

Towards a unified localized description of the electronic structure of saturated organic molecules

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Abstract

The common one-electron density matrix (DM) for saturated organic molecules in the basis of bond orbitals (BOs) and the relevant representation matrix of the localized MOs (LMOs) are expected to be interrelated analogously to those of alkanes (V. Gineityte, *J. Mol. Struct. (Theochem)*, 288 (1993) 111). Accordingly, a single procedure yielding both matrices and implying the feasibility of a unified localized description of saturated molecules is being sought. To this end two relevant non-canonical problems, i.e. the commutation relation for the DM and the respective hamiltonian matrix and the Brillouin theorem for LMOs, are analyzed and compared. The $2n$ -dimensional space of BOs for a saturated system containing $2n$ electrons is divided into two n -dimensional subspaces of bonding and antibonding BOs, respectively. The off-diagonal intersubspace blocks of both the LMO representation matrix and the DM are shown to be determined by common equations, whereas the relevant diagonal blocks are expressed algebraically in terms of the off-diagonal ones. Solving the above common equations is concluded to be sufficient to obtain the LMOs and DM of saturated organic molecules on a unified basis.

1. Introduction

The principal features of the electronic structure of molecules are commonly expected to resemble those of atoms. Accordingly, similar approximations are used when solving the relevant Schrödinger equations, and it is the canonical Hartree–Fock method [1,2] that will be mentioned here in the first place. The resulting one-electron orbitals, i.e. AOs and canonical MOs for atoms and molecules, respectively, prove to be delocalized over the whole system. The reliability of such a common approach to atoms and molecules has been verified many times by comparing the results obtained with the numerous spectroscopical data. Hence, there can be no doubt that the canonical

MO method allows the electronic structure of a molecule as a whole to be described adequately.

Nevertheless, additional aspects of the electronic structure of molecules against that of atoms reveal themselves as well, and these are associated mainly with local regions in molecules. Thus, numerous local characteristics, e.g. chemical shifts in the NMR and ESCA spectra [3], are studied experimentally. Furthermore, certain total characteristics of molecules, e.g. dipole moments, polarizabilities, energies of formation, etc., are successfully estimated as sums of local increments associated with similar bonds or functional groups [4–6].

So far as classical chemistry is concerned, the local point of view with regard to molecular structure is prevailing here [7]. Thus, the concept

of local chemical reactivity forms the basis of the theory of chemical reactions [8]. Moreover, the most fundamental chemical concepts, such as atoms in molecules, localized interatomic bonds, etc., originate only from the above local point of view. Accordingly, the concept of electron pairs pertinent to chemical bonds and lone electron pairs has been accepted in chemistry for a long time [9].

It is no surprise in this context that localized approaches are also being continuously developed in quantum chemistry [4], and these are intended mostly for describing the local peculiarities of the electronic structure of molecules.

In the framework of the most popular one-electron model, the localized approach consists of the employment of the non-canonical MOs under certain localization requirements, which are commonly referred to as localized MOs (LMOs) [1,2,4]. These orbitals may be obtained as a result of both the transformation of the occupied canonical MOs into a set of LMOs using various localization criteria [4] and direct calculation by means of the Brillouin theorem [4,10–13]. The optimum LMOs for saturated systems prove to be composed of the main contribution pertaining to a chemical bond or lone electron pair and tails extending over the neighbouring bonds [14,15].

It should be noted here that the greater popularity of the “a posteriori” ways of obtaining LMOs from the canonical MOs gave rise to an opinion [4] of LMOs being of a subsidiary nature. However, the possibility of obtaining LMOs directly on the basis of the Brillouin theorem [4,10–13] speaks in favour of equivalence between both sets of MOs. Moreover, additional advantages prove to be inherent to LMOs against the canonical one-electron orbitals. Thus, apart from the above-mentioned relation of LMOs to the chemical concepts (chemical bonds and lone electron pairs) [2,4,6], the possibility of deriving the common expressions for LMOs of definite large sets of molecules, e.g. alkanes [12,13], and the relation of the LMO representation matrix to the relevant one-electron density matrix (DM) [12,13,16] rank among these advantages. The latter peculiarity of LMOs deserves special attention here.

The one-electron DM may be regarded as one of the most fundamental quantum-mechanical

characteristics of molecules related to numerous observed properties [1,2]. Moreover, in contrast to LMOs, the DM is a unique characteristic of the given molecule. This, in turn, implies an increased significance both of the LMOs related to the DM as close as possible and of the localized approach to the electronic structure of molecules in general.

An especially close relation between the LMOs and DM has been established for alkanes [12]. Thus, both the DM and the LMO representation matrix in the basis of bond orbitals (BOs) proved to contain the same combinations of the hamiltonian matrix blocks with different coefficients. Otherwise, both the LMOs and DM of alkanes consist of the same system-structure-dependent matrices as building blocks. This result promotes an assumption that a single problem for the above common building blocks may be formulated and solved instead of two separate problems for the LMOs and DM.

Such a common way of obtaining both matrices (if feasible) implies a unified localized description of the systems under study, wherein LMOs and DM play the role of two alternative representations of the electronic structure. To discover the above-expected common way, the non-canonical problems for the LMOs and DM are to be analyzed and compared.

The Brillouin theorem for the orthogonal LMOs [4,12,13] serves as the first of these problems. As to the DM, this matrix may be obtained either by the indirect way of summing coefficients within the occupied MOs or by the direct way. The latter consists of the solution of the commutation equation for the DM and the respective hamiltonian matrix [17], and this equation may be regarded as the non-canonical problem for the DM. Therefore, revealing the relation between the commutation equation for the DM and the Brillouin theorem for LMOs becomes important.

This paper is aimed at accomplishing this scheme for saturated organic molecules with alkanes as a particular case. To this end the non-canonical problems for the relevant DM and LMOs are analyzed separately in sections 2 and 3. Common equations determining the building blocks of both the LMO representation matrix and the DM follow from this comparative analysis. The main features

of these equations and of their solutions are discussed in section 4.

2. The non-canonical problem for the one-electron density matrix of saturated organic molecules

The common form of the Hückel-type model hamiltonian matrices for alkanes required when stating and solving the non-canonical problem for the DM has been constructed in Refs. [12,13,18,19] on the basis of taking into account the most essential properties of the respective self-consistent Fockians. Similar considerations are employed here when discussing saturated organic molecules.

As in Refs. [12,13], the basis of BOs is used. The bonding BOs (BBOs) $\phi_{(+)}$ and the antibonding BOs (ABOs) $\phi_{(-)}$ are defined as eigenfunctions of the respective two-dimensional hamiltonian matrix blocks in the basis of two sp^3 -hybrid AOs or one sp^3 -hybrid AO and one $1s_H$ AO belonging to the same chemical bond. The orbitals associated with the lone electron pairs of the system under study (if any) may also be included in the initial basis set. In order to retain the even total number of orbitals ($2n$), being convenient for further deriving the expressions for the DM and LMOs, the respective number of faked antibonding orbitals attributed to the lone electron pairs are also assumed to be included in the initial basis set. These orbitals are presumed to be situated at sufficiently high positive energies so as to exert no influence upon the final results. For simplicity let us term the whole set of orbitals the BO basis. Let us assume also that the $2n$ -dimensional set of BOs is orthogonal.

The first-order magnitude of the interactions (resonance integrals) between BOs compared with the differences in the BBO and ABO energies was the main assumption when constructing the common hamiltonian matrix for alkanes [12,13]. These ratios between the matrix elements in the basis of BOs originated from the large values of the neighbouring resonance integrals against the remaining non-diagonal elements in the basis of sp^3 -hybrid AOs and $1s_H$ AOs [18–22] and were related to the tetrahedral local structure of alkanes. Hence, similar assumptions may be accepted also in the case of

any saturated organic molecule of tetrahedral local structure.

Let the first n BOs coincide with BBOs and the remaining n BOs correspond to ABOs. Then the hamiltonian matrix H is conveniently represented in terms of four $n \times n$ -dimensional blocks. Diagonal and off-diagonal blocks of this matrix contain resonance integrals inside subspaces of BBOs and ABOs and those between BOs of different types, respectively. In accordance with the above-discussed relative values of the hamiltonian matrix elements, let the off-diagonal blocks of the matrix H be of first-order magnitude compared with the diagonal ones. Such a requirement allows zero-order resonance integrals inside subspaces of BBOs and ABOs and includes the assumptions of Refs. [12,13] as a particular case. Moreover, zero-order intrasubspace blocks are in line with the expectations [18,20] about the largest values of the resonance integrals between pairs of nearest (geminal) BBOs compared to other types of non-diagonal elements in the BO basis.

Let the two diagonal blocks of the matrix H be represented as sums of respective zero-order terms $E_{(+)}$ and $E_{(-)}$, and of the respective first-order terms S and Q , the subscripts “+” and “-” here and further referring to BBOs $\phi_{(+)}$ and ABOs $\phi_{(-)}$. Then the total hamiltonian matrix H for any saturated organic molecule takes the form

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

where

$$H_{(0)} = \begin{vmatrix} E_{(+)} & 0 \\ 0 & -E_{(-)} \end{vmatrix} \quad (2)$$

and

$$H_{(1)} = \begin{vmatrix} S & R \\ R^+ & Q \end{vmatrix} \quad (3)$$

and the zero- and first-order hamiltonian matrices, respectively. Accordingly, the first-order intersubspace resonance integrals are contained within the matrix R of Eq. (3). The superscript “+” of Eq. (3) designates the transposed matrix, while the negative sign in front of $E_{(-)}$ of Eq. (2) is introduced for convenience. In the case of blocks $E_{(+)}$ and $E_{(-)}$ being proportional to the n -dimensional unit matrix

$I_{(n)}$, the hamiltonian matrix of alkanes suggested in Refs. [12,13] follows from Eqs. (1)–(3).

As with the case of alkanes, no necessity for specifying either the structure of blocks within Eqs. (2) and (3) or their dimension (n) arises when formulating and solving the problems for both the DM and LMOs of saturated organic molecules. Let us assume only that the energy reference point is chosen so that both $E_{(+)}$ and $E_{(-)}$ are negative definite matrices [23]. In the case of $E_{(+)}$ and $E_{(-)}$ being diagonal matrices, such an assumption resolves itself into negative values of the BBO energies and positive values for the ABO energies.

The common expression for the one-electron DM (bond-order matrix) P of alkanes and their derivatives has been constructed in Refs. [12,13, 18,19] by means of the so-called density matrix formalism. The essence of this method consists of solving the following system of equations [17]

$$[H, Y]_- = 0 \quad (4)$$

$$Y^2 = I \quad (5)$$

$$\text{Spur } Y = 0 \quad (6)$$

formulated in terms of the residual charge matrix Y connected with P by the relation $Y = P - I$. The notation $[\dots]_-$ indicates a commutator of matrices.

The different nature of Eqs. (4), (5) and (6) should be noted in the first place. Thus, the commutation condition of Eq. (4) may be considered as the main physical requirement determining the matrix Y and thereby the DM P . The relation of Eq. (4) results from Dirac's equation in the case of the time-independent hamiltonian [17]. Alternatively, Eqs. (5) and (6) are additional system-structure-independent restrictions following from the idempotence requirement $\Pi^2 = \Pi$ for the projector $\Pi = (1/2)P$ and from the charge conservation condition, respectively.

The matrix P has been sought in Refs. [12,13, 18,19] in the form of power series

$$P = I + Y = I + Y_{(0)} + Y_{(1)} + Y_{(2)} + \dots \quad (7)$$

and general expressions for the corrections $Y_{(k)}$ have been obtained using the perturbation theory (PT) for the DM [17]. However, this way of solving Eqs. (4)–(6) allows no comparison of the problems

for the DM and LMOs. That is why a direct way of solving Eqs. (4)–(6) for the hamiltonian matrix H defined by Eqs. (1)–(3) is proposed here.

In common with the general PT for DM [17], let us substitute Eqs. (1) and (7) into Eq. (4), collect terms of the same order and impose the zero-matrix requirement within each order separately. As with the case of alkanes [12,13], let us consider terms to within the second order. We then obtain the relations

$$[H_{(0)}, Y_{(0)}]_- = 0 \quad (8)$$

$$[H_{(0)}, Y_{(1)}]_- + W_{(1)} = 0 \quad (9)$$

$$[H_{(0)}, Y_{(2)}]_- + W_{(2)} = 0 \quad (10)$$

where

$$W_{(1)} = [H_{(1)}, Y_{(0)}]_- \quad W_{(2)} = [H_{(1)}, Y_{(1)}]_- \quad (11)$$

Similarly, after substituting Eq. (7) into Eq. (5), the relations

$$Y_{(0)}^2 = I \quad (12)$$

$$[Y_{(0)}, Y_{(1)}]_+ = 0 \quad (13)$$

$$[Y_{(0)}, Y_{(2)}]_+ + Y_{(1)}Y_{(1)} = 0 \quad (14)$$

follow. The notation $[\dots]_+$ indicates an anti-commutator of matrices. And finally from Eq. (6) it follows that

$$\text{Spur } Y_{(k)} = 0 \quad (15)$$

for any k .

The matrix $Y_{(0)}$ complying with the zero-order relations shown in Eqs. (8), (12) and (15) for $k = 0$ is

$$Y_{(0)} = \begin{vmatrix} I & 0 \\ 0 & -I \end{vmatrix} \quad (16)$$

This matrix determines the zero-order DM $P_{(0)}$ ($P_{(0)} = I + Y_{(0)}$) representing the initial occupation numbers of BOs equal to 2 and 0 for BBOs and ABOs, respectively. The intrasubspace interactions contained within the zero-order blocks $E_{(+)}$ and $E_{(-)}$ of Eq. (2) exert no influence on the initial populations of BOs.

Let us consider the equation

$$[H_{(0)}, Y_{(k)}]_- + W_{(k)} = 0 \quad (17)$$

including both Eq. (9) and Eq. (10). Let the

Hermitian correction $Y_{(k)}$ be represented in the form of four $n \times n$ blocks, i.e.

$$Y_{(k)} = \begin{pmatrix} C_{(k)} & F_{(k)} \\ F_{(k)}^+ & D_{(k)} \end{pmatrix} \quad (18)$$

After substituting Eqs. (2) and (18) into Eq. (17), the zero-matrix requirements for the diagonal blocks of the left-hand side of Eq. (17) yield the relations

$$[E_{(+)}, C_{(k)}]_- + W_{(k)11} = 0 \quad (19)$$

$$[D_{(k)}, E_{(-)}]_- + W_{(k)22} = 0 \quad (20)$$

whereas the relevant requirements for the off-diagonal blocks lead to the relation

$$E_{(+)}F_{(k)} + F_{(k)}E_{(-)} + W_{(k)12} = 0 \quad (21)$$

where $W_{(k)ij}$ ($i, j = 1, 2$) are the respective $n \times n$ blocks of the matrix $W_{(k)}$ defined by Eq. (11). From this definition of $W_{(k)}$ as a commutator of two Hermitian matrices, it follows that $W_{(k)21} = -W_{(k)12}^+$. Accordingly, the last of four relations resulting from Eq. (17) and containing $W_{(k)21}$ proves to be the complex conjugate counterpart of Eq. (21) and is not worth considering.

The relations shown in Eqs. (19)–(21) belong to the matrix equations of the form

$$AX + XB = aC \quad (22)$$

where X is the matrix being sought and “ a ” is a constant. According to the theory of these equations [23], a unique solution is peculiar to Eq. (22) if the matrices A and $-B$ possess no common eigenvalues. Given that such a condition is satisfied and the matrices A and B are negative definite matrices, the unique solution of Eq. (22) may be presented in the integral form [23]

$$X = -a \int_0^\infty e^{At} C e^{Bt} dt \quad (23)$$

Therefore, the relations shown in Eqs. (19) and (20) and corresponding to the case $A = -B$ possess no unique solutions, whereas that of Eq. (21) presents the opposite case. As a result, only the off-diagonal blocks $F_{(k)}$ of the corrections $Y_{(k)}$ may be expected to be unambiguously determined by the commutation relation of Eq. (4). Alternatively, unique diagonal blocks $C_{(k)}$ and $D_{(k)}$ may be

assumed to follow after invoking the additional conditions of Eqs. (5) and (6) resolving themselves into Eqs. (13)–(15).

To make sure this is the case, let us consider the first- and second-order corrections separately.

The blocks of the matrix $W_{(1)}$ defined by Eq. (11) are

$$W_{(1)12} = -2R \quad W_{(1)11} = W_{(1)22} = 0 \quad (24)$$

(Eqs. (3) and (16) are used here). Substituting Eq. (24) into Eq. (21) and making use of Eq. (23) we obtain

$$F_{(1)} = -2G_{(1)} \quad (25)$$

where

$$G_{(1)} = \int_0^\infty e^{E_{(+)}t} R e^{E_{(-)}t} dt \quad (26)$$

Accordingly, the relation that the matrix $G_{(1)}$ complies with takes the form

$$E_{(+)}G_{(1)} + G_{(1)}E_{(-)} + R = 0 \quad (27)$$

To find the diagonal blocks $C_{(1)}$ and $D_{(1)}$ of the correction $Y_{(1)}$ let us turn to Eq. (13). Substituting Eqs. (16) and (18) for $k = 1$ into Eq. (13) we obtain

$$C_{(1)} = D_{(1)} = 0 \quad (28)$$

It should be noted here that no additional conditions for $F_{(1)}$ result from Eq. (13). Besides, Eq. (15) is also fulfilled after substituting Eq. (28). Moreover, the zero diagonal blocks $C_{(1)}$ and $D_{(1)}$ comply with Eqs. (19) and (20) for $k = 1$, the latter resolving themselves into the commutation requirements for the matrices $E_{(+)}$ and $C_{(1)}$ and $E_{(-)}$ and $D_{(1)}$, respectively.

As a result, the whole first-order correction $Y_{(1)}$ becomes

$$Y_{(1)} = -2 \begin{pmatrix} 0 & G_{(1)} \\ G_{(1)}^+ & 0 \end{pmatrix} \quad (29)$$

The diagonal and off-diagonal blocks of this correction actually follow from different conditions, namely from the requirement of Eq. (5) and from the commutation relation of Eq. (4), respectively.

Let us turn now to the second-order correction $Y_{(2)}$. The blocks of the relevant matrix $W_{(2)}$ defined

by Eq. (11) are

$$\mathbf{W}_{(2)11} = 2(\mathbf{G}_{(1)}\mathbf{R}^+ - \mathbf{R}\mathbf{G}_{(1)}^+)$$

$$\mathbf{W}_{(2)22} = 2(\mathbf{G}_{(1)}^+\mathbf{R} - \mathbf{R}^+\mathbf{G}_{(1)}) \quad (30)$$

$$\mathbf{W}_{(2)12} = -2\mathbf{V} \quad (31)$$

where

$$\mathbf{V} = \mathbf{S}\mathbf{G}_{(1)} - \mathbf{G}_{(1)}\mathbf{Q} \quad (32)$$

Accordingly, the off-diagonal blocks $\mathbf{F}_{(2)}$ of the correction $\mathbf{Y}_{(2)}$ result from Eq. (21) for $k = 2$. These are

$$\mathbf{F}_{(2)} = -2\mathbf{G}_{(2)} \quad (33)$$

where

$$\mathbf{G}_{(2)} = \int_0^\infty e^{\mathbf{E}_{(+)}t} \mathbf{V} e^{\mathbf{E}_{(-)}t} dt \quad (34)$$

and the relation that the matrix $\mathbf{G}_{(2)}$ complies with is

$$\mathbf{E}_{(+)}\mathbf{G}_{(2)} + \mathbf{G}_{(2)}\mathbf{E}_{(-)} + \mathbf{V} = 0 \quad (35)$$

The diagonal blocks $\mathbf{C}_{(2)}$ and $\mathbf{D}_{(2)}$ of the matrix $\mathbf{Y}_{(2)}$ follow from Eq. (14) after substituting Eqs. (16), (18) and (29). These are

$$\mathbf{C}_{(2)} = -2\mathbf{G}_{(1)}\mathbf{G}_{(1)}^+ \quad \mathbf{D}_{(2)} = 2\mathbf{G}_{(1)}^+\mathbf{G}_{(1)} \quad (36)$$

As with Eq. (13), no restrictions for $\mathbf{F}_{(2)}$ result from Eq. (14). Similarly, Eq. (15) is also fulfilled and $\mathbf{C}_{(2)}$ and $\mathbf{D}_{(2)}$ of Eq. (36) comply with the conditions resulting from Eqs. (19) and (20) for $k = 2$ after substituting $\mathbf{W}_{(2)11}$ and $\mathbf{W}_{(2)22}$ shown in Eq. (30). To prove the latter statement, the relation of Eq. (27) is to be used. As a result, the whole correction $\mathbf{Y}_{(2)}$ takes the form

$$\mathbf{Y}_{(2)} = -2 \begin{vmatrix} \mathbf{G}_{(1)}\mathbf{G}_{(1)}^+ & \mathbf{G}_{(2)} \\ \mathbf{G}_{(2)}^+ & -\mathbf{G}_{(1)}^+\mathbf{G}_{(1)} \end{vmatrix} \quad (37)$$

Therefore, analysis of the non-canonical problem for the one-electron DM shown in Eqs. (4)–(6) indicates that only the off-diagonal blocks $\mathbf{F}_{(k)}$ of the corrections $\mathbf{Y}_{(k)}$ are determined by the physical condition of Eq. (4), whereas the diagonal blocks $\mathbf{C}_{(k)}$ and $\mathbf{D}_{(k)}$ result from the additional system-structure-independent requirement of Eq. (5). Furthermore, using the off-diagonal part of the commutation relation shown in Eq. (4) suffices to

obtain the blocks $\mathbf{F}_{(k)}$ and the actual equation determining these blocks takes the form

$$\{[\mathbf{H}_{(0)}, \mathbf{Y}_{(k)}]_- + \mathbf{W}_{(k)}\}_{12} = \{[\mathbf{H}_{(0)}, \mathbf{Y}_{(k)}]_- + \mathbf{W}_{(k)}\}_{21} = 0 \quad (38)$$

where the subscripts 12 and 21 indicate the off-diagonal blocks of the total matrix within the braces. The relations of Eq. (38), in turn, resolve themselves into Eqs. (27) and (35) for the principal matrices $\mathbf{G}_{(1)}$ and $\mathbf{G}_{(2)}$ containing the dependence on the structure of the given system. Alternatively, the diagonal blocks $\mathbf{C}_{(k)}$ and $\mathbf{D}_{(k)}$ of the correction $\mathbf{Y}_{(k)}$ prove to be merely certain combinations of the above principal matrices $\mathbf{G}_{(1)}$ and $\mathbf{G}_{(2)}$. Hence, the relations of Eqs. (27) and (35) may be considered as the main system-structure-dependent equations determining the DM.

It should be noted that the above result about the blocks $\mathbf{C}_{(k)}$, $\mathbf{D}_{(k)}$ and $\mathbf{F}_{(k)}$ following from different conditions is in line with the general conclusions drawn in Ref. [17]. These concerned the commuting $\mathbf{Y}_{(k)+}$ and anticommuting $\mathbf{Y}_{(k)-}$ with the matrix $\mathbf{Y}_{(0)}$ parts of the total corrections $\mathbf{Y}_{(k)}$ ($\mathbf{Y}_{(k)} = \mathbf{Y}_{(k)+} + \mathbf{Y}_{(k)-}$): the term $\mathbf{Y}_{(k)+}$ has been established to result from Eq. (5), whereas $\mathbf{Y}_{(k)-}$ followed from Eq. (4). Again, it may be easily shown that in the particular case of the matrix $\mathbf{Y}_{(0)}$ taking the form of Eq. (16), the term $\mathbf{Y}_{(k)+}$ acquires a block-diagonal form, whereas $\mathbf{Y}_{(k)-}$ proves to contain non-zero off-diagonal blocks only.

3. The Brillouin theorem for the LMOs of saturated organic molecules

Let us dwell in this section on the non-canonical problem for the LMOs based on the perturbation theory and the Brillouin theorem [10–13]. The latter consists of the zero-matrix requirement for the off-diagonal blocks of the hamiltonian matrix \mathbf{H}' in the basis of LMOs. Let \mathbf{T} be the transformation matrix from the BO into the LMO basis. Then the transformed hamiltonian matrix is

$$\mathbf{H}' = \mathbf{T}^{-1}\mathbf{H}\mathbf{T} \quad (39)$$

and the Brillouin theorem resolves itself into the

requirements

$$\{\mathbf{H}'\}_{12} = \{\mathbf{H}'\}_{21} = 0 \quad (40)$$

or

$$\{\mathbf{T}^{-1}\mathbf{HT}\}_{12} = \{\mathbf{T}^{-1}\mathbf{HT}\}_{21} = 0 \quad (40a)$$

where the meaning of the subscripts 12 and 21 is similar to that of Eq. (38). As in Refs. [12,13], let us impose on the matrix \mathbf{T} the unitarity condition

$$\mathbf{TT}^+ = \mathbf{I} \quad (41)$$

which serves as an additional system-structure-independent requirement within the non-canonical problem for LMOs. Similarly to the case of alkanes [12,13], let us look for the matrix \mathbf{T} in the form of a power series with respect to parameters contained within the term $\mathbf{H}_{(1)}$ of Eq. (1). Since the member $\mathbf{H}_{(0)}$ of Eq. (2) complies with the Brillouin theorem from the outset, the zero-order term of the series for \mathbf{T} may be assumed to coincide with the $2n$ -dimensional unit matrix. Then the series being sought takes the form

$$\mathbf{T} = \mathbf{I} + \mathbf{T}_{(1)} + \mathbf{T}_{(2)} + \dots \quad (42)$$

The requirement $\mathbf{T}_{(0)} = \mathbf{I}$ contained in Eq. (42) is evidently not imperative. Indeed, the unit matrix may be replaced here by any unitary matrix involving zero off-diagonal blocks. However, the above choice of $\mathbf{T}_{(0)}$ proves to be essential when relating the problems for the LMOs and the DM.

The equality $\mathbf{T}_{(0)} = \mathbf{I}$ represents the coincidence requirement between BOs and the respective zero-order LMOs. Hence, it implies confinement to the class of the BO-like LMOs, and the subsequent discussion refers to the Brillouin theorem for the orthogonal BO-like LMOs.

Similarity of conditions shown in Eqs. (5) and (41) may also be noted. Thus, because of the equality $\mathbf{Y}^+ = \mathbf{Y}$, the requirement of Eq. (5) may be rewritten in the form $\mathbf{Y}^+\mathbf{Y} = \mathbf{I}$ indicating unitarity of the matrix \mathbf{Y} . However, an implicit difference between the requirements of Eqs. (5) and (41) lies in the non-Hermitian nature of the matrix \mathbf{T} .

To obtain further terms of the series shown in Eq. (42), let us substitute the latter into Eqs. (40a) and (41). Collecting terms of the same order in the

product $\mathbf{T}^+\mathbf{T}$ of Eq. (41) we obtain

$$\mathbf{T}_{(0)}^+\mathbf{T}_{(0)} = \mathbf{I} \quad (43)$$

$$\mathbf{T}_{(1)}^+ + \mathbf{T}_{(1)} = 0 \quad (44)$$

$$\mathbf{T}_{(2)}^+ + \mathbf{T}_{(2)} + \mathbf{T}_{(1)}^+\mathbf{T}_{(1)} = 0 \quad (45)$$

These relations are somewhat similar to those shown in Eqs. (12)–(14).

An analogous collecting of terms in the product $\mathbf{T}^+\mathbf{HT}$ and imposing the conditions of Eq. (40a) within each order separately yields the relations

$$\begin{aligned} & \{\mathbf{T}_{(1)}^+\mathbf{H}_{(0)} + \mathbf{H}_{(0)}\mathbf{T}_{(1)} + \mathbf{H}_{(1)}\}_{12} \\ & = \{\mathbf{T}_{(1)}^+\mathbf{H}_{(0)} + \mathbf{H}_{(0)}\mathbf{T}_{(1)} + \mathbf{H}_{(1)}\}_{21} = 0 \end{aligned} \quad (46)$$

$$\begin{aligned} & \{\mathbf{T}_{(2)}^+\mathbf{H}_{(0)} + \mathbf{H}_{(0)}\mathbf{T}_{(2)} \\ & + \mathbf{T}_{(1)}^+\mathbf{H}_{(1)} + \mathbf{H}_{(1)}\mathbf{T}_{(1)} + \mathbf{T}_{(1)}^+\mathbf{H}_{(0)}\mathbf{T}_{(1)}\}_{12} \\ & = \{\mathbf{T}_{(2)}^+\mathbf{H}_{(0)} + \mathbf{H}_{(0)}\mathbf{T}_{(2)} + \mathbf{T}_{(1)}^+\mathbf{H}_{(1)} \\ & + \mathbf{H}_{(1)}\mathbf{T}_{(1)} + \mathbf{T}_{(1)}^+\mathbf{H}_{(0)}\mathbf{T}_{(1)}\}_{21} = 0 \end{aligned} \quad (47)$$

After replacing $\mathbf{T}_{(1)}^+$ by $-\mathbf{T}_{(1)}$ on the basis of Eq. (44), a new version of Eq. (46) results

$$\begin{aligned} & \{[\mathbf{H}_{(0)}, \mathbf{T}_{(1)}]_- + \mathbf{H}_{(1)}\}_{12} \\ & = \{[\mathbf{H}_{(0)}, \mathbf{T}_{(1)}]_- + \mathbf{H}_{(1)}\}_{21} = 0 \end{aligned} \quad (48)$$

Similarly, replacing $\mathbf{T}_{(2)}^+$ of Eq. (47) by $-\mathbf{T}_{(2)} - \mathbf{T}_{(1)}^+\mathbf{T}_{(1)}$ in accordance with Eq. (45) leads to the equation

$$\begin{aligned} & \{[\mathbf{H}_{(0)}, \mathbf{T}_{(2)}]_- + \mathbf{U}_{(2)}\}_{12} \\ & = \{[\mathbf{H}_{(0)}, \mathbf{T}_{(2)}]_- + \mathbf{U}_{(2)}\}_{21} = 0 \end{aligned} \quad (49)$$

where

$$\mathbf{U}_{(2)} = [\mathbf{H}_{(1)}, \mathbf{T}_{(1)}]_- + \mathbf{T}_{(1)}^+\mathbf{H}_{(0)}\mathbf{T}_{(1)} - \mathbf{T}_{(1)}^+\mathbf{T}_{(1)}\mathbf{H}_{(0)} \quad (50)$$

Therefore, in the case of an unitary matrix \mathbf{T} expressed in the form of a power series as shown in Eq. (42), the Brillouin theorem becomes equivalent to the relation

$$\begin{aligned} & \{[\mathbf{H}_{(0)}, \mathbf{T}_{(k)}]_- + \mathbf{U}_{(k)}\}_{12} \\ & = \{[\mathbf{H}_{(0)}, \mathbf{T}_{(k)}]_- + \mathbf{U}_{(k)}\}_{21} = 0 \end{aligned} \quad (51)$$

where $\mathbf{U}_{(1)} = \mathbf{H}_{(1)}$ and $\mathbf{U}_{(2)}$ is defined by Eq. (50).

Comparison of Eqs. (38) and (51) shows that both relations are of similar form. This promotes an expectation that the off-diagonal blocks of the corrections $T_{(k)}$ are determined by Eq. (51), whereas the relevant diagonal blocks follow after invoking Eqs. (44) and (45).

To make sure this is the case, let us represent the correction $T_{(k)}$ in terms of four $n \times n$ blocks

$$T_{(k)} = \begin{vmatrix} M_{(k)} & N_{(k)} \\ K_{(k)} & L_{(k)} \end{vmatrix} \quad (52)$$

Different off-diagonal blocks are introduced in Eq. (52) in connection with the non-Hermitian nature of the matrix $T_{(k)}$.

It is noteworthy that the off-diagonal blocks both of the matrix $W_{(1)}$ defined by Eq. (11) and shown in Eq. (24) and of $U_{(1)} = H_{(1)}$ shown in Eq. (3) are proportional to the matrices R and R^+ . This proportionality results from the simple structure of the matrix $Y_{(0)}$ of Eq. (16). Indeed, only the signs of blocks of the matrix $H_{(1)}$ change after multiplying it by $Y_{(0)}$ when building up the matrix $W_{(1)}$ in accordance with Eq. (11). As a result, the matrices R and R^+ keep taking the off-diagonal positions when passing from $H_{(1)}$ to $W_{(1)}$. The established proportionality between the off-diagonal blocks of matrices $W_{(1)}$ and $U_{(1)}$ contributes significantly to the implicit similarity of Eqs. (38) and (51).

After substituting Eq. (52) for $k = 1$ into Eq. (51), the two relations of the latter take the form

$$E_{(+)}N_{(1)} + N_{(1)}E_{(-)} + R = 0 \quad (53)$$

$$-E_{(-)}K_{(1)} - K_{(1)}E_{(+)} + R^+ = 0 \quad (54)$$

Eqs. (53) and (54) belong to the matrix equations shown in Eq. (22) and the relevant unique solutions are

$$N_{(1)} = G_{(1)} \quad K_{(1)} = -G_{(1)}^+ \quad (55)$$

It should be noted that in contrast to Eq. (13) the relation shown in Eq. (44) does not determine the unique blocks $M_{(1)}$ and $L_{(1)}$ of the matrix $T_{(1)}$. The reason for that is the non-Hermitian nature of the matrix $T_{(1)}$. As with the case of alkanes [12], zero matrices $M_{(1)}$ and $L_{(1)}$ ($M_{(1)} = L_{(1)} = 0$) follow from Eq. (44) after accepting additional

requirements

$$M_{(1)}^+ = M_{(1)} \quad L_{(1)}^+ = L_{(1)} \quad (56)$$

Accordingly, the total matrix $T_{(1)}$ takes the form

$$T_{(1)} = \begin{vmatrix} 0 & G_{(1)} \\ -G_{(1)}^+ & 0 \end{vmatrix} \quad (57)$$

which proves to be as close to $Y_{(1)}$ of Eq. (29) as possible.

Substituting $T_{(1)}$ from Eq. (57) into Eq. (50) shows that zero off-diagonal blocks are inherent in the two last terms of the expression for $U_{(2)}$. This allows the matrix $U_{(2)}$ to be replaced by

$$U'_{(2)} = [H_{(1)}, T_{(1)}]_- \quad (58)$$

and the matrix $U'_{(2)}$ proves to be defined similarly to $W_{(2)}$ of Eq. (11). Furthermore, the off-diagonal blocks of $U'_{(2)}$ coincide with the matrices V and V^+ of Eq. (32). The reason for that is the similarity of $Y_{(1)}$ and $T_{(1)}$ evident from comparing Eqs. (29) and (57). Then the relevant two equations resulting from Eq. (51) for $k = 2$ and determining the off-diagonal blocks $N_{(2)}$ and $K_{(2)}$ of the second-order correction $T_{(2)}$ are

$$E_{(+)}N_{(2)} + N_{(2)}E_{(-)} + V = 0 \quad (59)$$

$$-E_{(-)}K_{(2)} - K_{(2)}E_{(+)} + V^+ = 0 \quad (60)$$

The unique solutions of Eqs. (59) and (60) may be expressed in terms of the matrix $G_{(2)}$ defined by Eq. (34)

$$N_{(2)} = G_{(2)} \quad K_{(2)} = -G_{(2)}^+ \quad (61)$$

Likewise, from both Eq. (45) and the additional requirements

$$M_{(2)} = M_{(2)}^+ \quad L_{(2)} = L_{(2)}^+ \quad (62)$$

it follows that

$$M_{(2)} = -\frac{1}{2}G_{(1)}G_{(1)}^+ \quad L_{(2)} = -\frac{1}{2}G_{(1)}^+G_{(1)} \quad (63)$$

As a result, the total matrix $T_{(2)}$ takes the form

$$T_{(2)} = \begin{vmatrix} -\frac{1}{2}G_{(1)}G_{(1)}^+ & G_{(2)} \\ -G_{(2)}^+ & -\frac{1}{2}G_{(1)}^+G_{(1)} \end{vmatrix} \quad (64)$$

It may be concluded, therefore, that the off-diagonal blocks $N_{(k)}$ and $K_{(k)}$ of the correction $T_{(k)}$

are determined by the physical condition shown in Eq. (51), whereas the diagonal blocks follow from the unitarity requirement of Eq. (41). However, in contrast to Eq. (38), the relation of Eq. (51) involves not only the Brillouin theorem, but also the additional unitarity requirement. This indicates an essential role of the latter requirement when relating the problems for LMOs and the DM.

The relations of Eqs. (53), (54), (59) and (60) resulting from Eq. (51) resemble Eqs. (27) and (35) of the previous section. Furthermore, the equality

$$\mathbf{K}_{(k)} = -\mathbf{N}_{(k)}^+ \quad (65)$$

for $k = 1, 2$ follows from Eqs. (44) and (45). Hence, solving Eqs. (53) and (59) and making use of Eq. (65) yields Eqs. (55) and (61) without regard to Eqs. (54) and (60). Again, Eqs. (53) and (59) coincide with Eqs. (27) and (35), respectively.

Therefore, common system-structure-dependent equations shown in Eqs. (27) and (35) are inherent in the non-canonical problems for both the LMOs and the DM. Solving Eqs. (27) and (35), or using the respective integral solutions shown in Eqs. (26) and (34), allows the principal matrices $\mathbf{G}_{(1)}$ and $\mathbf{G}_{(2)}$ to be obtained, to which the off-diagonal blocks of the corrections $\mathbf{Y}_{(k)}$ and $\mathbf{T}_{(k)}$ are proportional. The diagonal blocks of these corrections are expressed algebraically in terms of the same matrices $\mathbf{G}_{(1)}$ and $\mathbf{G}_{(2)}$. Hence, if Eqs. (27) and (35) are solved for a given molecule, the corrections inside the LMOs and the DM may be obtained on a unified basis. This implies the feasibility of a unified localized description of saturated organic molecules, wherein LMOs and the DM play the role of two alternative representations of electronic structure.

4. Discussion of the main features of the unified localized description of the electronic structure of saturated organic molecules

As is seen from Eqs. (7), (16), (29), (37), (42), (57) and (64), both the DM \mathbf{P} and the LMO representation matrix \mathbf{T} contain the same matrices $\mathbf{G}_{(1)}$, $\mathbf{G}_{(2)}$, $\mathbf{G}_{(1)}\mathbf{G}_{(1)}^+$ and $\mathbf{G}_{(1)}^+\mathbf{G}_{(1)}$ as building blocks. Hence, the LMOs and the DM rows (columns) of saturated organic molecules prove to be interrelated and

characterized by the same dependence on the structure of the system as was the case with alkanes [12].

The matrix $\mathbf{G}_{(1)}^+$ determines both the first-order tails of the occupied LMOs containing ABOs and the bond orders between BBOs and ABOs, whereas the matrix $\mathbf{G}_{(2)}^+$ causes the analogous second-order quantities. Similarly, the matrix $\mathbf{G}_{(1)}\mathbf{G}_{(1)}^+$ describes the tails of the occupied LMOs containing BBOs and the bond orders between the latter, whereas $\mathbf{G}_{(1)}^+\mathbf{G}_{(1)}$ represents the tails of vacant LMOs containing ABOs and the bond orders between ABOs.

Let us discuss the dependence of the matrices $\mathbf{G}_{(1)}$ and $\mathbf{G}_{(2)}$ on the hamiltonian matrix blocks $\mathbf{E}_{(+)}$, $\mathbf{E}_{(-)}$, \mathbf{R} , \mathbf{S} and \mathbf{Q} . Three cases may be distinguished here:

(1) The case of alkanes described by the matrices $\mathbf{E}_{(+)}$ and $\mathbf{E}_{(-)}$ proportional to the n -dimensional unit matrix [12,13], i.e.

$$\mathbf{E}_{(+)} = \mathbf{E}_{(-)} = \beta \mathbf{I} \quad (66)$$

where β is the negative energy unit. (Energies of all BBOs and of all ABOs are assumed to be similar for alkanes and the intrasubspace interactions are assumed to be of first-order magnitude.) In this case Eqs. (27) and (35) may be solved algebraically and we obtain

$$\mathbf{G}_{(1)}^{(a)} = -\frac{1}{2\beta}\mathbf{R} \quad \mathbf{G}_{(2)}^{(a)} = \frac{1}{4\beta^2}(\mathbf{SR} - \mathbf{RQ}) \quad (67)$$

where the superscript (a) refers to the case of alkanes. The elements of these matrices are

$$\mathbf{G}_{(1)il}^{(a)} = \mathbf{G}_{(1)li}^{+(a)} = -\frac{1}{2\beta}\mathbf{R}_{il} = -\frac{1}{2\beta}\mathbf{R}_{li}^+ \quad (68a)$$

$$\mathbf{G}_{(2)il}^{(a)} = \mathbf{G}_{(2)li}^{+(a)} = \frac{1}{4\beta^2} \left(\sum_j^{\text{BBOs}} \mathbf{S}_{ij}\mathbf{R}_{jl} - \sum_k^{\text{ABOs}} \mathbf{R}_{ik}\mathbf{Q}_{kl} \right) \quad (68b)$$

where the superscripts i and j describe BBOs, while k and l refer to ABOs.

Properties of the matrices $\mathbf{G}_{(1)}^{(a)}$ and $\mathbf{G}_{(2)}^{(a)}$ shown in Eqs. (67) and (68) have been studied in Ref. [12]. Thus, the element $\mathbf{G}_{(1)il}^{+(a)}$ proportional to the respective hamiltonian matrix element \mathbf{R}_{li}^+ and inversely proportional to the difference (2β) between the BBO energy and the ABO energy has been concluded to describe the direct through-space interaction

between the BBO $\phi_{(+i)}$ and ABO $\phi_{(-l)}$. The magnitude of this interaction was expected to decrease rapidly when the relevant interbond distance increases. Alternatively, the element $G_{(2)li}^{+(a)}$ proved to represent the indirect interaction of the same BOs by means of BBOs $\phi_{(+j)}$ and/or ABOs $\phi_{(-k)}$ playing the role of mediators. This interaction was expected to be of a more long-range nature compared with the through-space one. As is seen from Eq. (68b), the intrasubspace interactions contained within the matrices S and Q play an essential part in the formation of the indirect interaction between the BBO $\phi_{(+i)}$ and ABO $\phi_{(-l)}$.

(2) The case of molecules described by diagonal matrices $E_{(+)}$ and $E_{(-)}$, i.e. by intrasubspace interactions of first-order magnitude. Explicit expressions for particular elements of the two relevant matrices $G_{(1)il}^{(d)}$ and $G_{(2)il}^{(d)}$, but not for the matrices themselves, follow in this case from Eqs. (26) and (34)

$$G_{(1)il}^{(d)} = G_{(1)il}^{+(d)} = -\frac{R_{il}}{E_{(+i)} + E_{(-l)}} \quad (69a)$$

$$G_{(2)il}^{(d)} = G_{(2)il}^{+(d)} = \frac{1}{E_{(+i)} + E_{(-l)}} \times \left(\sum_j^{\text{BBOs}} \frac{S_{ij}R_{jl}}{E_{(+j)} + E_{(-l)}} - \sum_k^{\text{ABOs}} \frac{R_{ik}Q_{kl}}{E_{(+i)} + E_{(-k)}} \right) \quad (69b)$$

where the superscript (d) refers to the case of diagonal matrices $E_{(+)}$ and $E_{(-)}$ with the elements $E_{(+i)}$ and $E_{(-l)}$. Comparing Eqs. (68) and (69) shows that cases (1) and (2) differ only in denominators of the relevant expressions for the matrix elements. As a result, the conclusions referring to case (1) hold true for case (2) as well.

(3) The most general case of molecules described by arbitrary negative definite matrices $E_{(+)}$ and $E_{(-)}$. No simple relation between the elements of the matrices $G_{(1)}$ and $G_{(2)}$, on the one hand, and that of the blocks S , R , Q , $E_{(+)}$ and $E_{(-)}$, on the other hand, may be established in this case. Hence, the element $G_{(1)il}$ may not be interpreted as a direct through-space interaction between the BBO $\phi_{(+i)}$ and the ABO $\phi_{(-l)}$. Accordingly, the interaction between these BOs may be expected to be of a non-local nature in this case.

Let us consider the occupation numbers (populations) of BOs. These follow from the diagonal elements of the matrices $P_{(0)} = I + Y_{(0)}$ and $Y_{(2)}$ shown in Eqs. (16) and (37). Thus, the populations of the BBO $\phi_{(+i)}$ and the ABO $\phi_{(-m)}$ are

$$X_{(+i)} = 2 - 2 \sum_l^{\text{ABOs}} G_{(1)il} G_{(1)li}^+ = 2 \left(1 - \sum_l^{\text{ABOs}} (G_{(1)li}^+)^2 \right) \quad (70)$$

$$X_{(-m)} = 2 \sum_i^{\text{BBOs}} (G_{(1)im})^2 \quad (71)$$

In case (2) the expressions for $G_{(1)li}^{+(d)}$ and $G_{(1)im}^{(d)}$ shown in Eqs. (69a) and (69b) may be substituted into Eqs. (70) and (71). We then obtain

$$X_{(+i)}^{(d)} = 2 \left(1 - \sum_l^{\text{ABOs}} \frac{(R_{il})^2}{(E_{(+i)} + E_{(-l)})^2} \right) \quad (72)$$

and

$$X_{(-m)}^{(d)} = 2 \sum_i^{\text{BBOs}} \frac{(R_{im})^2}{(E_{(+i)} + E_{(-m)})^2} \quad (73)$$

As is seen from Eqs. (72) and (73), alterations of the occupation numbers against the respective initial values equal to 2 and 0 for BBOs and ABOs, respectively, are determined by sums of contributions associated with the direct interactions of the BBO (ABO) under study and the remaining ABOs (BBOs). Hence, the additive nature of the occupation numbers may be concluded on the basis of Eqs. (72) and (73), provided that the matrices $E_{(+)}$ and $E_{(-)}$ are diagonal.

From Eqs. (72) and (73) it follows also that changes in the occupation numbers of BOs when building up the molecule are determined by the interactions between BOs of different types (BBOs and ABOs). This conclusion may be considered as a generalization of the relevant rules for two-level systems. Indeed, interactions between either two occupied or two vacant orbitals are known to lead to no charge transfer, whereas interactions between an occupied and a vacant orbital present the opposite situation. When discussing

saturated organic molecules we have to work with a set of n initially occupied BBOs and with a set of n initially vacant ABOs.

Let us now look for the relations between the occupation numbers of BOs $X_{(+i)}$ and $X_{(-m)}$ and the respective LMOs. Let us consider the general case (3) of arbitrary negative definite matrices $E_{(+)}$ and $E_{(-)}$. The occupied LMO $\Psi_{(+i)}$ to within first-order terms follows from Eqs. (42) and (57) and takes the form

$$\Psi_{(+i)} = \phi_{(+i)} - \sum_I^{\text{ABOs}} \phi_{(-)I} \mathbf{G}_{(1)Ii}^+ \quad (74)$$

As in Ref. [12], let us define the delocalization coefficient $\mathbf{D}_{(+i)}$ of the LMO $\Psi_{(+i)}$

$$\mathbf{D}_{(+i)} = \sum_I^{\text{ABOs}} (\mathbf{G}_{(1)Ii}^+)^2 \quad (75)$$

Then the occupation number $X_{(+i)}$ of the BBO $\phi_{(+i)}$ shown in Eq. (70) proves to be related to the delocalization coefficient $\mathbf{D}_{(+i)}$

$$X_{(+i)} = 2(1 - \mathbf{D}_{(+i)}) \quad (76)$$

Hence, the population of the BBO $\phi_{(+i)}$ lost when making up the LMO $\Psi_{(+i)}$ appears to be proportional to the total delocalization of the latter. Accordingly, for an ABO $\phi_{(-)m}$ we obtain

$$X_{(-)m} = 2\mathbf{D}_{(-)m} \quad (77)$$

where

$$\mathbf{D}_{(-)m} = \sum_I^{\text{BBOs}} (\mathbf{G}_{(1)Im})^2 \quad (78)$$

is the delocalization coefficient of the vacant LMO $\Psi_{(-)m}$. Hence, the population $X_{(-)m}$ that the ABO $\phi_{(-)m}$ acquires when making up the respective LMO $\Psi_{(-)m}$ is proportional to the total delocalization of this LMO.

Therefore, the relations between the populations of BOs and the extent of delocalization of respective LMOs established in Ref. [12] for alkanes are valid for any saturated molecule.

The explicit interrelations between the corrections $Y_{(k)}$ and $T_{(k)}$ obtained in Ref. [12] for

alkanes

$$Y_{(1)} + \mathbf{T}_{(1)}^+ Y_{(0)} + Y_{(0)} \mathbf{T}_{(1)} = 0 \quad (79)$$

$$Y_{(2)} + Y_{(0)} \mathbf{T}_{(2)} + \mathbf{T}_{(2)}^+ Y_{(0)} + \mathbf{T}_{(1)}^+ Y_{(0)} \mathbf{T}_{(1)} + \mathbf{T}_{(1)}^+ Y_{(1)} + Y_{(1)} \mathbf{T}_{(1)} = 0 \quad (80)$$

also prove to be valid for any saturated molecule. Coincidence between the occupation numbers of BOs and those of respective LMOs suffices to prove this statement. Indeed, no more is required here to substitute Eqs. (7) and (42) into the product $\mathbf{T}^+ \mathbf{P} \mathbf{T}$ describing the DM in the LMO basis, and then to use the equality

$$\mathbf{T}^+ \mathbf{P} \mathbf{T} = \mathbf{I} + Y_{(0)} \quad (81)$$

which implies zero-matrix conditions for the transformed corrections $Y'_{(1)}$ and $Y'_{(2)}$.

Let us eliminate $\mathbf{T}_{(1)}^+$ and $\mathbf{T}_{(2)}^+$ from Eqs. (79) and (80) on the basis of Eqs. (44) and (45) as was performed in the case of Eqs. (46) and (47). We then obtain

$$[Y_{(0)}, \mathbf{T}_{(k)}]_- + \mathbf{Z}_{(k)} = 0 \quad (82)$$

instead of Eqs. (79) and (80), where

$$\mathbf{Z}_{(1)} = Y_{(1)} \quad (83)$$

$$\mathbf{Z}_{(2)} = [Y_{(1)}, \mathbf{T}_{(1)}]_- + \mathbf{T}_{(1)}^+ Y_{(0)} \mathbf{T}_{(1)} - \mathbf{T}_{(1)}^+ \mathbf{T}_{(1)} Y_{(0)} + Y_{(2)} \quad (84)$$

Comparing Eqs. (82), (17) and (51) indicates a similarity of these equations. As with Eqs. (17) and (51), the relation of Eq. (82) may be shown to determine the off-diagonal blocks of the corrections $\mathbf{T}_{(k)}$ in terms of blocks of the corrections $Y_{(k)}$.

Therefore, equations for LMOs with respect to DM instead of the hamiltonian matrix may be formulated and these resemble the relevant equations of Eq. (51) based on the Brillouin theorem. However, in contrast to Eqs. (17) and (51) containing the block-diagonal matrix $\mathbf{H}_{(0)}$, Eq. (82) involves the diagonal matrix $Y_{(0)}$ of Eq. (16). Hence, Eq. (82) may be solved algebraically for any saturated organic molecule. This gives rise to the mutual proportionality between the respective

blocks of the corrections $Y_{(k)}$ and $T_{(k)}$ seen from comparison of Eqs. (29), (37) (57) and (64).

On the whole, the interrelations between the LMOs and the DM of saturated molecules discussed in this section also contribute to the equivalence of the two localized representations of the electronic structure.

5. Concluding remarks

As is seen from the above analysis, the different initial problems for the LMOs and the DM become similar after taking into account the specific structure of the hamiltonian matrix for saturated organic molecules. The block-diagonal form of the zero-order term $H_{(0)}$ and the constitution of the zero-order corrections $Y_{(0)}$ and $T_{(0)}$ play the most important part in the formation of this similarity. As a result, common equations determining the building blocks $G_{(1)}$ and $G_{(2)}$ of both the LMOs and the DM follow, and these prove to be the only system-structure-dependent equations within the relevant non-canonical problems. Therefore, a single physical condition determining the electronic structure of saturated organic molecules may be assumed to underlie both the commutation relation for the DM and the Brillouin theorem for the orthogonal LMOs.

The above investigation also shows that the commutation relation of Eq. (4) contains excessive requirements relative to that which is sufficient for obtaining the unique DM of saturated molecules. Indeed, the zero-matrix condition for the off-diagonal blocks of the commutator $[H, Y]_-$ suffices to determine the DM. Again, additional requirements, such as the unitarity condition and the equality $T_{(0)} = I$, prove to be necessary when reformulating the Brillouin theorem into the form similar to the off-diagonal part of the commutation relation. As a result, it is the set of the orthogonal BO-like LMOs that serves as an alternative to the DM when describing saturated organic molecules in a localized way.

In contrast to the canonical eigenvalue problems for the hamiltonian matrices, different roles of the diagonal intrasubspace blocks and of the off-diagonal intersubspace blocks are revealed in the non-canonical problems under discussion. Thus,

equations determining the principal matrices $G_{(1)}$ and $G_{(2)}$ follow from the off-diagonal blocks both of the commutator $[H, Y]_-$ and of the transformed hamiltonian matrix T^+HT . Again, it is the off-diagonal blocks of the corrections $Y_{(k)}$ and $T_{(k)}$ that follow from these hamiltonian-containing requirements. Therefore, the physical conditions determining the electronic structure of saturated organic molecules may be concluded to act between the subspaces of BBOs and ABOs and not inside the latter.

References

- [1] L. Zuelicke, *Quantenchemie, Vol.1, Grundlagen und Allgemeine Methoden*, VEB, Berlin, 1973.
- [2] R. McWeeny and B.T. Sutcliffe, *Methods of Molecular Quantum Mechanics*, Academic Press, London, 1969.
- [3] R. Drago, *Physical Methods in Chemistry*, W.B. Saunders, Philadelphia, 1977.
- [4] O. Chalvet (Ed.), *Localization and Delocalization in Quantum Chemistry, Atoms and Molecules in the Ground State*, Vol. 1, Reidel, Dordrecht, 1975.
- [5] A.J. Gordon and R.A. Ford, *The Chemist's Companion. The Handbook of Practical Data, Techniques and References*, Interscience-Wiley, New York, 1972.
- [6] M.J.S. Dewar, *J. Am. Chem. Soc.*, 106 (1984) 669.
- [7] R. Hoffmann, *Solid and Surfaces: A Chemist's View of Bonding in Extended Structures*, VCH, 1988.
- [8] H.G.O. Becker, *Einführung in die Elektronentheorie Organisch-chemischen Reaktionen*, VEB, Berlin, 1974.
- [9] V.I. Kuznecov (Ed.), *Development of the Valency Concept*, Khimia, Moscow, 1977.
- [10] P.R. Surjan, I. Mayer and M. Kertez, *J. Chem. Phys.*, 77 (1982) 2454.
- [11] I. Mayer and P.R. Surjan, *J. Chem. Phys.*, 80 (1984) 5649.
- [12] V. Gineityte, *J. Mol. Struct. (Theochem)*, 288 (1993) 111.
- [13] V. Gineityte, *J. Mol. Struct. (Theochem)*, 342 (1995) 219.
- [14] X. Cao and J. Wang, *Chem. Phys. Lett.*, 146 (1988) 41.
- [15] E. Kapui, R. Daudel and C. Kozmutza, *J. Mol. Struct. (Theochem)*, 181 (1988) 237.
- [16] A.V. Luzanov, *Zh. Strukt. Khim.*, 21 (1980) 3.
- [17] M.M. Mestechkin, *Metod Matricy Plotnosti v Teorii Molekul*, Naukova Dumka, Kiev, 1977.
- [18] V. Gineityte and D. Shatkovskaya, *J. Mol. Struct. (Theochem)*, 201 (1989) 49.
- [19] V. Gineityte and D. Shatkovskaya, *Int. J. Quantum Chem.*, 39 (1991) 11.
- [20] J.A. Pople and D.P. Santry, *Mol. Phys.*, 7 (1963–64) 269.
- [21] V. Gineityte and D. Shatkovskaya, *Zh. Strukt. Khim.*, 25 (1984) 152.
- [22] V. Gineityte and D. Shatkovskaya, *Zh. Strukt. Khim.*, 26 (1985) 42.
- [23] P. Lancaster, *Theory of Matrices*, Academic Press, New York, 1969.