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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 λV is chosen to be an antialternant operator. A configuration interaction space X_n generated by n electrons moving over $2n$ orthonormalised orbitals is considered. This space splits into two mutually complementary subspaces X_n^+ and X_n^- containing alternant-like states. These states have characteristic properteis of the eigenstates associated with neutral alternant hydrocarbon systems. If the eigenstate $\Phi \in X_n$ of the unperturbed Hamiltonian H_0 is nondegenerate, then it is alternant-like, *i. e.* either $\Phi \in X_n^+$ or $\Phi \in X_n^-$, and without loss of generality one can assume $\Phi = \Phi^+ \in X_n^+$. 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 λ, 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_n^+, while all odd corrections are contained in the space X_n^-. The corresponding eigenvalue $E(\lambda)$ is an even function of the expansion parameter λ. Also, the expectation value of each alternant operator is an even function of λ, while the expectation value of each antialternant operator is an odd function of λ. 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 λV, where λ is a parameter

$$H = H_0 + \lambda V \tag{1}$$

All the properties of a system, like eigenvalues, expectation values of different operators *etc.* are then expanded in the power series of the parameter λ. 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 λV 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[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.[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.[1,2]. Secondly, if the configuration interaction (CI) space X_n generated by n electrons moving over $2n$ orthonormalised orbitals χ_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.[1-3] In particular, they have uniform charge density distribution over all orbitals χ_i, vanishing bond orders between orbitals of the same parity *etc.*[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.[1-3] Hence polarised states, which have arbitrary charge density distribution and arbitrary bond orders, necessarily have nonvanishing 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.[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 λ (Ψ_1, Ψ_2, Ψ_3, *etc.*) 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 Ψ_2, Ψ_4, *etc.* are also contained in the space X_n^+, while all odd corrections Ψ_1, $\Psi_3, \ldots$ *etc.* 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 λ (corollary 1), the expectation value of each alternant operator is an even function of λ (corollary 2), and finally, the expectation value of each antialternant operator is an odd function of λ (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 $\boldsymbol{\gamma}$ is an even function of λ if vertices (i) and (j) are of the opposite parity, and an odd function of λ otherwise. Concerning diagonal matrix elements $\gamma_{ii}(\lambda)$, it is shown that the expression $[\gamma_{ii}(\lambda) - 1/2]$ is an odd function of λ *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[6,7] Hamiltonian H is usually written in the form (1) where H_0 is an unperturbed Hamiltonian, V is a perturbation, and λ is a real parameter. If Φ_0 is a nondegenerated eigenstate of the unperturbed Hamiltonian H_0

$$H_0 \Phi_0 = E_0 \Phi_0 \tag{2}$$

then there is a unique eigenstate $\Psi = \Psi(\lambda)$ of the Hamiltonian H which is a continuous function of λ and which for $\lambda = 0$ coincides with Φ_0

$$\begin{aligned} H\Psi(\lambda) &= E(\lambda)\Psi(\lambda) \\ \Psi(0) &= \Phi_0 \end{aligned} \tag{3}$$

the norm of this state being normalised with the condition

$$\langle \Psi \mid \Phi_0 \rangle = 1 \tag{3a}$$

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

$$E(\lambda) = E_0 + \lambda\varepsilon_1 + \lambda^2\varepsilon_2 + \lambda^3\varepsilon_3 + \ldots \tag{4a}$$

$$\Psi(\lambda) = \Phi_0 + \lambda\Psi_1 + \lambda^2\Psi_2 + \lambda^3\Psi_3 + \ldots \tag{4b}$$

and the condition (3a) is equivalent to

$$\langle \Psi_1 \mid \Phi_0 \rangle = \langle \Psi_2 \mid \Phi_0 \rangle = \ldots = \langle \Psi_k \mid \Phi_0 \rangle = \ldots = 0 \tag{3b}$$

Energies ε_k are given by

$$\varepsilon_k = \langle \Phi_0 \mid V \mid \Psi_{k-1} \rangle \tag{5}$$

while vectors Ψ_k can be expanded in terms of the eigenstates Φ_i of the unperturbed Hamiltonian H_0

$$\Psi_k = \sum_{i \neq 0} \langle \Phi_i \mid \Psi_k \rangle \mid \Phi_i \rangle \tag{6a}$$

where

$$\begin{aligned} \langle \Phi_i \mid \Psi_1 \rangle &= \langle \Phi_i \mid V \mid \Phi_0 \rangle / [E_0 - E_i] \\ \langle \Phi_i \mid \Psi_k \rangle &= [\langle \Phi_i \mid V - \varepsilon_1 \mid \Psi_{k-1} \rangle - \varepsilon_2 \langle \Phi_i \mid \Psi_{k-2} \rangle - \\ &- \ldots - \varepsilon_k \langle \Phi_i \mid \Phi_0 \rangle]/[E_0 - E_i], \qquad k > 1 \end{aligned} \tag{6b}$$

and[6,7]

$$H_0 \Phi_i = E_i \Phi_i \tag{6c}$$

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

Assume now that the Hamiltonian is partitioned in the following way

$$H = H_{al} + \lambda H_{nal} \tag{1a}$$

where the unperturbed Hamiltonian $H_0 = H_{al}$ is an alternant operator, while the perturbation $\lambda V = \lambda H_{nal}$ is an antialternant operator. Since the eigenstate Φ_0 of the unperturbed Hamiltonian is assumed nondegenerate, it follows from the splitting theorem that it is alternant-like.[1,2] 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 $H = H_{\rm al} + \lambda H_{\rm nal}$ be the symmetric Hamiltonian operator constructed out of $2n$ creation and $2n$ annihilation operators η_i^+ and η_i, respectively. Assume that the unperturbed Hamiltonian $H_{\rm al}$ is an alternant operator, and that the perturbation $H_{\rm nal}$ is an antialternant operator. Further let Φ_0 be a nondegenerate n-particle eigenstate of the unperturbed Hamiltonian $H_{\rm al}$, and let $\Psi(\lambda)$ be the eigenstate of H continuous in λ and coinciding with Φ_0 for $\lambda = 0$. Then the state Φ_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 λ is then

$$\Psi(\lambda) = \Phi_0^+ + \lambda \Psi_1^- + \lambda^2 \Psi_2^+ + \lambda^3 \Psi_3^- + \lambda^4 \Psi_4^+ + \dots \tag{7}$$

where $\Psi_k^+ \in X_n^+$ and $\Psi_k^- \in X_n^-$. In other words, corrections to all orders in the expansion parameter λ (Ψ_1, Ψ_2, Ψ_3, *etc.*) 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 λ

$$E(\lambda) = E_0 + \lambda^2 \varepsilon_2 + \lambda^4 \varepsilon_4 + \lambda^6 \varepsilon_6 + \dots \tag{8}$$

i. e. all odd corrections ε_1, ε_3, *etc.* 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 λ, *i. e* we will first show that $\varepsilon_1 = 0$ and $\Psi_1 = \Psi_1^- \in X_n^-$.

According to the relation (5) $\varepsilon_1 = \langle \Phi_0^+ | H_{\rm nal} | \Phi_0^+ \rangle$. Since the perturbation $H_{\rm nal}$ is an antialternant operator, the splitting theorem implies $\varepsilon_1 = 0$. Further, according to this theorem all eigenstates Φ_i of the unperturbed Hamiltonian $H_{\rm al}$ 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

$$\langle \Phi_i | \Psi_1 \rangle = \langle \Phi_i | H_{\rm nal} | \Phi_0^+ \rangle / [E_0 - E_i] = 0 \tag{9}$$

whenever $\Phi_i \in X_n^+$. The state Ψ_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 λ.

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

a) $\varepsilon_i = 0$ 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 λ as well.

Consider first the case of even k. According to the above assumption $\Psi_k = \Psi_k^+ \in X_n^+$. Since H_{nal} is an antialternant operator the relation (5) and the splitting theorem imply

$$\varepsilon_{k+1} = \langle \Phi_0^+ | H_{nal} | \Psi_k^+ \rangle = 0 \tag{10}$$

where $k + 1$ is now odd. Further, one has

$$\langle \Phi_i | \Psi_{k+1} \rangle = [\langle \Phi_i | H_{nal} | \Psi_k^+ \rangle - \varepsilon_2 \langle \Phi_i | \Psi_{k-1}^- \rangle - \\ - \varepsilon_4 \langle \Phi_i | \Psi_{k-3}^- \rangle - \ldots - \varepsilon_k \langle \Phi_i | \Psi_1^- \rangle]/[E_0 - E_i] \tag{11}$$

If now $\Phi_i \in X_n^+$ one obtains $\langle \Phi_i | \Psi_{k+1} \rangle = 0$ since by the splitting theorem $\langle \Phi_i | H_{nal} | \Psi_k^+ \rangle = 0$, while all overlaps $\langle \Phi_i | \Psi_{k-1}^- \rangle \ldots \langle \Phi_i | \Psi_1^- \rangle$ vanish. The state Ψ_{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 $k \geqslant 1$, 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 Φ_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 $\Phi_0 \in X_n^+$ can be allowed to be degenerate, provided all the eigenstates of H_{al} with the same eigenvalue as Φ_0 are also contained in the space X_n^+.[5] 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 $E(\lambda) = \langle \Psi(\lambda) | H | \Psi(\lambda) \rangle / \langle \Psi(\lambda) | \Psi(\lambda) \rangle$ and using the splitting theorem. In a similar manner the following corollaries can be derived

Corollary 2

The expectation value $\langle \hat{O}_{al} \rangle_\lambda = \langle \Psi(\lambda) | \hat{O}_{al} | \Psi(\lambda) \rangle / \langle \Psi(\lambda) | \Psi(\lambda) \rangle$ of an alternant operator $\hat{O}_{al}$ in the state $\Psi(\lambda)$ is an even function of λ, *i. e.*

$$\langle \hat{O}_{al} \rangle_\lambda = O_0 + \lambda^2 O_2 + \lambda^4 O_4 + \ldots \tag{12}$$

where $O_0 = \langle \Phi_0 | \hat{O}_{al} | \Phi_0 \rangle$, while O_2, O_4, *etc.* are coefficients which can be obtained by performing the actual perturbation expansion.

Corollary 3

The expectation value $\langle \hat{O}_{nal} \rangle_\lambda$ of an antialternant operator $\hat{O}_{nal}$ in the state $\Psi(\lambda)$ is an odd function of the parameter λ, *i. e.*

$$\langle \hat{O}_{nal} \rangle_\lambda = \lambda O_1 + \lambda^3 O_3 + \lambda^5 O_5 + \ldots \tag{13}$$

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[1,2], *i. e.* in the form (1a), and hence one can in most cases apply the above approach. It is only required that the eigenstate Φ_0 of the unperturbed Hamiltonian be an n-particle nondegenerate 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 λ, 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 λ 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 $O_0 = \langle \Phi_0 | \hat{O}_{al} | \Phi_0 \rangle$, which is the expectation value of the alternant operator $\hat{O}_{al}$ in the unperturbed state Φ_0. In general, the expectation value of an alternant operator can always be evaluated up to some even order in the expansion parameter λ, 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 λ to obtain the result which is exactly one order higher. Furthermore, the definition of alternant and antialternant operators depends on the partition $B \rightarrow \{B^{\circ}, B^{*}\}$ 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 partitition $B \rightarrow \{B^{\circ}, B^{*}\}$, and the flexibility in the choice of source and sink vertices can be used in order to make the antialternant perturbation λH_{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_{al}, since its eigenstates are alternant-like, and hence have a uniform charge density distribution with vanishing bond orders between vertices of the same parity *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 sence that the unperturbed Hamiltonian H_{al} is relatively easy to diagonalise, while the perturbation λH_{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 $\hat{R}_{ij}$ and $\hat{R}_{ij,\,kl}$. 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 $\Psi(\lambda)$[8]:

a) *One-Particle Density Matrices*

Matrix elements $\gamma_{ij}(\lambda)$[1]

$$\gamma_{ij}(\lambda) = \langle \Psi(\lambda) | \hat{A}_{ij}/2 | \Psi(\lambda) \rangle / \langle \Psi(\lambda) | \Psi(\lambda) \rangle \tag{14}$$

of a one-particle density matrix $\boldsymbol{\gamma}$ satisfy

$$\gamma_{ii}(\lambda) = 1/2 + \lambda \cdot \gamma_{ii}^{(1)} + \lambda^3 \cdot \gamma_{ii}^{(3)} + \lambda^5 \cdot \gamma_{ii}^{(5)} + \dots \tag{15a}$$

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

$$i \text{ and } j \text{ are of opposite parity} \tag{15b}$$

and

$$\gamma_{ij}(\lambda) = \lambda\, \gamma_{ij}^{(1)} + \lambda^3 \gamma_{ij}^{(3)} + \dots$$

$$i \text{ and } j \text{ are of the same parity, } (i \neq j) \tag{15c}$$

where

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

while

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

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 λ. Similarly, the off-diagonal matrix element $\gamma_{ij}(\lambda)$ is an odd function of λ if vertices i and j are of the same parity and an even function of λ otherwise.

Orbitals $|\chi_i\rangle = |i\rangle = \eta_i^+|0\rangle$ $(i = 1, \dots, 2n)$ which build up the CI space X_n are arbitrary, except for the orthogonality condition.[1-3] In most cases one assumes that there are n spin-α orbitals $\chi_i = w_i\,\alpha$ and n spin-β orbitals $\overline{\chi_i} = w_i\,\beta$, where w_i are orthonormalised atomic orbitals, while α and β are spin-α and spin-β states, respectively. Source and sink orbitals can now be defined in such a way that if χ_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-α orbital χ_i. For the sake of reference we call this model with the above conventions model A.[1] One can now define spin-α (γ^α), spin-β (γ^β) and cross ($\gamma^{\alpha\beta}$) density matrices.[1] These matrices satisfy relations (15). However, in the case of the cross density matrix $\gamma^{\alpha\beta}$ one has to be careful: since χ_i and $\overline{\chi_i}$ are of opposite parity, diagonal elements $\gamma_{ii}^{\alpha\beta}(\lambda)$ are even functions of the expansion parameter λ (compare with Eq. 15a). Similarly, matrix element $\gamma_{ij}^{\alpha\beta}(\lambda)$ is an even function of the expansion parameter λ if vertices (i) and (j) are of the same parity (spin orbitals χ_i and $\overline{\chi_j}$ are then of the opposite parity), and odd functions of λ otherwise (compare with relations 15b and 15c). One can now define spin-independent density matrix $\varrho = \gamma^\alpha + \gamma^\beta$ to obtain for the diagonal elements

$$Q_i(\lambda) = Q_i^\alpha(\lambda) + Q_i^\beta(\lambda) = 1 + \lambda \cdot Q_i^{(1)} + \lambda^3 \cdot Q_i^{(3)} + \dots \tag{16}$$

where $Q_i^\alpha(\lambda) = \gamma_{ii}^\alpha(\lambda)$, $Q_i^\beta(\lambda) = \gamma_{ii}^\beta(\lambda)$ and $Q_i(\lambda) = \varrho_{ii}(\lambda)$ are spin-α, spin-β 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 λ. Similarly, total bond orders $P_{ij}(\lambda) = \varrho_{ij}(\lambda) = \gamma_{ij}^\alpha(\lambda) + \gamma_{ij}^\beta(\lambda)$ between atomic orbitals w_i and w_j are found to be even functions of λ if vertices (i) and (j) are of opposite parity, and odd functions of λ otherwise.

b) *Two-Particle Density Matrices*

Matrix elements $\Gamma_{ij,kl}(\lambda)$[1]

$$\Gamma_{ij,kl}(\lambda) = \langle \Psi(\lambda) \,|\, \hat{A}_{ij,lk}/4 \,|\, \Psi(\lambda) \rangle / \langle \Psi(\lambda) \,|\, \Psi(\lambda) \rangle \tag{17}$$

of a two-particle density matrix $\mathbf{\Gamma}$ satisfy

$$\Gamma_{ij,kl}(\lambda) = R^{(0)}_{ij,kl} + \lambda^2 R^{(2)}_{ij,kl} + \lambda^4 R^{(4)}_{ij,kl} + \dots$$

even number of source vertices, $(i \neq j \neq k \neq l)$ (18a)

$$\Gamma_{ij,kl}(\lambda) = \lambda \cdot R^{(1)}_{ij,kl} + \lambda^3 R^{(3)}_{ij,kl} + \lambda^5 R^{(5)}_{ij,kl} + \dots$$

odd number of source vertices, $(i \neq j \neq k \neq l)$ *(18b)*

$$\Gamma_{il,jl}(\lambda) - \frac{1}{4}\gamma_{ij}(\lambda) = R^{(0)}_{il,jl} + \lambda^2 R^{(2)}_{il,jl} + \lambda^4 R^{(4)}_{il,jl} + \dots$$

i and j are of the same parity, $(i \neq j \neq l)$ (19a)

$$\Gamma_{il,jl}(\lambda) - \frac{1}{4}\gamma_{ij}(\lambda) = \lambda R^{(1)}_{il,jl} + \lambda^3 R^{(3)}_{il,jl} + \lambda^5 R^{(5)}_{il,jl} + \dots$$

i and j are of the opposite parity, $(l \neq i, j)$ (19b)

$$\Gamma_{ij,ij}(\lambda) - [\gamma_{ii}(\lambda) + \gamma_{jj}(\lambda)]/4 = R^{(0)}_{ij,ij} + \lambda^2 R^{(2)}_{ij,ij} + \lambda^4 R^{(4)}_{ij,ij} + \dots$$

$(i \neq j)$ (20)

where $R^{(r)}_{ij,kl}$ 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 λ. The last relation is particularly interesting, since $2\,\Gamma_{ij,ij} = \langle \eta_i^+ \eta_i \eta_j^+ \eta_j \rangle$ is the pair correlation function[9,10]. 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-determinental function (no correlation) it factorises into $2\,\Gamma_{ij,ij} = \gamma_{ii}\gamma_{jj} - \gamma_{ij}\gamma_{ij}$.[9,10] According to the relation (20), the pair correlation function alone is neither even nor odd function of the expansion parameter λ. However, a particular linear combination of this function and particle densities at vertices (i) and (j) is an even function of λ. 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 λ, depending on the number of source vertices.

If orbitals $|\,\chi_i\,\rangle = \eta_i^+\,|\,0\,\rangle$ are chosen to be spin-α and spin-β orbitals, in accord with model A above[1], then matrix elements of the spin-α ($\Gamma^{\alpha\alpha}$), spin-β ($\Gamma^{\beta\beta}$) and cross ($\Gamma^{\alpha\beta}$ and $\Gamma^{\beta\alpha}$) density matrices[1] satisfy relations (18)—(20). Hence matrix elements $P_{ij,kl}$[1]

$$P_{ij,kl} = \Gamma^{\alpha\alpha}_{ij,kl} + \Gamma^{\alpha\beta}_{ij,kl} + \Gamma^{\beta\alpha}_{ij,kl} + \Gamma^{\beta\beta}_{ij,kl} \tag{21}$$

of the two-particle spin-independent density matrix $\mathbf{P}$ 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, $(i \neq j \neq k \neq l)$ (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, $(i \neq j \neq k \neq l)$ (22b)

$$P_{il,\,jl}(\lambda) - \frac{1}{2}\varrho_{ij}(\lambda) = P^{(0)}_{il,\,jl} + \lambda^2 P^{(2)}_{il,\,jl} + \lambda^4 P^{(4)}_{il,\,jl} + \ldots$$

i and j are of the same paritiy, $(i \neq j \neq l)$ (23a)

$$P_{il,\,jl}(\lambda) - \frac{1}{2}\varrho_{ij}(\lambda) = \lambda P^{(1)}_{il,\,jl} + \lambda^3 P^{(3)}_{il,\,jl} + \lambda^5 P^{(5)}_{il,\,jl} + \ldots$$

i and j are of the opposite parity, $(l \neq i,\ j)$ (23b)

$$P_{ij,\,ij}(\lambda) - [Q_i(\lambda) + Q_j(\lambda)]/2 = P^{(0)}_{ij,\,ij} + \lambda^2 P^{(2)}_{ij,\,ij} + \lambda^4 P^{(4)}_{ij,\,ij} + \ldots \tag{24}$$

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 λ. Further, in the case $\lambda = 0$, the above expressions reduce to the relations obtained in the previous paper for the case of alternant system.[1] 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 Ψ is a one-determinental function, the two-particle density matrix $\mathbf{\Gamma}$ satisfies[1,8–10]

$$\Gamma_{ij,\,kl} = \frac{1}{2}[\gamma_{ik}\gamma_{jl} - \gamma_{il}\gamma_{jk}] \tag{25a}$$

and hence spin-independent density matrix $\mathbf{P}$ is found to satisfie

$$P_{ij,\,kl} = \frac{1}{2}[\varrho_{ik}\varrho_{jl} - \varrho_{il}\varrho_{jk}] \tag{25b}$$

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 Ψ is a one-determinental function. For example, relation (25a) implies $\Gamma_{ij,\,ij} - (\gamma_{ii} + \gamma_{jj})/4 = (\gamma_{ii}\gamma_{jj} - \gamma_{ij}\gamma_{ij})/2 - (\gamma_{ii} + \gamma_{jj})/4 = [(\gamma_{ii} - 1/2)(\gamma_{jj} - 1/2) - \gamma_{ij}\gamma_{ij} - 1/4]/2$. According to the relation (15a) expressions $(\gamma_{ii} - 1/2)$ and $(\gamma_{jj} - 1/2)$ are odd functions λ, and hence $(\gamma_{ii} - 1/2)(\gamma_{jj} - 1/2)$ is an even function of λ. Similarly, relations (15b) and (15c) imply that $\gamma_{ij}\gamma_{ij}$ is an even function of λ. Hence the expression $[\Gamma_{ij,\,ij} - (\gamma_{ii} + \gamma_{jj})/4]$ is an even function of λ 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-determinental 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 π-electron system. In the Hückel approach the Hamiltonian H of this system is (expressed in Hückel β units)

$$H = H_{al} + \lambda (\hat{q}_1 - 1) \tag{26}$$

where H_{al} is the Hückel Hamiltonian of the benzene molecule, while $\hat{q}_1 = \hat{q}_1^{\alpha} + \hat{q}_1^{\beta} = a_1^{+} a_1 + b_1^{+} b_1$ is the charge density operator associated with the vertex (1) (a_i^{+} and b_i^{+} being spin-α and spin-β creation operators, respectively[1]). The expansion parameter λ 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 α_1, while the resonance integrals β_{12} and β_{16} are assumed to be unaffected. The unperturbed Hamiltonian H_{al} is an alternant operator, while the perturbation $\hat{q}_1 - 1 = (\hat{R}_{11}^{\alpha} + \hat{R}_{11}^{\beta})/2$ 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 λ (Figure 2).

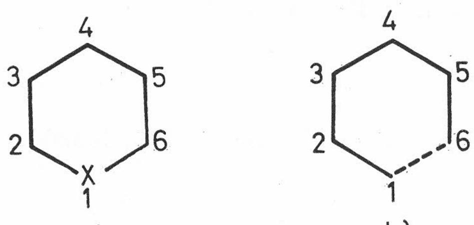

Figure 1. a) Example of an alternant system perturbed by an antialternant perturbation. The calculation is done within the Hückel approach, and the unperturbed system represents the benzene molecule. The perturbation is due to the presence of the heteroatom X, and it is represented by the operator $\lambda(\hat{q}_1 - 1)$ 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 $\hat{p}_{16}$ which is an alternant operator. Figures 6 to 8 illustrate the lack of symmetry with respect to the expansion parameter λ. 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 λ. In a similar way bond orders $P_{14}(\lambda)$ and $P_{26}(\lambda)$ are found to be even functions of λ. The total π-electron energy $E(\lambda)$ is also an even function of λ (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 λ, (Figure 4), as implied by relations

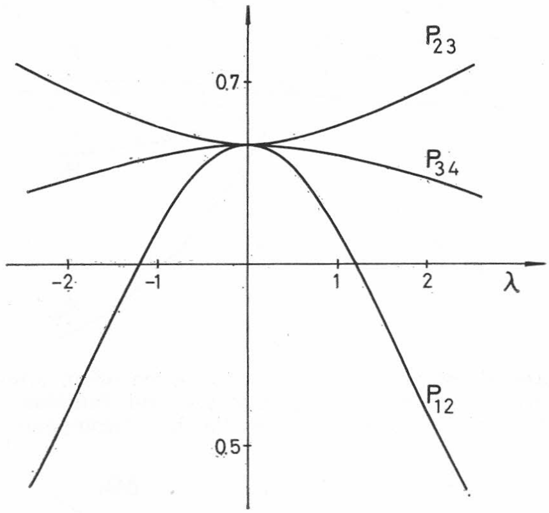

Figure 2. In the case of the antialternant perturbation of an alternant system bond orders between vertices of the opposite parity are even functions of the expansion parameter λ. This Figure corresponds to the heterocompound in Figure 1a.

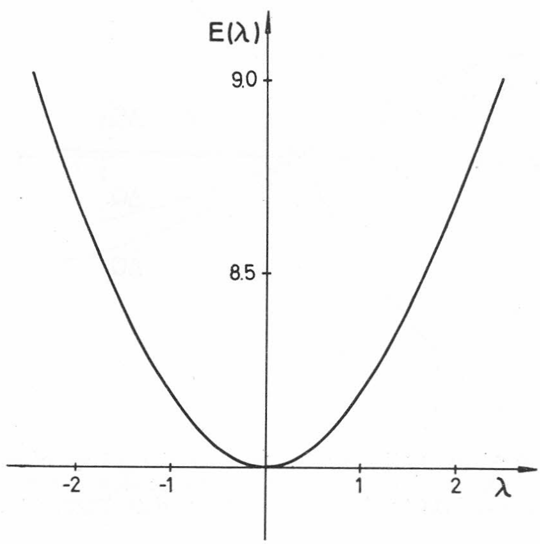

Figure 3. In the case of the antialternant perturbation of an alternant system the total energy is an even function of the expansion parameter λ. This Figure corresponds to the heterocompound in Figure 1a.

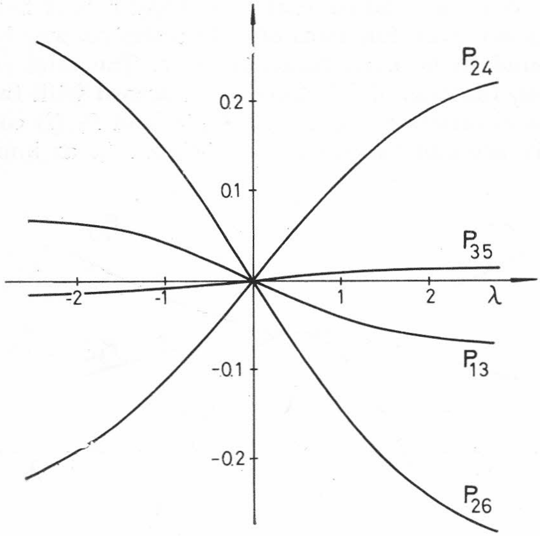

Figure 4. In the case of the antialternant perturbation of an alternant system bond orders between vertices of the same parity are odd functions of the expansion parameter λ. This Figure corresponds to the heterocompound in Figure 1a.

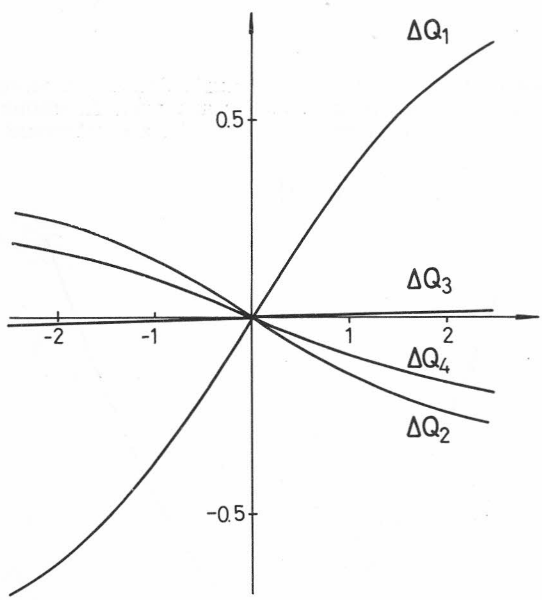

Figure 5. In the case of the antialternant perturbation of an alternant system netto charges $\Delta Q_i = Q_i - 1$ are odd functions of the expansion parameter λ. This Figure corresponds to the heterocompound in Figure 1a.

(15c). Similarly, perturbed total charges $\Delta Q_1 = Q_1 - 1$, ΔQ_2, ΔQ_3 and ΔQ_4 are also odd functions of λ (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-α and spin-β 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 Ψ is a one-determinental 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 β_{16} between vertices (1) and (6) as a perturbation (Figure 1b). In the Hückel approach the corresponding Hamiltonian is

$$H = H_{\mathrm{al}} + \lambda \hat{p}_{16} \tag{27}$$

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 λ. Similarly, bond orders $P_{14}(\lambda)$ and $P_{25}(\lambda)$ have no definite symmetry properties with respect to λ (Figure 7). Finally, the total π-electron energy $E(\lambda)$ is also neither an even nor an odd function of λ (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 λ. Similarly, total charges $Q_1(\lambda)$, $Q_2(\lambda), \ldots, Q_6(\lambda)$ are

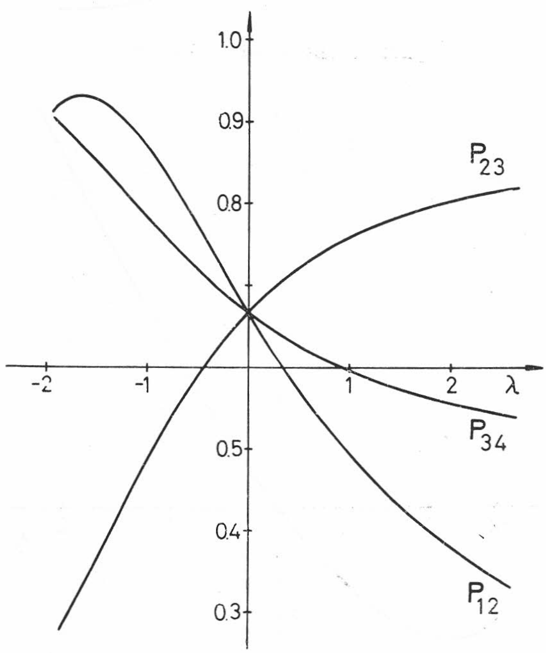

Figure 6. If the perturbation is not antialternant bond orders between vertices of the opposite parity are neither even nor odd functions of the expansion parameter λ. This Figure corresponds to the system represented in Figure 1b.

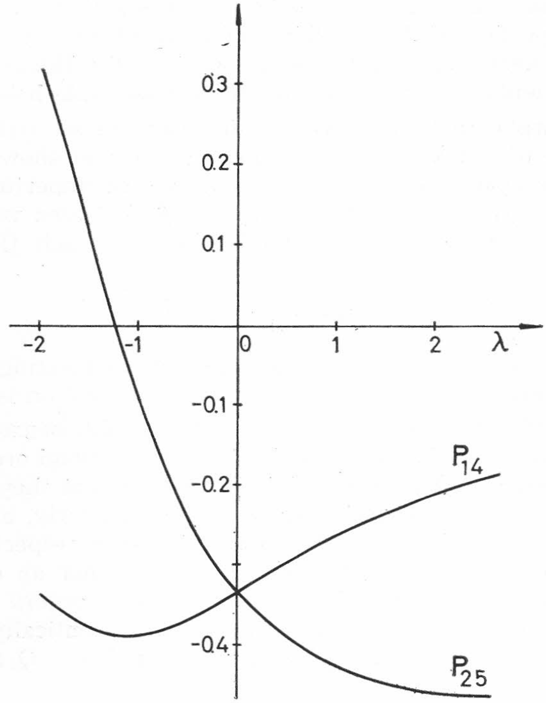

Figure 7. The same as Figure 6.

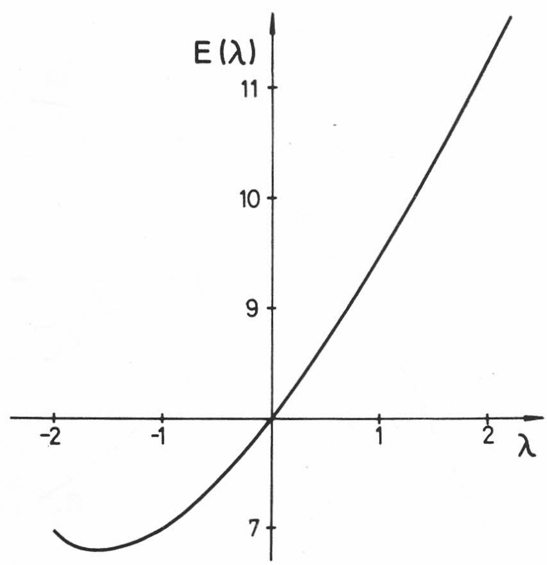

Figure 8. If the perturbation is not antialternant the total energy is neither an even nor an odd function of the expansion parameter λ. This Figure corresponds to the system represented in Figure 1b.

identically equal to one, *i. e.* they are also even functions of λ. However, this is a trivial consequence of the fact that the Hamiltonian (27) is an alternant operator, since the perturbation $\hat{p}_{16}$ 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 λ.

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[1], 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 λV 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 Φ_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 λ 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 λ, the expectation value of each alternant operator is an even function of λ, and the expectation value of each antialternant operator is an odd function of λ. 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.[1] 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.*[1]. An »arbitrary« state $\Psi(\lambda)$ is thus expanded in terms of functions with very particular and special properties. In addition, successive corrections $\Psi_k, \Psi_{k+1}, \ldots$ 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 evalution 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 Ψ_2^+, there is a double summation, and hence the number of terms is reduced roughly by the factor four, in the evalution of Ψ_3^- by the factor of eight, *etc.* Of course, one usually does not consider the complete CI space X_n, 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 evalution 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 considerebly simplify[5], 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°) and sink (B^*) subsets. The flexibility in the partition $B \rightarrow \{B^\circ, B^*\}$ can be efficiently used in order to make the antialternant perturbation λV as »small« as possible, especially in the case of the ground state.[5] 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.[1] 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 λ.

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 Φ_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.[5] 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 $\Phi_0^+ \in X_n^+$.[5] 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.[5] 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.[5]

In conclusion, the expansion theorem is valid quite generally, either in the present form, or with some modifications.[5]

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.[1-5] 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.[11] The critical discussion of these approaches can be found elsewhere.[3]

A1. *Alternant and Antialternant Operators*

Building blocks for the construction of alternant and antialternant operators are reduced operators $\hat{R}_{ij}$ and $\hat{R}_{ij,\,kl}$[1,2]

$$\hat{R}_{ij} = \hat{A}_{ij} - \delta_{ij} \tag{A1}$$

$$\hat{R}_{ij,kl} = \hat{A}_{ij,kl} \qquad (i \neq j \neq k \neq l) \tag{A2}$$

$$\hat{A}_{ik,\,jk} = 2\,\hat{A}_{ik,\,jk} + \hat{A}_{ij} \qquad (i \neq j \neq k) \tag{A3}$$

$$\hat{R}_{ij,\,ij} = 2\,\hat{A}_{ij,\,ij} + \hat{A}_{ii} + \hat{A}_{jj} - 1 \qquad (i \neq j) \tag{A4}$$

where

$$\begin{aligned} \hat{A}_{ij} &= \eta_i^+ \eta_j + \eta_j^+ \eta_i \\ \hat{A}_{ij,\,kl} &= \eta_i^+ \eta_j^+ \eta_k \eta_l + \eta_l^+ \eta_k^+ \eta_j \eta_i \end{aligned} \tag{A5}$$

and η_i^+ and η_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.[1,2] By definition, they satisfy symmetry relations

$$\begin{aligned} \hat{R}_{ij} &= \hat{R}_{ji} \\ \hat{R}_{ij,\,kl} &= -\hat{R}_{ji,\,kl} = \hat{R}_{kl,\,ij} \end{aligned} \tag{A6}$$

in order to mimic analogous symmetry relations satisfied by operators $\hat{A}_{ij}$ and $\hat{A}_{ij,\,kl}$.

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.[1,2]

Let there be $2n$ (an even number) of creation (annihilation) operators. Partition the set $B = \{i\}$ of $2n$ vertices (i) into subsets B° and B^* containing n vertices each.[1-3] The creation operator η_i^+, the annihilation operator η_i, the one-particle state (orbital) $|i\rangle = \eta_i^+|0\rangle$ and the vertex (i) are »source« if $(i) \in \{B^\circ\}$ and »sink« if $(i) \in \{B^*\}$.[1-3] Relative to this partition, each reduced operator is either »alternant« or »antialternant«:

a) Reduced alternant operators are[1,2]:

I	a unit operator	
$\hat{R}_{ij}$	i and j are of the opposite parity	(A7)
$\hat{R}_{ij,\,kl}$	even number of source vertices	

b) Reduced antialternant operators are [1,2]:

$$\hat{R}_{ij} \quad i \text{ and } j \text{ are of the same parity}$$
$$\hat{R}_{ij,\,kl} \quad \text{odd number of source vertices} \qquad \text{(A8)}$$

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 Theorem*[1-3]

Let X_n be the configuration interaction (CI) space spanned by all n-particle states $|\Delta_\nu\rangle = \eta_{i1}^+ \eta_{i2}^+ \ldots \eta_{in}^+ |0\rangle$ where $|0\rangle$ is a vacuum state

$$\eta_i |0\rangle = 0 \qquad i = 1, \ldots, 2n \qquad \text{(A9)}$$

The partition $B \to \{B^\circ, B^*\}$ uniquely determines the partition of the space X_n into two complementary subspaces X_n^+ and X_n^-.[1,3] 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 satisfy[1,2]

The splitting theorem

a) The expectation value $\langle \Psi^+ | \hat{O}_{al} | \Psi^- \rangle$ of each alternant operators $\hat{O}_{al}$ between states $\Psi^+ \in X_n^+$ and $\Psi^- \in X_n^-$ vanishes.

b) The expectation value $\langle \Psi_1 | \hat{O}_{nal} | \Psi_2 \rangle$ of each antialternant operator $\hat{O}_{nal}$ between states Ψ_1 and Ψ_2 vanishes whenever either $\Psi_1, \Psi_2 \in X_n^+$ or $\Psi_1, \Psi_2 \in X_n^-$.

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SAŽETAK

Antialternantne perturbacije alternantnih sistema

Tomislav P. Živković

Rayleigh-Schrödingerov račun smetnje primijenjen je na sistem gdje je neperturbirani hamiltonian H_0 alternantni operator, dok je smetanja λV antialternantni operator. Razmatran je konfiguracijsko-interakcijski prostor X_n što ga tvori n elektrona nad $2n$ ortonormiranih orbitala. Taj se prostor cijepa na komplementarne potprostore X_n^+ i X_n^- koji sadrže »alternantna« stanja. Ta stanja imaju karakteristična svojstva vlastitih stanja neutralnih alternantnih ugljikovodika. Ako vlastito stanje $\Phi_0 \in X_n$ neperturbiranog hamiltonijana H_0 nije degenerirano, tada je ono alternantno i može se bez gubitka općenitosti pretpostaviti $\Phi_0 = \Phi_0^+ \in X_n^+$. U tom je slučaju razvoj vlastitog stanja $\Psi(\lambda)$ totalnog hamiltonijana $H = H_0 + \lambda V$ u red potencija po parametru λ dan relacijom $\Psi(\lambda) = \Phi_0^+ + \lambda \Psi_1^- + \lambda^2 \Psi_2^+ + \lambda^3 \Psi_3^- + \ldots$, gdje su sve korekcije $\Psi_1^-, \Psi_2^+, \ldots$ alternantna stanja. Nadalje, sve parne korekcije sadržane su u prostoru X_n^+, a sve neparne korekcije sadražane su u prostoru X_n^-. Odgovarajuća vlastita vrijednost $E(\lambda)$ parna je funkcija od λ. Također, srednja vrijednost svakog alternantnog operatora parna je funkcija od λ, a srednja vrijednost svakoga antialternantnog operatora neparna je funkcija od λ. Ti su rezultati primijenjeni na matrične elemente jednočestičnih i dvočestičnih matrica gustoće, i dan je jednostavan primjer koji ilustrira ta svojstva.