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# Block Diagonalization Problem for a Fockian Matrix of Molecule and Its Solution by Means of Noncommutative Rayleigh–Schrödinger Perturbation Theory

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**ABSTRACT:** The block diagonalization problem for a Fockian or a Huckel-type model Hamiltonian matrix ( $\mathbf{H}$ ) of molecule originating from the Brillouin theorem and determining the noncanonical molecular orbitals (NCMOs) has been studied. An alternative form of the problem, viz. the so-called eigenblock equation for the matrix  $\mathbf{H}$ , has been suggested, which formally resembles the usual secular equation for certain two-dimensional matrix. The operator analog of the eigenblock equation also has been derived, and it acquired the form of the usual secular problem for an operator. However, the multidimensional eigenblocks of the matrix  $\mathbf{H}$ , playing the role of eigenvalues in this new equation, do not commute with the respective multidimensional eigenfunctions. A noncommutative Rayleigh–Schrödinger perturbation theory (PT) has been developed for the solution of operator problems of the above-mentioned type. It has been shown that the PT used previously when obtaining the NCMOs of saturated organic molecules on the basis of the Brillouin theorem [V. Gineityte, *J. Mol. Struct. (Theochem)* **343**, 183 (1995)] actually corresponds to the case of two eigenfunctions (eigenvalues) of the noncommutative Rayleigh–Schrödinger PT. On the whole, search for NCMOs of molecules is shown to be related to a nontrivial generalization of a two-level problem, where multidimensional (noncommutative) characteristics stand for the usual ones. © 1998 John Wiley & Sons, Inc. *Int J Quant Chem* **68**: 119–127, 1998

**Key words:** Brillouin theorem; noncanonical MOs; Rayleigh–Schrödinger perturbation theory; saturated organic molecules

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## Introduction

**E**lectronic structures of molecules are most commonly studied in terms of molecular orbitals (MOs) resulting from the canonical Hartree–Fock (HF) equation [1, 2]. Since the MOs are usually sought in the form of linear combination of certain basis functions [e.g., atomic orbitals (AOs)], the canonical HF equation resolves itself into the diagonalization problem for the Fockian matrix. Owing to the relation of eigenvalues of this matrix to ionization potentials of molecule (the Koopmans theorem [3]), the canonical MOs (CMOs) are especially popular in molecular spectroscopy.

The set of CMOs, however, is not the only possible set of one-electron states of molecule [1, 2, 4]. Moreover, certain advantages of other (i.e., non-canonical) MOs against the CMOs are known.

Thus, orbitals localized mostly on separate fragments of molecule (including chemical bonds and lone electron pairs) may be found just among noncanonical MOs (NCMOs) [4, 5]. As a result, relations may be established between the classical chemical concepts (such as that of localized two-electron bond) and quantum chemical characteristics [localized MOs (LMOs), respectively]. The possibility of deriving common expressions for NC-MOs of large sets of similar molecules discussed below, and the relation between the NC-MO representation matrix and the one-electron density matrix [6–9] also rank among the advantages of the NC-MOs.

Constitution and properties of LMOs have been studied extensively for various molecules (see, e.g., [10, 11]), but this does not refer to NC-MOs in general. Moreover, the greater popularity of the indirect ways of obtaining LMOs from CMOs gave rise to an opinion [5] of LMOs being of a subsidiary nature vs. CMOs. However, the possibility of obtaining NC-MOs directly from the Brillouin theorem [5–8, 12–14] speaks against such an opinion.

Among particular forms of the Brillouin theorem there is a zero value requirement for an off-diagonal element of the Fockian operator referring to an occupied and a vacant MO [1]. In its matrix form, the requirement resolves itself into the zero-matrix condition for the occupied–vacant off-diagonal block (submatrix) of the total Fockian matrix in the basis of NC-MOs being sought [6–8, 12–14]. Hence, the block diagonalization problem for the

Fockian matrix arises and it may be evidently traced back to the noncanonical HF equation [1]. In this context, the alternative way of interpretation of electronic structures in terms of NC-MOs seems to be a more general approach as compared to the canonical one.

Investigations in this field started with a contribution [12] where the existence of nonorthogonal LMOs containing a single strictly localized bond orbital (BO) and tails consisting of vacant BOs have been proved. Moreover, explicit algebraic expressions for these tails in terms of elements of the initial Huckel-type Hamiltonian matrix have been obtained using a perturbative approach [12–14] where interorbital interactions (resonance parameters) were included into the perturbation matrix.

The more general nature of the noncanonical approach vs. the canonical one becomes especially evident if we look for a common quantum chemical description of a class of molecules as a whole [6–8], e.g., of alkanes [7, 8]. Indeed, the diagonalization problem underlying the canonical approach may be solved for a particular matrix only. It is no surprise, therefore, that the early attempts in development of the electronic structure theory of saturated molecules (including alkanes) based on the canonical one-electron problem in the framework both of the Huckel-type models [15–19] and of the extended Huckel theory [20] did not avoid certain specifying of the structure of particular compound, to say nothing of more sophisticated (self-consistent) approaches [21–23].

Alternatively, the block diagonalization problem proved to be solvable in terms of entire submatrices (blocks) of the initial matrix without specifying either the structures and dimensions of submatrices themselves or the nature of approximations used when constructing the initial matrix [6–8]. Such a solution actually refers to certain class of matrices. As a result, common expressions have been derived for orthogonal NC-MOs of saturated organic molecules in general [6] and of alkanes in particular [7, 8] in the framework of the Huckel model using a certain matrix form of perturbation theory (PT). Zero-order resonance parameters between either two occupied BOs or two vacant ones were allowed in Ref. [6] in contrast to previous investigations [7, 8, 12–14].

In the framework of the above-mentioned PT the entire representation matrix of NC-MOs ( $C$ ) in the basis of BOs has been sought in the form of power series [6]. It is noteworthy that no explicit expressions have been obtained for separate cor-

rections ( $C_{(k)}$ ) of this series in contrast to the usual Rayleigh–Schrödinger PT [2, 24, 25]. In their place, matrix equations determining separate blocks of these corrections have been derived.

This promotes an expectation that certain non-trivial generalization corresponds to the problem under discussion vs. diagonalization of a particular matrix by means of the usual PT. This study deals with investigation of the nature of this generalization.

The standard Rayleigh–Schrödinger PT [2, 24, 25] is commonly applied to secular equations for Hamiltonian operators. Hence, to compare the PT of Ref. [6] to the conventional Rayleigh–Schrödinger PT, a new form of the Brillouin theorem is required, which would resemble a secular equation for an operator as closely as possible.

To this end, we reformulate the block diagonalization problem into the so-called eigenblock equation at first, so that the new equation looks like the secular problem for certain two-dimensional matrix (second section). Thereupon, we rewrite the eigenblock equation into an operator form (third section) which formally resembles the usual secular equation for an operator; however, the multi-dimensional analog of the eigenvalue does not commute with that of the respective eigenfunction. Then we develop a generalized version of the PT (fourth section) suitable for solution of operator equations of the above-mentioned type. And finally, we make sure that the PT of Ref. [6] corresponds to the two-level case of the noncommutative Rayleigh–Schrödinger PT.

### Alternative Form of the Block Diagonalization Problem

Let us consider a molecule containing  $2n$  electrons and a set of  $p$  orthogonal basis orbitals  $\{\varphi_i\}$ ,  $i = 1, 2, \dots, p$ . In accordance with the Brillouin theorem [1, 12–14], turning from the basis  $\{\varphi_i\}$  to the relevant set of NCMOS  $\{\psi_j\}$  may be carried out by transforming the initial Fockian or Huckel-type Hamiltonian matrix  $\mathbf{H}$  of our molecule into the following block-diagonal form:

$$\mathbf{H}' = \mathbf{C}^{-1}\mathbf{H}\mathbf{C} = \begin{vmatrix} \mathbf{E}_1^{(n \times n)} & 0 \\ 0 & \mathbf{E}_2^{(s \times s)} \end{vmatrix}, \quad (1)$$

where  $\mathbf{C}$  is the transformation matrix. The superscripts of submatrices (blocks)  $\mathbf{E}_1$  and  $\mathbf{E}_2$  indicate

their dimensions ( $n$  coincides with the number of occupied NCMOs, whereas  $s = p - n$  stands for the number of vacant NCMOs).

Let us assume now that the initial matrix  $\mathbf{H}$  may be divided (at least formally) into four submatrices, viz.

$$\mathbf{H} = \begin{vmatrix} \mathbf{H}_{11}^{(n \times n)} & \mathbf{H}_{12}^{(n \times s)} \\ \mathbf{H}_{21}^{(s \times n)} & \mathbf{H}_{22}^{(s \times s)} \end{vmatrix}. \quad (2)$$

Then the matrix  $\mathbf{C}$  being sought also may be represented as shown in Eq. (2). As a result, an analogy may be traced between the problem of Eq. (1) and the diagonalization problem for a two-dimensional matrix  $\mathbf{h}$ , the latter corresponding to the case  $n = s = 1$ . Given that an additional unitarity condition is imposed on the matrix  $\mathbf{C}$ , i.e.,

$$\mathbf{C}^+\mathbf{C} = \mathbf{I}, \quad (3)$$

the above-mentioned analogy allows the problem of Eq. (1) to be rewritten in the form

$$\mathbf{H}\mathbf{C} = \mathbf{C}\mathbf{E} \quad (4)$$

where  $\mathbf{E}$  stands for the total block-diagonal matrix of the right-hand side of Eq. (1). Equation (4) resembles the eigenvalue problem for the matrix  $\mathbf{h}$ , and it has been called the eigenblock equation [7].

The secular problem for a two-dimensional matrix is known to be solvable algebraically in terms of matrix elements. This fact along with the analogy between Eq. (4) and the secular problem for the matrix  $\mathbf{h}$  promotes an expectation that a general solution of Eq. (4) and thereby of the block diagonalization problem in terms of entire submatrices  $\mathbf{H}_{11}^{(n \times n)}$ ,  $\mathbf{H}_{12}^{(n \times s)}$ ,  $\mathbf{H}_{21}^{(s \times n)}$ , and  $\mathbf{H}_{22}^{(s \times s)}$  is feasible, and it may be found without specifying the internal constitution of submatrices. Then the submatrices are likely to play the role of usual matrix elements.

Such a solution, however, has been obtained for a particular case only. This case corresponds to saturated organic molecules where two subsets of basis orbitals separated by a large energy gap vs. the intersubset interactions have been revealed within the initial basis set [6]. The first subset contained the bonding bond orbitals (BBOs) along with lone pair orbitals (if any), while the second one consisted of antibonding BOs (ABOs). As a result, first-order magnitude of the off-diagonal blocks  $\mathbf{H}_{12}^{(n \times s)}$  and  $\mathbf{H}_{21}^{(s \times n)}$  of Eq. (2) vs. the diagonal ones  $\mathbf{H}_{11}^{(n \times n)}$  and  $\mathbf{H}_{22}^{(s \times s)}$  has been assumed. The

latter, in turn, have been represented as sums of respective zero-order terms  $\mathbf{E}_{(0)1}$  and  $\mathbf{E}_{(0)2}$  and of the respective first-order terms  $\mathbf{T}$  and  $\mathbf{Q}$ . Then the total Hamiltonian (Fockian) matrix  $\mathbf{H}$  takes the form

$$\mathbf{H} = \mathbf{H}_{(0)} + \mathbf{V}, \quad (5)$$

where

$$\mathbf{H}_{(0)} = \begin{vmatrix} \mathbf{E}_{(0)1} & 0 \\ 0 & \mathbf{E}_{(0)2} \end{vmatrix} \quad (6)$$

and

$$\mathbf{V} = \begin{vmatrix} \mathbf{T} & \mathbf{R} \\ \mathbf{R}^+ & \mathbf{Q} \end{vmatrix} \quad (7)$$

are the zero-order and first-order matrices, respectively;  $\mathbf{R}$  stands for the off-diagonal block  $\mathbf{H}_{12}^{(n \times s)}$ , and the superscript  $+$  designates the Hermitian conjugate matrix.

The form of the matrix  $\mathbf{H}$  shown in Eqs. (5)–(7) allowed a perturbative approach to be applied when solving Eq. (4). As a result, the solution of the eigenblock equation has been obtained in terms of entire submatrices  $\mathbf{E}_{(0)1}$ ,  $\mathbf{E}_{(0)2}$ ,  $\mathbf{T}$ ,  $\mathbf{R}$ , and  $\mathbf{Q}$ . This solution will be discussed later.

## Operator Form of the Brillouin Theorem

It is well-known that the eigenvalue equations for matrices may be reformulated into those for respective operators [2]. For example, the operator of the form

$$\hat{h} = \sum_{i,j=1}^2 |\varphi_i\rangle h_{ij} \langle \varphi_j| \quad (8)$$

corresponds to any two-dimensional matrix  $\mathbf{h}$  containing the elements  $h_{ij}$  ( $i, j = 1, 2$ ), and  $|\varphi_i\rangle$  and  $\langle \varphi_j|$  are basis functions of the two-level system in the form of ket and bra vectors, respectively. Moreover, the secular equation

$$\hat{h}|\psi_m\rangle = |\psi_m\rangle e_m \quad (9)$$

is the operator analog of the matrix problem

$$\mathbf{h}\mathbf{c}_m = \mathbf{c}_m e_m, \quad (10)$$

where  $|\psi_m\rangle$  is an eigenfunction of the operator  $\hat{h}$ ,  $e_m$  is the respective eigenvalue, and  $\mathbf{c}_m$  stands for the column matrix of two coefficients  $c_{km}$  ( $k = 1, 2$ ) contained within the linear combination

$$|\psi_m\rangle = \sum_{k=1}^2 |\varphi_k\rangle c_{km}. \quad (11)$$

Let us look now for the operator form of the eigenblock equation of Eq. (4). To this end, let us define  $n$ - and  $s$ -dimensional row matrices consisting of basis functions  $\varphi_1, \varphi_2, \dots, \varphi_n$  and  $\varphi_{n+1}, \varphi_{n+2}, \dots, \varphi_p$ , in accordance with the partition of the matrix  $\mathbf{H}$  shown in Eq. (2). These row matrices will be called multiorbitals and will be designated by ket vectors  $|\Phi_1\rangle$  and  $|\Phi_2\rangle$ . Then the bra vectors  $\langle \Phi_1|$  and  $\langle \Phi_2|$  coincide with column matrices containing the respective complex-conjugate basis orbitals.

The total matrix  $\mathbf{H}$  of Eq. (2) may be considered as consisting of four multidimensional elements  $H_{ij}$  ( $i, j = 1, 2$ ), each of them corresponding to a submatrix. Let us define an operator

$$\hat{H} = \sum_{i,j=1}^2 |\Phi_i\rangle H_{ij} \langle \Phi_j| \quad (12)$$

where

$$\mathbf{H}_{ij} = \langle \Phi_i | \hat{H} | \Phi_j \rangle \quad (13)$$

and

$$\langle \Phi_i | \Phi_j \rangle = \mathbf{I} \delta_{ij} \quad (14)$$

is the respective orthonormalization condition.

It is evident that after substituting a column and a row matrix for the bra and ket vector  $\langle \Phi_i|$  and  $|\Phi_j\rangle$ , respectively, into Eq. (13), a multidimensional Hamiltonian matrix element results. Accordingly, the product  $\langle \Phi_i | \Phi_j \rangle$  of Eq. (14) yields the relevant overlap matrix of basis orbitals. Furthermore, projectors into the multiorbitals  $|\Phi_1\rangle$  and  $|\Phi_2\rangle$  may be defined

$$\hat{P}_1 = |\Phi_1\rangle \langle \Phi_1| \equiv \sum_{i=1}^n |\varphi_i\rangle \langle \varphi_i| \quad (15a)$$

$$\hat{P}_2 = |\Phi_2\rangle \langle \Phi_2| \equiv \sum_{i=n+1}^p |\varphi_i\rangle \langle \varphi_i|. \quad (15b)$$

It is seen that  $\hat{P}_1$  and  $\hat{P}_2$  coincide with projectors into subspaces of basis orbitals  $\varphi_1, \varphi_2, \dots, \varphi_n$  and  $\varphi_{n+1}, \varphi_{n+2}, \dots, \varphi_p$ .

Let us consider the operator equation of the form

$$\hat{H}|\Psi_m\rangle = |\Psi_m\rangle\mathbf{E}_m, \quad (16)$$

where  $|\Psi_m\rangle$  is a row matrix either of occupied or of vacant NCMOs, and it may be called the multi-eigenfunction. Accordingly,  $\mathbf{E}_m$  stands for the respective eigenblock playing the role of a multidimensional eigenvalue. It is evident that  $\mathbf{E}_m$  does not commute with  $|\Psi_m\rangle$  within Eq. (16).

It may be easily verified that Eq. (16) is the operator form of the Brillouin theorem being sought. To this end, Eq. (12) along with the multi-eigenfunction  $|\Psi_m\rangle$  in the form of linear combination

$$|\Psi_m\rangle = \sum_{k=1}^2 |\Phi_k\rangle\mathbf{C}_{km} \quad (17)$$

containing the multidimensional coefficients  $\mathbf{C}_{km}$  should be substituted into Eq. (16) and Eq. (14) should be used.

Let us dwell now on the particular case of the matrix  $\mathbf{H}$  shown in Eqs. (5)–(7). From these expressions it follows that

$$\mathbf{H}_{ij} = \mathbf{H}_{(0)ij} + \mathbf{V}_{ij} \quad (18)$$

for any  $i$  and  $j$ . Hence, zero- and first-order Hamiltonian operators may be introduced:

$$\hat{H}_{(0)} = \sum_{i,j=1}^2 |\Phi_i\rangle\mathbf{H}_{(0)ij}\langle\Phi_j| \quad (19)$$

$$\hat{V} = \sum_{i,j=1}^2 |\Phi_i\rangle\mathbf{V}_{ij}\langle\Phi_j|, \quad (20)$$

and the total operator  $\hat{H}$  consists of a sum of these operators.

Therefore, the eigenblock equation for the matrix  $\mathbf{H}$  has been rewritten into an equation for the operator  $\hat{H}$ . The eigenblocks of the matrix  $\mathbf{H}$  and row matrices containing separate sets of NCMOs play the role of eigenvalues and eigenfunctions, respectively, in this new problem. As a result, noncommutativeness between any multidimensional eigenvalue and the respective multi-eigenfunction proves to be the main distinctive feature of this operator problem.

In the next section we are about to formulate a generalized version of the PT suitable for the solution of operator equations like that of Eq. (16).

## Noncommutative Rayleigh–Schrödinger Perturbation Theory

Let us start with the following operator problem:

$$\hat{H}|\Psi_a\rangle = |\Psi_a\rangle\mathbf{E}_a, \quad (21)$$

where  $\hat{H}$  stands for the initial Hamiltonian operator,  $\mathbf{E}_a$  designates a multidimensional eigenvalue, and  $|\Psi_a\rangle$  is the respective row matrix being called the multi-eigenfunction. The only difference of Eq. (21) from Eq. (16) consists in the allowance for an arbitrary number of multi-eigenvalues and multi-eigenfunctions.

Furthermore, the operator  $\hat{H}$  is supposed to consist of the zero-order term  $\hat{H}_{(0)}$  and of the first-order term  $\hat{V}$ , the latter being called the perturbation operator, i.e.,

$$\hat{H} = \hat{H}_{(0)} + \hat{V}. \quad (22)$$

We will assume also that the zero-order operator  $\hat{H}_{(0)}$  complies with the respective zero-order equation

$$\hat{H}_{(0)}|\Psi_{(0)i}\rangle = |\Psi_{(0)i}\rangle\mathbf{E}_{(0)i}. \quad (23)$$

The zero-order multi-eigenfunctions  $|\Psi_{(0)i}\rangle$  are supposed to be orthonormalized, i.e.,

$$\langle\Psi_{(0)m}|\Psi_{(0)i}\rangle = \mathbf{I}\delta_{im}. \quad (24)$$

As with the usual PT [2, 24, 25], let us represent the multi-eigenfunction  $|\Psi_a\rangle$  of the operator  $\hat{H}$  in the form of linear combination of the zero-order multi-eigenfunctions

$$|\Psi_a\rangle = \sum_i |\Psi_{(0)i}\rangle\mathbf{C}_{ia}, \quad (25)$$

where  $\mathbf{C}_{ia}$  are multidimensional coefficients.

Thereupon, Eq. (25) will be substituted into Eq. (21) and the relations of Eqs. (22) and (23) will be used. We then obtain

$$\sum_i [|\Psi_{(0)i}\rangle\mathbf{E}_{(0)i}\mathbf{C}_{ia} + \hat{V}|\Psi_{(0)i}\rangle\mathbf{C}_{ia}] = \sum_i |\Psi_{(0)i}\rangle\mathbf{C}_{ia}\mathbf{E}_a. \quad (26)$$

After multiplying Eq. (26) by the complex-conjugate function  $\langle\Psi_{(0)m}|$  from the left-hand side of

this relation and taking into account Eq. (24), we obtain the principal equation of our PT in terms of matrices:

$$\mathbf{C}_{ma}\mathbf{E}_a - \mathbf{E}_{(0)m}\mathbf{C}_{ma} = \sum_i \mathbf{V}_{mi}\mathbf{C}_{ia}, \quad (27)$$

where  $\mathbf{V}_{mi} = \langle \Psi_{(0)m} | \hat{V} | \Psi_{(0)i} \rangle$  are elements of the operator  $\hat{V}$ .

It is seen that the distinctive feature of Eq. (27) vs. the relevant analog of the usual PT [24] consists in noncommutativeness of factors within the products of the former. Moreover, the different relative order of factors within the two terms of the left-hand side of Eq. (27) proves to be essential.

Let us look for the coefficients  $\mathbf{C}_{ia}$  and the eigenvalues  $\mathbf{E}_a$  in the usual form of power series:

$$\begin{aligned} \mathbf{C}_{ia} &= \mathbf{C}_{(0)ia} + \mathbf{C}_{(1)ia} + \mathbf{C}_{(2)ia} + \dots \\ \mathbf{E}_a &= \mathbf{E}_{(0)a} + \mathbf{E}_{(1)a} + \mathbf{E}_{(2)a} + \dots \end{aligned} \quad (28)$$

and substitute Eq. (28) into Eq. (27).

Let us start with the zero-order equation

$$\mathbf{C}_{(0)ma}\mathbf{E}_{(0)a} - \mathbf{E}_{(0)m}\mathbf{C}_{(0)ma} = 0, \quad (29)$$

which belongs to matrix equations of the form [26]

$$\mathbf{A}\mathbf{X} + \mathbf{X}\mathbf{B} = a\mathbf{D}, \quad (30)$$

where  $\mathbf{X}$  is the matrix being sought and  $a$  is a constant. Indeed, Eq. (29) coincides with the particular case of Eq. (30) when  $\mathbf{D} = 0$ . Two cases may be distinguished here:

1. If  $\mathbf{E}_{(0)a} \neq \mathbf{E}_{(0)m}$ , the only zero solution  $\mathbf{C}_{(0)ma} = 0$  may be expected to be peculiar to Eq. (29) (see the Appendix). The eigenfunction  $|\Psi_a\rangle$  would contain first-order terms only in this case, and such a result is not compatible with the expression for the operator  $\hat{H}$  where the zero-order term is also present [see Eq. (22)].

2. If  $\mathbf{E}_{(0)a} = \mathbf{E}_{(0)m}$ , the solution  $\mathbf{C}_{(0)ma} = \mathbf{I}$  complies with Eq. (29). At the same time, this solution resembles the respective expression of the usual PT [24]. Hence, let us accept the equalities

$$\mathbf{E}_{(0)a} = \mathbf{E}_{(0)m}, \quad \mathbf{C}_{(0)am} = \mathbf{I}\delta_{am}. \quad (31)$$

Then the subscripts  $m, i, k$ , etc., describing the zero-order multieigenfunctions of Eq. (23), may be used also when denoting those of the total Hamiltonian operator  $\hat{H}$ .

The first-order equation for  $a = k$  takes the form

$$\mathbf{C}_{(0)mk}\mathbf{E}_{(1)k} + \mathbf{C}_{(1)mk}\mathbf{E}_{(0)k} - \mathbf{E}_{(0)m}\mathbf{C}_{(1)mk} = \mathbf{V}_{mk}. \quad (32)$$

For  $m \neq k$ , we then obtain

$$\mathbf{E}_{(0)m}\mathbf{C}_{(1)mk} - \mathbf{C}_{(1)mk}\mathbf{E}_{(0)k} + \mathbf{V}_{mk} = 0. \quad (33)$$

It is seen that in the case of commutative parameters Eq. (33) yields the usual expression for the coefficient  $c_{(1)mk}$ . In the general case Eq. (33) belongs to matrix equations of the form shown in Eq. (30) and may be solved as discussed in the Appendix.

Let us look now for the coefficient  $\mathbf{C}_{(1)kk}$ . This may be obtained on the basis of the orthonormalization requirement for multieigenfunctions:

$$\langle \Psi_k | \Psi_m \rangle = \mathbf{I}\delta_{km}. \quad (34)$$

To this end, let us write  $\langle \Psi_k |$  and  $|\Psi_m\rangle$  in the form

$$\begin{aligned} |\Psi_m\rangle &= |\Psi_{(0)m}\rangle + \sum_{i \neq m} |\Psi_{(0)i}\rangle \mathbf{C}_{im} \\ \langle \Psi_k | &= \langle \Psi_{(0)k} | + \sum_{j \neq k} \mathbf{C}_{jk}^+ \langle \Psi_{(0)j} |. \end{aligned} \quad (35)$$

After substituting Eq. (35) into (34) and collecting the first-order terms, we obtain

$$\mathbf{C}_{(1)mk}^+ + \mathbf{C}_{(1)km} = 0. \quad (36)$$

In the case  $m = k$ , from Eq. (36) it follows that

$$\mathbf{C}_{(1)kk}^+ + \mathbf{C}_{(1)kk} = 0. \quad (37)$$

Equation (37) implies a zero-matrix condition for the Hermitian (symmetric) part of the correction  $\mathbf{C}_{(1)kk}$ , whereas the skew-Hermitian (skew-symmetric) part remains undefined. The analog of this result within the usual PT coincides with the zero-value requirement for the real part of the coefficient  $c_{(1)kk}$  following from the orthonormalization condition for the eigenfunction being sought [25]. The imaginary part of this coefficient is also taken to be zero in the usual PT [24, 25], and this additional assumption corresponds to a certain choice of the phase of the wave function [25]. On the basis of this analogy let us assume that

$$\mathbf{C}_{(1)kk}^+ = \mathbf{C}_{(1)kk} = 0. \quad (38)$$

(This does not imply, however, that other choices of  $\mathbf{C}_{(1)kk}^+ - \mathbf{C}_{(1)kk}$  and thereby other solutions of our problem are impossible).

Let us take now the case  $m = k$  within Eq. (32) and use Eq. (38). We then obtain

$$\mathbf{E}_{(1)k} = \mathbf{V}_{kk}, \quad (39)$$

and this result also coincides with the usual one [2, 24, 25].

The second-order equation of our PT takes the form

$$\delta_{mk} \mathbf{E}_{(2)k} + \mathbf{C}_{(1)mk} \mathbf{V}_{kk} + \mathbf{C}_{(2)mk} \mathbf{E}_{(0)k} - \mathbf{E}_{(0)m} \mathbf{C}_{(2)mk} = \sum_i \mathbf{V}_{mi} \mathbf{C}_{(1)ik}, \quad (40)$$

where  $\mathbf{V}_{kk}$  stands for  $\mathbf{E}_{(1)k}$  in accordance with Eq. (39).

In the case  $m \neq k$  the relation of Eq. (40) becomes

$$\mathbf{E}_{(0)m} \mathbf{C}_{(2)mk} - \mathbf{C}_{(2)mk} \mathbf{E}_{(0)k} + \mathbf{W}_{mk} = 0, \quad (41)$$

where

$$\mathbf{W}_{mk} = \sum_i \mathbf{V}_{mi} \mathbf{C}_{(1)ik} - \mathbf{C}_{(1)mk} \mathbf{V}_{kk}. \quad (42)$$

The relation of Eq. (41) for  $\mathbf{C}_{(2)mk}$  proves to be similar to that for  $\mathbf{C}_{(1)mk}$  shown in Eq. (33). The coefficient  $\mathbf{C}_{(2)kk}$  may be obtained from the second-order terms of the requirement shown in Eq. (34). Then the following relation results

$$\mathbf{C}_{(2)mk}^+ + \mathbf{C}_{(2)km} + \sum_{i \neq k, m} \mathbf{C}_{(1)ik}^+ \mathbf{C}_{(1)im} = 0. \quad (43)$$

As with the first-order term  $\mathbf{C}_{(1)kk}$ , let us accept the equality

$$\mathbf{C}_{(2)kk}^+ = \mathbf{C}_{(2)kk}. \quad (44)$$

Then the relation of Eq. (43) for  $m = k$  yields the expression

$$\mathbf{C}_{(2)kk} = -\frac{1}{2} \sum_{i \neq k} \mathbf{C}_{(1)ik}^+ \mathbf{C}_{(1)ik}. \quad (45)$$

In the case  $m = k$  the second-order correction  $\mathbf{E}_{(2)k}$  for the generalized eigenvalue  $\mathbf{E}_k$  follows from Eq. (40):

$$\mathbf{E}_{(2)k} = \sum_i \mathbf{V}_{ki} \mathbf{C}_{(1)ik} - \mathbf{C}_{(2)kk} \mathbf{E}_{(0)k} + \mathbf{E}_{(0)k} \mathbf{C}_{(2)kk}. \quad (46)$$

Using Eq. (44) for  $\mathbf{C}_{(2)kk}$  we obtain

$$\mathbf{E}_{(2)k} = \sum_i (1 - \delta_{ki}) [\mathbf{V}_{ki} \mathbf{C}_{(1)ik} + \frac{1}{2} \mathbf{C}_{(1)ik}^+ \mathbf{E}_{(0)k} \mathbf{C}_{(1)ik} - \frac{1}{2} \mathbf{E}_{(0)k} \mathbf{C}_{(1)ik}^+ \mathbf{C}_{(1)ik}]. \quad (47)$$

This expression for  $\mathbf{E}_{(2)k}$  may be simplified considerably. To this end let us substitute  $\mathbf{E}_{(0)i} \mathbf{C}_{(1)ik} + \mathbf{V}_{ik}$  and  $\mathbf{C}_{(1)ki} \mathbf{E}_{(0)i} - \mathbf{V}_{ki}$  for  $\mathbf{C}_{(1)ik} \mathbf{E}_{(0)k}$  and  $\mathbf{E}_{(0)k} \mathbf{C}_{(1)ik}^+ \equiv -\mathbf{E}_{(0)k} \mathbf{C}_{(1)ki}$ , respectively, in accordance with Eqs. (33) and (36). We then obtain

$$\mathbf{E}_{(2)k} = \frac{1}{2} \sum_i (1 - \delta_{ki}) (\mathbf{V}_{ki} \mathbf{C}_{(1)ik} - \mathbf{C}_{(1)ki} \mathbf{V}_{ik}). \quad (48)$$

Therefore, the coefficients  $\mathbf{C}_{(1)mk}$  and  $\mathbf{C}_{(2)mk}$  of the noncommutative Rayleigh–Schrödinger PT are determined by matrix equations of Eqs. (33) and (41), whereas  $\mathbf{C}_{(1)kk}$  and  $\mathbf{C}_{(2)kk}$  prove to be defined algebraically in terms of the former. Given that the principal equations of Eqs. (33) and (41) are solved, the multieigenfunctions and multidimensional eigenvalues of the operator  $\hat{H}$  may be easily obtained on the basis of Eqs. (31), (38), (39), (45), and (48).

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## Discussion of the Particular Case of Saturated Organic Molecules: Summarizing Remarks

The results corresponding to the Hamiltonian (Fockian) matrix of saturated organic molecules shown in Eqs. (5)–(7) follow directly from the expressions given in the preceding section if the number of multieigenfunctions is assumed to be equal to 2. Thus, let the subscripts  $m$ ,  $l$ , and  $k$  of the preceding section coincide with either 1 and 2 (see above). Then the following expressions:

$$\mathbf{V}_{12} = \mathbf{R}, \quad \mathbf{W}_{12} = \mathbf{T} \mathbf{C}_{(1)12} - \mathbf{C}_{(1)12} \mathbf{Q} \quad (49)$$

should be substituted into Eqs. (33) and (41). As a result, the above-mentioned matrix equations determine the off-diagonal blocks of the matrix  $\mathbf{C}$ . These are

$$\mathbf{E}_{(0)1} \mathbf{C}_{(1)12} - \mathbf{C}_{(1)12} \mathbf{E}_{(0)2} + \mathbf{R} = 0, \quad (50)$$

$$\mathbf{E}_{(0)1} \mathbf{C}_{(2)12} - \mathbf{C}_{(2)12} \mathbf{E}_{(0)2} + \mathbf{W}_{12} = 0, \quad (51)$$

and coincide with the respective equations of Ref. [6]. Accordingly, the diagonal blocks of the matrix  $\mathbf{C}$  follow from Eq. (45):

$$\mathbf{C}_{(2)11} = -\frac{1}{2} \mathbf{C}_{(1)12} \mathbf{C}_{(1)12}^+, \quad \mathbf{C}_{(2)22} = -\frac{1}{2} \mathbf{C}_{(1)12}^+ \mathbf{C}_{(1)12}, \quad (52)$$

and this result also is in agreement with the relevant expressions of Ref. [6]. And finally, from Eqs.

(39) and (48) we obtain that

$$\begin{aligned} E_1 &= E_{(0)1} + T - \frac{1}{2}(C_{(1)12}R^+ + RC_{(1)12}), \\ E_2 &= E_{(0)2} + Q + \frac{1}{2}(C_{(1)12}^+R + R^+C_{(1)12}). \end{aligned} \quad (53)$$

Therefore, the matrix form of the PT developed in Ref. [6] for saturated organic molecules actually coincides with the case of two multieigenfunctions of the noncommutative Rayleigh–Schrödinger PT. In this connection, additional conclusions may be drawn about the nature of generalization underlying the common quantum mechanical description of saturated organic molecules based on the block diagonalization problem for the respective common Huckel-type Hamiltonian matrix [6].

So far as the matrix representation of the problem is concerned, the essence of the generalization consists in passing from one-dimensional (commutative) to multidimensional (noncommutative) Hamiltonian matrix parameters.

The operator form of the same problem follows from the results given in the third section provided that the multidimensional parameters  $H_{ij}$  are taken from Eqs. (5)–(7). Accordingly, Eq. (12) may be considered as a definition of the common Hamiltonian operator of saturated organic molecules. In this connection, noncommutativity of a multidimensional eigenfunction, and of the respective multidimensional eigenvalue of the Hamiltonian operator of saturated organic molecules, may be regarded as an alternative formulation of the nature of the generalization under discussion.

Similar conclusions refer also to the noncanonical approach to the investigation of the electronic structure of molecules in general. Thus, application of the Brillouin theorem for obtaining NCMOs of any molecule is associated with passing to multidimensional (noncommutative) quantum chemical characteristics. The question whether these characteristics may be derived by means of the noncommutative Rayleigh–Schrödinger PT should be examined in each particular case separately.

### Appendix: On the Solution of the Matrix Equations $AX + XB = aD$

The general theory of matrix equations

$$AX + XB = aD \quad (A1)$$

where  $A$  and  $B$  are square matrices,  $a$  is a constant and  $X$  is the matrix being sought, may be found in

Ref. [26]. In particular, a unique solution of Eq. (A1) has been proved to exist if the real parts of eigenvalues of both matrices  $A$  and  $B$  are negative. Moreover, this solution may be presented as an integral:

$$X = -a \int_0^\infty \exp(At)D \exp(Bt) dt. \quad (A2)$$

Given that  $A$  and  $B$  are Hermitian matrices, the negative-value requirement refers to eigenvalues themselves.

In the case of saturated organic molecules, we obtain

$$A = E_{(0)1}, \quad B = -E_{(0)2} \quad (A3)$$

and thereby both  $A$  and  $B$  are Hermitian matrices.

One-electron energies of BBOs (ABOs) of these molecules acquire the negative (positive) values after an appropriate choice of the energy reference point [6]. Moreover, absolute values of these energies are known to be sufficiently large vs. the interorbital resonance parameters [27–29] standing in the off-diagonal positions of matrices  $E_{(0)1}$  and  $E_{(0)2}$ . Hence, the eigenvalues of matrices  $E_{(0)1}$  and  $-E_{(0)2}$  may be expected to be negative, and the solution of Eq. (A1) shown in Eq. (A2) is likely to be valid in this case.

Given that the particular structures of matrices  $A$  and  $B$  are known, these may be diagonalized using unitary matrices  $U$  and  $V$ :

$$A^* = U^+AU, \quad B^* = V^+BV, \quad (A4)$$

where  $A^*$  and  $B^*$  are diagonal matrices involving elements  $\alpha_i$  and  $\beta_j$ , respectively, i.e.,

$$A_{ik}^* = \alpha_i \delta_{ik}, \quad B_{kj}^* = \beta_j \delta_{kj}. \quad (A5)$$

Then the initial problem of Eq. (A1) may be rewritten in the form

$$A^*X^* + X^*B^* = aD^*, \quad (A6)$$

where  $X^* = U^+XV$  and  $D^* = U^+DV$ . After further rewriting of Eq. (A6) into components and using Eq. (A5), the elements of the matrix  $X^*$  follow:

$$X_{ij}^* = aD_{ij}^*/(\alpha_i + \beta_j). \quad (A7)$$

Then the matrix  $X$  equals to

$$X = UX^*V^+. \quad (A8)$$

This algorithm may be regarded as a practical way of solving Eq. (A1).



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