# The common quantum-mechanical problem for the whole class of alkanes as a matrix generalization of the definite two-level problem

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## Abstract

The common hamiltonian matrix for the whole class of alkanes ($H$) has been considered as a generalization of the definite two-dimensional matrix ($h$), where the usual Coulomb and resonance parameters are replaced by the $N \times N$-dimensional matrices ($N$ stands for the number of chemical bonds in an alkane). A similar relation between the two analytical expressions for the one-electron density matrices of alkanes and of the relevant two-level two-electron system described by the hamiltonian matrix $h$ has been established. The block-diagonalization procedure for the matrix $H$ following from the Brillouin theorem and resulting in the localized MOs (LMOs) of alkanes has been shown to be an analogous matrix generalization of the usual eigenvalue problem for the two-dimensional matrix $h$. These results imply a kind of similarity between the class of alkanes and the unique two-level system and form the basis for describing the former as a single quantum-mechanical object. The relation between the actual occupation numbers of the bond orbitals and the extent of delocalization of the respective LMOs and the proportionality of the stabilization energy to the total delocalization of the occupied LMOs have been shown to result from the established similarity between alkanes and the two-level system.

## 1. Introduction

Revealing certain classes of closely related objects characterized by common features and studying such a class as a single object may be regarded as one of the basic approaches used in natural sciences. In cases when the number of possible representatives of the class under study is infinite, their common properties become of great importance.

The same situation arises when dealing with chemical compounds. Indeed, classes of related molecules, e.g. alkanes, alkenes, etc. [1], are usually distinguished on the basis of similar structures, and properties. Moreover, along with the unique properties of the individual molecules and the rules

inherent in their series, common properties of the classes of related chemical compounds make up the subject of chemistry.

In this context, a single quantum-chemical approach orientated towards revealing the common peculiarities of the electronic structure of the large sets of related molecules is also advisable. It should be mentioned here that both the exact Schroedinger's equation and the relevant approximations [2], e.g. the Hartree–Fock–Rothaan method, are formulated for a single molecule. Nevertheless, certain achievements in stating and solving the generalized problems for chemical classes and other large sets of molecules may also be mentioned, and it is the simplest version of

the Hückel-type hamiltonian that proves to be the basis for these approaches. Thus, common peculiarities of the one-electron spectra and of the one-electron density matrices (bond-order matrices) for the alternant conjugated hydrocarbons [3] resulting from the common form of the relevant hamiltonian matrices may be considered as the most well-known achievement of the above-discussed type, although these hydrocarbons are not regarded as a chemical class of molecules. Furthermore, the stating and solving of the single problem for the one-electron density matrix (DM) [4–7] and for the localized MOs (LMOs) [7] of alkanes also ranks among the generalized quantum-chemical approaches.

The two examples given here are promising with respect to the feasibility of similar results for other large sets of related molecules. Therefore, it is essential to determine the place the generalized quantum-mechanical problems take in molecular electronic structure theory, i.e. their relation to the usual problems for individual molecules.

The above-mentioned common problems for alkanes stated and solved in Refs. [4–7] were based both on the common form of the relevant hamiltonian matrix containing four peculiar $N \times N$-dimensional blocks ($N$ stands for the number of bonds in an alkane) and on the possibility of expressing the relevant DM and the LMO representation matrix in terms of these blocks in the general case without regard for their specific structure and dimension ($N$). This result resembles the algebraic solution of the two-level problem described by the Coulomb and resonance parameters, which may be obtained in a wide range of numerical values of the latter. This analogy promotes an assumption that the above common problem for alkanes is a matrix generalization of the two-level problem, where the usual parameters (matrix elements) are replaced by the $N \times N$-dimensional matrices.

The paper is aimed at demonstrating the above-assumed relation between the two-level problem and the common problem for alkanes, and discussing the consequences of this relation.

## 2. Comparison of the relevant hamiltonian matrices

The two most popular basis sets giving rise to the

hamiltonian matrices of alkanes of a regular and coordinate-system-independent structure are used here. The first one $\{\chi\}$ contains the $sp^3$ hybrid AOs (HAOs) of the carbon atoms and the 1s AOs of the hydrogen atoms (for simplicity let us call them both the HAO basis). The second one $\{\phi\}$ involves the bonding $\{\phi_{(+)}\}$ and antibonding $\{\phi_{(-)}\}$ bond orbitals (BOs) defined as normalized sums and differences of the mutually directed (neighboring) pairs of HAOs. Both the HAOs and BOs are assumed to be orthogonal. The concrete relation between the orbitals $\{\chi\}$ and $\{\phi\}$, i.e. the respective transformation matrix, is not essential here.

Let us start with the HAO basis. The non-neighboring resonance integrals and the differences both between various neighboring resonance integrals and between diagonal elements may be considered [4–6] as the first-order terms with respect to the mean value $(\beta_0)$ of the neighboring resonance integrals. The averaged diagonal element $(\alpha_0)$ and the above-defined parameter $\beta_0$ have been used as the reference point and the energy unit, respectively; the equalities $\alpha_0 = 0$ and $\beta_0 = 1$ have been accepted.

Let us divide the initial $2N$-dimensional basis set of HAOs $\{\chi\}$ into two $N$-dimensional subsets $\{\chi'\}$ and $\{\chi''\}$ so that the strongly overlapping pairs of the neighboring orbitals find themselves in different subsets. Furthermore, let us enumerate the basis functions in such a way that the neighboring pairs of orbitals acquire the coupled numbers $i$ and $N + i$. Then the initial Hückel-type hamiltonian matrix $(H)$ for any alkane in the basis of HAOs may be presented as a sum of zero-order $(H_{(0)})$ and first-order $(H_{(1)})$ terms, the former containing the average neighboring resonance integrals equal to 1 in the positions $(i, N + i)$, and the latter involving the remaining terms

$$H = H_{(0)} + H_{(1)} = \begin{vmatrix} 0 & I_{(N)} \\ I_{(N)} & 0 \end{vmatrix} + \begin{vmatrix} A & B \\ B^+ & C \end{vmatrix} \quad (1)$$

where $I_{(N)}$ is the $N$-dimensional unit matrix and $A, C$ and $B$ are the $N \times N$-dimensional matrices corresponding to the subsets $\{\chi'\}$ and $\{\chi''\}$ and to their interactions, respectively; the superscript (+) designates the transposed matrix.

Alternatively, the bonding BOs (BBOs) $\{\phi_{(+)}\}$

and the antibonding BOs (ABOs) $\{\phi_{(-)}\}$ make up the two $N$-dimensional subsets in the BO basis. As in Ref. [7], let us consider the resonance integrals between BOs as the first-order terms with respect to the differences between the BBO and ABO energies. Moreover, nearly identical values of all BBO energies and of all ABO energies may be assumed [7]. Finally, the BO energy mean value ($\alpha'_0$) and the difference ($\beta'_0$) between the latter and the averaged BBO energy served as the reference point and the energy unit, respectively; the equalities $\alpha'_0 = 0$ and $\beta'_0 = 1$ have been accepted in the BO basis. Then the relevant common hamiltonian matrix of alkanes takes the form

$$H' = H'_{(0)} + H'_{(1)} = \begin{vmatrix} I_{(N)} & 0 \\ 0 & -I_{(N)} \end{vmatrix} + \begin{vmatrix} S & R \\ R^+ & Q \end{vmatrix} \tag{2}$$

where the diagonal zero-order term $H'_{(0)}$ contains the BO energies and the first-order term $H'_{(1)}$ consists of four $N \times N$-dimensional blocks, $S$, $Q$ and $R$, representing the intra- and intersubset resonance integrals, respectively.

It should be noted here that no need arises for specifying either the structure of the blocks $A, B, C, S, R$ and $Q$ or their dimension ($N$) when seeking the common results for the whole class of alkanes, e.g. the expressions for the DM [4] and the LMOs [7].

As is seen from Eqs. (1) and (2), the matrices $H$ and $H'$ may be considered as the matrix generalizations of the two-dimensional matrices

$$h = h_{(0)} + h_{(1)} = \begin{vmatrix} 0 & 1 \\ 1 & 0 \end{vmatrix} + \begin{vmatrix} \alpha & \beta \\ \beta & \gamma \end{vmatrix} \tag{3}$$

$$h' = h'_{(0)} + h'_{(1)} = \begin{vmatrix} 1 & 0 \\ 0 & -1 \end{vmatrix} + \begin{vmatrix} \sigma & \rho \\ \rho & \kappa \end{vmatrix} \tag{4}$$

respectively, where $\alpha, \beta, \gamma, \sigma, \rho$ and $\kappa$ are small parameters compared to 1. The generalization under discussion involves substitution of the $N \times N$-dimensional matrices $I_{(N)}, A, B \ldots$ for the usual parameters $1, \alpha, \beta \ldots$. However, it is the emergence of the $N$-dimensional unit matrices ($I_{(N)}$) instead of the one-dimensional units (1)

when passing from $h$ and $h'$ to $H$ and $H'$, respectively, that makes the essence of this generalization. Indeed, the similarity between the matrices $H$ and $h$, as well as between $H'$ and $h'$, lies not in the possibility of presenting the $2N \times 2N$-dimensional matrices $H$ and $H'$ in terms of four $N \times N$ blocks (such a form is possible for any even-dimensional matrix), but only in the similarity of the relevant zero-order terms of the related matrices.

The hamiltonian matrix of Eq. (3) describes a two-level system characterized by the large resonance integral $(1 + \beta)$ vs. the difference in the Coulomb integrals $(\alpha - \gamma)$, whereas the matrix of Eq. (4) corresponds to the opposite case. Accordingly, the matrices $H$ and $H'$ shown in Eqs. (1) and (2) represent the respective generalized systems involving two $N$ dimensional subsets of orbitals described by large intersubset interactions vs. the difference in the intrasubset ones and vice versa.

Therefore, it is not an arbitrary two-dimensional matrix that is related to the common hamiltonian matrix of alkanes. Indeed the ratio between the parameters of the former is determined by the nature of the interactions between the two orbitals of alkanes belonging to the same chemical bond in the basis under consideration. A reason for that is the first-order magnitude of the interbond interactions vs. the intrabond ones in the model employed here. Thus, a pair of HAOs pertinent to a chemical bond is characterized by a large resonance integral and two similar Coulomb integrals, and the relation between the matrices $H$ and $h$ shown in Eqs. (1) and (3), respectively, results. Alternatively, the relevant BOs (a BBO and the coupled ABO) are separated by a large energy gap and this gives rise to the relation between the matrices $H'$ and $h'$ of Eqs. (2) and (4).

## 3. The analogy between the DMs of alkanes and of the appropriate two-level system

The above-discussed similarity between the hamiltonian matrices of alkanes and of the definite two-level systems does not necessarily imply the resemblance between the solutions of the relevant quantum-mechanical problems. This is evident when dealing with the respective secular

polynomials (SPs). Thus, the SP of the matrix $h$ shown in Eq. (3) is

$$\text{Det}|h - \lambda I_{(2)}| = \text{Det} \begin{vmatrix} \alpha - \lambda & 1 + \beta \\ 1 + \beta & \gamma - \lambda \end{vmatrix}$$

$$= (\alpha - \lambda)(\gamma - \lambda) - (1 + \beta)^2 \qquad (5)$$

Again, the SP of the matrix $H$ shown in Eq. (1)

$$\text{Det}|H - \lambda I_{(2N)}| = \text{Det} \begin{vmatrix} A - \lambda I_{(N)} & I_{(N)} + B \\ I_{(N)} + B^+ & C - \lambda I_{(N)} \end{vmatrix}$$

(5a)

may not be written in the form shown in the last relation of Eq. (5), as the $N \times N$-dimensional blocks $A - \lambda I_{(N)}, I_{(N)} + B$, etc. do not commute with each other [8]. Therefore, passing from the two-level system to the class of alkanes is by no means a trivial generalization.

Nevertheless, the solutions of the non-canonical problems for the DM and the LMOs of alkanes may be shown to be analogous to the relevant solutions for the two-electron two-level system. It is noteworthy that no need for diagonalizing the hamiltonian matrices or obtaining their SPs arises when solving these problems, only the perturbation theory (PT) in the matrix representation is applied.

To demonstrate the above analogy, let us discuss the non-canonical problem for the DM in this section. To establish not only the very fact of the similarity between the DMs of alkanes and of the respective two-level system, but also the origins of this similarity, let us recall the way the DMs of alkanes were obtained in Refs. [4–7]. The residual charge matrices ($Y$) proportional to the relevant DMs ($P$) (these matrices are connected by the relation $Y = P - I$) resulted from the system of equations [9]

$$[H, Y]_- = 0 \qquad Y^2 = I \qquad \text{Spur } Y = 0 \qquad (6)$$

where the notation $[..,..]_-$ indicates a commutator of matrices. Similar systems of equations may also be written for the hamiltonian matrices $H'$, $h$ and $h'$. The PT for the DM [9] has been used to solve Eq. (6), and a power series with respect to parameters included in the first-order hamiltonian has

been obtained:

$$P = I + Y_{(0)} + Y_{(1)} + Y_{(2)} + \cdots \qquad (7)$$

The zero-order matrices $Y_{(0)}$ [4–6], $Y'_{(0)}$ [7], $y_{(0)}$ and $y'_{(0)}$ result from the equations like that shown in Eq. (6), only the zero-order terms $H_{(0)}, H'_{(0)}, h_{(0)}$ and $h'_{(0)}$, respectively, stand for the initial hamiltonians. These matrices are

$$Y_{(0)} = \begin{vmatrix} 0 & I_{(N)} \\ I_{(N)} & 0 \end{vmatrix} \qquad Y'_{(0)} = \begin{vmatrix} I_{(N)} & 0 \\ 0 & -I_{(N)} \end{vmatrix}$$

$$y_{(0)} = \begin{vmatrix} 0 & 1 \\ 1 & 0 \end{vmatrix} \qquad y'_{(0)} = \begin{vmatrix} 1 & 0 \\ 0 & -1 \end{vmatrix} \qquad (8)$$

The structures of the zero-order DMs shown in Eq. (8) coincide with those of the respective zero-order hamiltonian matrices $H_{(0)}, H'_{(0)}, h_{(0)}$ and $h'_{(0)}$, respectively. Again, the matrices $Y_{(0)}$ and $y_{(0)}$, as well as $Y'_{(0)}$ and $y'_{(0)}$, are of similar structure, only the dimensions of the unit matrices are increased from 1 to $N$ when passing from the two-level system to the class of alkanes.

The simple structure of the zero-order DMs shown in Eq. (8) provides for the equalities

$$H_{(0)} Y_{(0)} = H'_{(0)} Y'_{(0)} = I_{(2N)}$$

$$h_{(0)} y_{(0)} = h'_{(0)} y'_{(0)} = I_{(2)} \qquad (9)$$

which allow the original expressions for the next corrections $Y_{(k)}$ $k = 1, 2$ [9] to be simplified considerably. These are finally determined by the relations

$$Y_{(1)} = \tfrac{1}{2} (H_{(1)} - Y_{(0)} H_{(1)} Y_{(0)}) \qquad (10)$$

$$Y_{(2)} = -\tfrac{1}{2} Y_{(0)} Y_{(1)} Y_{(1)} + \tfrac{1}{4} [[H_{(1)}, Y_{(1)}]_-, Y_{(0)}]_- \qquad (11)$$

Similar expressions may also be written for $Y'_{(1)}, Y'_{(2)}, y_{(1)}$, etc.

The origin of the subsequent similarity between $Y_{(k)}$ and $y_{(k)}$, as well as between $Y'_{(k)}$ and $y'_{(k)}$, follows from the structure of the relations shown in Eqs. (10) and (11). Thus, the corrections $Y_{(1)}$ and $Y_{(2)}$ involve the matrices $H_{(1)}, H_{(1)} \times Y_{(1)}, Y_{(1)} \times H_{(1)}$ and $Y_{(1)} \times Y_{(1)}$ multiplied by $Y_{(0)}$. Multiplying any matrix, e.g. $H_{(1)}$, by $Y_{(0)}$ shown in Eq. (8) does not destroy the internal structure of the

$N \times N$ blocks of the former, only the positions of these blocks change. Accordingly, only the signs of the $N \times N$ blocks may change as a consequence of multiplying the respective matrices $H'_{(1)}$, $H'_{(1)} \times Y'_{(1)}$ etc. by $Y'_{(0)}$. As a result, entire $N \times N$ blocks $A, B$ and $C$ and $S, Q$ and $R$ appear in the final expressions for $Y_{(k)}$ and $Y'_{(k)}$ whatever the dimension of these blocks $N$. Thus, in the HAO basis the first-order corrections $Y_{(1)}$ [4–6] and $y_{(1)}$ are

$$Y_{(1)} = \frac{1}{2} \begin{vmatrix} A - C & B - B^+ \\ B^+ - B & C - A \end{vmatrix}$$

$$y_{(1)} = \frac{1}{2} \begin{vmatrix} \alpha - \gamma & 0 \\ 0 & \gamma - \alpha \end{vmatrix} \tag{12}$$

whereas the second-order corrections $Y_{(2)}$ [4–6] and $y_{(2)}$ are

$$Y_{(2)} = \begin{vmatrix} L & M \\ M^+ & K \end{vmatrix} \qquad y_{(2)} = \begin{vmatrix} l & m \\ m & k \end{vmatrix} \tag{13}$$

where

$$L = \tfrac{1}{4}(CB + B^+C - AB^+ - BA)$$
$$\quad - \tfrac{1}{8}[(A - C),(B - B^+)]_-$$

$$K = -\tfrac{1}{4}(CB + B^+C - AB^+ - BA)$$
$$\quad - \tfrac{1}{8}[(A - C),(B - B^+)]_- \tag{14}$$

$$M = \tfrac{1}{4}([A,(A - C)]_- + B^+B^+ - BB)$$
$$\quad - \tfrac{1}{8}\{(A - C)^2 - (B - B^+)^2\}$$

and

$$l = \tfrac{1}{2}(\gamma - \alpha)\beta \quad k = \tfrac{1}{2}(\alpha - \gamma)\beta \quad m = -\tfrac{1}{8}(\alpha - \gamma)^2 \tag{15}$$

Comparing Eqs. (12)–(15) shows that the corrections $y_{(k)}$ for the two-level system follow from the respective general expression for $Y_{(k)}$, if the one-dimensionality of the matrices $I, A, B$ and $C$ is assumed. The latter, in turn, implies the commutation of the blocks $A, B$ and $C$, and the equality $B = B^+$. Therefore, the case of the two-level system is noted only for the natural consequences of the one-dimensionality of the blocks $I, A, B$ and $C$.

It is noteworthy that in common with the corrections $y_{(k)}$ valid for any numerical values of the parameters $\alpha, \beta$ and $\gamma$ (provided that these are small compared to 1), the corrections $Y_{(k)}$ described any alkane. Accordingly, Eqs. (8), (12) and (13) have been regarded in Refs. [4–6] as the common expressions for the DMs of alkanes.

Similar conclusions follow from the comparison of the residual charge matrices $y'$ and $Y'$ in the BO basis. The relevant expressions for the corrections $Y'_{(k)}$ and $y'_{(k)}$ are of much simpler structure as compared with Eqs. (12) and (13) and take the form

$$Y'_{(1)} = \begin{vmatrix} 0 & R \\ R^+ & 0 \end{vmatrix} \qquad y'_{(1)} = \begin{vmatrix} 0 & \rho \\ \rho & 0 \end{vmatrix} \tag{16}$$

$$Y'_{(2)} = \frac{1}{2} \begin{vmatrix} -RR^+ & W \\ W^+ & R^+R \end{vmatrix}$$

$$y'_{(2)} = \frac{1}{2} \begin{vmatrix} -\rho^2 & (\kappa - \sigma)\rho \\ (\kappa - \sigma)\rho & \rho^2 \end{vmatrix} \tag{17}$$

where $W = RQ - SR$. As is seen from Eqs. (16) and (17), $y'_{(1)}$ and $y'_{(2)}$ result from $Y'_{(1)}$ and $Y'_{(2)}$, if the matrices $Q, S$ and $R$ are replaced by the respective one-dimensional parameters $\kappa, \sigma$ and $\rho$.

Therefore, the expressions for the DMs of alkanes and of the appropriate two-level system may be concluded to be similar. The origin of this similarity lies in the peculiar structure of the zero-order terms of both the hamiltonian matrix and the DMs of alkanes involving the $N$-dimensional unit matrices $I_{(N)}$.

## 4. The Brillouin theorem for alkanes as a generalized eigenvalue problem for the two-dimensional matrix

Let us consider in this section the non-canonical problem for the LMOs of alkanes based on the Brillouin theorem [7,10,11]. The essence of this theorem lies in the zero-value requirement for the hamiltonian matrix elements associated with the interactions between the occupied and vacant LMOs [12].

Let the BOs be the initial basis set. Since the total number of electrons $(2N)$ coincides with the number of basis functions in any alkane, the matrix

form of the Brillouin theorem resolves itself into the zero-matrix requirement for the $N \times N$-dimensional off-diagonal blocks of the hamiltonian matrix transformed into the LMO basis [7], i.e.

$$\tilde{H}' = T^{-1} H' T = \begin{vmatrix} \Lambda_1 & 0 \\ 0 & \Lambda_2 \end{vmatrix} = \Lambda \qquad (18)$$

where $T$ is the transformation matrix containing the LMOs represented in the basis of BOs, $H'$ is to be taken from Eq. (2), and $\Lambda_1$ and $\Lambda_2$ are the $N \times N$-dimensional diagonal blocks specified below. Hence, the non-canonical problem for the LMOs of alkanes consists of obtaining the matrix $T$ fulfilling the condition of Eq. (18).

A unitary matrix $T$ complying with both Eq. (18) and the appropriate requirement

$$T^+ T = I_{(2N)} \qquad (19)$$

has been obtained in Ref. [7] in the form of a power series, i.e.

$$T = T_{(0)} + T_{(1)} + T_{(2)} + \cdots \qquad (20)$$

The terms of Eq. (20) are

$$T_{(0)} = I_{(2N)} \qquad T_{(1)} = \frac{1}{2} \begin{vmatrix} 0 & -R \\ R^+ & 0 \end{vmatrix}$$

$$T_{(2)} = \frac{1}{4} \begin{vmatrix} -\frac{1}{2} R R^+ & -W \\ W^+ & -\frac{1}{2} R^+ R \end{vmatrix} \qquad (21)$$

The matrix $W$ of Eq. (21) is determined in Eq. (17).

The relevant transformed diagonal blocks $\Lambda_1$ and $\Lambda_2$ of Eq. (18) are

$$\Lambda_1 = I + S + \frac{1}{2} R R^+ + \cdots$$

$$\Lambda_2 = -I + Q - \frac{1}{2} R^+ R + \cdots \qquad (22)$$

The reason why the members of the series for the matrix $T$ shown in Eq. (21) are expressed in terms of entire blocks $S$, $Q$, and $R$ lies in the nature of the requirement shown in Eq. (18). Indeed, zero-matrix condition is imposed here on the entire off-diagonal blocks of the transformed hamiltonian $\tilde{H}'$ whatever the dimension of these blocks ($N$). Such a condition implies certain requirements (equations) for the entire blocks of the matrix $T$ being sought

[7], which served to obtain the expressions for the blocks of the corrections $T_{(k)}$, $k = 0, 1, 2$ in terms of the matrices $S$, $Q$ and $R$ as shown in Eq. (21). In addition, the presence of the unit matrix $I_{(N)}$ in the initial hamiltonian $H'$ of Eq. (2) played an essential role in simplifying the above-mentioned equations. The similar series for the diagonal blocks $\Lambda_1$ and $\Lambda_2$ shown in Eq. (22) is a direct consequence of the above-discussed structure of the matrix $T$. Therefore, as with the case of the DM, the dimension of the blocks $S$, $Q$ and $R$ plays no part in the formation of the expressions for the LMO representation matrix $T$.

The block-diagonal form of a $2N$-dimensional matrix as shown in Eq. (18) is evidently a generalization of the diagonal form of a two-dimensional matrix. Accordingly, transformation $T$ shown in Eqs. (20) and (21) describes passing into a new basis consisting of two $N$-dimensional non-interacting subspaces, whereas the usual diagonalization of a two-dimensional matrix represents passing into the basis of two non-interacting one-dimensional vectors.

It is no surprise in this context that a similar two-dimensional matrix ($t$) containing the usual parameters $\rho$, $\kappa$ and $\sigma$ instead of the $N \times N$ blocks $R$, $Q$ and $S$, respectively.

$$t = t_{(0)} + t_{(1)} + t_{(2)} + \cdots = \begin{vmatrix} 1 & 0 \\ 0 & 1 \end{vmatrix} + \frac{1}{2} \begin{vmatrix} 0 & -\rho \\ \rho & 0 \end{vmatrix}$$

$$+ \frac{1}{4} \begin{vmatrix} -\frac{1}{2}\rho^2 & (\sigma - \kappa)\rho \\ (\kappa - \sigma)\rho & -\frac{1}{2}\rho^2 \end{vmatrix} + \cdots \qquad (23)$$

leads to the eigenvalues of the matrix $h'$

$$\lambda_1 = 1 + \sigma + \frac{1}{2}\rho^2 + \cdots, \qquad \lambda_2 = -1 + \kappa - \frac{1}{2}\rho^2 + \cdots \qquad (24)$$

Comparing Eqs. (22) and (24) shows that the relation between the eigenvalues $\lambda_1$ and $\lambda_2$ of the matrix $h'$ and the diagonal blocks $\Lambda_1$ and $\Lambda_2$ of the matrix $\tilde{H}'$ is also of the above-discussed nature: the matrices $I_{(N)}$, $S$, $Q$ and $R$ are replaced by the parameters $1$, $\sigma$, $\kappa$ and $\rho$, respectively, when passing from alkanes to the two-level system. Therefore, the transformation shown in Eqs. (18), (20)

and (21) proves to be the matrix generalization of the usual diagonalization procedure for the two-dimensional matrix $h'$.

Accordingly, the structure of the LMOs of alkanes may be shown to resemble that of the MOs of the two-electron two-level system described by the hamiltonian matrix $h'$. Thus, the row-matrix of the occupied LMOs of alkanes $\langle \Psi_{(+)}|$ and the only occupied MO of the two level system follow from Eqs. (21) and (23). These are

$$\langle \Psi_{(+)}| = \langle \phi_{(+)}|(I_{(N)} - \tfrac{1}{8}RR^+) + \tfrac{1}{2}\langle \phi_{(-)}|(R^+ + \tfrac{1}{2}W^+)$$
(25)

$$\psi_{(+)} = \eta_{(+)}(1 - \tfrac{1}{8}\rho^2) + \tfrac{1}{2}\eta_{(-)}\{\rho + \tfrac{1}{2}(\kappa - \sigma)\rho\}$$
(26)

where $\langle \phi_{(+)}|$ and $\langle \phi_{(-)}|$ are the row-matrices of the BBOs and ABOs, respectively, whereas $\eta_{(+)}$ and $\eta_{(-)}$ stand for the relevant basis orbitals of the two-level system. It is seen from Eq. (25) that the entire row-matrices $\langle \phi_{(+)}|$ and $\langle \phi_{(-)}|$ play the role of the generalized basis functions when expressing the LMOs of alkanes.

The diagonalization procedure for any matrix in the orthogonal basis is known to be equivalent to the relevant eigenvalue equation [8]. Accordingly, Eq. (18) may be rewritten in the form

$$H'T = T\Lambda$$
(18a)

which may be described as the $N \times N$ eigenblock equation for the $2N \times 2N$-dimensional matrix $H'$. Hence, LMOs of alkanes may be considered as generalized eigenvectors of the relevant common hamiltonian matrix $H'$.

It should be noted at the end of this section that the hamiltonian matrix $H$ of Eq. (1) may also be transformed into a block-diagonal form like that shown in Eq. (18). The first step towards this form lies in applying the simple transformation matrix

$$U_{(0)} = 2^{-\frac{1}{2}} \begin{vmatrix} I_{(N)} & I_{(N)} \\ I_{(N)} & -I_{(N)} \end{vmatrix}$$
(27)

The resulting transformed hamiltonian $U_{(0)}^+ H \, U_{(0)}$ becomes similar to $H'$ of Eq. (2) and the next steps towards the form complying with the Brillouin theorem are similar to those developed in Ref. [7].

Accordingly, the expressions for the complete transformation matrix $U$ in terms of the entire blocks $A, B$ and $C$ of the first hamiltonian $H_{(1)}$ of Eq. (1) may be obtained whatever the dimension ($N$) of these blocks. As a result, the analogy between the matrix $U$ and the diagonalization matrix $u$ for the two-dimensional hamiltonian $h$ of Eq. (3) may be easily established.

Therefore, the Brillouin theorem for alkanes proves to be the matrix generalization of the usual eigenvalue problem for the respective two-level system.

## 5. Common regularities of the electronic structure of alkanes resulting from their relation to the unique two-level system

The established relation between the whole class of alkanes and the unique two-level system forms the basis for describing the former as a single quantum-mechanical object. Such a description consists both of the common expressions for the LMOs and DM of alkanes shown in Eqs. (8), (12), (14), (16), (17) and (21) and of the resulting regularities of the electronic structure.

Let us discuss in this section the most general of these regularities, namely those independent of the specific structure of the blocks $S, Q$ and $R$.

The expressions for the DM of alkanes, shown in Eqs. (16) and (17), on the one hand, and that for the LMOs of Eq. (21), on the other hand, involve similar combinations of the blocks $S, Q$ and $R$ with different coefficients. As a result, the LMOs and DM rows (columns) of alkanes proved to be interrelated and these two matrices have been considered as containing the same information on the specific structure of the given alkane [7]. Furthermore, the bond-orbital-and-tail structure of the LMOs follows from both the series for the matrix $T$ and the equality $T_{(0)} = I_{(2N)}$ shown in Eqs. (20) and (21), respectively. As a result, the one-to-one correspondence between the BOs and LMOs may be established, i.e. each LMO is related to the concrete BO. Since the possibility of expressing both $T$ and $Y$ in terms of the same matrices arises owing to the relation of alkanes to the unique two-level system, the above common

peculiarities of the LMOs and DM rows (columns) may be considered as a result of this relation.

Another consequence of the similarity between alkanes and the two-level system lies in the relation of the actual occupation numbers (populations) of BOs of alkanes to the extent of delocalization of the respective LMO. Let us consider this relation in more detail.

Let us start with the two-electron two-level system described by the hamiltonian matrix $h'$ of Eq. (4). The only occupied MO of this system shown in Eq. (26) contains the term $1/2\,(\rho\eta_{(-)})$ as the main correction to the orbital $\eta_{(+)}$. This term describes the extent of delocalization of the orbital $\eta_{(+)}$ when making up the respective MO $\psi_{(+)}$. Let us define the positive delocalization coefficient of this MO

$$d_{(+)} = (\tfrac{1}{2}\rho)^2 = \tfrac{1}{4}\rho^2 \tag{28}$$

Then the actual occupation number $x_{(+)}$ of the initially doubly-occupied orbital $\eta_{(+)}$ is

$$x_{(+)} = 2 - \tfrac{1}{2}\rho^2 = 2(1 - d_{(+)}) \tag{29}$$

It follows from Eq. (29) that the occupation number $x_{(+)}$ decreases when the delocalization coefficient $d_{(+)}$ increases, i.e. the more delocalized the orbital becomes the more charge it loses.

Similarly, the actual occupation number $x_{(-)}$ of the initially vacant basis function $\eta_{(-)}$ is

$$x_{(-)} = 2d_{(-)} \tag{30}$$

where the respective delocalization coefficient $d_{(-)}$ of the MO $\psi_{(-)}$ coincides with $d_{(+)}$ of Eq. (28). Hence, the population $x_{(-)}$ that the orbital $\eta_{(-)}$ acquires is proportional to its delocalization when making up the respective MO $\psi_{(-)}$. On the whole, the populations $x_{(+)}$ and $x_{(-)}$ are interrelated by the charge conservation condition

$$x_{(+)} + x_{(-)} = 2 \tag{31}$$

These rules may be easily generalized to the case of the alkanes. To do this, let us rewrite Eq. (25) to within the first-order terms using the relevant matrix elements

$$\Psi_{(+)i} = \phi_{(+)i} + \tfrac{1}{2} \sum_{l}^{\text{ABOs}} \phi_{(-)l} R_{li}^+ \tag{32}$$

The term $\tfrac{1}{2}R_{li}^+$ represents the contribution of the

ABO $\phi_{(-)l}$ to the LMO $\Psi_{(+)i}$. That is why the quantity

$$D_{(+)il} = (\tfrac{1}{2}R_{li}^+)^2 = \tfrac{1}{4}(R_{li}^+)^2 \tag{33}$$

may be considered as the partial delocalization coefficient of the LMO $\Psi_{(+)i}$ over the ABO $\phi_{(-)l}$.

Again, the actual occupation number of the BBO $\phi_{(+)i}$ follows from Eqs. (7), (8) and (17) and equals

$$X_{(+)i} = 2 - \tfrac{1}{2}\sum_{l}^{\text{ABOs}} R_{il}R_{li}^+ = 2 - \tfrac{1}{2}\sum_{l}^{\text{ABOs}}(R_{li}^+)^2$$

$$= 2\left(1 - \sum_{l}^{\text{ABOs}} D_{(+)il}\right) \tag{34}$$

where the last equality is the result of substitution of Eq. (33). Let us introduce the total delocalization coefficient of the LMO $\Psi_{(+)i}$ over all ABOs

$$D_{(+)i} = \sum_{l}^{\text{ABOs}} D_{(+)il} \tag{35}$$

Then the relation

$$X_{(+)i} = 2(1 - D_{(+)i}) \tag{36}$$

follows from Eq. (34) and it is true for any pair of BBO $\phi_{(+)i}$ and the respective LMO $\Psi_{(+)i}$. The similarity of Eqs. (29) and (36) is obvious. As a result, the population of the BBO $\phi_{(+)i}$ lost when making up the LMO $\Psi_{(+)i}$ is proportional to the total delocalization of the latter.

An analogous relation is valid for an ABO $\phi_{(-)m}$ and the respective vacant LMO $\Psi_{(-)m}$. Thus, the occupation number of the former is

$$X_{(-)m} = 2D_{(-)m} \tag{37}$$

where

$$D_{(-)m} = \sum_{i}^{\text{BBOs}} D_{(-)mi} \tag{38}$$

is the total delocalization coefficient of the vacant LMO $\Psi_{(-)m}$ over all BBOs, whereas $D_{(-)mi}$ is the respective partial delocalization coefficient of the same LMO over the particular BBO $\phi_{(+)i}$

$$D_{(-)mi} = (\tfrac{1}{2}R_{im})^2 = \tfrac{1}{4}(R_{im})^2 \tag{39}$$

As is seen from Eq. (37), the population $X_{(-)m}$ that the ABO $\phi_{(-)m}$ acquires when making up the LMO

$\Psi_{(-)m}$ is proportional to the total delocalization of this LMO.

Therefore, despite the fact that LMOs of alkanes involve tails extending over the whole molecule, the relation between the occupation number of any particular BO and the extent of delocalization of the respective single LMO is similar to the relevant relation for the two-level system.

It follows from the definition of the partial delocalization coefficients shown in Eqs. (33) and (39) and the equality $R_{mi}^{+} = R_{im}$ that

$$D_{(-)mi} = D_{(+)im} \tag{40}$$

This result implies the coincidence between the partial delocalization coefficients of the occupied LMO $\Psi_{(+)i}$ over the ABO $\phi_{(-)m}$ and that of the vacant LMO $\Psi_{(-)m}$ over the BBO $\phi_{(+)i}$. However, the two total delocalization coefficients $D_{(+)i}$ and $D_{(-)m}$ associated with the same chemical bond are not interrelated. This result is due to the non-Hermitian nature of the matrix $R$ of Eq. (2) and implies a possibility of an interbond charge transfer in alkanes.

Let us introduce the complete delocalization coefficients of all occupied LMOs

$$D_{(+)} = \sum_{i}^{BBOs} D_{(+)i} \tag{41}$$

and that of all vacant LMOs

$$D_{(-)} = \sum_{m}^{ABOs} D_{(-)m} \tag{42}$$

Then the equality

$$D_{(+)} = D_{(-)} \tag{43}$$

and the respective charge conservation condition for the whole molecule

$$\sum_{i}^{BBOs} X_{(+)i} + \sum_{m}^{ABOs} X_{(-)m} = 2N \tag{44}$$

may be easily proved by using Eqs. (35), (38), (40), (36) and (37).

Finally, let us dwell on the total energy of alkanes.

Two definitions of this quantity are possible

$$E = \text{Spur}(PH) \tag{45}$$

and

$$E = 2\text{Spur } \Lambda_1 \tag{46}$$

and both result in the same expression of the energy as a sum of two members

$$E = E_1 + E_2 \tag{47}$$

The first term of Eq. (47) is

$$E_1 = 2\text{Spur}(I + S) \tag{48}$$

and contains the sum of the BBO energies, whereas the second one

$$E_2 = \text{Spur } (RR^+) \tag{49}$$

may be interpreted as the total stabilization (resonance) energy. Using Eqs. (33), (35), (41) and (49) we obtain

$$E_2 = 4D_{(+)} \tag{50}$$

Accordingly, from Eqs. (24) and (28) the respective resonance energy for the two-level system follows

$$\varepsilon_2 = 4d_{(+)} \tag{51}$$

Therefore, the stabilization (resonance) energy of both alkanes and the respective two-level system is proportional to the complete delocalization of the occupied LMOs and of the single MO.

On the whole, the results of this section contribute to the substantiation of the above conclusion that the LMOs and not the canonical MOs of alkanes are the direct generalizations of the MOs of the respective two-level system. It is noteworthy in this context that the two MOs of the latter comply with the Brillouin theorem shown in Eq. (18) and may be regarded as both the canonical MOs and the non-canonical ones, i.e. the LMOs of the two-level system described by the hamiltonian matrix $h'$ of Eq. (4).

## 6. Concluding remarks

The $N$-dimensional unit matrices $I_{(N)}$ contained in the hamiltonian matrices of Eqs. (1) and (2) and

forming the basis for the established relation between alkanes and the respective two-level system, represent the set of $N$ chemical bonds of alkanes assumed to be equivalent to within the zero-order terms in the employed model. Such an equivalence of bonds has been described in Ref. [7] as topological, and it has been related to the tetrahedral symmetry of the nearest environment of the carbon atoms [13]. As a result of the latter relation, the above two peculiarities of the structure of alkanes acquired the joint denomination of the common topological structure of these system. Accordingly, the relation between alkanes and the definite two-level system may be concluded to reveal itself owing to the common topological structure of the former.

Consequently, the presence of approximately equivalent bonds may be regarded as the main common feature of the structure of alkanes. Again, the specific constitution of a particular molecule is described by the number of bonds and the pattern of their spatial arrangement. These peculiarities are represented by the dimension $N$ and the specific structure of the $N \times N$ blocks $S, Q$ and $R$ and/or $A, B$ and $C$. In this context, passing to the case of $N = 1$, i.e. replacing the above $N \times N$-dimensional blocks by usual parameters, may be regarded as turning to a single effective bond inherent to any alkane. Hence, the two-dimensional hamiltonian matrices $h$ and/or $h'$ may be concluded to describe an effective chemical bond common to the whole class of alkanes.

Furthermore, the obtained results show that certain common regularities of the electronic structure of alkanes may be established without regard for the dimension of the system $N$ and these are similar to the relevant regularities for the two-level system. Therefore, the obtained two-dimensional hamiltonian matrices $h$ and/or $h'$ may be used when modeling the main regularities of the electronic structure of alkanes. Therefore, the effective chemical bond may be concluded to be the smallest building block of alkanes, which keeps the main peculiarities of the electronic structure of the whole class.

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