The Matrix Form of the Noncanonical Theory of Molecular Orbitals

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ABSTRACT: The eigenblock equation for a Fockian- or Hückel-type Hamiltonian matrix of a molecule being an alternative form of the Brillouin theorem and determining the noncanonical molecular orbitals (NCMOs) was generalized to the case of nonorthogonal initial basis sets. As in the Löwdin's partitioning technique, the initial set of basis orbitals was divided into two subsets. This allowed the problem to be formulated in terms of these subsets and the respective submatrices. A perturbative approach was developed for the solution of the new matrix equation in terms of entire submatrices (blocks) of both Fockian and overlap matrices without specifying either the structures or dimensions of these submatrices. Two multidimensional molecular orbitals (MMOs) containing the subsets of occupied and vacant noncanonical MOs (NCMOs), respectively, were defined for any molecule, and these MMOs were expressed in the form of linear combinations of two subsets of basis orbitals with matrix coefficients. A linear combination of this type may be considered as a generalization of the usual LCAO approximation for an MO of a two-level system. The relevant common form of the bond-order matrix was shown to be obtainable on the basis of the projector to a single occupied MMO. These results allowed us to conclude that the generalized matrix problem obtained in this article forms the basis of the noncanonical MO theory of electronic structures of molecules in its matrix representation. The new matrix problem along with its solution was compared to related problems and methods. © 1999 John Wiley & Sons, Inc. Int J Quant Chem 72: 559–570, 1999

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Introduction

One-electron orbitals of molecules (molecular orbitals) are usually sought in the form of linear combinations of certain nonorthogonal basis functions (e.g., AOs). As a result, the operator equations determining these orbitals turn into respective matrix problems [1–3].

In the case of the canonical Hartree–Fock (HF) equation [1, 2] one obtains the diagonalization problem for the Fockian matrix of molecule along with orthonormalization condition for molecular

orbitals (MOs) being sought (these MOs are usually referred to as the canonical MOs (CMOs)). Owing to the relation of eigenvalues of the Fockian matrix to the ionization potentials of a molecule (the Koopmans theorem [4]) the sets of CMOs are especially popular in molecular spectroscopy. It is also noteworthy that the CMOs are, as a rule, delocalized over the whole molecule [1–3, 5].

In contrast to the unique canonical HF equation, various forms of the noncanonical one-electron problem are possible. Such a variety may be traced back to the fact that the general version of the HF equation containing off-diagonal Lagrange multipliers has no unique solution [1, 2]. As delocalized MOs may be more easily obtained from the canonical HF equation, the noncanonical one-electron problem is usually adapted [5] to look for orbitals localized mostly on separate fragments of molecule and thereby being more closely related to chemical concepts of bonds, lone electron pairs, etc. [5–7]. Furthermore, to obtain a set of MOs being as localized as possible [8], the orthogonality requirement for these orbitals is given up in addition, although the problem becomes both more involved and more ambiguous in this case.

The well-known Adams–Gilbert equation [5, 9–12] and its various modifications [8, 13–16] serve as an example of the above-mentioned adaptation. The respective initial problem takes the form of an eigenvalue equation for an ambiguous effective operator in this case. After introducing an appropriate localization criterion for orbitals being sought into this operator, an eigenvalue equation for effective Fockian of a subsystem (fragment) embedded into the molecule under study follows. In particular, the criterion of minimal self-energy of an atom yields an equation for atoms (ions) in molecules and/or crystals [9, 10, 12] being closely related to the theory of pseudopotentials [8, 15]. It is evident that these equations also resolve themselves into diagonalization problems when turning to respective matrix representations.

In this context, the Brillouin theorem [1, 5, 17–24] deserves particular attention. Indeed, application of this theorem is equivalent to solution of the noncanonical HF equation as shown in [1]. On the other hand, the theorem itself contains no particular localization criterion and, consequently, it may be used to obtain various types of noncanonical MOs (NCMOs). The existence of NCMOs of the desired type also may be verified on the basis of the Brillouin theorem. This possibility may be exemplified by the results of [18] where the existence of nonorthogonal NCMOs containing a single strictly localized bond orbital and tails consisting of vacant BOs has been proved under certain conditions.

The most important feature of the Brillouin theorem, however, consists of the fact that it yields a new and more general matrix problem after turning to matrix representation. Let us discuss this point in more detail.

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, this 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 NCMOs being sought [18–24]. As a result, the block-diagonalization problem for the Fockian matrix arises and it includes the diagonalization problem as a particular case [22, 24].

The more general nature of the block-diagonalization problem versus the diagonality requirement allowed us to expect that the former has more general solutions, for example, for entire classes of matrices. This expectation has been supported by the results of [21–24], wherein the block-diagonalization problem was solved in an orthogonal basis in terms of entire submatrices (blocks) of the initial matrix without specifying either the internal constitutions or dimensions of these blocks. Moreover, these solutions proved to be independent of approximations made within the initial matrix including the use of the Hückel-type model.

Inasmuch as nonorthogonal basis sets of AOs are most commonly used in quantum chemistry, generalization of the above-mentioned solution to the case of a nonorthogonal basis becomes an important task. Now, the solution is expected to be expressed in terms of submatrices of both Fockian and overlap matrices. It is precisely the accomplishing of this generalization that this article was aimed at.

Furthermore, we intend to demonstrate that the solution of the block-diagonalization problem in terms of submatrices may be used directly to form other quantum chemical characteristics of molecules including the bond order (BO) matrix. This, in turn, implies a feasibility of constructing a general matrix form of the noncanonical theory of MOs.

Formulation of the Block-diagonalization Problem in the Case of a Nonorthogonal Basis Set

Let us consider a molecule containing $2n$ electrons and a set of p nonorthogonal basis orbitals $\{\varphi_i\}$, $i = 1, 2 \cdots p$. The overlap matrix of these orbitals will be designated by S.

In accordance with the Brillouin theorem in its matrix representation [18–24], turning from the basis $\{\varphi_i\}$ to the relevant set of NCMOs $\{\psi_j\}$ may be carried out by transforming the initial Fockian- or Hückel-type Hamiltonian matrix H of our molecule into a block-diagonal form. Thus, let us look for a transformation matrix C determined by the following block-diagonality condition:

$$C^+ H C = E \equiv \begin{vmatrix} E_1^{(n \times n)} & 0^{(n \times k)} \\ 0^{(k \times n)} & E_2^{(k \times k)} \end{vmatrix}, \qquad (1)$$

which coincides with the respective requirement in the case $S = I$ [23, 24]. The superscript "+" within the left side of Eq. (1) designates the Hermitian-conjugate (transposed) matrix, whereas those of submatrices (blocks) of the matrix E indicate the dimensions of these blocks (n coincides with the number of occupied NCMOs, whereas $k = p - n$ stands for the number of vacant NCMOs).

As in [21–24], let us impose an orthogonality condition on NCMOs being sought. In the case of a nonorthogonal basis set $\{\varphi_i\}$, this condition takes the form [2, 3]

$$C^+ S C = I^{(p \times p)}, \qquad (2)$$

where $I^{(p \times p)}$ is the p-dimensional unit matrix.

Let us invoke now the Löwdin's partitioning technique originally developed [3, 25–28] for transforming the eigenvalue problems for matrices into effective problems of lower dimensions. The central idea of this technique consists of partitioning the basis set into two subsets and in reformulating the initial matrix problem in terms of these subsets and the respective submatrices.

Thus, let us assume that the initial basis set $\{\varphi_i\}$ may be divided (at least formally) into two subsets containing n and k basis functions, respectively. Then, n- and k-dimensional row matrices consisting of basis orbitals $\varphi_1, \varphi_2, \ldots \varphi_n$ and $\varphi_{n+1}, \varphi_{n+2}, \ldots \varphi_p$ may be defined. These row matrices will be designated by ket-vectors $|\Phi_1\rangle$ and $|\Phi_2\rangle$,

respectively, and further referred to as multidimensional basis orbitals (MBOs). The bra-vectors $\langle\Phi_1|$ and $\langle\Phi_2|$ evidently coincide with column matrices containing the respective complex-conjugate orbitals.

Accordingly, the matrices H, S, and C may be represented in terms of four submatrices (blocks), for example:

$$H = \begin{vmatrix} H_{11}^{(n \times n)} & H_{12}^{(n \times k)} \\ H_{21}^{(k \times n)} & H_{22}^{(k \times k)} \end{vmatrix}. \qquad (3)$$

Then, the block-diagonality condition of Eq. (1) may be considered as a generalization of the diagonalization problem for a two-dimensional matrix h, the latter corresponding to the case $n = k = 1$ [22, 24]. The generalization consists of passing from one-dimensional to multidimensional matrix elements. The same conclusion is evidently valid for the orthonormalization condition of Eq. (2). Hence, the matrix problems of Eqs. (1) and (2) make up a generalization of the two-level problem in the basis of two nonorthogonal basis functions $|\varphi_1\rangle$ and $|\varphi_2\rangle$. As with the latter, the requirements of Eqs. (1) and (2) may be rewritten as a single matrix equation [3]:

$$HC = SCE, \qquad (4)$$

where E stands for the block-diagonal matrix of Eq. (1).

Let us revert for a while to the case of orthonormalized basis functions $\{\varphi_i\}$ described by the equality $S = I^{(p \times p)}$ [21–24]. Then, the eigenblock equation [22] for the matrix H

$$HC = CE \qquad (5)$$

follows from Eq. (4). The solution of Eq. (5) was obtained in terms of entire submatrices (blocks) $H_{11}^{(n \times n)}$, $H_{12}^{(n \times k)}$, $H_{21}^{(k \times n)}$, and $H_{22}^{(k \times k)}$ in a particular case only [23, 24]. The case was described by an additional assumption that the two subsets of basis orbitals are separated by a large energy gap versus the intersubset interactions contained within the submatrix $H_{12}^{(n \times k)}$. This promotes an expectation that the matrix problem of Eq. (4) also may be solved in terms of entire submatrices H_{ij} and S_{ij} ($i, j = 1, 2$) under small-matrix conditions for both $H_{12}^{(n \times k)}$ and $S_{12}^{(n \times k)}$. This solution will be obtained and analyzed in the third section.

Before finishing this section, let us define additional multidimensional electronic-structure characteristics necessary for further studies. Thus, let

us introduce a row matrix $|\Psi_m\rangle$ containing either the set of occupied NCMOs ($m = 1$) or of vacant ones ($m = 2$). Given that the solution of the matrix problem shown in Eq. (4) is obtained and thereby the four submatrices C_{jm} ($j = 1, 2$) of the matrix C are known, the row matrix $|\Psi_m\rangle$ may be expressed as a linear combination of two MBOs, that is,

$$|\Psi_m\rangle = |\Phi_1\rangle C_{1m} + |\Phi_2\rangle C_{2m} \equiv \sum_{j=1}^{2} |\Phi_j\rangle C_{jm}, \quad (6)$$

where the submatrices C_{jm} of the matrix C play the role of coefficients. In the case $n = k = 1$, Eq. (6) evidently turns into an usual expression for an MO of the two-level system described by the Hamiltonian matrix h. Hence, Eq. (6) may be considered as a generalization of the usual LCAO approximation for MOs. In this context, the row matrices $|\Psi_1\rangle$ and $|\Psi_2\rangle$ may be called the multidimensional MOs (MMOs). This concept is evidently immanent in the NCMO method.

It is also evident that the relevant one-electron density matrix (DM) may be defined as a projector onto the occupied MMO $|\Psi_1\rangle$ multiplied by the occupation number 2, that is,

$$P(r|r') = 2|\Psi_1(r)\rangle\langle\Psi_1(r')|. \quad (7)$$

Indeed, the right-hand side of Eq. (7) actually contains a sum of projectors to all occupied NCMOs. If we rewrite the expressions for $|\Psi_1(r)\rangle$ and $\langle\Psi_1(r')|$ shown in Eq. (6) into the form

$$|\Psi_1(r)\rangle = ||\Phi_1(r)\rangle|\Phi_2(r)\rangle| \begin{vmatrix} C_{11} \\ C_{21} \end{vmatrix} \quad (8a)$$

$$\langle\Psi_1(r')| = |C_{11}^+ \quad C_{21}^+| \begin{vmatrix} \langle\Phi_1(r')| \\ \langle\Phi_2(r')| \end{vmatrix} \quad (8b)$$

and substitute Eqs. (8a, b) into Eq. (7), the following expression for the DM $P(r|r')$ in terms of four multidimensional elements of the BO matrix results in

$$P(r|r') = \sum_{i,j=1}^{2} |\Phi_i(r)\rangle P_{ij}\langle\Phi_j(r')|, \quad (9)$$

which serves as a generalization of the well-known bilinear form of the DM in terms of individual basis functions [1–3]. The elements P_{ij} of the BO matrix P are

$$P_{11} = 2C_{11}C_{11}^+, \qquad P_{22} = 2C_{21}C_{21}^+ \quad (10)$$

and

$$P_{12} = 2C_{11}C_{21}^+. \quad (11)$$

The $n \times n$- and $k \times k$-dimensional matrices P_{11} and P_{22} are the multidimensional analogs of the occupation numbers (populations) of basis functions and these may be called the intrasubset population matrices. Accordingly, the matrix P_{12} defined by Eq. (11) may be referred to as the intersubset BO matrix.

Solution of the Problem in the Case of Small Intersubset Interaction

Let us turn now to the case when the subsets of basis orbitals $\varphi_1, \varphi_2 \cdots \varphi_n$ and $\varphi_{n+1}, \varphi_{n+2} \cdots \varphi_p$ may be assumed to be separated by a large energy gap versus the intersubset interactions contained within the submatrix $H_{12}^{(n \times k)}$ [23, 24] (see also the subsection The Main Features . . .). The energy reference point will be supposed to be located inside this energy gap so that the one-electron energies referring to orbitals of the first subset are negative, whereas those of the second subset are positive. As a result, the first-order magnitude of the submatrix $H_{12}^{(n \times k)}$ as compared to the diagonal blocks $H_{11}^{(n \times n)}$ and $H_{22}^{(k \times k)}$ will be accepted. The latter matrices, in turn, will be represented as sums of zero-order terms $H_{(0)1}$ and $H_{(0)2}$ and of the first-order terms T_1 and T_2, respectively. Then, the total matrix H takes the form

$$H = H_{(0)} + H_{(1)}, \quad (12)$$

where

$$H_{(0)} = \begin{vmatrix} H_{(0)1} & 0 \\ 0 & H_{(0)2} \end{vmatrix}, \qquad H_{(1)} = \begin{vmatrix} T_1 & R \\ R^+ & T_2 \end{vmatrix} \quad (13)$$

are the zero-order and the first-order matrices, respectively, and R stands for the total submatrix $H_{12}^{(n \times k)}$. Inasmuch as the off-diagonal elements of the Fockian matrix (resonance parameters) are usually assumed to be proportional to the respective overlap integrals of basis functions [29], a similar assumption about the first-order magnitude of the off-diagonal submatrices versus the diagonal ones is valid in the case of the overlap matrix as well [30]. Thus, the latter also will be supposed to contain a block-diagonal zero-order

term $S_{(0)}$ and a first-order term $S_{(1)}$, namely:

$$S = S_{(0)} + S_{(1)}, \tag{14}$$

where

$$S_{(0)} = \begin{vmatrix} S_{(0)1} & 0 \\ 0 & S_{(0)2} \end{vmatrix} \qquad S_{(1)} = \begin{vmatrix} V_1 & Z \\ Z^+ & V_2 \end{vmatrix}. \tag{15}$$

Before turning to the solution of Eqs. (1) and (2) for the above-described matrices H and S, two essential features of the problem are worth discussing:

First, the problem may be simplified considerably if we start with performing the zero-order (intrasubset) orthogonalization. To show this, let us introduce a block-diagonal matrix

$$S_{(0)}^{-1/2} = \begin{vmatrix} S_{(0)1}^{-1/2} & 0 \\ 0 & S_{(0)2}^{-1/2} \end{vmatrix} \tag{16}$$

where the Löwdin's orthogonalization matrix [31, 32] is used. Then, the problems of Eqs. (1) and (2) may be rewritten as follows:

$$E = C^+ S_{(0)}^{1/2} S_{(0)}^{-1/2} H S_{(0)}^{-1/2} S_{(0)}^{1/2} C \tag{17}$$

$$C^+ S_{(0)}^{1/2} S_{(0)}^{-1/2} S S_{(0)}^{-1/2} S_{(0)}^{1/2} C = I^{(p \times p)}. \tag{18}$$

If we define new matrices

$$\tilde{C} = S_{(0)}^{1/2} C, \qquad \tilde{S} = S_{(0)}^{-1/2} S S_{(0)}^{-1/2}, \\ \tilde{H} = S_{(0)}^{-1/2} H S_{(0)}^{-1/2}, \tag{19}$$

and use them to rewrite Eqs. (17) and (18), the latter acquire the form of Eqs. (1) again, that is:

$$E = \tilde{C}^+ \tilde{H} \tilde{C}, \tag{20}$$

$$\tilde{C}^+ \tilde{S} \tilde{C} = I^{(p \times p)}. \tag{21}$$

However, an essential simplification of the problem consisting of the equality

$$\tilde{S}_{(0)} = I^{(p \times p)} \tag{22}$$

follows from this transformation. Hence, we may solve Eqs. (20) and (21) along with Eq. (22) at first and, thereupon, turn back to the matrix C using Eq. (19).

Second, the diagonal blocks $\tilde{C}_{rr}$ ($r = 1, 2$) of our solution $\tilde{C}$ are not defined unambiguously by the requirements of Eqs. (20) and (21), and an additional condition may be imposed on these blocks before solving the problem. To do this, let us start with the following statement: Given that $\tilde{C}$ is a solution of Eqs. (20) and (21), the matrix $\tilde{C}' = \tilde{C}U$ is also a solution of the same problem, where U is an unitary block-diagonal matrix of the form

$$U = \begin{vmatrix} U_1 & 0 \\ 0 & U_2 \end{vmatrix}, \qquad U_1^+ U_1 = I^{(n \times n)}, \\ U_2^+ U_2 = I^{(k \times k)}. \tag{23}$$

To prove this statement, let us consider the matrix $\tilde{C}'^+ \tilde{S} \tilde{C}'$ and the off-diagonal block of the matrix $\tilde{C}'^+ \tilde{H} \tilde{C}'$, the latter being denoted by the subscript (12). We then obtain

$$\tilde{C}'^+ \tilde{S} \tilde{C}' = U^+ \tilde{C}^+ \tilde{S} \tilde{C} U = U^+ U = I^{(p \times p)} \tag{24}$$

and

$$(\tilde{C}'^+ \tilde{H} \tilde{C}')_{12} = (U^+ \tilde{C}^+ \tilde{H} \tilde{C} U)_{12} \\ = U_1^+ (\tilde{C}^+ \tilde{H} \tilde{C})_{12} U_2 = 0^{(n \times k)}. \tag{25}$$

Now, let $\tilde{C}$ be a generic solution of Eqs. (20) and (21). Let us build up the matrix U containing the diagonal blocks of the form

$$U_r = \left(\tilde{C}_{rr}^+ \tilde{C}_{rr} \right)^{-1/2} \tilde{C}_{rr}^+ \qquad (r = 1, 2). \tag{26}$$

Then, the diagonal blocks $\tilde{C}'_{rr}$ of the matrix $\tilde{C}'$ become Hermitian matrices. Indeed, these blocks are

$$\tilde{C}'_{rr} = \tilde{C}_{rr} U_r = \tilde{C}_{rr} \left(\tilde{C}_{rr}^+ \tilde{C}_{rr} \right)^{-1/2} \tilde{C}_{rr}^+ \qquad (r = 1, 2) \tag{27}$$

and $\tilde{C}'^+_{rr} = \tilde{C}'_{rr}$. Hence, we may "a priori" confine ourselves to matrices $\tilde{C}$ described by the property

$$\tilde{C}_{rr}^+ = \tilde{C}_{rr}. \tag{28}$$

As in [21–23], let us look now for the transformation matrix $\tilde{C}$ in the form of power series, that is,

$$\tilde{C} = \sum_{m=0}^{\infty} \tilde{C}_{(m)} = \tilde{C}_{(0)} + \tilde{C}_{(1)} + \tilde{C}_{(2)} + \cdots . \tag{29}$$

Thereupon, let us substitute Eq. (29) into Eqs. (20), (21), and (28) and collect terms of the same order within these requirements.

Thus, the zero-order equations

$$\left(\tilde{C}_{(0)}^+ \tilde{H}_{(0)} \tilde{C}_{(0)}\right)_{12} = 0^{(n \times k)}, \qquad \tilde{C}_{(0)}^+ \tilde{S}_{(0)} \tilde{C}_{(0)} = I^{(p \times p)} \tag{30}$$

along with Eq. (28) yield the requirements

$$\tilde{C}_{(0)rr}^+ \tilde{C}_{(0)rr} = I, \qquad \tilde{C}_{(0)rr}^+ = \tilde{C}_{(0)rr}, \qquad (r = 1, 2)$$

$$\tilde{C}_{(0)11}^+ \tilde{H}_{(0)11} \tilde{C}_{(0)12} + \tilde{C}_{(0)21}^+ \tilde{H}_{(0)22} \tilde{C}_{(0)22} = 0^{(n \times k)} \tag{31}$$

that may be easily met if we take the zero-order matrix $\tilde{C}_{(0)}$ equal to the unit matrix, that is,

$$\tilde{C}_{(0)} = I^{(p \times p)}. \tag{32}$$

In addition, the zero-order eigenblocks follow from the diagonal blocks of the matrix $\tilde{C}_{(0)}^+ \tilde{H}_{(0)} \tilde{C}_{(0)}$, namely:

$$E_{(0)r} = \tilde{H}_{(0)r} \qquad (r = 1, 2). \tag{33}$$

The first-order equations take the form

$$\tilde{C}_{(1)}^+ \tilde{S}_{(0)} \tilde{C}_{(0)} + \tilde{C}_{(0)}^+ \tilde{S}_{(0)} \tilde{C}_{(1)} + \tilde{C}_{(0)}^+ \tilde{S}_{(1)} \tilde{C}_{(0)} = 0 \tag{34a}$$

$$\left(\tilde{C}_{(1)}^+ \tilde{H}_{(0)} \tilde{C}_{(0)} + \tilde{C}_{(0)}^+ \tilde{H}_{(0)} \tilde{C}_{(1)} + \tilde{C}_{(0)}^+ \tilde{H}_{(1)} \tilde{C}_{(0)}\right)_{12} = 0. \tag{34b}$$

After taking into account Eqs. (22) and (32), we obtain

$$\tilde{C}_{(1)}^+ + \tilde{C}_{(1)} + \tilde{S}_{(1)} = 0 \tag{35}$$

$$\tilde{C}_{(1)21}^+ \tilde{H}_{(0)2} + \tilde{H}_{(0)1} \tilde{C}_{(1)12} + \tilde{R} = 0. \tag{36}$$

Diagonal blocks of Eq. (35) along with Eq. (28) yield

$$\tilde{C}_{(1)rr} = -\frac{1}{2} \tilde{V}_r \qquad (r = 1, 2). \tag{37}$$

Then, the first-order corrections to the eigenblocks follow from the diagonal blocks of the whole matrix within the parentheses of Eq. (34b), namely:

$$E_{(1)r} = \tilde{H}_{(1)rr} + \tilde{C}_{(1)rr}^+ \tilde{H}_{(0)r} + \tilde{H}_{(0)r} \tilde{C}_{(1)rr}$$

$$= \tilde{T}_r - \frac{1}{2}\left(\tilde{V}_r \tilde{H}_{(0)r} + \tilde{H}_{(0)r} \tilde{V}_r\right). \tag{38}$$

Again, a system of two matrix equations

$$\tilde{C}_{(1)21}^+ + \tilde{C}_{(1)12} + \tilde{Z} = 0$$

$$\tilde{C}_{(1)21}^+ \tilde{H}_{(0)2} + \tilde{H}_{(0)1} \tilde{C}_{(1)12} + \tilde{R} = 0 \tag{39}$$

results from the off-diagonal blocks of Eqs. (35) and (36). The solution of these equations is described in the Appendix. Let us introduce the notations

$$\tilde{C}_{(1)21}^+ = \tilde{K}_{(1)}, \qquad \tilde{C}_{(1)12} = \tilde{L}_{(1)}. \tag{40}$$

Then, the total matrix $\tilde{C}_{(1)}$ takes the form

$$\tilde{C}_{(1)} = \begin{vmatrix} -\dfrac{1}{2}\tilde{V}_1 & \tilde{L}_{(1)} \\ \tilde{K}_{(1)}^+ & -\dfrac{1}{2}\tilde{V}_2 \end{vmatrix}, \tag{41}$$

where

$$\tilde{K}_{(1)} = \int_0^\infty \exp\left(\tilde{H}_{(0)1} t\right)\left[-\tilde{R} + \tilde{H}_{(0)1}\tilde{Z}\right]$$

$$\times \exp\left(-\tilde{H}_{(0)2} t\right) dt \tag{42}$$

$$\tilde{L}_{(1)} = \int_0^\infty \exp\left(\tilde{H}_{(0)1} t\right)\left[\tilde{R} - \tilde{Z}\tilde{H}_{(0)2}\right]\exp\left(-\tilde{H}_{(0)2} t\right) dt. \tag{43}$$

The second-order equations may be solved similarly—only more intricate expressions follow in this case. Thus, the second-order analog of Eq. (35) is

$$\tilde{C}_{(2)}^+ + \tilde{C}_{(2)} + \tilde{N}_{(2)} = 0, \tag{44}$$

where

$$\tilde{N}_{(2)} = \tilde{C}_{(1)}^+ \tilde{S}_{(1)} + \tilde{C}_{(1)}^+ \tilde{C}_{(1)} + \tilde{S}_{(1)} \tilde{C}_{(1)}. \tag{45}$$

The diagonal blocks of Eq. (44) along with Eq. (28) yield the respective second-order analog of Eq. (37), namely:

$$\tilde{C}_{(2)rr} = -\frac{1}{2} \tilde{N}_{(2)rr} \qquad (r = 1, 2). \tag{46}$$

On the other hand, the following matrix equation

$$\tilde{C}_{(2)21}^+ \tilde{H}_{(0)2} + \tilde{H}_{(0)1} \tilde{C}_{(2)12} + \tilde{M}_{(2)12} = 0 \tag{47}$$

results instead of Eq. (36), where

$$\tilde{M}_{(2)} = \tilde{C}_{(1)}^+ \tilde{H}_{(1)} + \tilde{C}_{(1)}^+ \widetilde{H_{(0)}} \tilde{C}_{(1)} + \tilde{H}_{(1)} \tilde{C}_{(1)}. \tag{48}$$

The off-diagonal block of Eq. (44) and Eq. (47) yields a system of two matrix equations like those of Eq. (39), namely:

$$\tilde{C}_{(2)21}^{+} + \tilde{C}_{(2)12} + \tilde{N}_{(2)12} = 0$$

$$\tilde{C}_{(2)21}^{+} \tilde{H}_{(0)2} + \tilde{H}_{(0)1} \tilde{C}_{(2)12} + \tilde{M}_{(2)12} = 0. \quad (49)$$

As a result, the total second-order matrix $\tilde{C}_{(2)}$ takes the form

$$\tilde{C}_{(2)} = \begin{vmatrix} -\frac{1}{2}\tilde{N}_{(2)11} & \tilde{L}_{(2)} \\ \tilde{K}_{(2)}^{+} & -\frac{1}{2}\tilde{N}_{(2)22} \end{vmatrix}, \quad (50)$$

where

$$\tilde{K}_{(2)} = \int_{0}^{\infty} \exp\left(\tilde{H}_{(0)1} t\right)\left[-\tilde{M}_{(2)12} + \tilde{H}_{(0)1} \tilde{N}_{(2)12}\right]$$
$$\times \exp\left(-\tilde{H}_{(0)2} t\right) dt \quad (51)$$

$$\tilde{L}_{(2)} = \int_{0}^{\infty} \exp\left(\tilde{H}_{(0)1} t\right)\left[\tilde{M}_{(2)12} - \tilde{N}_{(2)12} \tilde{H}_{(0)2}\right]$$
$$\times \exp\left(-\tilde{H}_{(0)2} t\right) dt. \quad (52)$$

The second-order corrections to the eigenblocks E_r ($r = 1, 2$) may be expressed as follows:

$$E_{(2)r} = \tilde{M}_{(2)rr} - \frac{1}{2}\left(\tilde{N}_{(2)rr} \tilde{H}_{(0)r} + \tilde{H}_{(0)r} \tilde{N}_{(2)rr}\right). \quad (53)$$

Equation (53) is the second-order analog of Eq. (38). Diagonal blocks of matrices $\tilde{N}_{(2)}$ and $\tilde{M}_{(2)}$

defined by Eqs. (45) and (48), respectively, should be substituted into Eq. (53) to obtain the final form of the $E_{(2)r}$.

Therefore, we have derived the expressions for the first three terms of the power series of Eq. (29). Obtaining of the subsequent terms also meets no considerable difficulties.

Using Eqs. (19), (32), (41), and (50), the multidimensional MOs $|\Psi_1\rangle$ and $|\Psi_2\rangle$ defined by Eq. (6) may be expressed as follows:

$$|\Psi_1\rangle = |\Phi_1\rangle S_{(0)1}^{-1/2}\left[I^{(n\times n)} - \frac{1}{2}\left(\tilde{V}_1 + \tilde{N}_{(2)11}\right)\right]$$
$$+ |\Phi_2\rangle S_{(0)2}^{-1/2}\left(\tilde{K}_{(1)}^{+} + \tilde{K}_{(2)}^{+}\right) \quad (54)$$

$$|\Psi_2\rangle = |\Phi_2\rangle S_{(0)2}^{-1/2}\left[I^{(k\times k)} - \frac{1}{2}\left(\tilde{V}_2 + \tilde{N}_{(2)22}\right)\right]$$
$$+ |\Phi_1\rangle S_{(0)1}^{-1/2}\left(\tilde{L}_{(1)} + \tilde{L}_{(2)}\right). \quad (55)$$

The BO matrix P also may be expressed in the form of power series, that is,

$$P = \sum_{m=0}^{\infty} P_{(m)} = P_{(0)} + P_{(1)} + P_{(2)} + \cdots . \quad (56)$$

The first three terms of Eq. (56) are

$$P_{(0)} = 2\begin{vmatrix} S_{(0)1}^{-1} & 0 \\ 0 & 0 \end{vmatrix} \quad (57a)$$

$$P_{(1)} = 2\begin{vmatrix} -S_{(0)1}^{-1/2}\tilde{V}_1 S_{(0)1}^{-1/2} & S_{(0)1}^{-1/2}\tilde{K}_{(1)} S_{(0)2}^{-1/2} \\ S_{(0)2}^{-1/2}\tilde{K}_{(1)}^{+} S_{(0)1}^{-1/2} & 0 \end{vmatrix} \quad (57b)$$

$$P_{(2)} = 2\begin{vmatrix} \frac{1}{4}S_{(0)1}^{-1/2}\left(\tilde{V}_1\right)^2 S_{(0)1}^{-1/2} - S_{(0)1}^{-1/2}\tilde{N}_{(2)11} S_{(0)1}^{-1/2} & S_{(0)1}^{-1/2}\left[-\frac{1}{2}\tilde{V}_1 \tilde{K}_{(1)} + \tilde{K}_{(2)}\right]S_{(0)2}^{-1/2} \\ S_{(0)2}^{-1/2}\left[-\frac{1}{2}\tilde{K}_{(1)}^{+}\tilde{V}_1 + \tilde{K}_{(2)}^{+}\right]S_{(0)1}^{-1/2} & S_{(0)2}^{-1/2}\tilde{K}_{(1)}^{+}\tilde{K}_{(1)} S_{(0)2}^{-1/2} \end{vmatrix}. \quad (57c)$$

Equations (10) and (11) should be used when obtaining Eqs. (57a–c).

The total energy of our system (ϵ) may be easily obtained either on the basis of the eigenblock E_1 or using the above-described DM P. Indeed, two alternative definitions of the total energy are possible, namely:

$$\epsilon = 2TrE_1 \quad (58a)$$

or [3, 33]

$$\epsilon = Tr(PH). \quad (58b)$$

Discussion

COMPARISON OF THE MATRIX PROBLEM OF EQ. (4) TO RELATED PROBLEMS

The problem of Eq. (4) is the most general matrix form of the Brillouin theorem determining orthogonal sets of noncanonical MOs of molecules. This problem forms the basis of the noncanonical MO method in its matrix representation. Hence, comparison of Eq. (4) to related problems is of interest.

First, Eq. (4) is a nontrivial generalization of a two-dimensional eigenvalue problem, where multidimensional quantities (submatrices) stand for the usual matrix elements (third section). Similarly, the NCMO approach as a whole may be regarded as a generalization of the usual (canonical) MO theory for two-electron systems in the basis of two nonorthogonal basis functions.

Second, the problem of Eq. (4) is a generalization of the eigenblock equation shown in Eq. (5) to the case of a nonorthogonal basis set ($S \neq I$). Accordingly, the solution of Eq. (4) discussed in the third section turns into the respective solution of Eq. (5) obtained in [23] if the equality $S = I$ is assumed.

Thus, the matrices $\tilde{K}_{(1)}$, $\tilde{L}_{(1)}$, $\tilde{K}_{(2)}$, and $\tilde{L}_{(2)}$ of the third section, taking the off-diagonal positions within the corrections $\tilde{C}_{(1)}$ and $\tilde{C}_{(2)}$, turn into matrices $-G_{(1)}$, $G_{(1)}$, $-G_{(2)}$ and $G_{(2)}$, respectively, where $G_{(1)}$ and $G_{(2)}$ are determined by matrix equations

$$H_{(0)1}G_{(1)} - G_{(1)}H_{(0)2} + R = 0 \qquad (59a)$$

$$H_{(0)1}G_{(2)} - G_{(2)}H_{(0)2} + M = 0 \qquad (59b)$$

and $M = T_1 G_{(1)} - G_{(1)} T_2$. The matrices $G_{(1)}$ and $G_{(2)}$ coincide with the principal matrices used in [23] when expressing the solution of Eq. (5) (The minus sign in front of $H_{(0)2}$ within the initial matrix $H_{(0)}$ of [23] should be taken into consideration when comparing Eqs. (59a, b) of the present article to Eqs. (27) and (35) of [23].)

As to diagonal blocks of corrections $\tilde{C}_{(1)}$ and $\tilde{C}_{(2)}$, Eq. (37) yields zero matrices for $\tilde{C}_{(1)11} \equiv C_{(1)11}$ and $\tilde{C}_{(1)22} \equiv C_{(1)22}$ when turning to the case $S = I$. For $C_{(2)11}$ and $C_{(2)22}$, in turn, simple algebraic expressions result from Eqs. (46), and these may be traced back to the nonzero product $\tilde{C}_{(1)}^+ \tilde{C}_{(1)}$ within the expression of Eq. (45) for the matrix $\tilde{N}_{(2)}$.

Finally, the requirement of Eq. (28) turns into the equality $C_{rr}^+ = C_{rr}$ assumed in [23] and is equivalent to a zero-matrix condition for the anti-Hermitian (skew-symmetrix) part of the submatrix C_{rr}. The analog of this assumption within the usual Rayleigh–Schrödinger perturbation theory (see, e.g., [34, 35]) corresponds to certain choice of the phase of the wave function [35] as discussed in [24].

In this context, the relation of the perturbative approach of the third section to the standard Rayleigh–Schrödinger perturbation theory (RSPT) deserves attention. Thus, the solution of Eq. (5) obtained in [23] has been shown to be actually based on application of the so-called noncommutative RSPT developed in [24] and is a generalization of the standard RSPT (see, e.g., [34, 35]) to the case of noncommutative (multidimensional) matrix elements. Both the standard and the noncommutative RSPTs refer to an orthogonal basis set. The standard RSPT may be generalized to the case of a nonorthogonal basis set as shown in [36–39]. In this context, certain generalization of the noncommutative RSPT to the case $S \neq I$ seems to be feasible. This task, however, is not accomplished yet.

Let us compare now our solutions of Eqs. (4) and (5) with the relevant results of the pioneering contributions in this field [17–20]. Thus, the solutions of the block-diagonalization problem for a Hückel-type Hamiltonian matrix in an orthogonal [18, 19] and in a nonorthogonal basis [20] were obtained in these articles in terms of individual elements of this matrix. The same refers also to the iterative approach to the linearized version of the Brillouin theorem for the Fockian operator [17]. Again, our solutions of Eqs. (4) and (5) were expressed in terms of entire submatrices (blocks) of the initial matrix. Moreover, zero-order resonance parameters inside subspaces of basis functions $\varphi_1, \varphi_2, \ldots \varphi_n$ and $\varphi_{n+1}, \varphi_{n+2}, \ldots \varphi_p$ are allowed in the latter case in contrast to [17–20]. The above-mentioned two points make up the content of generalization made when passing from [17–20] to [23] and the present contribution. On the other hand, an orthogonality requirement for NCMOs being sought is added in [23] and in the present article in contrast to [17–20]. In this respect, the results of [17–20] correspond to a more general type of NCMOs. It should be noted, however, that the Brillouin theorem cannot be represented in the matrix form of Eqs. (4) and (5) without imposing the orthogonality condition for NCMOs.

THE MAIN FEATURES OF THE NONCANONICAL MOs RESULTING FROM THE PERTURBATIVE SOLUTION OF EQ. (4)

The main features of our NCMOs are determined by both the nature of the initial basis functions $\{\varphi_i\}$ and the peculiarities of the solution of Eq. (4) itself. Let us start with the first of these factors:

The perturbative solution of Eq. (4) (third section) was based on an assumption that the two subsets of basis orbitals are separated by a large energy gap versus the intersubset resonance parameters. This requirement may be most easily met for basis functions $\{\varphi_i\}$ coinciding with either the MOs of the whole ''unperturbed'' system or with the orbitals localized on its separate fragments, for example, on chemical bonds. Indeed, coincidence between the dimension of the first subset (n) and the total number of pairs of electrons (third section) allows the bonding basis orbitals to be included into the first subset, while the antibonding orbitals find themselves within the second subset. Inasmuch as bonding and antibonding orbitals are usually separated by a large energy gap, the main assumption of our solution is valid provided that intersubset resonance parameters are not too large.

Choice of the basis functions $\{\varphi_i\}$ coinciding with strictly localized orbitals may be exemplified by the results of [21−23, 40, 41], wherein NCMOs of saturated organic molecules have been sought in the basis of bonding and antibonding bond orbitals. As a result, NCMOs of the bond-orbital-and-tail structure were obtained. Similar orbitals were derived also in [17−20].

Delocalized basis orbitals coinciding with CMOs of the ''unperturbed'' system make an alternative type of basis sets. For example, NCMOs of aromatic heterocycles may be sought in the basis of CMOs of respective parent hydrocarbons [42], and delocalized NCMOs result in this case.

It is also noteworthy in this context that the principal assumption of the third section may hardly be met for ordinary AOs. Thus, the perturbative solution of Eq. (4) is unlikely to be applicable for investigation of ''atoms in molecules.'' Hence, the NCMOs of the third section may be considered as an alternative to those resulting from the Adams−Gilbert equation: The latter proved to be most applicable to ions in inorganic molecules and crystals [9, 10, 12], whereas the perturbative solution of Eq. (4) refers mostly to organic molecules containing covalent bonds.

Let us discuss now the main peculiarities of our solution of Eq. (4). As seen from the third section, this solution is not unique, and this especially refers to diagonal blocks of matrix C. In this context, the assumptions of Eqs. (28) and (32) may be considered as representing a choice of a particular solution.

Thus, the equality $\tilde{C}_{(0)} = I$ ensures that the zero-order corrections within the multidimensional MOs $|\Psi_1\rangle$ and $|\Psi_2\rangle$ shown in Eqs. (54) and (55) coincide with matrices $S_{(0)1}^{-1/2}$ and $S_{(0)2}^{-1/2}$ describing the intrasubset orthogonalization. As the Löwdin's orthogonalization is known to yield a set of orthonormal functions which minimize the sum of squared distances between each initial function and a corresponding function of the orthonormal set [43], the zero-order NCMOs prove to be as close to the initial basis functions $\{\varphi_i\}$ as possible. Given that the latter are localized, the respective NCMOs are as localized as is possible within the class of orthogonal MOs. On this basis, the NCMOs of the third section may be related to localized MOs obtained using the so-called projection criterion [5]. Equations (54) and (55) also indicate that the extent of intrasubset delocalization is proportional to the relevant overlap integrals of basis functions.

Intersubset delocalization of NCMOs arises within the first-order corrections only, and it is represented by matrices $\tilde{K}_{(1)}^{+}$ and $\tilde{L}_{(1)}$, each of them consisting of two terms as shown in Eqs. (42) and (43), respectively. The first $\tilde{R}$-containing terms may be traced back to intersubset resonance parameters involved within the matrix R, while the second $\tilde{Z}$-containing terms are related to the intersubset overlap integrals.

ANALYSIS OF THE BOND-ORDER MATRIX

Let us start by verifying the adequacy of the BO matrix obtained on the basis of a projector to a single occupied MMO. It may be easily proved that the BO matrix shown in Eqs. (56) and (57a−c) complies with the system of equations [44−46]

$$Tr(PS) = 2n \qquad (60)$$

$$PSP = 2P \qquad (61)$$

$$SPH = HPS \qquad (62)$$

to within the second-order terms inclusive. Equations (60)−(62) correspond to generalizations of the

charge conservation condition, the idempotence requirement, and the commutation equation for the respective representations of the Hamiltonian and one-electron density matrices, respectively, to the case of a nonorthogonal basis set.

To make the above-mentioned proof, Eqs. (12)–(15), (56), and (57) should be substituted into Eqs. (60)–(62) and terms of the same order should be collected. In particular, the following matrix relation

$$\tilde{H}_{(0)1}\tilde{K}_{(1)} - \tilde{K}_{(1)}\tilde{H}_{(0)2} = \tilde{R} - \tilde{H}_{(0)1}\tilde{Z} \qquad (63)$$

easily resulting from Eqs. (39) and (40) should be used to verify Eq. (62). The fact that the BO matrix P obtained on the basis of the projector to the MMO $|\Psi_1\rangle$ complies with the requirements of Eqs. (60)–(62) serves to bear out the suggested way of obtaining this matrix in the framework of the NCMO method.

Let us turn now to comparison of the BO matrix P to the MMOs $|\Psi_1\rangle$ and $|\Psi_2\rangle$. Indeed, these matrices are expressed in terms of the same submatrices ($\tilde{V}_1$, $\tilde{K}_1$, etc.) as is seen from Eqs. (54), (55), and (57a, b, c). Hence, elements of the BO matrix may be expected to be related to delocalizational characteristics of NCMOs.

In the case $S = I$ studied in [21–24], the relation between the diagonal elements of the BO matrix (occupation numbers of basis orbitals) and the extents of delocalization of respective NCMOs acquired an extremely simple form, namely, the alterations in the occupation numbers versus their initial values (equal to 2 and 0 for bonding and antibonding basis orbitals, respectively) were shown to coincide with the total delocalization coefficients [23, 24] of the respective NCMOs. As occupation numbers are invariant to unitary transformations, the above relation implies that a certain special choice of NCMOs was actually made in [21–24], namely, NCMOs, the extents of delocalization of which were related to the unique populations of basis orbitals, were obtained. The above-discussed relation, however, becomes considerably more involved if we turn to the general case $S \neq I$.

Similarly, certain relations also may be expected between the shapes of NCMOs and the off-diagonal elements of the matrix P determining the overlap populations [47] of basis orbitals. Interrelations of this type are likely to be applicable for substantiation of the Magnasco–Perico criterion

[48, 49] for obtaining localized NCMOs based on the so-called partial occupation numbers of NCMOs being expressed in terms of overlap populations [5].

Appendix: on the Solution of a System of Two Linear Matrix Equations

Let us consider a system of two linear matrix equations

$$A_1 X_1 + X_2 A_2 + B = 0$$
$$X_1 + X_2 + D = 0, \qquad (A1)$$

where A_1, A_2, B, and D are assumed to be known matrices and X_1 and X_2 are matrices being sought. Let us start with reformulating the system of Eq. (A1) into two independent equations. To this end, let us turn to matrices Y_1 and Y_2 related to X_1 and X_2 as follows:

$$X_1 = Y_2 - Y_1 A_2, \qquad X_2 = -Y_2 + A_1 Y_1. \quad (A2)$$

Indeed, substituting Eq. (A2) into Eq. (A1) yields two independent equations for matrices Y_1 and Y_2, namely:

$$A_1 Y_2 - Y_2 A_2 + B = 0$$
$$A_1 Y_1 - Y_1 A_2 + D = 0. \qquad (A3)$$

Moreover, both of these equations are of the well-studied form

$$AX + XC + aF = 0. \qquad (A4)$$

The general theory of Eqs. (A4) may be found in [50]. In particular, a unique solution of Eq. (A4) was proved to exist if the real parts of eigenvalues of both matrices A and C are negative. This solution may be presented as an integral

$$X = a \int_0^\infty \exp(At) F \exp(Ct)\, dt. \qquad (A5)$$

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

Using Eqs. (A3) and (A5), we then obtain

$$Y_1 = \int_0^\infty \exp(A_1 t) D \exp(-A_2 t)\, dt,$$
$$\qquad\qquad\qquad\qquad\qquad (A6)$$
$$Y_2 = \int_0^\infty \exp(A_1 t) B \exp(-A_2 t)\, dt.$$

Owing to commutation of matrices A and $\exp(At)$ [50], the final solution of Eq. (A1) may be presented in the form

$$X_1 = \int_0^\infty \exp(A_1 t)[B - DA_2]\exp(-A_2 t)\, dt$$

$$X_2 = \int_0^\infty \exp(A_1 t)[-B + A_1 D]\exp(-A_2 t)\, dt.$$
(A7)

In the case studied in the third section, we obtain

$$A_1 = \tilde{H}_{(0)1} = S_{(0)1}^{-1/2} H_{(0)1} S_{(0)1}^{-1/2}$$
$$A_2 = \tilde{H}_{(0)2} = S_{(0)2}^{-1/2} H_{(0)2} S_{(0)2}^{-1/2}$$
(A8)

and both A_1 and A_2 are Hermitian matrices. The question whether the eigenvalues of matrices A_1 and $-A_2$ are negative should be solved in each case separately. It should be noted that only eigenvalues of matrices $H_{(0)1}$ and $-H_{(0)2}$ are expected to be negative, at least for saturated organic molecules [24].

Let us discuss now the use of solution shown in Eq. (A7) in practice. To this end, particular structures of the involved matrices are evidently required. Let us start with Eq. (A4) and its solution shown in Eq. (A5) for Hermitian matrices A and C.

Given that the structures of matrices A and C are specified, these may be diagonalized using unitary matrices U and V, namely:

$$A^* = U^+ A U, \qquad C^* = V^+ C V, \qquad \text{(A9)}$$

where A^* and C^* are diagonal matrices involving elements α_i and γ_j. As a result, the matrices $\exp(At)$ and $\exp(Ct)$ may be expressed as follows [50]:

$$\exp(At) = U\exp(A^* t)U^+$$
$$\exp(Ct) = V\exp(C^* t)V^+,$$
(A10)

where $\exp(A^* t)$ and $\exp(C^* t)$ also are diagonal matrices containing elements $\exp(\alpha_i t)$ and $\exp(\gamma_j t)$, respectively. Then, the solution X of Eq. (A5) becomes

$$X = aUX^* V^+, \qquad \text{(A11)}$$

where

$$X^* = a\int_0^\infty \exp(A^* t)F^*\exp(C^* t)\, dt \quad \text{(A12)}$$

and

$$F^* = U^+ F V. \qquad \text{(A13)}$$

It may be easily seen that particular elements X_{ij}^* of the matrix X^* defined by Eq. (A12) may be obtained in an explicit form, namely:

$$X_{ij}^* = a\int_0^\infty \exp(\alpha_i t)F_{ij}^*\exp(\gamma_j t)\, dt = -\frac{aF_{ij}^*}{\alpha_i + \gamma_j},$$
(A14)

where $\exp[(\alpha_i + \gamma_j)t]$ is assumed to turn to zero for $t \to \infty$ (this requirement is met for negative value of $\alpha_i + \gamma_j$).

This version of solution shown in Eq. (A5) is equivalent to that discussed in [24]. It is also evident that it may be applied to obtain matrices Y_1 and Y_2 of Eq. (A3). Thereupon, the matrices X_1 and X_2 follow directly from Eq. (A2).

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