambda \Psi^+_1 + \lambda^2 \Psi^+_2 + \lambda^3 \Psi^+_3 + \ldots$, where corrections to all orders are alternant-like states. In addition, all even corrections are contained in the space $X_+$, while all odd corrections are contained in the space $X_-$. The corresponding eigenvalue $E(\lambda)$ is an even function of the expansion parameter $\lambda$. Also, the expectation value of each alternant operator is an even function of $\lambda$, while the expectation value of each antialternant operator is an odd function of $\lambda$. In particular, these results are applied to the matrix elements of one- and two-particle density matrices, and a simple example illustrating these properties is given.

1. INTRODUCTION

Perturbation expansion is a very powerful scheme in the treatment of various quantum chemical problems. The Hamiltonian $H$ of the system is usually written as a sum of two parts, the unperturbed Hamiltonian $H_0$, and the perturbation $\lambda V$, where $\lambda$ is a parameter

$$H = H_0 + \lambda V$$

(1)

All the properties of a system, like eigenvalues, expectation values of different operators etc. are then expanded in the power series of the parameter $\lambda$. In principle, the splitting (1) is arbitrary. However, the unperturbed Hamiltonian $H_0$ is usually chosen in such a way that it can be easily diagonalised, while the perturbation $\lambda V$ is required to be »small« in order to obtain fast convergence.

This paper deals with a special kind of perturbation expansion where the unperturbed Hamiltonian is chosen to be an »alternant« operator, while the
perturbation is chosen to be an »antialternant« operator. The definition and properties of alternant and antialternant operators can be found in the preceding paper\textsuperscript{1}, as well as in Refs. 2 and 3. We follow throughout this paper the notation and conventions of Ref. 1.

The notion of these operators and related spaces is obtained within the wider scope of the molecular orbital resonance theory (MORT) approach, which is discussed elsewhere.\textsuperscript{2-4} However, for the purpose of this paper, a few points should be emphasized: firstly, each symmetric operator can be written as a sum of an alternant and an antialternant operator, and there is a simple algorithm to obtain this splitting.\textsuperscript{1,2} Secondly, if the configuration interaction (CI) space \( X_n \) generated by \( n \) electrons moving over \( 2n \) ortho-normalised orbitals \( \psi_i \) is considered, then the eigenstates of an alternant operator are »alternant-like« in the sense that they have all the characteristic properties of the eigenstates of neutral alternant hydrocarbon (AH) systems.\textsuperscript{1-3} In particular, they have uniform charge density distribution over all orbitals \( \psi_i \), vanishing bond orders between orbitals of the same parity etc.\textsuperscript{1-3} It can be shown that the space \( X_n \) can be split into two mutually orthogonal subspaces \( X_n^+ \) and \( X_n^- \) such that each state \( \psi = \psi' \in X_n^+ \) as well as each state \( \psi = \psi' \in X_n^- \) is alternant-like.\textsuperscript{1-3} Hence polarised states, which have arbitrary charge density distribution and arbitrary bond orders, necessarily have non-vanishing components in both subspaces \( X_n^+ \) and \( X_n^- \). This suggests that it should be much easier to diagonalise the Hamiltonian \( H_0 \) having alternant-like eigenstates, than to diagonalise the complete Hamiltonian \( H \) of the system. One can further show that the antialternant perturbation is usually »small«, at least when the ground state is considered.\textsuperscript{5} In conclusion, the splitting of an arbitrary symmetric Hamiltonian into its alternant and antialternant part is easy to perform and promises to yield a rather rapid convergence. This is already quite a good reason to try to perform such an expansion. There are however some additional rather interesting properties of this expansion, and these properties are the subject of this paper.

The most important result is the expansion theorem derived in the second section. This theorem states essentially the following: if the eigenstate \( \Phi_0 \in X_n \) of the unperturbed Hamiltonian is nondegenerate, then this eigenstate, as well as corrections to all orders in \( \lambda \) (\( \psi_1, \psi_2, \psi_3, \ldots ) \) in the expansion \( \psi (\lambda) = \Phi_0 + \lambda \psi_1 + \lambda^2 \psi_2 + \ldots \), are alternant-like. In addition, provided that \( \Phi_0 \in X_n^+ \) (which can be assumed without loss of generality), all even corrections \( \psi_2, \psi_4, \psi_6, \ldots \) are also contained in the space \( X_n^+ \), while all odd corrections \( \psi_1, \psi_3, \ldots \) are contained in the space \( X_n^- \). From this theorem three simple corollaries are derived: the corresponding eigenvalue \( E (\lambda) \) is an even function of \( \lambda \) (corollary 1), the expectation value of each alternant operator is an even function of \( \lambda \) (corollary 2), and finally, the expectation value of each antialternant operator is an odd function of \( \lambda \) (corollary 3). In the third section these corollaries are used in order to derive some relations satisfied by matrix elements of one- and two-particle density matrices. For example, it is shown that the off-diagonal matrix element \( \gamma_{ij} (\lambda) \) of a one-particle density matrix \( \gamma \) is an even function of \( \lambda \) if vertices (i) and (j) are of the opposite parity, and an odd function of \( \lambda \) otherwise. Concerning diagonal matrix elements \( \gamma_{ii} (\lambda) \), it is shown that the expression \( [\gamma_{ii} (\lambda) - 1/2] \) is an odd function of \( \lambda \) etc. Finally, in the fourth section a simple example illustrating the above properties of the antialternant perturbation is given.
2. THE EXPANSION THEOREM

In the standard time-independent perturbation theory Hamiltonian $H$ is usually written in the form (1) where $H_0$ is an unperturbed Hamiltonian, $V$ is a perturbation, and $\lambda$ is a real parameter. If $\Phi_0$ is a nondegenerated eigenstate of the unperturbed Hamiltonian $H_0$

$$H_0 \Phi_0 = E_0 \Phi_0$$

then there is a unique eigenstate $\Psi = \Psi(\lambda)$ of the Hamiltonian $H$ which is a continuous function of $\lambda$ and which for $\lambda = 0$ coincides with $\Phi_0$

$$H \Psi(\lambda) = E(\lambda) \Psi(\lambda)$$

$$\Psi(0) = \Phi_0$$

the norm of this state being normalised with the condition

$$\langle \Psi | \Phi_0 \rangle = 1$$

If the perturbation $\lambda \cdot V$ is «small», one can expand $E(\lambda)$ and $\Psi(\lambda)$ in the power series of $\lambda$

$$E(\lambda) = E_0 + \lambda \varepsilon_1 + \lambda^2 \varepsilon_2 + \lambda^3 \varepsilon_3 + \ldots$$

$$\Psi(\lambda) = \Phi_0 + \lambda \Psi_1 + \lambda^2 \Psi_2 + \lambda^3 \Psi_3 + \ldots$$

and the condition (3a) is equivalent to

$$\langle \Psi_1 | \Phi_0 \rangle = \langle \Psi_2 | \Phi_0 \rangle = \ldots = \langle \Psi_k | \Phi_0 \rangle = \ldots = 0$$

Energies $\varepsilon_k$ are given by

$$\varepsilon_k = \langle \Phi_0 | V | \Psi_{k-1} \rangle$$

while vectors $\Psi_k$ can be expanded in terms of the eigenstates $\Phi_i$ of the unperturbed Hamiltonian $H_0$

$$\Psi_k = \Sigma_{i=0}^{k} \langle \Phi_i | \Psi_k \rangle | \Phi_i \rangle$$

where

$$\langle \Phi_i | \Psi_1 \rangle = \langle \Phi_i | V | \Phi_0 \rangle/[E_0 - E_i]$$

$$\langle \Phi_i | \Psi_k \rangle = [\langle \Phi_i | V - \varepsilon_1 | \Psi_{k-1} \rangle - \varepsilon_2 \langle \Phi_i | \Psi_{k-2} \rangle - \ldots - \varepsilon_k \langle \Phi_i | \Phi_0 \rangle]/[E_0 - E_i], \quad k > 1$$

and

$$H_0 \Phi_i = E_i \Phi_i$$

This is a standard procedure of the Rayleigh-Schrödinger perturbation theory.

Assume now that the Hamiltonian is partitioned in the following way

$$H = H_{al} + \lambda H_{nal}$$

where the unperturbed Hamiltonian $H_0 = H_{al}$ is an alternant operator, while the perturbation $\lambda \cdot V = \lambda H_{nal}$ is an antialternant operator. Since the eigenstate $\Phi_0$ of the unperturbed Hamiltonian is assumed nondegenerate, it follows from the splitting theorem that it is alternant-like. Without loss of generality one can assume $\Phi_0 \in X_n^+$, and to stress this fact we write $\Phi_0 = \Phi_0^+$. We will now
show that under these assumptions $\Psi_k \in X_n^+$ implies $\Psi_{k+1} \in X_n^-$ and $\Psi_k \in X_n^-$ implies $\Psi_{k+1} \in X_n^+$. In other words, we will derive

Theorem 1 (the Expansion Theorem)

Let $H = H_{al} + \lambda H_{nal}$ be the symmetric Hamiltonian operator constructed out of $2n$ creation and $2n$ annihilation operators $\eta_i^+$ and $\eta_i^-$, respectively. Assume that the unperturbed Hamiltonian $H_{al}$ is an alternant operator, and that the perturbation $H_{nal}$ is an antialternant operator. Further let $\Phi_0$ be a nondegenerate $n$-particle eigenstate of the unperturbed Hamiltonian $H_{al}$, and let $\Psi(\lambda)$ be the eigenstate of $H$ continuous in $\lambda$ and coinciding with $\Phi_0$ for $\lambda = 0$. Then the state $\Phi_0$ is alternant-like, i.e. either $\Phi_0 = \Phi_0^+ \in X_n^+$ or $\Phi_0 = \Phi_0^- \in X_n^-$, and without loss of generality one can assume $\Phi_0 = \Phi_0^+$. The expansion of the eigenstate $\Psi(\lambda)$ in the power series of the parameter $\lambda$ is then

$$\Psi(\lambda) = \Phi_0^+ + \lambda \Psi_1^+ + \lambda^2 \Psi_2^+ + \lambda^3 \Psi_3^- + \lambda^4 \Psi_4^+ + \ldots$$

where $\Psi_{k^+} \in X_n^+$ and $\Psi_{k^-} \in X_n^-$. In other words, corrections to all orders in the expansion parameter $\lambda$ are alternant-like. In addition, all even corrections are contained in the space $X_n^+$, while all odd corrections are contained in the complementary space $X_n^-$. 

Simultaneously with the above theorem we will also derive the following

Corollary 1

The eigenvalue $E(\lambda)$ of the Hamiltonian $H$ corresponding to the eigenstate $\Psi(\lambda)$ is an even function of $\lambda$

$$E(\lambda) = E_0 + \lambda^2 e_2 + \lambda^4 e_4 + \lambda^6 e_6 + \ldots$$

i.e. all odd corrections $e_1, e_3, e_5, \ldots$ in the expansion (4a) vanish.

In order to prove this theorem and the corollary we will first show that they are true up to the first order in the expansion parameter $\lambda$, i.e we will first show that $e_1 = 0$ and $\Psi_1 = \Psi_1^- \in X_n^-$. 

According to the relation (5) $e_1 = \langle \Phi_0^+ | H_{nal} | \Phi_0^+ \rangle$. Since the perturbation $H_{nal}$ is an antialternant operator, the splitting theorem implies $e_1 = 0$. Further, according to this theorem all eigenstates $\Phi_i$ of the unperturbed Hamiltonian $H_{al}$ can be chosen to be alternant-like, i.e. either $\Phi_i \in X_n^+$ or $\Phi_i \in X_n^-$. From the relations (6b) it now follows

$$\langle \Phi_i | \Psi_1^- \rangle = \langle \Phi_i | H_{nal} | \Phi_0^+ \rangle / [E_0 - E_1] = 0$$

whenever $\Phi_i \in X_n^+$. The state $\Psi_1$ has no component in the space $X_n^+$, and hence $\Psi_1 = \Psi_1^- \in X_n^-$. This proves the expansion theorem and the corollary 1 up to the first order in the expansion parameter $\lambda$.

Assume now that this theorem and the corollary are true up to some $k$-th ($k \geq 1$) order in the expansion parameter $\lambda$, i.e. assume that for each $i \leq k$

- a) $e_i = 0$ and $\Psi_i = \Psi_i^- \in X_n^-$ if $i$ is odd and
- b) $\Psi_i = \Psi_i^+ \in X_n^+$ if $i$ is even

We will show that under this assumption the above theorem and corollary are true up to the $(k+1)$-th order in the expansion parameter $\lambda$ as well.
Consider first the case of even \( k \). According to the above assumption \( \Psi_k = \Psi_k^* \in X_n^* \). Since \( H_{\text{sal}} \) is an antialternant operator the relation (6) and the splitting theorem imply
\[
\varepsilon_{k+1} = \langle \Phi_k^* | H_{\text{sal}} | \Psi_k^* \rangle = 0 \tag{10}
\]
where \( k + 1 \) is now odd. Further, one has
\[
\langle \Phi_k^* | \Psi_{k+1}^* \rangle = \langle \Phi_k^* | H_{\text{sal}} | \Psi_k^* \rangle - \varepsilon_k \langle \Phi_k^* | \Psi_{k-1}^* \rangle - \ldots - \varepsilon_2 \langle \Phi_k^* | \Psi_1^* \rangle - E_0 = E_k
\tag{11}
\]
If now \( \Psi_1^* \in X_n^* \) one obtains \( \langle \Phi_1^* | \Psi_{k+1}^* \rangle = 0 \) since by the splitting theorem \( \langle \Phi_1^* | H_{\text{sal}} | \Psi_k^* \rangle = 0 \), while all overlaps \( \langle \Phi_i^* | \Psi_{k-1}^* \rangle \ldots \langle \Phi_i^* | \Psi_1^* \rangle \) vanish. The state \( \Psi_{k+1}^* \) has no component in the space \( X_n^* \), and hence \( \Psi_{k+1} = \Psi_{k+1}^* \in X_n^* \).

The case of odd \( k \) can be treated in a similar way. Thus, if the above assumption is true for some \( k \geq 1 \), then it is also true for \( k + 1 \). But we have shown that it is true for \( k = 1 \), and hence it is true for each \( k \). This completes the proof.

The above theorem and corollary are derived under the assumption that the unperturbed eigenstate \( \Psi_0 \) is nondegenerate. For the ground state this is usually the case. However, it should be noted that this condition can be also somewhat relaxed. Namely, the unperturbed eigenstate \( \Psi_0 \in X_n^* \) can be allowed to be degenerate, provided all the eigenstates of \( H_{\text{sal}} \) with the same eigenvalue as \( \Psi_0 \) are also contained in the space \( X_n^* \). In other words, if the unperturbed eigenstate is contained in one complementary space, then no other eigenstate corresponding to the same eigenvalue is allowed to be contained in the other complementary space.

The expansion theorem and corollary 1 have been derived here simultaneously. However, it is proper to consider relation (8) as a corollary since it is really a consequence of the expansion theorem. Namely, once this theorem is assumed, corollary 1 can be obtained by simply inserting the expansion (7) in the expression
\[
E(2) = \langle \Psi (2) | H | \Psi (2) \rangle / \langle \Psi (2) | \Psi (2) \rangle
\]
and using the splitting theorem. In a similar manner the following corollaries can be derived

**Corollary 2**

The expectation value \( \langle \hat{O}_{\text{sal}} | \lambda \rangle = \langle \Psi (\lambda) | \hat{O}_{\text{sal}} | \Psi (\lambda) \rangle / \langle \Psi (\lambda) | \Psi (\lambda) \rangle \) of an antialternant operator \( \hat{O}_{\text{sal}} \) in the state \( \Psi (\lambda) \) is an even function of \( \lambda \), i.e.
\[
\langle \hat{O}_{\text{sal}} | \lambda \rangle = O_0 + \lambda^2 O_2 + \lambda^4 O_4 + \ldots \tag{12}
\]
where \( O_0 = \langle \Psi_0 | \hat{O}_{\text{sal}} | \Psi_0 \rangle \), while \( O_2, O_4 \) etc. are coefficients which can be obtained by performing the actual perturbation expansion.

**Corollary 3**

The expectation value \( \langle \hat{O}_{\text{sal}} | \lambda \rangle \) of an antialternant operator \( \hat{O}_{\text{sal}} \) in the state \( \Psi (\lambda) \) is an odd function of the parameter \( \lambda \), i.e.
\[
\langle \hat{O}_{\text{sal}} | \lambda \rangle = \lambda O_1 + \lambda^3 O_3 + \lambda^5 O_5 + \ldots \tag{13}
\]
where coefficients \( O_1, O_3, O_5 \ldots \) can be obtained by performing the actual perturbation expansion.
The expansion theorem and the above corollaries describe the behaviour of an alternant system subjected to an antialternant perturbation, and they are quite general. Firstly, each symmetric Hamiltonian $H$ can be written as a sum of an alternant and an antialternant operator, i.e., in the form (1a), and hence one can in most cases apply the above approach. It is only required that the eigenstate $\Phi_0$ of the unperturbed Hamiltonian be an $n$-particle non-degenerate state, and the condition of nondegeneracy can be also somewhat relaxed\(^5\). Perturbation approach is then highly simplified by the special form of the expansion (7). Expectation values of alternant and antialternant operators are then even and odd functions of the expansion parameter $\lambda$, respectively. Since there is a simple algorithm to partition an arbitrary symmetric operator into its alternant and antialternant part\(^1,2\), this permits quite general qualitative analysis. It also simplifies quantitative predictions. Thus, it suffices to evaluate the expectation value of an alternant operator up to the zeroth order in the expansion parameter $\lambda$ in order to obtain results exact up to the first order, since according to corollary 2 all odd orders vanish. The zeroth order is however $O_0 = \langle \Phi_0 | O_{\text{alt}} | \Phi_0 \rangle$, which is the expectation value of the alternant operator $O_{\text{alt}}$ in the unperturbed state $\Phi_0$. In general, the expectation value of an alternant operator can always be evaluated up to some even order in the expansion parameter $\lambda$, which automatically yields the result which is exactly one order higher. Similarly, expectation value of an antialternant operator can be always evaluated up to some odd order in the expansion parameter $\lambda$ to obtain the result which is exactly one order higher. Furthermore, the definition of alternant and antialternant operators depends on the partition $B \rightarrow \{B^c, B^s\}$ of the set $B$ into source and sink subsets.\(^1,2\) Hence the partition of the Hamiltonian $H$ on the alternant and antialternant component also depends on the partition $B \rightarrow \{B^c, B^s\}$, and the flexibility in the choice of source and sink vertices can be used in order to make the antialternant perturbation $\lambda H_{\text{nal}}$ as small as possible.\(^5\) The above perturbation expansion can hence be expected to be relatively rapidly convergent. In addition, it is usually much easier to diagonalise the alternant Hamiltonian $H_{\text{alt}}$, since its eigenstates are alternant-like, and hence have a uniform charge density distribution with vanishing bond orders between vertices of the same parity \(\text{etc.}^1-3\). This leads to the simplification and even cancellation of many matrix elements.\(^5\) The splitting (1a) is hence rather natural in the sense that the unperturbed Hamiltonian $H_{\text{alt}}$ is relatively easy to diagonalise, while the perturbation $\lambda H_{\text{nal}}$ can usually be chosen to be »small«.

3. ANTIALTERNANT PERTURBATIONS AND DENSITY MATRICES

Corollaries 2 and 3 refer to arbitrary alternant and antialternant operators. In particular, they apply to reduced operators $R_{ij}^A$ and $R_{ij, kl}^A$. Using expressions (A1)—(A8) defining these operators, one can obtain the following relations satisfied by the matrix elements of one- and two-particle density matrices associated with the state $\Psi (\lambda)^A$:

a) One-Particle Density Matrices

Matrix elements $\gamma_{ij}^\lambda (\lambda)$

$$\gamma_{ij}^\lambda (\lambda) = \langle \Psi (\lambda) | A_{ij}/2 | \Psi (\lambda) \rangle / \langle \Psi (\lambda) | \Psi (\lambda) \rangle$$

(14)
of a one-particle density matrix $\gamma$ satisfy

$$\gamma_{ii}(\lambda) = 1/2 + \lambda \cdot \gamma_{ii}^{(1)} + \lambda^2 \cdot \gamma_{ii}^{(2)} + \lambda^3 \cdot \gamma_{ii}^{(3)} + \ldots \quad (15a)$$

$$\gamma_{ij}(\lambda) = \gamma_{ij}^{(0)} + \lambda^2 \cdot \gamma_{ij}^{(3)} + \lambda^3 \cdot \gamma_{ij}^{(4)} + \ldots$$

i and j are of opposite parity

and

$$\gamma_{ij}(\lambda) = \lambda \gamma_{ij}^{(1)} + \lambda^2 \gamma_{ij}^{(2)} + \ldots$$

i and j are of the same parity, \(i \neq j\)

where

$$\gamma_{ij}^{(0)} = \langle \Phi_0 \mid \hat{A}_{ij}/2 \mid \Phi_0 \rangle,$$

while

$$\gamma_{ij}^{(1)}, \gamma_{ij}^{(2)}, \ldots \text{ etc.}$$

are coefficients which can be determined by performing the actual perturbation expansion. According to these relations, the expression \([\gamma_{ii}(\lambda) - 1/2]\) is an odd function of the expansion parameter $\lambda$. Similarly, the off-diagonal matrix element $\gamma_{ij}(\lambda)$ is an odd function of $\lambda$ if vertices $i$ and $j$ are of the same parity and an even function of $\lambda$ otherwise.

Orbitals $|\chi_i\rangle = |i\rangle = \eta_{i^z}|0\rangle$ (\(i = 1, \ldots, 2n\)) which build up the CI space $X_n$ are arbitrary, except for the orthogonality condition.\(^1\) In most cases one assumes that there are $n$ spin-$\alpha$ orbitals $\chi_i = w_i\alpha$ and $n$ spin-$\beta$ orbitals $\bar{\chi}_i = w_i\beta$, where $w_i$ are orthonormalised atomic orbitals, while $\alpha$ and $\beta$ are spin-$\alpha$ and spin-$\beta$ states, respectively. Source and sink orbitals can now be defined in such a way that if $\chi_i$ is source, then $\bar{\chi}_i$ is sink, and vice versa (see Appendix and Ref. 1). The parity of the vertex (i) and atomic orbital $w_i$ is chosen to coincide with the parity of the spin-$\alpha$ orbital $\chi_i$. For the sake of reference we call this model with the above conventions model $A$.\(^1\) One can now define spin-$\alpha$ ($\gamma_{ii}^\alpha$), spin-$\beta$ ($\gamma_{ii}^\beta$) and cross ($\gamma_{ii}^{\alpha\beta}$) density matrices.\(^1\) These matrices satisfy relations (15). However, in the case of the cross density matrix $\gamma_{ii}^{\alpha\beta}$ one has to be careful: since $\chi_i$ and $\bar{\chi}_i$ are of opposite parity, diagonal elements $\gamma_{ii}^{\alpha\beta}(\lambda)$ are even functions of the expansion parameter $\lambda$ (compare with Eq. 15a). Similarly, matrix element $\gamma_{ij}^{\alpha\beta}(\lambda)$ is an even function of the expansion parameter $\lambda$ if vertices (i) and (j) are of the same parity (spin orbitals $\chi_i$ and $\bar{\chi}_i$ are then of the opposite parity), and odd functions of $\lambda$ otherwise (compare with relations 15b and 15c). One can now define spin-independent density matrix $Q = \gamma^\alpha + \gamma^\beta$ to obtain for the diagonal elements

$$Q_i(\lambda) = Q_{i\alpha}(\lambda) + Q_{i\beta}(\lambda) = 1 + \lambda \cdot \gamma_{i\alpha}^{(1)} + \lambda^2 \cdot \gamma_{i\alpha}^{(2)} + \gamma_{i\beta}^{(3)} + \ldots \quad (16)$$

where $Q_{i\alpha}(\lambda) = \gamma_{ii}^{\alpha}(\lambda)$, $Q_{i\beta}(\lambda) = \gamma_{ii}^{\beta}(\lambda)$ and $Q_i(\lambda) = Q_{ii}(\lambda)$ are spin-$\alpha$, spin-$\beta$ and total charges, respectively.\(^1\) The quantity $[Q_i(\lambda) - 1]$, where $Q_i(\lambda)$ is the total charge at the atomic orbital $w_i$, is an odd function of the expansion parameter $\lambda$. Similarly, total bond orders $P_{ij}(\lambda) = Q_{ij}(\lambda) = \gamma_{ij}^{\alpha}(\lambda) + \gamma_{ij}^{\beta}(\lambda)$ between atomic orbitals $w_i$ and $w_j$ are found to be even functions of $\lambda$ if vertices (i) and (j) are of opposite parity, and odd functions of $\lambda$ otherwise.
b) Two-Particle Density Matrices

Matrix elements $\Gamma_{ij,kl}(\lambda)$

$$\Gamma_{ij,kl}(\lambda) = \langle \Psi(\lambda) | \hat{A}_{ij,kl} | \Psi(\lambda) \rangle$$

(17)

of a two-particle density matrix $\Gamma$ satisfy

$$\Gamma_{ij,kl}(\lambda) = R_{ij,kl}^{(0)} + \lambda^2 R_{ij,kl}^{(2)} + \lambda^4 R_{ij,kl}^{(4)} + \ldots$$

(18a)

even number of source vertices, $(i \neq j \neq k \neq l)$

$$\Gamma_{ij,kl}(\lambda) = \lambda \cdot R_{ij,kl}^{(1)} + \lambda^3 R_{ij,kl}^{(3)} + \lambda^5 R_{ij,kl}^{(5)} + \ldots$$

(18b)

odd number of source vertices, $(i \neq j \neq k \neq l)$

$$\Gamma_{ij,kl}(\lambda) = \frac{1}{4} \gamma_{ij}(\lambda) = R_{i\bar{i},j\bar{j}}^{(0)} + \lambda^2 R_{i\bar{i},j\bar{j}}^{(2)} + \lambda^4 R_{i\bar{i},j\bar{j}}^{(4)} + \ldots$$

(19a)

$i$ and $j$ are of the same parity, $(i \neq j \neq l)$

$$\Gamma_{ij,kl}(\lambda) = \frac{1}{4} \gamma_{ij}(\lambda) = \lambda R_{i\bar{i},j\bar{j}}^{(1)} + \lambda^3 R_{i\bar{i},j\bar{j}}^{(3)} + \lambda^5 R_{i\bar{i},j\bar{j}}^{(5)} + \ldots$$

(19b)

$i$ and $j$ are of the opposite parity, $(i \neq i, j)$

$$\Gamma_{ij,ij}(\lambda) = [\gamma_{ii}(\lambda) + \gamma_{jj}(\lambda)]/4 = R_{ij,ij}^{(0)} + \lambda^2 R_{ij,ij}^{(2)} + \lambda^4 R_{ij,ij}^{(4)} + \ldots$$

(20)

where $R_{ij,kl}^{(p)}$ are coefficients which can be obtained by performing the actual perturbation expansion. Each of the above expressions is either even or odd function of the expansion parameter $\lambda$. The last relation is particularly interesting, since $2\Gamma_{ii,ij}^{(0)} = \langle \eta^\alpha_i \eta^\beta_i | \eta^\beta_j | \eta^\alpha_j \rangle$ is the pair correlation function. This function gives the probability of finding simultaneously two particles, one particle at the vertex (i), and another at the vertex (j). This function measures the correlation between the two particles, and in the case of the one-determinantal function (no correlation) it factorises into $2\Gamma_{ii,ij}^{(0)} = 0$. According to the relation (20), the pair correlation function alone is neither even nor odd function of the expansion parameter $\lambda$. However, a particular linear combination of this function and particle densities at vertices (i) and (j) is an even function of $\lambda$. A similar interpretation can be given to relations (19), while according to relations (18) matrix elements $\Gamma_{ij,kl}(\lambda)$ $(i \neq j \neq k \neq l)$ are already either even or odd functions of the expansion parameter $\lambda$, depending on the number of source vertices.

If orbitals $| \chi_i \rangle = \eta^\alpha_i | 0 \rangle$ are chosen to be spin-$\alpha$ and spin-$\beta$ orbitals, in accord with model $A$ above, then matrix elements of the spin-$\alpha$ ($\Gamma^{\alpha\alpha}$), spin-$\beta$ ($\Gamma^{\beta\beta}$) and cross ($\Gamma^{\alpha\beta}$ and $\Gamma^{\beta\alpha}$) density matrices satisfy relations (18)—(20). Hence matrix elements $P_{ij,kl}$

$$P_{ij,kl} = \Gamma^{\alpha\alpha}_{ij,kl} + \Gamma^{\alpha\beta}_{ij,kl} + \Gamma^{\beta\alpha}_{ij,kl} + \Gamma^{\beta\beta}_{ij,kl}$$

(21)

of the two-particle spin-independent density matrix $P$ satisfy
\[ P_{ij,kl}(\lambda) = P^{(0)}_{ij,kl} + \lambda^2 P^{(2)}_{ij,kl} + \lambda^4 P^{(4)}_{ij,kl} + \ldots \]

even number of source vertices, \((i \neq j \neq k \neq l)\) \hspace{1cm} (22a)

\[ P_{ij,kl}(\lambda) = \lambda P^{(1)}_{ij,kl} + \lambda^3 P^{(3)}_{ij,kl} + \lambda^5 P^{(5)}_{ij,kl} + \ldots \]

odd number of source vertices, \((i \neq j \neq k \neq l)\) \hspace{1cm} (22b)

\[ P_{ij,kl}(\lambda) \rightarrow \frac{1}{2} \quad \text{even number of source vertices, (i \neq j \neq k \neq l)} \]

\[ P_{ij,kl}(\lambda) \rightarrow \frac{1}{2} \quad \text{odd number of source vertices, (i \neq j \neq k \neq l)} \]

\[ i \text{ and } j \text{ are of the same parity, (i \neq j \neq l)} \hspace{1cm} (23a) \]

\[ i \text{ and } j \text{ are of the opposite parity, (i \neq i, j)} \hspace{1cm} (23b) \]

According to the above expressions, particular matrix elements of one- and two-particle density matrix (e.g. relations (15b), (15c), (18) etc.), as well as some linear combinations of these matrix elements (e.g. relations (15a), (19), (20) etc.) are either odd or even functions of the expansion parameter \(\lambda\). Further, in the case \(\lambda = 0\), the above expressions reduce to the relations obtained in the previous paper for the case of alternant system. These relations are hence generalisations to an arbitrary nonalternant system. They are generally not true if the unperturbed Hamiltonian is not alternant and/or if the perturbation is not antialternant. The above regularities are thus due to the particular splitting (1a) of the Hamiltonian \(H\) into the alternant and antialternant part.

Note finally that in the case when \(\Psi\) is a one-determinental function, the two-particle density matrix \(\Gamma\) satisfies\(^{1,8,10}\)

\[ \Gamma_{ij,kl} = \frac{1}{2} [\gamma_{ik} \gamma_{jl} - \gamma_{il} \gamma_{jk}] \] \hspace{1cm} (25a)

and hence spin-independent density matrix \(P\) is found to satisfy

\[ P_{ij,kl} = \frac{1}{2} [\varrho_{ik} \varrho_{jl} - \varrho_{il} \varrho_{jk}] \] \hspace{1cm} (25b)

It can now easily be shown that relations (18)—(24) involving matrix elements of the two-particle density matrix follow from relations (15) involving matrix elements of the one-particle density matrix, provided \(\Psi\) is a one-determinental function. For example, relation (25a) implies \(\Gamma_{ij,ij} = (\gamma_{ii} + \gamma_{jj})/4 = (\gamma_{ii} \gamma_{jj} - \gamma_{ij} \gamma_{ij})/2 - (\gamma_{ii} + \gamma_{jj})/4 = (\gamma_{ii} - 1/2)(\gamma_{jj} - 1/2) - \gamma_{ij} \gamma_{ij}/4)/2\). According to the relation (15a) expressions \((\gamma_{ii} - 1/2)\) and \((\gamma_{jj} - 1/2)\) are odd functions \(\lambda\), and hence \((\gamma_{ii} - 1/2)(\gamma_{jj} - 1/2)\) is an even function of \(\lambda\). Similarly, relations (15b) and (15c) imply that \(\gamma_{ij} \gamma_{ij}\) is an even function of \(\lambda\). Hence the expression \([\Gamma_{ij,ij} = (\gamma_{ii} + \gamma_{jj})/4\) is an even function of \(\lambda\) as well, in accord with the relation (20). Analogously, all other expressions involving matrix elements of the two-particle density matrix can be derived from the expressions (15) involving
matrix elements of the one-particle density matrix, provided relations (25) are satisfied, i.e. in the case of one-determinantal functions. This applies to various self-consistent field (SCF) approaches. However, relations (18)—(24) are much more general, and they remain valid irrespective of relations (25).

4. AN EXAMPLE OF THE ANTIALTERNANT PERTURBATION OF AN ALTERNANT SYSTEM

In order to understand better the above relations, let us give a simple example. Consider a heterocompound such as pyridine or pyrylium (Figure 1a) where the heteroatom X donates one electron to the \( n \)-electron system. In the Hückel approach the Hamiltonian \( H \) of this system is (expressed in Hückel \( \beta \) units)

\[
H = H_{al} + \lambda (q_1 - 1)
\]

where \( H_{al} \) is the Hückel Hamiltonian of the benzene molecule, while \( q_1 = q_1^\alpha + q_1^\beta \) is the charge density operator associated with the vertex (1) \( (a_1^\alpha \text{ and } b_1^\beta \text{ being spin-}\alpha \text{ and spin-}\beta \text{ creation operators, respectively)} \). The expansion parameter \( \lambda \) depends on the heteroatom X and it expresses the strength of the perturbation. In this simple picture the sole effect of the heteroatom X is to change the coulomb integral \( a_1 \), while the resonance integrals \( \beta_{12} \) and \( \beta_{16} \) are assumed to be unaffected. The unperturbed Hamiltonian \( H_{al} \) is an alternant operator, while the perturbation \( q_1 - 1 = (R_{11}^\alpha + R_{11}^\beta)/2 \) is antialternant. Hence the Hamiltonian (26) represents an alternant system subjected to an antialternant perturbation, and its eigenstates should satisfy all the properties discussed in sections 2 and 3. These properties are illustrated in Figures 2 to 5. Thus bond orders \( P_{12} (\lambda), P_{23} (\lambda) \) and \( P_{34} (\lambda) \) associated with the ground state \( \Psi (\lambda) \) are even functions of the expansion parameter \( \lambda \) (Figure 2).

![Figure 1](image)

**Figure 1.** a) Example of an alternant system perturbed by an antialternant perturbation. The calculation is done within the Hückel approach, and the unperturbed system represents the benzene molecule. The perturbation is due to the presence of the heteroatom X, and it is represented by the operator \( \lambda (q_1 - 1) \) which is antialternant. Symmetry properties of different observables associated with this system are shown in Figures 2 to 5. b) Example of an alternant system perturbed by the perturbation which is not antialternant. In this particular case the perturbation is represented by the bond order operator \( P_{16} \) which is an alternant operator. Figures 6 to 8 illustrate the lack of symmetry with respect to the expansion parameter \( \lambda \). In an arbitrary case, the perturbation is neither alternant nor antialternant, i.e. it is nonalternant.
This is in accord with our finding that total bond orders between vertices of the opposite parity are even functions of $\lambda$. In a similar way bond orders $P_{14}(\lambda)$ and $P_{26}(\lambda)$ are found to be even functions of $\lambda$. The total $\pi$-electron energy $E(\lambda)$ is also an even function of $\lambda$ (Figure 3), in accord with the corollary 1. On the other hand, bond orders $P_{13}(\lambda)$, $P_{24}(\lambda)$, $P_{26}(\lambda)$ and $P_{35}(\lambda)$ connecting vertices of the same parity are odd functions of $\lambda$, (Figure 4), as implied by relations

Figure 2. In the case of the antialternant perturbation of an alternant system bond orders between vertices of the opposite parity are even functions of the expansion parameter $\lambda$. This Figure corresponds to the heterocompound in Figure 1a.

Figure 3. In the case of the antialternant perturbation of an alternant system the total energy is an even function of the expansion parameter $\lambda$. This Figure corresponds to the heterocompound in Figure 1a.
Figure 4. In the case of the antialternant perturbation of an alternant system bond orders between vertices of the same parity are odd functions of the expansion parameter $\lambda$. This Figure corresponds to the heterocompound in Figure 1a.

Figure 5. In the case of the antialternant perturbation of an alternant system netto charges $\Delta Q_i = Q_i - 1$ are odd functions of the expansion parameter $\lambda$. This Figure corresponds to the heterocompound in Figure 1a.

(15c). Similarly, perturbed total charges $\Delta Q_i = Q_i - 1$, $\Delta Q_2$, $\Delta Q_3$ and $\Delta Q_4$ are also odd functions of $\lambda$ (Figure 5), as predicted by the relations (16). These are properties of spin-independent one-particle density matrix. It is now easy
to show that spin-$\alpha$ and spin-$\beta$ density matrices satisfy relations (15). Concerning the properties of the matrix elements of the two-particle density matrix, they are here automatically satisfied since the Hückel ground state $\Psi$ is a one-determinantal function, and hence relations (25) hold.

One might argue that the above regularities are an artifact of the symmetry properties of the benzene molecule. In order to show that this is not the case, consider again the benzene molecule as the unperturbed system, but take now the change in the resonance integral $\beta_{16}$ between vertices (1) and (6) as a perturbation (Figure 1b). In the Hückel approach the corresponding Hamiltonian is

$$\hat{H} = \hat{H}_{3s} + \lambda \hat{p}_{16}$$

where $\hat{p}_{16} = \hat{p}_{16}^\alpha + \hat{p}_{16}^\beta$ is the bond-order operator connecting vertices (1) and (6). This is an alternant operator, and thus the perturbation is alternant.

Note that while the case $\lambda = 0$ corresponds to the benzene molecule, the case $\lambda = -1$ corresponds to the hexatriene molecule. Bond orders $P_{12}(\lambda)$, $P_{23}(\lambda)$ and $P_{34}(\lambda)$ are shown in Figure 6 and it is obvious that they are neither odd nor even functions of the expansion parameter $\lambda$. Similarly, bond orders $P_{14}(\lambda)$ and $P_{25}(\lambda)$ have no definite symmetry properties with respect to $\lambda$ (Figure 7). Finally, the total $\pi$-electron energy $E(\lambda)$ is also neither an even nor an odd function of $\lambda$ (Figure 8). In this simple example bond orders $P_{13}(\lambda)$, $P_{15}(\lambda)$ and $P_{24}(\lambda)$ connecting vertices of the same parity are identically zero, i.e. they are even functions of $\lambda$. Similarly, total charges $Q_1(\lambda), Q_2(\lambda), \ldots, Q_6(\lambda)$ are

Figure 6. If the perturbation is not antialternant bond orders between vertices of the opposite parity are neither even nor odd functions of the expansion parameter $\lambda$. This Figure corresponds to the system represented in Figure 1b.
Figure 7. The same as Figure 6.

Figure 8. If the perturbation is not antialternant the total energy is neither an even nor an odd function of the expansion parameter $\lambda$. This Figure corresponds to the system represented in Figure 1b.
identically equal to one, i.e. they are also even functions of $\lambda$. However, this is a trivial consequence of the fact that the Hamiltonian (27) is an alternant operator, since the perturbation $p_{16}$ is alternant. In a general case when a perturbation is nonalternant, i.e. when it is a nontrivial linear combination of an alternant and an antialternant operator, these bond orders and charges have no definite symmetry properties with respect to the expansion parameter $\lambda$.

The above example is only an illustration of the symmetry properties of matrix elements of one- and two-particle density matrices. Though an example within the Hückel approach is considered, these symmetry properties are valid much more generally, as implied by the expansion theorem.

5. CONCLUSION

The results obtained in this paper are generalisations of the properties of alternant systems as discussed in the previous paper, to arbitrary nonalternant systems. The most important result is the expansion theorem which refers to the special kind of the perturbation expansion where the unperturbed Hamiltonian $H_0$ is chosen to be an alternant operator, while the perturbation $\lambda V$ is chosen to be an antialternant operator. The eigenstate $\Psi(\lambda)$ of the full Hamiltonian $H = H_0 + \lambda V$, the corresponding energy $E(\lambda)$, as well as expectation values of alternant and antialternant operators have special properties: provided the unperturbed eigenstate $\Phi_0$ is nondegenerate, and if $\Phi_0 = \Phi_0^+ \in X_n^+$ (which can be assumed without loss of generality), the expansion of the eigenstate $\Psi(\lambda)$ in terms of the expansion parameter $\lambda$ is $\Psi(\lambda) = \Phi_0^+ + \lambda \Psi_1^+ + \lambda^2 \Psi_2^+ + \lambda^3 \Psi_3^+ + \ldots$. As a consequence, the corresponding energy $E(\lambda)$ is an even function of $\lambda$, the expectation value of each alternant operator is an even function of $\lambda$, and the expectation value of each antialternant operator is an odd function of $\lambda$. These are the most important results discussed in this paper.

The expansion of the eigenstate $\Psi(\lambda)$ is really remarkable: each term in this expansion is an alternant-like state possessing all the nice properties discussed in the previous paper. These properties are essentially the characteristic properties of the eigenstates associated with neutral alternant hydrocarbons, like uniform charge density distribution, vanishing bond orders between vertices of the same parity, etc. An »arbitrary« state $\Psi(\lambda)$ is thus expanded in terms of functions with very particular and special properties. In addition, successive corrections $\Psi_1$, $\Psi_{k+1}$, ... alternate in complementary spaces $X_n^+$ and $X_n^-$. Namely, if $\Psi_k \in X_n^+$ then $\Psi_{k+1} \in X_n^-$, and vice versa. Beside undeniable conceptual appeal of such a picture, the actual numerical advantage is also apparent: since $\Psi_1^+ \in X_n^-$ the summation involved in the evaluation of the first order correction need not be performed over vectors contained in the space $X_n^+$, and hence the number of terms is reduced by the factor two. Similarly, in the evaluation of the second order correction $\Psi_2^-$, there is a double summation, and hence the number of terms is reduced roughly by the factor four, in the evaluation of $\Psi_3^-$ by the factor of eight, etc. Of course, one usually does not consider the complete CI space $X_m$, but rather some subspace of this space containing energetically low lying and most important structures. However, whatever the approximation used, the fact that $\Psi_1^- \in X_n^-$, $\Psi_2^- \in X_n^+$, $\Psi_3^- \in X_n^-$ etc. further reduces the numerical evaluation
of these corrections by the factor two, four, eight etc., respectively. In addition, since corrections to all orders are alternant-like states, many matrix elements either vanish or considerably simplify, and this still further reduces the number of terms which should be considered. Finally, note that the decomposition of the Hamiltonian $H$ in the alternant and antialternant component, depends on the partition of the set $B$ on source ($B^0$) and sink ($B^*$) subsets. The flexibility in the partition $B \rightarrow \{B^0, B^*\}$ can be efficiently used in order to make the antialternant perturbation $\lambda V$ as «small» as possible, especially in the case of the ground state. In conclusion, the perturbation expansion suggested here is likely to converge rapidly and to be mathematically very feasible involving a small number of terms.

There is no need to discuss in detail the three corollaries which follow from the expansion theorem, and which refer to the expectation values of different operators in the state $\Psi(\lambda)$. In addition to the obvious conceptual insight into the structure and behaviour of quantum systems, these corollaries take over from the expansion theorem all the numerical feasibility in the evaluation of different expectation values. It should be noted that there is an efficient and simple algorithm to decompose an arbitrary symmetric operator into its alternant and antialternant component. Hence the expectation value of an arbitrary symmetric operator can be analysed in terms of corollaries 2 and 3 referring to alternant and antialternant operators, respectively. In particular, one can easily identify even and odd components of the expansion of the expectation value of an arbitrary symmetric operator in terms of the parameter $\lambda$.

At the end, the limitations of the expansion theorem should be noted. There are essentially three restrictions to the validity of this theorem as formulated here: the Hamiltonian $H$ is assumed to be symmetric, the unperturbed eigenstate $\Phi_0$ is assumed nondegenerate, and finally, the CI space $X_n$ generated by $n$ electrons moving over exactly $2n$ orbitals is considered. The first restriction (Hamiltonian $H$ is symmetric) is not so serious, and the expansion theorem can be generalised to arbitrary Hamiltonians with essentially no change. The second restriction (unperturbed eigenstate $\Phi_0^+ \in X_n^+$ is nondegenerate), can be generalised with minor changes to the case when $\Phi_0^+ \in X_n^+$ is degenerate, but only with eigenstates contained in the same space $X_n^+$. In other words, there should be no unperturbed eigenstate $\Phi^- \in X_n^-$ of the operator $H_0$ with the same energy as $\Phi_0^+ \in X_n^+$. If however $\Phi_0^+ \in X_n^+$ is degenerate with some eigenstate $\Phi^- \in X_n^-$, the generalisation of the expansion theorem is still possible, but it is now quite radical, and a substantial modification of this theorem is required. Finally, the last restriction that only the CI space $X_n$ is considered can be also relaxed. The expansion theorem can be generalised to an arbitrary CI space $X_{n,N}$ generated by $n$ electrons moving over $N$ orbitals ($n$ and $N$ arbitrary), but again with substantial modifications.

In conclusion, the expansion theorem is valid quite generally, either in the present form, or with some modifications. The notion of alternant and antialternant operators, as well as the splitting theorem, can be consistently derived within the molecular orbital resonance theory (MORT) approach. Here are presented only these results which are relevant for the understanding of this paper. For more details see the preceding paper, as well

APPENDIX

The notion of alternant and antialternant operators, as well as the splitting theorem, can be consistently derived within the molecular orbital resonance theory (MORT) approach. Here are presented only these results which are relevant for the understanding of this paper. For more details see the preceding paper, as well...
as Refs. 2 and 3. It should be noted that in the connection with the remarkable properties of neutral AH compounds, various authors have considered different alternant systems. The critical discussion of these approaches can be found elsewhere.

A.1. Alternant and Antialternant Operators

Building blocks for the construction of alternant and antialternant operators are reduced operators $R_{ij}$ and $R_{ij,kl}^{1,2}$

$$R_{ij} = \delta_{ij}$$
$$R_{ij,kl} = A_{ij,kl} \quad (i \neq j \neq k \neq l)$$

$$A_{ij,kl} = 2A_{ij} + A_{ij} \quad (i \neq j \neq k)$$

$$R_{ij,ij} = 2A_{ij,ij} + A_{ij} + A_{ij} - 1 \quad (i \neq j)$$

where

$$A_{ij} = \eta^*_i \eta_j + \eta^*_j \eta_i$$

and $\eta^*_i$ and $\eta_i$ are fermion creation and annihilation operators, respectively. A unit operator is a reduced operator as well. Reduced operators are symmetric, hermitian, and hence real operators. By definition, they satisfy symmetry relations

$$R_{ij} = R_{ji}$$
$$R_{ij,kl} = -R_{ij,kl} = R_{kl,ij}$$

in order to mimic analogous symmetry relations satisfied by operators $A_{ij}$ and $A_{ij,kl}$.

The set of all reduced operators is complete in the space of symmetric operators, i.e. each symmetric operator can be represented as a linear combination of reduced operators.

Let there be $2n$ (an even number) of creation (annihilation) operators. Partition the set $B = \{i\}$ of $2n$ vertices (i) into subsets $B^0$ and $B^*$ containing $n$ vertices each.

The creation operator $\eta_i^*$, the annihilation operator $\eta_i$, the one-particle state (orbital) $|i\rangle = \eta^*_i |0\rangle$ and the vertex (i) are »source« if $(i) \in \{B^0\}$ and »sink« if $(i) \in \{B^*\}$.

Relative to this partition, each reduced operator is either »alternant« or »antialternant«:

a) Reduced alternant operators are:

$$\hat{R}_{ij} \quad i \text{ and } j \text{ are of the opposite parity}$$

$$\hat{R}_{ij,kl} \quad \text{even number of source vertices}$$
Reduced antialternant operators are  
\[ R_{ij} \quad i \text{ and } j \text{ are of the same parity} \]
\[ R_{ij, kl} \quad \text{odd number of source vertices} \]  
(A8)

Each linear combination of reduced alternant operators is an alternant operator, and each linear combination of reduced antialternant operators is an antialternant operator. There is a simple and efficient algorithm to represent an arbitrary symmetric operator as a sum of an alternant and an antialternant operator.1–2

A2. The Splitting Theorem1–3

Let \( X_n \) be the configuration interaction (CI) space spanned by all \( n \)-particle states \( | \Lambda_i \rangle = \eta_{i1} \eta_{i2}^* \ldots \eta_{in}^* | 0 \rangle \) where \( | 0 \rangle \) is a vacuum state
\[ \eta_i | 0 \rangle = 0 \quad i = 1, \ldots, 2n \]  
(A9)

The partition \( B \rightarrow \{ B^0 , B^* \} \) uniquely determines the partition of the space \( X_n \) into two complementary subspaces \( X_n^+ \) and \( X_n^- \). These subspaces are of the same dimension, and each state \( \Psi \in X_n \) can be uniquely written in the form \( \Psi = \Psi^+ + \Psi^- \) where \( \Psi^+ \in X_n^+ \) and \( \Psi^- \in X_n^- \). In addition, alternant and antialternant operators satisfy1–2

The splitting theorem

a) The expectation value \( \langle \Psi^+ | O_{\text{al}} | \Psi^- \rangle \) of each alternant operator \( O_{\text{al}} \) between states \( \Psi^+ \in X_n^+ \) and \( \Psi^- \in X_n^- \) vanishes.

b) The expectation value \( \langle \Psi_1 | O_{\text{al}} | \Psi_2 \rangle \) of each antialternant operator \( O_{\text{al}} \) between states \( \Psi_1 \) and \( \Psi_2 \) vanishes whenever either \( \Psi_1 , \Psi_2 \in X_n^+ \) or \( \Psi_1 , \Psi_2 \in X_n^- \).

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REFERENCES
8. In the present paper density matrices as defined in Ref. 1 are used.
SAZETAK
Antialternantne perturbacije alternantnih sistema

Tomislav P. Zivković

Rayleigh-Schrödingerov račun smetnje primijenjen je na sistem gdje je neper-
turbirani hamiltonijan $H_0$ alternantni operator, dok je smetanja $V$ antialternantni
operator. Razmatran je konfiguracijsko-interakcijski prostor $X$, što ga tvori n elektrona nad $2n$ ortonormiranih orbitala. Taj se prostor cijepa na komplementarne potprostore $X_+$ i $X_-$ koji sadrže »alternantna« stanja. Ta stanja imaju karakteri-
stična svojstva vlastitih stanja neutralnih alternantnih ugljikovodika. Ako vlastito
stanje $\Phi_0 \in X_+$ neperurbiranog hamiltonijana $H_0$ nije degenerirano, tada je ono alter-
nantno i može se bez gubitka opcenitosti pretpostaviti $\Phi_0 = \Psi_0 + \Phi_0^\perp$. U tom je slu-
čaju razvoj vlastitog stanja $\Psi(\lambda)$ totalnog hamiltonijana $H = H_0 + \lambda V$ u red poten-
cija po parametru $\lambda$ dan relacijom $\Psi(\lambda) = \Psi_0 + \lambda \Psi'_0 + \lambda^2 \Psi''_0 + \lambda^3 \Psi'''_0 + \ldots$, gdje su sve korekcije $\Psi'_0$, $\Psi''_0$, $\ldots$ alternantna stanja. Nadalje, sve parne korekcije sadržane su u prostoru $X_+$, a sve nerparne korekcije sadržane su u prostoru $X_-$. Odgovarajuća vlastita vrijednost $E(\lambda)$ parna je funkcija od $\lambda$. Također, srednja vrijednost svakog alternantnog operatora parna je funkcija od $\lambda$, a srednja vrijednost svakog antial-
nenantnog operatora neparna je funkcija od $\lambda$. Ti su rezultati primijenjeni na matrične elemente jednocestičnih i dvocestičnih matrica gustote, i dan je jedno-
stavan primjer koji ilustrira ta svojstva.