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Substantiation of the basis set orthogonality assumption for saturated molecules and crystals on account of their common topological structure

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Abstract

The overlap matrices of saturated (tetrahedral) systems in the basis of sp^3 hybrid AOs have been presented as a single matrix (S) consisting of zero-order and first-order terms. The common expression for the respective Löwdin's orthogonalization matrix ($S^{-1/2}$) has been obtained in the form of a power series and the structure of the orthogonalized basis orbitals has been analyzed. The relevant common hamiltonian matrix (H) has been transformed into the basis of the orthogonalized orbitals and the resulting matrix \tilde{H} has been compared with the initial one. The similarity between the most essential qualitative peculiarities of the matrices H and \tilde{H} has been established: the presence of the zero-order terms of similar structure and first-order terms, the local nature of the relation between the hamiltonian matrix elements and the structure of the system, and the transferability of the elements associated with the similar atoms and bonds, are inherent to both H and \tilde{H} . These results follow from the common topological structure of saturated molecules and crystals and serve to support the basis set orthogonality assumption extensively used in qualitative quantum chemistry.

Keywords: Basis set orthogonality assumption; Crystals; Saturated molecules; Topological structure

1. Introduction

Two current trends may be distinguished in quantum chemistry. The quantitative one is orientated mainly toward calculating the electronic structure of a molecule as accurately as possible, and the relevant results contribute to the development of quantum chemistry's predicting ability.

Alternatively, the qualitative quantum chemistry is principally intended to account for the actual electronic structure regularities inherent in the whole series or a class of molecules. Simple models are being developed in this case, and the obtained

conclusions serve the classification and interpretation of the entire information on the molecular structure and reactivity.

The Hückel-type hamiltonian matrix [1,2] may be considered as one of the most popular qualitative models. It is this approach that resulted in the well-known qualitative theory of the electronic structure of the conjugated hydrocarbons, including the alternant ones [2]. It is noteworthy that the basis set orthogonality assumption usually accepted in this method essentially contributes to the simplicity of the results obtained.

A similar Hückel-type hamiltonian in common

with the basis set orthogonality requirement has also been applied to the investigation of saturated hydrocarbons (alkanes) and their derivatives [3–6] and of the related tetrahedral crystals [7]. It has been shown that the relevant hamiltonian matrices may be presented in the form of the single matrix (H) both in the sp^3 hybrid AO (HAO) basis [3–5,7] and in the basis of their simple linear combinations described as bond orbitals (BOs) [6]. Such a common form of the matrix H has allowed the single quantum-mechanical problem to be formulated and solved algebraically for any saturated system. As a result, the common expression for the relevant one-electron density matrix (DM) [3–7] and the similar expression for the localized MOs (LMOs) [6] have been obtained. Moreover, the common peculiarities of the resulting matrices, i.e. of the DM and the LMO representation matrix, have been established. The local nature of the relation between the elements of these matrices and the structure of the system and the transferability of these elements pertaining to the identical atoms and bonds rank among these common peculiarities.

Furthermore, the well-known more involved semiempirical methods, e.g. CNDO, MINDO [8], taking an intermediate place between the qualitative and quantitative trends of quantum chemistry, are based on the so-called zero differential overlap (ZDO) approximation closely related to the basis set orthogonality requirement. These methods have been extensively applied to the investigation of both conjugated and saturated molecules [8].

Therefore the basis set orthogonality is one of the basic assumptions in qualitative quantum chemistry, and justifying this assumption serves to support the above-discussed results and conclusions.

Many attempts to achieve this end have been undertaken, especially in the context of the analysis of the assumptions underlying the semiempirical ZDO methods. The relevant contributions dealing with conjugated molecules [9–11] and organic compounds in general [10–12] may be mentioned. These are based on transforming the initial hamiltonian matrix represented in the non-orthogonal basis to the symmetrically orthogonalized (SO)

basis using the Löwdin's transformation matrix $S^{-1/2}$ [13,14] (S is the overlap matrix of the initial AOs), and on relating the semi-empirical parameters to the elements of the transformed matrix \tilde{H} . Then the results obtained under the basis set orthogonality assumption are looked upon as corresponding to the SO basis [9–12].

The overlap integrals between the neighboring $2p_z$ AOs of the conjugated molecules do not exceed 0.25 [10,11] and a converging power series with respect to the difference $S-I$ (I stands for the unit matrix) may be constructed for the relevant matrix $S^{-1/2}$ [9–11]. In turn, the general expressions for the elements of the transformed hamiltonian \tilde{H} follow from these series. Analysis of such expressions has shown that the differences in the values of the respective hamiltonian matrix elements in the initial and in the SO basis are sufficiently small for the conjugated systems [9–11]. For that reason the basis set orthogonality assumption is usually considered as justified in this case.

Alternatively, the whole set of valent AOs for each atom is to be included in the initial basis when studying the saturated systems, and relatively large elements emerge in the relevant overlap matrices. As a result, the power series of the above type does not converge [10–12]. Moreover, a non-local relation between the respective elements of H and \tilde{H} has been predicted in this case [15]. All this gave rise to some doubts as to the validity of the basis set orthogonality assumption for saturated molecules [10–12].

This paper is aimed at justifying the above-discussed assumption for saturated molecules and crystals. Using this example, we are about to demonstrate that the validity of the basis set orthogonality assumption for a certain type of molecule or crystal is related to the definite peculiarities of their structure rather than to the smallness of the overlap integrals. Moreover, we intend to show in this paper that no small value requirement for the matrix $S-I$ is imperative for expanding the matrix $S^{-1/2}$ in the form of a converging power series. The peculiarities of the relevant orthogonalized orbitals are also studied and the analysis of the transformed hamiltonian matrix intended for comparing its structure with that accepted in our previous papers [3–7] is carried out.

2. Expansion in the form of power series for Löwdin's orthogonalization matrix $S^{-1/2}$ of a saturated system

Let us consider a saturated system of tetrahedral structure, e.g. alkane, substituted alkane, or a finite diamond crystal. No lone electron pairs are assumed to be inherent to our system. This requirement, however, is not imperative, and the results obtained below may be easily generalized to a system containing such pairs.

Let us compile the initial basis set $\{\chi\}$ including four sp^3 HAOs of each internal (most commonly carbon) atom and the 1s AOs of the hydrogen atoms (if any). Let us term the set $\{\chi\}$ the HAO basis. The use of the HAOs instead of the ordinary AOs leads to a correspondence between the spatial arrangement of the basis functions and that of the chemical bonds. As a result, the tetrahedral structure of our system manifests itself in the considerable differences [3–7,16,17] in the relative values of the neighboring and non-neighboring overlap integrals (the pairs of the mutually directed HAOs are described as neighboring). Hence, the non-neighboring integrals may be regarded as the first-order terms with respect to the neighboring ones [3–7]. Moreover, the neighbouring overlap integrals prove to be of nearly identical value for different types of bonds in saturated systems. This last conclusion follows from the calculations of the overlap integrals using the formulae derived by Roothaan [18] and from other estimations [16,17,19]. For example, the neighboring overlap integrals pertinent to the C–C and C–H bonds in alkanes equal 0.647 and 0.686 [19] respectively, whereas the non-neighboring ones do not exceed 0.2 [16]. Therefore the differences between the actual values of the neighboring overlap integrals and their mean value σ may also be considered as first-order terms. Then the initial overlap matrix S may be presented as a sum of zero-order ($S_{(0)}$) and first-order ($S_{(1)}$) terms

$$S = S_{(0)} + S_{(1)} \quad (1)$$

where $S_{(0)}$ contains the diagonal elements of the matrix S equal to unity and the averaged neighboring overlap integrals equal to σ , and $S_{(1)}$ involves the non-neighboring overlaps and the differences

between σ and the actual values of the neighboring ones.

Further, let us divide the initial $2N$ -dimensional basis set $\{\chi\}$ (N stands for the total number of bonds in the system under study) into two N -dimensional subsets $\{\chi'\}$ and $\{\chi''\}$ so that the strongly overlapping pairs of the neighboring orbitals find themselves in the different subsets. Let the pairs of the neighboring orbitals require the coupled numbers i and $N+i$, where $i = 1, 2, \dots, N$. Then both $S_{(0)}$ and $S_{(1)}$ may be presented in the form of four $(N \times N)$ -dimensional blocks corresponding to the subsets $\{\chi'\}$ and $\{\chi''\}$ and to the inter-subset overlaps

$$S_{(0)} = \begin{vmatrix} I & \sigma I \\ \sigma I & I \end{vmatrix} \quad S_{(1)} = \sigma \begin{vmatrix} X & Z \\ Z^+ & Y \end{vmatrix} \quad (2)$$

where I is the N -dimensional unit matrix and the superscript $+$ designates the transposed matrix. The averaged neighboring overlap integrals make up the off-diagonal blocks σI in the zero-order term $S_{(0)}$, whereas the constant σ in front of the second matrix of Eq. (2) is introduced for convenience. It is seen from Eq. (2) that the two subspaces $\{\chi'\}$ and $\{\chi''\}$ are strongly non-orthogonal.

Therefore, the zero-order term $S_{(0)}$ of simple and common structure shown in Eq. (2) may be revealed in the overlap matrices of saturated systems. As with the zero-order hamiltonian $H_{(0)}$ [6], the matrix $S_{(0)}$ represents the common topological structure of our systems, consisting of both tetrahedral symmetry of the nearest environment of the internal atoms and the rough topological equivalence of all bonds (which is associated with the nearly identical values of the neighboring overlap integrals). It is noteworthy that these two aspects of the structure are closely interrelated. Indeed, it is the topological equivalence of the four bonds at the given internal atom that largely contributes to the tetrahedral symmetry of its nearest environment, provided that this symmetry is understood in terms of the overlap integrals and not in terms of the internuclear distances.

Again, the dimension N and the structure of the blocks X , Y and Z contain information on the specific constitution of the system under study. As with the LMOs [6] and DM [3–7], the expression

for the matrix $S^{-1/2}$ being sought may be constructed without regard to these specific peculiarities of the matrices X , Y and Z , and no necessity for specifying them arises. Let us note only that the non-diagonal elements of the matrices X , Y , Z and Z^+ situated in the identical positions, e.g. X_{ij} , Y_{ij} , Z_{ij} and Z_{ij}^+ , represent the four different non-neighboring overlaps associated with a definite pair of bonds. Indeed, let X_{ij} be the overlap integral between the orbitals χ'_i and χ'_j localized on the r th and p th bond, respectively (note that both χ'_i and χ'_j belong to the first subset $\{\chi'\}$ and thus $r \neq p$). Then the element Y_{ij} represents the overlap integral between the orbitals χ''_{N+i} and χ''_{N+j} being the neighbors of the orbitals χ'_i and χ'_j localized on the same pair of bonds. Accordingly, Z_{ij} and Z_{ij}^+ are associated with the remaining two combinations of the above-defined four orbitals.

Let us turn now to the construction of the common expression for the matrix $S^{-1/2}$. Since $S_{(0)} \neq I$ in Eq. (2), the power of the sum $S_{(0)} + S_{(1)}$ cannot be expanded in series directly, and a more involved procedure is necessary.

Let D and ω_i stand for the unitary matrix of the eigenvectors and the eigenvalues of the matrix S , respectively. Then, according to the definition of a power function of a matrix [20]

$$S = D \|\omega\| D^+ \quad S^{-1/2} = D \|\omega^{-1/2}\| D^+ \quad (3)$$

where the notation $\|\dots\|$ indicates a diagonal matrix. Let the matrix D be represented in the form of the product of two matrices D_1 and D_2 ($D = D_1 D_2$) and substitute this form into Eq. (3). After multiplying the two relations of Eq. (3) by D_1^+ and D_1 from the left and right side, respectively, and denoting

$$D_1^+ S D_1 = \Lambda \quad (4)$$

a modified expression for the matrix $S^{-1/2}$

$$S^{-1/2} = D_1 \Lambda^{-1/2} D_1^+ \quad (5)$$

results. Hence, if we find a common unitary matrix D_1 such that a converging power series for the $(-1/2)$ -th power of the transformed overlap matrix Λ resulting from Eq. (4) may be constructed, i.e. if a convergent expansion

$$\Lambda^{-1/2} = \Lambda_{(0)}^{-1/2} + \Lambda_{(1)}^{-1/2} + \Lambda_{(2)}^{-1/2} + \dots \quad (6)$$

exists, then the matrix $S^{-1/2}$ being sought follows from Eq. (5).

To find an appropriate matrix D_1 , the largest non-diagonal elements σ of the zero-order matrix $S_{(0)}$ given in Eq. (1) are to be eliminated in the first place. The unitary matrix

$$U = 2^{-1/2} \begin{vmatrix} I & I \\ I & -I \end{vmatrix} \quad (7)$$

serves as transformation matrix and represents the passing into the new basis $\{\varphi\}$ the functions of which are defined as sums $\{\varphi_{(+)}\}$ and differences $\{\varphi_{(-)}\}$ of the neighboring pairs of the initial orbitals $\{\chi\}$. In common with Ref. [6], let us describe the bonding and antibonding BOs (BBOs and ABOs) respectively. The transformed overlap matrix is

$$S' = U^+ S U = S'_{(0)} + S'_{(1)} = \begin{vmatrix} (1+\sigma)I & 0 \\ 0 & (1-\sigma)I \end{vmatrix} + \sigma \begin{vmatrix} V & R \\ R^+ & Q \end{vmatrix} \quad (8)$$

where

$$\begin{aligned} V &= \frac{1}{2}(X + Y + Z + Z^+) \\ R &= \frac{1}{2}(X - Y + Z^+ - Z) \\ Q &= \frac{1}{2}(X + Y - Z - Z^+) \end{aligned} \quad (9)$$

As seen from Eq. (8), it is the non-zero intersubspace blocks R and R^+ within the first-order term $S'_{(1)}$ that makes the expanding of the matrix $(S')^{-1/2}$ in the power series somewhat difficult. Hence, let us eliminate these blocks using the unitary transformation like that suggested in Ref. [6] for block-diagonalizing the relevant hamiltonian matrix containing the non-diagonal blocks of the first order vs. the diagonal ones. This transformation matrix has the form of a power series

$$T = T_{(0)} + T_{(1)} + T_{(2)} + \dots = \begin{vmatrix} I & 0 \\ 0 & I \end{vmatrix} + \frac{1}{2} \begin{vmatrix} 0 & -R \\ R^+ & 0 \end{vmatrix} + \frac{1}{4} \begin{vmatrix} -\frac{1}{2}RR^+ & -W \\ -\frac{1}{2}R^+R & \end{vmatrix} + \dots \quad (10)$$

where $W = RQ - VR$. The resulting transformed overlap matrix is

$$T^+ S' T = \begin{vmatrix} (1 + \sigma)I + \sigma V + \frac{1}{2}\sigma RR^+ + \dots & 0 \\ 0 & (1 - \sigma)I + \sigma Q - \frac{1}{2}\sigma R^+ R + \dots \end{vmatrix} = \begin{vmatrix} \Lambda_{(+)} & 0 \\ 0 & \Lambda_{(-)} \end{vmatrix} = \Lambda \quad (11)$$

and contains the intra-subspace overlap matrices $\Lambda_{(+)}$ and $\Lambda_{(-)}$ only. Therefore the matrix T may be considered as the inter-subspace orthogonalization matrix. The notation Λ coinciding with that used in Eqs. (4)–(6) is introduced into Eq. (11) purposely, because both $\Lambda_{(+)}$ and $\Lambda_{(-)}$ may be easily expanded in a power series. After collecting the terms of the same order we obtain the series of Eq. (6), the first three members of which are

$$\Lambda_{(0)}^{-1/2} = \begin{vmatrix} aI & 0 \\ 0 & bI \end{vmatrix} \quad \Lambda_{(1)}^{-1/2} = -\frac{\sigma}{2} \begin{vmatrix} cV & 0 \\ 0 & dQ \end{vmatrix}$$

$$\Lambda_{(2)}^{-1/2} = \frac{\sigma}{4} \begin{vmatrix} F & 0 \\ 0 & G \end{vmatrix} \quad (12)$$

where

$$a = (1 + \sigma)^{-1/2} \quad b = (1 - \sigma)^{-1/2}$$

$$c = (1 + \sigma)^{-3/2} \quad d = (1 - \sigma)^{-3/2}$$

$$F = 3\frac{\sigma}{2}(1 + \sigma)^{-5/2}V^2 - (1 + \sigma)^{-3/2}RR^+$$

$$G = 3\frac{\sigma}{2}(1 - \sigma)^{-5/2}Q^2 + (1 - \sigma)^{-3/2}R^+R \quad (13)$$

Note that the matrix $\Lambda^{-1/2}$ shown in Eqs. (6) and (12) may be regarded as the intra-subspace orthogonalization matrix. The matrix D_1 is

$$D_1 = UT \quad (14)$$

The common expression for D_1 , i.e. the expression independent of the particular structure of the blocks R , V and Q , follows from Eq. (14) after substituting Eqs. (7) and (10), and the matrix $S^{-1/2}$ results from Eq. (5)

$$S^{-1/2} = UTA^{-1/2}T^+U^+ = U(S')^{-1/2}U^+ \quad (15)$$

where

$$(S')^{-1/2} = T\Lambda^{-1/2}T^+ \quad (16)$$

is the respective orthogonalization matrix in the BO basis. It is seen from Eq. (15) that three

power series are multiplied when obtaining the matrices $S^{-1/2}$ and $(S')^{-1/2}$. The terms of these series do not commute in the general case, and the relevant commutators designated by the notation $[\cdot, \cdot]_{\pm}$ appear in the final expression for the series of Eq. (6). In the BO basis this series is of the simplest form

$$(S')_{(0)}^{-1/2} = \Lambda_{(0)}^{-1/2}$$

$$(S')_{(1)}^{-1/2} = \Lambda_{(1)}^{-1/2} + [T_{(1)}, \Lambda_{(0)}^{-1/2}]_{-}$$

$$(S')_{(2)}^{-1/2} = \Lambda_{(2)}^{-1/2} + [T_{(1)}, \Lambda_{(1)}^{-1/2}]_{-} + [T_{(2)}, \Lambda_{(0)}^{-1/2}]_{-}$$

$$+ [\Lambda_{(0)}^{-1/2} T_{(1)}, T_{(1)}]_{-} \quad (17)$$

The relevant terms in the HAO basis follow from Eqs. (15) and (17). Note that the relations

$$T_{(1)}^+ + T_{(1)} = 0 \quad T_{(2)}^+ + T_{(2)} + T_{(1)}^+ T_{(1)} = 0 \quad (18)$$

resulting from the unitarity of the matrix T [6] have been used when obtaining Eq. (17).

It is seen from Eq. (12) that $\Lambda_{(0)}^{-1/2}$ is virtually the renormalization matrix of BOs. Note that it is the renormalization of BOs that is mainly responsible for the non-unitarity of the matrices $\Lambda^{-1/2}$ and $S^{-1/2}$. Accordingly, the renormalization factors appear in front of the next terms of the series of Eq. (17). Thus, because of the block-diagonal form of $\Lambda_{(0)}^{-1/2}$ and $\Lambda_{(1)}^{-1/2}$ following from Eq. (12) and the anti-block-diagonal form of $T_{(1)}$ seen from Eq. (10), the structure of the commutators $[T_{(1)}, \Lambda_{(0)}^{-1/2}]_{-}$ and $[T_{(1)}, \Lambda_{(1)}^{-1/2}]_{-}$ resembles that of the matrix $T_{(1)}$, e.g.

$$[T_{(1)}, \Lambda_{(0)}^{-1/2}]_{-} = f \begin{vmatrix} 0 & R \\ R^+ & 0 \end{vmatrix} \quad (19)$$

where $f = \frac{1}{2}(a - b)$; a and b are shown in Eq. (13).

As a result, the first-order term $(\mathbf{S}')^{-1/2}$ of Eq. (17) takes the form of a sum of the intra-subspace orthogonalization matrix $\mathbf{\Lambda}_{(1)}^{-1/2}$ and the renormalized inter-subspace orthogonalization matrix shown in Eq. (19). However, no such additivity is inherent to the next terms of the series for $(\mathbf{S}')^{-1/2}$.

On the whole, the common form of the power series for Löwdin's orthogonalization matrix $\mathbf{S}^{-1/2}$ obtained above and valid whatever the structure of the blocks \mathbf{X} , \mathbf{Y} and \mathbf{Z} , is a direct consequence of the common form of the zero-order overlap matrix $\mathbf{S}_{(0)}$ shown in Eq. (2) and therefore of the common topological structure of saturated systems. As with the matrix $\mathbf{S}_{(0)}$, the zero-order term $\mathbf{S}_{(0)}^{-1/2}$ of this series is related to the topological structure. Moreover, the common expression for the matrix $\mathbf{S}^{-1/2}$ allows the common peculiarities of the orthogonalized orbitals to be expected for all saturated systems. These are analyzed in the next section.

3. The structure of the orthogonalized orbitals

The row-matrix of the orthogonalized BOs (OBOs) and the respective matrix of the orthogonalized HAOs (OHAOs) are [9–14]

$$\langle \tilde{\varphi} | = \langle \tilde{\varphi}_{(+)}, \tilde{\varphi}_{(-)} | = \langle \varphi_{(+)}, \varphi_{(-)} | (\mathbf{S}')^{-1/2} \quad (20)$$

$$\langle \tilde{\chi} | = \langle \tilde{\chi}', \tilde{\chi}'' | = \langle \chi', \chi'' | \mathbf{S}^{-1/2} \quad (21)$$

After substituting the series for $(\mathbf{S}')^{-1/2}$ and $\mathbf{S}^{-1/2}$ obtained above the zero-order orthogonalized orbitals follow:

$$\langle \tilde{\varphi}^{(0)} | = \langle \tilde{\varphi}_{(+)}, \tilde{\varphi}_{(-)} | = \langle a\varphi_{(+)}, b\varphi_{(-)} | \quad (22)$$

$$\langle \tilde{\chi}^{(0)} | = \langle \tilde{\chi}'^{(0)}, \tilde{\chi}''^{(0)} | = \langle e\chi' + f\chi'', f\chi' + e\chi'' | \quad (23)$$

where $e = \frac{1}{2}(a + b)$; a and b are shown in Eq. (13), and f has been defined in Eq. (19). The OBOs shown in Eq. (22) are virtually the renormalized BOs in accordance with the interpretation of the term $\mathbf{\Lambda}_{(0)}^{-1/2}$ given in the previous section.

The OHAOs shown in Eq. (23) completely coincide with the orthogonalized orbitals in the case of two orbitals only [21,22]. Since $|e| > |f|$, each OHAO $\tilde{\chi}_i^{(0)}$ in Eq. (23) has the largest coefficient

at the respective HAO $\chi_i^{(0)}$, i.e. a one-to-one coupling between HAOs and OHAOs takes place.

The first-order correction $\tilde{\varphi}_{(+)i}^{(1)}$ to an orthogonalized BBO $\tilde{\varphi}_{(+)i}^{(0)}$ is

$$\tilde{\varphi}_{(+)i}^{(1)} = \sum_j^{\text{BBO}} \varphi_{(+)j} \left(-\frac{1}{2} \sigma c V_{ji} \right) + \sum_k^{\text{ABO}} \varphi_{(-)k} f R_{ki}^+ \quad (24)$$

and contains contributions of both BBOs $\varphi_{(+)j}$ and ABOs $\varphi_{(-)k}$. The expressions for c , V and R are given in Eqs. (13) and (9). Since $f < 0$ (the relevant definition is shown just after Eq. (19)), $c > 0$ and $\sigma > 0$, both terms of Eq. (24) are negative. Hence, the total correction $\tilde{\varphi}_{(+)i}^{(1)}$ is also negative. It follows from Eq. (8) that $V_{ji} = \langle \varphi_{(+)j} | \varphi_{(+)i} \rangle$ and $R_{ki}^+ = \langle \varphi_{(-)k} | \varphi_{(+)i} \rangle$. Hence, the contributions of the BBOs and ABOs proportional to their direct overlaps with the BBO under consideration ($\varphi_{(+)i}$) appear within the first order. As in the case of the relevant hamiltonian matrix elements [23], such a direct overlap may be described as through-space. The magnitude of this overlap evidently decreases when the relevant inter-bond distance increases. Hence, in common with the LMOs [6], considerable contributions to the correction $\tilde{\varphi}_{(+)i}^{(1)}$ might be expected only for BBOs $\varphi_{(+)j}$ and ABOs $\varphi_{(-)k}$ pertinent to the nearest environment of the bond possessing the BBO under consideration, i.e. $\varphi_{(+)i}$. The number of neighboring (germinal) bonds are usually constant for all internal and for all external bonds in saturated systems and equal to six and three respectively. Therefore the transferability of the corrections $\tilde{\varphi}_{(+)i}^{(1)}$ should be expected, provided that the overlap integrals between the BBO under study and the neighboring BOs are transferable. In the case of alkanes such an assumption is supported by numerous estimations [16,17,19]. Note that the main difference in the structures of the LMOs [6] and OBOs to within the first order consists of the non-zero contributions of the neighboring BBOs to the latter as shown in Eq. (24), whereas the relevant LMOs contain the nearest ABOs only. This is because the only anti-block-diagonal transformation $\mathbf{T}_{(1)}$ has been used when passing from BOs to LMOs to within the first order [6], whereas the transformation $(\mathbf{S}')^{-1/2}$ leading to the respective OBOs contains also the term $\mathbf{\Lambda}_{(1)}^{-1/2}$

with the non-zero diagonal blocks as shown in Eqs. (17) and (12). Thus, the intra-subspace orthogonalization matrix $\Lambda_{(1)}^{-1/2}$ may be concluded to be responsible for the main differences in the structures of LMOs and OBOs.

The second-order correction to the same OBO is

$$\begin{aligned} \tilde{\varphi}_{(+)i}^{(2)} = & \sum_j^{\text{BBO}} \varphi_{(+)j} \left\{ \frac{1}{4} \sigma \mathbf{F} - \frac{1}{2} f \mathbf{R} \mathbf{R}^+ \right\}_{ji} \\ & + \sum_k^{\text{ABO}} \varphi_{(-)k} \left\{ \left(-\frac{1}{4} \sigma \right) (c \mathbf{R}^+ \mathbf{V} - d \mathbf{Q} \mathbf{R}^+) \right. \\ & \left. + \frac{1}{2} f \mathbf{W}^+ \right\}_{ki} \end{aligned} \quad (25)$$

where the matrices \mathbf{F} and \mathbf{W} and the functions c and d are defined in Eqs. (10) and (13). It follows from Eq. (25) and the definition of the matrix \mathbf{F} , that the contribution of the BBO $\varphi_{(+)j}$ consists of the sum of two terms proportional to the elements $(\mathbf{V}^2)_{ji}$ and $(\mathbf{R} \mathbf{R}^+)_{ji}$, respectively. The element

$$(\mathbf{V}^2)_{ji} = \sum_l^{\text{BBO}} \langle \varphi_{(+)j} | \varphi_{(+)l} \rangle \langle \varphi_{(+)l} | \varphi_{(+)i} \rangle \quad (26)$$

represents the indirect overlap of the BBOs $\varphi_{(+)j}$ and $\varphi_{(+)i}$ by means of the BBO $\varphi_{(+)l}$. Such an overlap may be described as through-bond [6,23] because a definite bond always corresponds to a BBO. Accordingly, the element $(\mathbf{R} \mathbf{R}^+)_{ji}$ represents the overlap of the BBOs $\varphi_{(+)i}$ and $\varphi_{(+)j}$ by means of the ABO $\varphi_{(-)k}$. Hence, the total contribution of the BBO $\varphi_{(+)j}$ to the correction $\tilde{\varphi}_{(+)i}^{(2)}$ consists of the sum of the separate terms representing the indirect overlaps of $\varphi_{(+)j}$ and $\varphi_{(+)i}$ by means of all possible mediators, i.e. the BBOs $\varphi_{(+)l}$ and the ABOs $\varphi_{(-)k}$. Such a structure of the OBO closely resembles that of the LMO of a saturated system to within the second order. In common with the LMOs [6], the corrections $\tilde{\varphi}_{(+)i}^{(2)}$ may be expected to decrease when the relevant inter-bond distance increases. This is because only the common neighbors of the two BBOs $\varphi_{(+)j}$ and $\varphi_{(+)i}$ appear to be effective mediators, and the number of such neighbors decreases with increasing inter-bond distance. Moreover, the constant numbers of the common geminal neighbors for various pairs of bonds in saturated systems [6] lead to the transferability of the corrections

under discussion. As a result, the OBOs are localized on the nearest environment of the relevant bond and depend on the structure of this part of the system only.

When passing to the basis of HAOs, the linear functions of the four elements X_{ij} , Y_{ij} , Z_{ij} and Z_{ij}^+ appear instead of each element V_{ij} and R_{ij} as seen from Eq. (9), and the relevant expressions for $\{\tilde{\chi}\}$ become somewhat more involved. Nevertheless, because of the above-discussed relation between the four elements X_{ij} , Y_{ij} , Z_{ij} and Z_{ij}^+ and the chemical bonds, localized and transferable nature is inherent to OHAOs $\{\tilde{\chi}\}$, too.

4. Analysis of the relevant transformed hamiltonian

From the known proportionality between the overlap and resonance integrals [8] it follows that the non-neighboring resonance integrals of saturated systems may be regarded as first-order terms with respect to the neighboring ones [3–7]. The same is true for the differences between the actual values of the neighboring integrals and their mean value β [3–7]. Let us confine ourselves to the case of small (i.e. first-order) differences in the values of the Coulomb integrals and introduce the respective mean value α . Such an approximation is completely justified for alkanes because of the small difference in the electronegativities of the C and H atoms [24]. Let us use the parameters α and β as the reference point and the energy unit, respectively, and accept the equalities $\alpha = 0$ and $\beta = 1$. Then using the same numbering of HAOs as in Eqs. (1) and (2), the initial common hamiltonian matrix \mathbf{H} may be presented as a sum of zero-order ($\mathbf{H}_{(0)}$) and first-order ($\mathbf{H}_{(1)}$) terms, each of them containing the $(N \times N)$ -dimensional blocks

$$\mathbf{H} = \mathbf{H}_{(0)} + \mathbf{H}_{(1)} = \begin{vmatrix} 0 & \mathbf{I} \\ \mathbf{I} & 0 \end{vmatrix} + \begin{vmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^+ & \mathbf{C} \end{vmatrix} \quad (27)$$

where $\mathbf{H}_{(0)}$ involves the averaged neighboring resonance integrals in the positions $(i, N+i)$ and $\mathbf{H}_{(1)}$ includes the remaining hamiltonian matrix elements. Thus, as with the zero-order overlap matrix $\mathbf{S}_{(0)}$ shown in Eq. (2), the zero-order hamiltonian $\mathbf{H}_{(0)}$ represents the common topological structure

of saturated systems [6].

The transformed hamiltonian matrix, i.e. that represented in the basis of OHAOs, is defined as follows [9–14]:

$$\tilde{H} = S^{-1/2} H S^{-1/2} \quad (28)$$

Since the three matrices of the right-hand side of Eq. (28) are expressed in power series, the new matrix \tilde{H} may also be presented in the form of a series

$$\tilde{H} = \tilde{H}_{(0)} + \tilde{H}_{(1)} + \tilde{H}_{(2)} + \dots \quad (29)$$

Because of the confinement to the first-order terms in the initial matrix H as shown in Eq. (27) [3–7], only the first two terms of Eq. (29)

$$\tilde{H}_{(0)} = S_{(0)}^{-1/2} H_{(0)} S_{(0)}^{-1/2} \quad (30)$$

$$\tilde{H}_{(1)} = \tilde{H}_{(1)}^{(h)} + \tilde{H}_{(1)}^{(s)} \quad (31)$$

where

$$\begin{aligned} \tilde{H}_{(1)}^{(h)} &= S_{(0)}^{-1/2} H_{(1)} S_{(0)}^{-1/2} \\ \tilde{H}_{(1)}^{(s)} &= S_{(0)}^{-1/2} H_{(0)} S_{(1)}^{-1/2} + S_{(1)}^{-1/2} H_{(0)} S_{(0)}^{-1/2} \end{aligned} \quad (32)$$

are worth considering. The terms relating to the first-order hamiltonian $H_{(1)}$ and to the first-order overlap matrix $S_{(1)}$ are designated in Eqs. (31) and (32) by the superscripts (h) and (s).

In the BO basis the initial hamiltonian matrix H' takes the form

$$\begin{aligned} H' &= U^+ H U = H'_{(0)} + H'_{(1)} \\ &= \begin{vmatrix} I & 0 \\ 0 & -I \end{vmatrix} + \begin{vmatrix} K & J \\ J^+ & L \end{vmatrix} \end{aligned} \quad (33)$$

where

$$\begin{aligned} K &= \frac{1}{2}(A + B + B^+ + C) & L &= \frac{1}{2}(A - B - B^+ + C) \\ J &= \frac{1}{2}(A - B + B^+ - C) \end{aligned} \quad (34)$$

and the relations similar to that given in Eqs. (28), (30), (31) and (32) are valid, provided that primes are added to all matrices involved.

The zero-order transformed hamiltonian matrices $\tilde{H}_{(0)}$ and $\tilde{H}'_{(0)}$ in the OHAO and OBO basis, respectively, may be obtained using Eqs. (27), (30) and (33):

$$\tilde{H}_{(0)} = \frac{1}{1 - \sigma^2} \begin{vmatrix} -\sigma I & I \\ I & -\sigma I \end{vmatrix} \quad (35)$$

$$\tilde{H}'_{(0)} = \begin{vmatrix} (1 + \sigma)^{-1} I & 0 \\ 0 & -(1 - \sigma)^{-1} I \end{vmatrix} \quad (36)$$

It follows from the comparison of Eqs. (35) and (27) that $\tilde{H}_{(0)}$ and $H_{(0)}$ are virtually of similar structure. Indeed, the identical neighboring resonance integrals $1/(1 - \sigma^2)$ and the identical diagonal elements $(-\sigma)/(1 - \sigma^2)$ appear in the transformed matrix. If the value $\sigma = 0.7$ [19] is accepted, the above elements prove to be equal to 2 and -1.4 respectively, i.e. the resonance integral is doubled, whereas the Coulomb integral is raised by -1.4 relative to the respective values in the HAO basis shown in Eq. (27). These results indicate that only the reference point and the energy unit are being changed when passing from $H_{(0)}$ to $\tilde{H}_{(0)}$. Again, these changes may be easily accounted for by the fact that our system to within the zero order coincides with the set of non-interacting two-level systems. For such a two-level system the orthogonalization-invariant eigenvalues in the initial and in the orthogonalized basis are [1]

$$\varepsilon_{1,2} = \frac{(\alpha \pm \beta)}{(1 \pm \sigma)} \quad \varepsilon_{1,2} = (\tilde{\alpha} \pm \tilde{\beta}) \quad (37)$$

It follows from Eq. (37) that in order to retain the same ε_1 and ε_2 , $\tilde{\alpha}$ is to be raised and $\tilde{\beta}$ is to be increased against the initial values α and β .

Similarly, the BBO and ABO energies are raised by $(1 + \sigma)^{-1}$ and $-(1 - \sigma)^{-1}$, respectively, when passing from $H'_{(0)}$ to $\tilde{H}'_{(0)}$ as shown in Eqs. (33) and (36).

Therefore it may be concluded that the topological structure of saturated systems is reflected either in the two matrices $H_{(0)}$ and $S_{(0)}$ or in the single one $\tilde{H}_{(0)}$ depending on the basis used.

Let us turn now to the first-order matrices $\tilde{H}'_{(1)}$ and $\tilde{H}_{(1)}$. First, let us dwell on the matrix $\tilde{H}'_{(1)}$ in the OBO basis. The first term of this matrix

involving the first-order hamiltonian $H'_{(1)}$ is

$$\begin{aligned} \tilde{H}'_{(1)}{}^{(h)} &= (S'_{(0)})^{-1/2} H'_{(1)} (S'_{(0)})^{-1/2} \\ &= \begin{vmatrix} (1+\sigma)^{-1}K & (1-\sigma^2)^{-1/2}J \\ (1-\sigma^2)^{-1/2}J^+ & (1-\sigma)^{-1}L \end{vmatrix} \end{aligned} \quad (38)$$

It is seen from Eqs. (33) and (38) that the interactions of BOs are being changed by the constant, i.e. molecular-structure-independent factors when passing from BOs to OBOs. Thus, the interactions between the BBOs are reduced by $(1+\sigma)^{-1}$, whereas those between ABOs are increased by $(1-\sigma)^{-1}$.

The second term of the matrix $\tilde{H}'_{(1)}$ containing the first-order overlap matrix $S'_{(1)}$ is

$$\begin{aligned} \tilde{H}'_{(1)}{}^{(s)} &= (S'_{(0)})^{-1/2} H'_{(0)} (S'_{(1)})^{-1/2} + (S'_{(1)})^{-1/2} H'_{(0)} (S'_{(0)})^{-1/2} \\ &= \begin{vmatrix} -\sigma(1+\sigma)^{-2}V & \{(1-\sigma^2)^{-1} - (1-\sigma^2)^{-1/2}\}R \\ \{(1-\sigma^2)^{-1} - (1-\sigma^2)^{-1/2}\}R^+ & \sigma(1-\sigma)^{-2}Q \end{vmatrix} \end{aligned} \quad (39)$$

and involves the relevant first-order overlap matrix blocks V , Q and R multiplied by the constant factors.

In the OHAO basis the respective two terms of $\tilde{H}'_{(1)}$, namely $\tilde{H}'_{(1)}{}^{(h)}$ and $\tilde{H}'_{(1)}{}^{(s)}$, contain the homogeneous linear functions of the blocks A , B , B^+ and C , and X , Y , Z^+ and Z , respectively, with the constant coefficients. For example,

$$\tilde{H}'_{(1)}{}^{(h)} = \begin{vmatrix} \tilde{A} & \tilde{B} \\ \tilde{B}^+ & \tilde{C} \end{vmatrix} \quad (40)$$

where

$$\begin{aligned} \tilde{A} &= \frac{1}{2} \{ (1-\sigma^2)^{-1}(A+C) + (1-\sigma^2)^{-1/2}(A-C) \\ &\quad - \sigma(1-\sigma^2)^{-1}(B+B^+) \} \\ \tilde{B} &= \frac{1}{2} \{ -\sigma(1-\sigma^2)^{-1}(A+C) \\ &\quad + (1-\sigma^2)^{-1/2}(B-B^+) \\ &\quad + (1-\sigma^2)^{-1}(B+B^+) \} \end{aligned}$$

$$\begin{aligned} \tilde{C} &= \frac{1}{2} \{ (1-\sigma^2)^{-1}(A+C) - (1-\sigma^2)^{-1/2}(A-C) \\ &\quad - \sigma(1-\sigma^2)^{-1}(B+B^+) \} \end{aligned} \quad (41)$$

It is seen from Eqs. (40) and (41) that the elements of the matrix $\tilde{H}'_{(1)}{}^{(h)}$ are the linear functions

$$kA_{ij} + lB_{ij} + mB_{ij}^+ + nC_{ij} \quad (42)$$

Similarly, the elements of the second term $\tilde{H}'_{(1)}{}^{(s)}$ are

$$uX_{ij} + tY_{ij} + oZ_{ij} + qZ_{ij}^+ \quad (43)$$

where k, l, m, n, u, t, o and q are σ -dependent constants. In the first section the four matrix elements involved in Eqs. (42) and (43) were demonstrated to be the four different non-neighboring resonance and overlap integrals pertinent to a definite pair of

bonds. Hence, a non-diagonal element $\tilde{H}'_{(1)ij}$ of the total first-order matrix $\tilde{H}'_{(1)}$ depends only on the four non-diagonal elements A_{ij} , B_{ij} , B_{ij}^+ and C_{ij} of the initial first-order hamiltonian $H'_{(1)}$ associated with the pair of bonds possessing the HAOs χ_i and χ_j and on the similar four elements of the overlap matrix $S'_{(1)}(X_{ij}, Y_{ij}, Z_{ij}$ and $Z_{ij}^+)$ and is independent of the remaining parts of the matrices $H'_{(1)}$ and $S'_{(1)}$. Given that the above-mentioned eight elements are transferable, the element $\tilde{H}'_{(1)ij}$ is also transferable. A similar relation to the characteristics of a definite bond may be obtained for the diagonal element $\tilde{H}'_{(1)ii}$.

In Refs. [3–7] it has been demonstrated that the blocks A , B , B^+ and C of Eq. (27) are of similar structure in the sense that their non-zero elements stand in the same positions. Otherwise, if $A_{ij} \neq 0$, then $B_{ij} \neq 0$, $B_{ij}^+ \neq 0$ and $C_{ij} \neq 0$ and vice versa. Indeed, A_{ij} , B_{ij} , B_{ij}^+ and C_{ij} belong to a definite pair of bonds and if this pair is a neighboring one, the four elements are of considerable value and vice versa. The analysis of the transformed hamiltonian \tilde{H} carried out above allows

us to conclude that the matrix \tilde{H} also contains four ($N \times N$)-dimensional blocks of similar constitution.

Therefore, both H and \tilde{H} involve zero-order terms of similar structure and first-order terms consisting of four blocks with the non-zero elements situated in the same positions. Moreover, the local nature of the relation between the hamiltonian matrix elements and the structure of the system, and the transferability of the hamiltonian elements pertinent to the identical atoms and bonds are inherent to both H and \tilde{H} . The model hamiltonian matrices of alkanes used in Refs. [3–7] were based on the above assumptions only and these matrices may be looked upon either as H or as \tilde{H} . Since the equations solved in Refs. [3–7] were formulated in the orthogonal basis, the relevant results should also be looked upon as corresponding to the orthogonal basis.

The above-mentioned orthogonalization-invariant peculiarities of the hamiltonian matrix may be considered as its main qualitative features. Again, the numerical values of the respective hamiltonian elements in the initial and in the SO basis may differ significantly. Hence, the basis set orthogonality assumption for saturated systems may be regarded as justified in the qualitative respect only, and therefore this assumption is acceptable when seeking qualitative results.

5. Conclusions

The common topological structure of saturated systems manifests itself in the simple and common form of the relevant zero-order overlap matrix of HAOs. This allows the basis set orthogonalization, consisting of passing into the basis of two almost orthogonal subspaces of BOs followed by the successive inter- and intra-subspace orthogonalization, to be carried out in the general case without specifying the size and composition of the system. Such a procedure leads to the single expression for the respective Löwdin's orthogonalization matrix $S^{-1/2}$ in the form of a power series and to the common peculiarities of the orthogonalized basis orbitals. The latter prove to be localized mainly on the nearest environment of a definite chemical

bond, dependent on the local structure of this part of the system only, and transferable in the case of transferability of the above-mentioned structure.

Furthermore, the orthogonalization-invariant qualitative peculiarities of the relevant common hamiltonian matrix result from the single expression obtained for the matrix $S^{-1/2}$, and these are also associated with the common topological structure of saturated systems. The invariant peculiarities of the hamiltonian matrix allow the basis set orthogonality assumption to be accepted in the qualitative models of the systems under study. Therefore the validity of such an assumption for saturated molecules and crystals is associated with the specific peculiarities of their structure and not with the smallness of the overlap integrals as in case of the conjugated molecules [9–11].

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