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Common Elementary Fragments for Alternant Hydrocarbons

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Abstract

The secular problem for the common Hückel type Hamiltonian matrix of alternant hydrocarbons (AHs) is studied by means of an alternative approach based on an initial reformulating of the problem itself in order to reveal the structures of eigenfunctions instead of the standard imposing of the zero- determinant condition and search for eigenvalues. As a result, a new representation is obtained for molecular orbitals (MOs) of AHs in the form of linear combinations of non- orthogonal local- structure- determined basis orbitals, each of them embracing a definite fragment of the whole system. Coefficients of these combinations are shown to follow from eigenvectors of the so-called interfragmental adjacency matrices, the latter being expressible in terms of entire submatrices (blocks) of respective initial Hamiltonian matrices. The above-specified basis orbitals, in turn, prove to be related to the usual MOs of respective fragments of the given AH. The principal outcome of passing to this new representation for MOs consists in revealing three types of elementary fragments in AHs (viz. ethenes, allyls and trimethylenemethanes) that are bound one with another in a uniform manner in addition. This result implies the AHs to meet the definition of a class of chemical compounds. A new mental image of electronic structures of AHs also is among the principal achievements. The results obtained are illustrated by consideration of specific examples.

1. Introduction

Molecular orbitals (MOs) are among the most popular quantum-chemical characteristics of organic compounds determining their spectral properties (see e.g. [1,2]) and chemical reactivity. The latter aspect may be illustrated by the well-known HOMO/LUMO concept [3,4] and the famous Woodward- Hoffmann rule [5]. Conjugated (aliphatic) and aromatic (benzenoid) hydrocarbons are no exceptions in this respect. Moreover, MOs of these hydrocarbons actually coincide with eigenvectors of adjacency matrices (AMs) of the relevant graphs of C-skeletons in the framework of the simple Hückel model (HMO theory) [6–8]. Inasmuch as the above-specified graphs represent the topological structure of the given system, some information about molecular topology is expected to be contained within MOs too. Regularities of this type are under an intensive search [9–17]. In particular, the so-called net sign approach [11–13] proved to be efficient for interpretation of overall nodal properties of Hückel MOs (HMOs) and their ordering in the energy scale. Again, select eigenvectors of AMs may be often traced back to subspectral fragments (subgraphs) embedded in the given graph [15–17].

Another perspective on constitution of MOs (HMOs) originates from the well-known perturbational MO (PMO) theory [18]. Indeed, this theory allows the MOs of an extended compound to be constructed in the form of linear combinations of orbitals of certain elementary fragments, often referred to as fragmental orbitals (FOs). [In terms of molecular graphs, elementary fragments coincide with subgraphs]. Besides, choice of particular fragments is usually based on chemical intuition. For example, the HMOs of butadiene take the form of normalized sums and differences of MOs of separate ethene fragments (C=C bonds). This simple approach provides us with mental images of electronic structures of composite molecules and thereby forms the basis for the qualitative chemical thinking. In general, specific FOs and coefficients of their linear combinations are correspondingly determined by constitution of underlying fragments and by the way these are bound together in the PMO theory. Accordingly, MOs of similar compounds prove to be interrelated. This especially refers to molecular systems of the same chemical class [Let us recall that a lot of molecules is usually understood to belong to the same class if common groups of atoms (elementary fragments) reveal themselves there and these are bound one with another in a uniform manner in addition].

Unfortunately, the very PMO theory is of a rather limited scope of applicability. So far as composite compounds are concerned, validity of this theory is restricted to the case of relatively weak interfragmental interactions vs. the intrafragmental ones. It is evident that the majority of molecules (including the benzenoid hydrocarbons) do not meet this requirement. Another and even more problematic point is that the nature of fragments themselves cannot be revealed straightforwardly in the respective chemical formulae. As for instance, if we try to distinguish separate double (C=C) bonds in the C-skeleton of benzene, we have to confine ourselves to a single Kekule structure of this molecule. The same state of things refers to any benzenoid hydrocarbon. Again, there are no doubts that these compounds consist of some repeated local substructures. This promotes an expectation that information about these substructures (elementary fragments) may be extracted from the relevant MOs (HMOs). To achieve this end, representation of the latter as linear combinations of FOs should be extended to the case of comparable (or even uniform) intra- and interfragmental interactions (resonance parameters), i.e. beyond the limits of the PMO theory. The present study adresses just this task.

We will dwell here on the case of alternant hydrocarbons (AHs) [6, 18] embracing the majority of the above-discussed conjugated and benzenoid systems. In other words, we are about to confine ourselves to hydrocarbons, the C-skeletons of which are representable by bipartite graphs [6–8]. It also deserves emphasizing here that several types of systems under current focus also belong to AHs, e.g. polyenes [19–22], polynuclear benzenoids [23–26], some hydrocarbon dendrimers [27] and most of carbon nanotubes [28–30]. Wide areas of both actual and potential applications of these systems exidently promote an interest in the underlying substructures (fragments). Another (and even more important) motive of our choice consists in constructability of a single Hückel type Hamiltonian matrix for C-skeletons of all AHs in the basis of $2p_z$ AOs of carbon atoms [6, 31, 32] and thereby representability of the consequent properties of their electronic structures in the form of general rules [6, 18, 31, 33–39]. For illustration, rules governing both constitutions of the usual (canonical) molecular orbitals of these hydrocarbons and the relevant one-electron energies deserve mentioning [6, 33, 34]. Common properties of charge-bond order matrices of AHs [31,34,35,38] also belong to achievements of the same type. Finally, rules underlying the formation of non-canonical (localized) MOs of the same systems [38, 39] may be added here too.

On the whole, the above-enumerated peculiarities of AHs give us a hint about existance of common elementary fragments in these systems. Given that this is the case, an important question arises whether the AHs may be regarded as a separate class of chemical compounds. Thus, we will look for common elementary fragments within C-skeletons of AHs by analyzing constitutions of their HMOs. In an attempt to represent the MOs concerned as linear combinations of certain FOs, we will study the secular equation for the above-specified common Hamiltonian matrix of AHs. The overall methodology to be invoked resembles that suggested previously for alkanes [40, 41]. It is discussed in the next Section in a more detail.

2. Eigenvalue- dependent basis orbitals for alternant hydrocarbons and their interpretation

Let us start with a brief description of the approach to be applied.

The experience of dealing with secular problems (eigenvalue equations) for Hamiltonian matrices of molecules shows that it is the decision upon the first step when solving the problem that determines the terms in which the results are expressed and interpreted [42]. The eigenfunctions (MOs) is no exception here. The first step of the standard solution procedure coincides with imposing the zero-determinant requirement and search for eigenvalues, whereas the second one lies in obtaining the eigenfunctions. As a result, the usual LCAO form is obtained for MOs. By contrast, the approach [42] to be applied below starts with reformulating the secular problem itself in order to reveal the structures of eigenfunctions, whilst the eigenvalues follow from the second step. A large part of the MO LCAO coefficients being sought is then initially eliminated from the original secular equation before specifying the energy variable (eigenvalue) ε. Consequently, the resulting MOs take the form of linear combinations of certain $\varepsilon-$dependent basis orbitals, the total number of which is much less than that of AOs. Moreover, these new basis functions appear to be strictly localized on separate local regions of systems under study. Hence, an alternative representation of MOs follows that is likely to provide us with information about underlying fragments. It deserves an additional emphasizing that no additional requirements are invoked here concerning relative values of intra- and interfragmental interactions.

Before turning to application of the above-described approach to the common Hückel type Hamiltonian matrix of AHs, let us dwell first on constructing the latter. Let us confine ourselves to the most common case of even AHs containing $2n$ carbon atoms. The relevant $2n-$dimensional basis set $\{\chi\}$ consists of $2p_z$ AOs of these atoms and always may be divided into two $n-$dimensional subsets $\{\chi^*\}$ and $\{\chi^\circ\}$ so that the intrasubset resonance parameters take zero values [6, 31, 32]. It happens so because the neighboring pairs of AOs referring to chemical bonds (and thereby characterized by non-zero resonance parameters in the Hückel model) get into different subsets. Moreover, the Coulomb parameters representing AOs usually are assumed to take uniform values α and the equality $\alpha = 0$ is accepted for convenience. As a result, the Hamiltonian matrices of our systems acquire a common form containing zero submatrices (blocks) in its diagonal positions, viz.

$$\mathbf{H} = \begin{vmatrix} \mathbf{0} & \mathbf{B} \\ \mathbf{B}^{+} & \mathbf{0} \end{vmatrix}. \tag{1}$$

Again, $\mathbf{B}$ and $\mathbf{B}^{+}$ are $n \times n-$dimensional off-diagonal blocks containing intersubset resonance parameters. Non-zero elements of these blocks represent the neighboring pairs of $2p_z$ AOs. The mean value of the latter β will be used here as a (negative) energy unit by accepting the equality $\beta = 1$. The superscript $+$ of Eq.(1) designates the transposed matrix $\mathbf{B}$ [Note that $\mathbf{B} \neq \mathbf{B}^{+}$ in the general case]. Besides, the matrix $\mathbf{H}$ of Eq.(1) actually coincides with the AM of a bipartite graph [6].

Let us turn now to the eigenvalue equation for the matrix $\mathbf{H}$ and represent it explicitly as follows

$$\begin{vmatrix} \mathbf{0} & \mathbf{B} \\ \mathbf{B}^{+} & \mathbf{0} \end{vmatrix} \begin{vmatrix} \mathbf{U} \\ \mathbf{V} \end{vmatrix} = \varepsilon \begin{vmatrix} \mathbf{U} \\ \mathbf{V} \end{vmatrix}, \tag{2}$$

where $\mathbf{U}$ and $\mathbf{V}$ are column- matrices of eigenvectors (MO LCAO coefficients) referring to subsets $\{\chi^{*}\}$ and $\{\chi^{\circ}\}$, respectively, and ε is the eigenvalue being sought. Two equations follow immediately from Eq.(2), viz.

$$\mathbf{BV} = \varepsilon\mathbf{U}, \quad \mathbf{B}^{+}\mathbf{U} = \varepsilon\mathbf{V}. \tag{3}$$

Let us assume now that $\varepsilon \neq 0$ [Note that no zero eigenvalues are peculiar to even AHs [31]]. The column-matrix $\mathbf{V}$ may be then expressed on the basis of the second relation of Eq.(3), i.e.

$$\mathbf{V} = \varepsilon^{-1}\mathbf{B}^{+}\mathbf{U}. \tag{4}$$

After substituting Eq.(4) into the first relation of Eq.(3), we obtain

$$(\mathbf{BB}^{+})\mathbf{U} = \varepsilon^{2}\mathbf{U}, \tag{5}$$

i.e. a secular equation for the $n \times n-$dimensional Hermitian (symmetric) matrix $\mathbf{BB}^{+}$, where ε^{2} playes the role of the eigenvalue. An analogous elimination of the column-matrix $\mathbf{U}$ yields the secular equation for the matrix $\mathbf{B}^{+}\mathbf{B}$, viz.

$$(\mathbf{B}^{+}\mathbf{B})\mathbf{V} = \varepsilon^{2}\mathbf{V}. \tag{6}$$

Moreover, matrices $\mathbf{BB}^+$ and $\mathbf{B}^+\mathbf{B}$ are similar [43] and thereby isospectral. The above two matrix equations have been originally derived a long time ago [44].

As is seen from Eqs.(5) and (6), the column- matrices $\mathbf{U}$ and $\mathbf{V}$ consist of coefficients of eigenvectors of Hermitian matrices. Thus, let us impose the following normalization conditions for elements U_i and V_k [31], viz.

$$\sum_{i=1}^{n} U_i^2 = \sum_{k=1}^{n} V_k^2 = 1. \tag{7}$$

Molecular orbitals of our AHs are then expressible as follows

$$\psi = \frac{1}{\sqrt{2}}[(\chi^*)\mathbf{U} + (\chi^\circ)\mathbf{V}] \equiv \frac{1}{\sqrt{2}}[\sum_{i=1}^{n} \chi_i^* U_i + \sum_{k=1}^{n} \chi_k^\circ V_k], \tag{8}$$

where (χ^*) and (χ°) stand for row-matrices of AOs of subsets $\{\chi^*\}$ and $\{\chi^\circ\}$, respectively. Let us substitute now the relation of Eq.(4) into Eq.(8). We then obtain

$$\psi^*(\varepsilon) = \frac{1}{\sqrt{2}}[(\chi^*) + \varepsilon^{-1}(\chi^\circ)\mathbf{B}^+]\mathbf{U}, \tag{9}$$

i.e. a certain unified eigenvalue- dependent form for all MOs, wherein the MO LCAO coefficients $V_k (k = 1, 2, 3...n)$ are no longer present. [The meaning of the additional superscript * of the left-hand side is clarified below]. The function $\psi^*(\varepsilon)$ may be conveniently called the generalized MO (GMO) of AHs. An alternative form of the same GMO is as follows

$$\psi^*(\varepsilon) = \frac{1}{\sqrt{2}} \sum_{i=1}^{n} \varphi_i^*(\varepsilon) U_i, \tag{10}$$

where

$$\varphi_i^*(\varepsilon) = \chi_i^* + \varepsilon^{-1} \sum_{k=1}^{n} \chi_k^\circ B_{ki}^+ \tag{11}$$

stands for an eigenvalue-dependent (generalized) basis orbital. It is seen that the GMO of AHs takes the form of a linear combination of these new basis orbitals. It also deserves a separate mentioning that no zero-determinant requirement concerning the initial secular problem of Eq.(2) is imposed hitherto. Moreover, no need for this requirement actually arises because both coefficients (U_i) of Eq.(10) and the eigenvalues are conditioned by the secular equation for the $n \times n-$dimensional matrix $\mathbf{BB}^+$ (i.e. by Eq.(5)). Finally, after substituting a particular eigenvalue ε_m along with the respective elements U_{im} of the appropriate column- matrix $\mathbf{U}_m$, the expression of Eq.(10) is naturally expected to yield the MO ψ_m, viz.

$$\psi_m = \frac{1}{\sqrt{2}} \sum_{i=1}^{n} \varphi_i^*(\varepsilon_m) U_{im}, \tag{12}$$

where

$$\varphi_i^*(\varepsilon_m) = \chi_i^* + \varepsilon_m^{-1} \sum_{k=1}^{n} \chi_k^\circ B_{ki}^+ \tag{13}$$

coincides with the ith adjusted basis orbital [Adjustment here and below implies employment of the specific eigenvalue ε_m instead of the energy parameter ε of Eq.(11)]. This anticipation is verified in Section 3 in a detail. Let us turn now to analysis of Eqs.(10)-(13).

First, one-to-one correspondence between AOs of the first subset χ_i^* and the generalized basis orbitals (GBOs) $\varphi_i^*(\varepsilon)$ follows from Eq.(11). Just this fact is reflected by the superscript *. Alternative basis orbitals $\varphi_k^\circ(\varepsilon)$ attached to AOs of the second subset χ_k° may be obtained analogously. The relevant GMO $\psi^\circ(\varepsilon)$ also is expressible in the form like that of Eq.(10), wherein $(1/\sqrt{2})V_k$ play the role of coefficients. Since the subsets $\{\chi^*\}$ and $\{\chi^\circ\}$ are entirely equivalent in even AHs, expressions of Eqs.(10)-(13) actually are sufficient for our further purposes.

Second, the dependence of the shape of the GBO $\varphi_i^*(\varepsilon)$ upon the one-electron energy ε deserves attention. In particular, basis orbitals of bonding nature correspond to occupied MOs of AHs characterized by positive energies ($\varepsilon > 0$) and vice versa. Since MOs of these hydrocarbons appear in pairs described by one-electron energies $\pm\varepsilon$ [6], the same refers also to the relevant basis orbitals. Moreover, the extent of localization of GBOs $\varphi_i^*(\varepsilon)$ over their principal AOs χ_i^* grows with the increasing absolute value of the energy ε. Hence, more delocalized basis orbitals underly the so-called frontier MOs (i.e. the HOMO and the LUMO), as the latter are characterized by lowest absolute values of ε.

Third, the extent of localization of a certain GBO $\varphi_i^*(\varepsilon)$ depends on the structure of the nearest environment of the respective principal AO χ_i^*. Indeed, an AO of the second subset (say χ_k°) contributes to the basis orbital $\varphi_i^*(\varepsilon)$ and/or $\varphi_i^*(\varepsilon_m)$, only if $B_{ki}^+ = B_{ik} \neq 0$, i.e. if AOs χ_i^* and χ_k° are characterized by a non-zero resonance parameter, and the relative value of this contribution is proportional to this particular parameter in addition. Non-zero resonance parameters, in turn, are usually ascribed to first-neighboring (chemically-bound) pairs of atoms and/or AOs in the standard Hückel model [6,45,47]. Consequently, the actual number of $\varepsilon-$dependent contributions to the GBO $\varphi_i^*(\varepsilon)$ depends on that of the first neighbors of the AO χ_i^* and thereby on valency of the Ith carbon atom (the AO χ_i^* is localized on). Since one-, two- and three-valent carbon atoms are present in AHs, three types of GBOs may be accordingly distinguished, viz.

$$\begin{aligned}
\varphi^*_{i(1)}(\varepsilon) &= \chi^*_i + \frac{1}{\varepsilon}B_{ik}\chi^\circ_k, &(14)\\
\varphi^*_{i(2)}(\varepsilon) &= \chi^*_i + \frac{1}{\varepsilon}(B_{ik}\chi^\circ_k + B_{il}\chi^\circ_l), &(15)\\
\varphi^*_{i(3)}(\varepsilon) &= \chi^*_i + \frac{1}{\varepsilon}(B_{ik}\chi^\circ_k + B_{il}\chi^\circ_l + B_{is}\chi^\circ_s), &(16)
\end{aligned}$$

where the respective valencies are represented by subscripts (1), (2) and (3) of the left-hand sides of Eqs.(14)-(16) and equalities $B^+_{ki} = B_{ik}$ are invoked in addition. It is seen that two-, three- and four-center GBOs are actually obtained here.

The fourth point of our discussion concerns non-orthogonality of GBOs. Let us assume for example that the AOs χ^*_i and χ^*_j possess a common neighbor χ°_k as it is typical in AHs. Consequently, the relevant two GBOs $\varphi^*_i(\varepsilon)$ and $\varphi^*_j(\varepsilon)$ contain contributions of the same AO χ°_k and thereby overlap one with another. Moreover, the relevant overlap integral is inversally proportional to the square of the one-electron energy ε. Thus, the overall extents of non-orthogonality of GBOs take the highest values for frontier MOs (HOMO and LUMO). Since AOs of the first subset and of the second one alternately reveal themselves in AHs in accordance with the definition of these hydrocarbons [6, 18, 33–36, 45], the GBOs of any AH form a continuously- overlapping set of basis functions. Finally, an interrelation deserves mentioning between the above-discussed shapes of GBOs and overlap integrals of their adjacent pairs: More delocalized GBOs (underlying the frontier MOs) overlap one with another more significantly and vice versa.

Let us turn now to interpretation of GBOs. To this end, let us start with consideration of the simplest AH, namely of the ethene molecule containing two $2p_z$ AOs χ^*_1 and χ°_2 (Fig.1a). One-dimensional quantities (B_{12}, U_1 and V_2) play the role of matrices ($\mathbf{B}, \mathbf{U}$ and $\mathbf{V}$, respectively) within Eqs.(2)-(6) in this case and we obtain

$$V_2 = \varepsilon^{-1}B_{12}U_1 \tag{17}$$

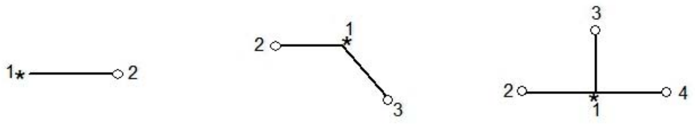
instead of Eq.(4). Substituting the above relation into the usual MO LCAO expression for ethene, viz.

$$\psi_e = \frac{1}{\sqrt{2}}(U_1\chi^*_1 + V_2\chi^\circ_2) \tag{18}$$

yields the relevant $\varepsilon-$dependent form

$$\psi_e(\varepsilon) = \frac{1}{\sqrt{2}}(\chi^*_1 + \frac{B_{12}}{\varepsilon}\chi^\circ_2), \tag{19}$$

where Eq.(7) also is invoked. It is seen that the function $\psi_e(\varepsilon)$ turns into the bonding MO of ethene if $\varepsilon = B_{12}$ and coincides with its antibonding counterpart if $\varepsilon = -B_{12}$. Thus, the $\varepsilon-$dependent orbital $\psi_e(\varepsilon)$ actually is the generalized MO of ethene. Again, comparison of Eqs.(14) and (19) indicates these formulae to contain the same orbital to within the normalization factor $1/\sqrt{2}$. Hence, the GBO $\varphi^*_{i(1)}(\varepsilon)$ of Eq.(14) may be interpreted as the generalized MO of the two-center (ethene-like) fragment of an AH involving the AOs χ^*_i and χ°_k.



(a) (b) (c)

Figure 1. Elementary fragments of AHs: ethene (a), allyl (b) and trimethylenemethane (c), as well as respective numberings of $2p_z$ AOs of carbon atoms.

Let us now consider an allyl system embracing three $2p_z$ AOs χ^*_1, χ°_2 and χ°_3 (Fig.1b). The principal matrices of this system are as follows

$$\mathbf{B} = \left| \begin{array}{cc} B_{12} & B_{13} \end{array} \right|, \quad \mathbf{U} = U_1, \quad \mathbf{V} = \left| \begin{array}{c} V_2 \\ V_3 \end{array} \right|. \tag{20}$$

¿From Eq.(3), we then obtain

$$B_{12}V_2 + B_{13}V_3 = \varepsilon U_1, \quad B^+_{21}U_1 = \varepsilon V_2, \quad B^+_{31}U_1 = \varepsilon V_3, \tag{21}$$

where $B^+_{21} = B_{12}$ and $B^+_{31} = B_{13}$. The second and the third relations of Eq.(21) easily yield expressions for matrix elements V_2 and V_3 in terms of U_1 as shown in Eq.(17). After substituting these expressions into the relevant LCAO form of MOs of allyl (ψ_a), viz.

$$\psi_a = \frac{1}{\sqrt{2}}(U_1\chi^*_1 + \ V_2\chi^\circ_2 + V_3\chi^\circ_3) \tag{22}$$

we obtain

$$\psi_a(\varepsilon) = \frac{1}{\sqrt{2}}(\chi^*_1 + \ \frac{B_{12}}{\varepsilon}\chi^\circ_2 + \frac{B_{13}}{\varepsilon}\chi^\circ_3), \tag{23}$$

where $U_1 = 1$ in accordance with Eq.(7). Equation (23) may be easily shown to yield the bonding and the antibonding MOs of allyl (but not its non-bonding MO corresponding to $\varepsilon = 0$). The simplest way of doing this consists in accepting the usual equalities $B_{12} = B_{13} = 1$ and in replacing the parameter ε by the respective one-electron energies $\pm\sqrt{2}$ [46]. Hence, the $\varepsilon-$dependent orbital $\psi_a(\varepsilon)$ of Eq.(23) actually is the GMO of allyl. Accordingly, comparison of functions exhibited in Eqs.(15) and (23) allows us to interpret the GBO $\varphi^*_{i(2)}(\varepsilon)$ as the GMO of an allyl-like fragment of AHs embracing the $2p_z$ AOs χ^*_i, χ°_k and χ°_l. Finally, an analogous consideration of the trimethylenemethane containing four AOs χ^*_1, $\chi^\circ_2, \chi^\circ_3$ and χ°_4 (Fig.1c) shows that the GBO $\varphi^*_{i(3)}(\varepsilon)$ of Eq.(16) is interpretable as the GMO of a four-center fragment covering the AOs χ^*_i, $\chi^\circ_k, \chi^\circ_l$ and χ°_s.

Hence, the newly-introduced eigenvalue-dependent representation for eigenfunctions of matrices provides us with a generalization of the usual perturbation-theory-based expressions for MOs as linear combinations of orbitals localized on separate fragments (FOs). Moreover, GMOs of ethenes, allylls and trimethylenemethanes play the role of basis orbitals (FOs) in our linear combinations for GMOs of AHs exhibited in Eq.(10). That is why the above-enumerated simple systems may be regarded as elementary fragments of AHs. The decisive role of valencies of carbon atoms in the formation of particular sets of elementary fragments also is among the conclusions.

It deserves adding here that ethene and allyl fragments are among substructures embedded in benzenoid hydrocarbons [15–17]. For particular AHs, however, our elementary fragments generally do not coincide with those embedded (Section 3). Such a conclusion causes little surprise because of entirely different methodologies underlying the derivetions of these substructures (Embedding is based on the concept of subspectrality [15–17], i.e. on search for substructures, the AMs of graphs of which possess eigenvalues common to those of the total AM concerned).

As already mentioned, coefficients of our principal linear combination of Eq.(12) (U_{im}) follow from eigenvectors of the matrix $\mathbf{BB}^+$ (see Eq.(5)). Thus, properties of this Hermitian matrix also deserve attention here. To discuss them, let us start with the one-to-one correspondence between diagonal elements of the matrix $\mathbf{BB}^+$ defined as follows

$$(\mathbf{BB}^+)_{ii} = \sum_{k=1}^{n} (B_{ik})^2 \tag{24}$$

and AOs χ^*_i of the first subset (the sum over k embraces here the AOs of the second subset $\{\chi^\circ\}$). If we assume in addition that $B_{ik} = 1$ for pairs of first-neighboring (adjacent) AOs χ^*_i and χ°_k and vanish elsewhere, the element $(\mathbf{BB}^+)_{ii}$ coincides with the total number of first neighbors of the AO χ^*_i and thereby with the valency of the Ith carbon atom.

Let us recall now that elementary fragments of AHs also were attached to AOs of the first subset $\{\chi^*\}$. Moreover, the nature of a certain fragment was determined by the valency of the respective carbon atom. Thus, diagonal elements of the matrix $\mathbf{BB}^+$ may be concluded to represent the respective set of elementary fragments of the given AH. Accordingly, numbers 1,2 and 3 correspond to ethenes, allyls and trimethylenemethanes in the principal diagonale. We may also conclude here that the higher is the valency of the Ith carbon atom, the lower is the relative position of the given elementary fragment in the energy scale. [Note that a negative energy unit is used in the present study].

Before passing to off-diagonal elements of the matrix $\mathbf{BB}^+$, let us define the so-called adjacent elementary fragments as those embracing a common carbon atom. These fragments are assumed to be attached to AOs χ_i^* and χ_j^* possessing a common first neighbor χ_k° . From the expression concerned, viz.

$$(\mathbf{BB}^+)_{ij} = \sum_{k=1}^{n} B_{ik} B_{jk} \tag{25}$$

then it follows that the element $(\mathbf{BB}^+)_{ij}, i \neq j$ coincides with 1, if the Ith and Jth fragments are adjacent, otherwise it vanishes. Thus, the off-diagonal elements of the matrix $\mathbf{BB}^+$ represent adjacencies of elementary fragments in the given AH. In this connection, the whole matrix $\mathbf{BB}^+$ will be referred to as the interfragmental adjacency matrix (IFAM). This matrix, in turn, may be represented by a certain graph, the latter being called the interfragmental graph for simplicity.

Therefore, equations (10) and (12) really represent the GMOs and the MOs of AHs, respectively, in terms of characteristics of elementary fragments. Again, a certain adjustment to the whole system under consideration also is peculiar to these fragments. In particular, eigenvalues of the total Hamiltonian matrix of the given AH (ε_m) stand instead of those of separate fragments in the linear combination of Eq.(12) for individual MOs (ψ_m). Nevertheless, orbitals of the same fragment prove to be recognizable in different AHs as demonstrated in the next section.

3. Consideration of specific examples

3.1. The benzene molecule

Let us start with the $\pi-$electron system of benzene. This six-orbital system contains carbon atoms of uniform valencies (equal to 2) and thereby it is among the simplest examples for illustration of our approach. Numbering of the relevant $2p_z$ AOs is shown in Fig.2a. Resonance parameters of all chemical bonds will be assumed to coincide with our energy unit. The principal matrices $\mathbf{B}$ and $\mathbf{BB}^+$ of benzene are then as follows

$$\mathbf{B}=\begin{vmatrix}1&0&1\\1&1&0\\0&1&1\end{vmatrix},\quad \mathbf{BB}^+=\begin{vmatrix}2&1&1\\1&2&1\\1&1&2\end{vmatrix}. \tag{26}$$

It is seen that diagonal elements of the IFAM $\mathbf{BB}^+$ coincide with 2 and thereby reflect the valencies of carbon atoms. Furthermore, these elements indicate three uniform allyl fragments to reveal themselves in benzene, namely C_6-C_1-C_4, C_4-C_2-C_5 and C_5-C_3-C_6. The off-diagonal elements of the same matrix, in turn, show all these fragments to be adjacent and thereby interacting one with another in addition [Besides, the graph underlying the matrix $\mathbf{BB}^+$ of Eq.(26) coincides with a symmetric triangle]. That is why eigenvalues of the AM of an isolated allyl ($\pm\sqrt{2}$) do not emerge in the spectrum of the total AM of benzene (Benzene can be embedded by ethene and, consequently, possesses an eigenvalue $\varepsilon = 1$ twice [16,17]. This embedding yields also an interpretation of one of the corresponding eigenvectors). On the other hand, use of GMOs of three allyl fragments (Section 2) provides us with interpretation of all HMOs of benzene.

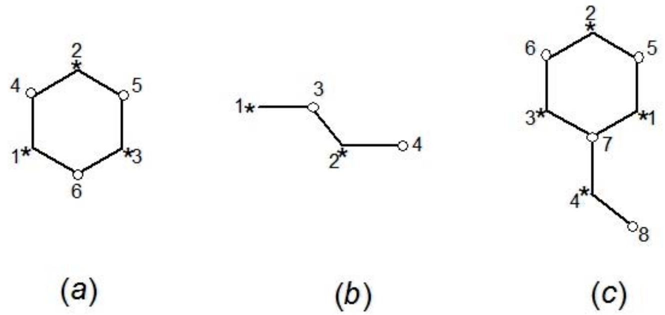


Figure 2. Numberings of $2p_z$ AOs of carbon atoms in benzene (a), butadiene (b) and styrene (c).

To verify the above predictions, let us now consider the MOs of benzene. The relevant three GBOs result from Eq.(15) and take the form

$$\begin{aligned}\varphi^*_{1(2)}(\varepsilon) &= \chi^*_1+\frac{1}{\varepsilon}(\chi^\circ_4+\chi^\circ_6),\\ \varphi^*_{2(2)}(\varepsilon) &= \chi^*_2+\frac{1}{\varepsilon}(\chi^\circ_4+\chi^\circ_5),\end{aligned} \tag{27}$$

$$\varphi^*_{3(2)}(\varepsilon) \;=\; \chi^*_3 + \frac{1}{\varepsilon}(\chi^\circ_5 + \chi^\circ_6).$$

Furthermore, substituting the eigenvalues (ε_m) and the coefficients of eigenvectors (U_{im}) of the matrix $\mathbf{BB}^+$ into Eq.(12) yields representations for individual MOs of benzene. As for instance, the lowest occupied MO ψ_1 takes the form of a symmetric linear combination of all GBOs, viz.

$$\psi_1 = \frac{1}{\sqrt{6}}[\varphi^*_{1(2)}(2) + \varphi^*_{2(2)}(2) + \varphi^*_{3(2)}(2)], \tag{28}$$

where the relevant eigenvalue coincides with 2. Meanwhile, the very adjusted GBOs of Eq.(28) may be examplified as follows

$$\varphi^*_{1(2)} = \chi^*_1 + \frac{1}{2}(\chi^\circ_4 + \chi^\circ_6) \tag{29}$$

and prove to be recognizable as the lowest MOs of allyl in spite of adjustment [The MO of allyl results from Eq.(23) after substituting the relations $B_{12} = B_{13} = 1$ and $\varepsilon = \sqrt{2}$ [46] and thereby contains the fraction $1/\sqrt{2}$ instead of $1/2$ of Eq.(29)]. To make sure that Eq.(28) really represents the lowest occupied MO of benzene, no more is required as to substitute GBOs like that of Eq.(29). We then obtain

$$\psi_1 = \frac{1}{\sqrt{6}}[\chi^*_1 + \frac{1}{2}(\chi^\circ_4 + \chi^\circ_6) + \chi^*_2 + \frac{1}{2}(\chi^\circ_4 + \chi^\circ_5) + \chi^*_3 + \frac{1}{2}(\chi^\circ_5 + \chi^\circ_6)]. \tag{30}$$

After summing up the increments of AOs of the second subset $\{\chi^\circ\}$, the MO ψ_1 takes the form of a normalized sum of all six AOs of benzene in accordance with the standard result [45–47].

Other MOs of benzene may be represented as linear combinations of adjusted GBOs analogously. Thus, the remaining occupied MOs (ψ_2 and ψ_3) characterized by the degenerate eigenvalue ($\varepsilon_2 = \varepsilon_3 = 1$) are expressible as follows

$$\psi_2 = \frac{1}{2\sqrt{3}}[2\varphi^*_{1(2)}(1) - \varphi^*_{2(2)}(1) - \varphi^*_{3(2)}(1)] \tag{31}$$

and

$$\psi_3 = \frac{1}{2}[\varphi^*_{2(2)}(1) - \varphi^*_{3(2)}(1)], \tag{32}$$

where GBOs are now of a simple constitution, e.g.

$$\varphi^*_{1(2)} = \chi^*_1 + \chi^\circ_4 + \chi^\circ_6. \tag{33}$$

These GBOs also closely resemble the lowest MO of allyl. Finally, substituting basis orbitals like that of Eq.(33) into Eqs.(31) and (32) allows us to derive the usual expressions for MOs ψ_2 and ψ_3. As for instance, from Eq.(31) we obtain

$$\psi_2 = \frac{1}{2\sqrt{3}}[2(\chi_1^* + \chi_4^\circ + \chi_6^\circ) - (\chi_2^* + \chi_4^\circ + \chi_5^\circ) - (\chi_3^* + \chi_5^\circ + \chi_6^\circ)] \tag{34}$$

and this formula easily yields the usual form of the respective HOMO of benzene. Thus, MOs of benzene are expressible as linear combinations of three uniform adjusted GBOs representing the respective allyl fragments in accordance with our expectation.

Comparison of expressions for GBOs underlying different MOs also is of interest. As is seen from Eqs.(29) and (33), more compact (less delocalized) GBOs refer to the lowest MO ψ_1 of benzene. Meanwhile, GBOs underlying the HOMOs ψ_2 and ψ_3 are relatively more delocalized and thereby overlap one with another more significantly. Thus, just the HOMOs may be concluded to be principally responsible for formation of the entire system of $\pi-$ electrons in benzene. Again, the lowest occupied MO ψ_1 may be considered as being delocalized mostly for symmetry reasons as it is usually the case with MOs consisting of inner shell (e.g. $1s$) AOs.

3.2. The butadiene molecule

The $\pi-$electron system of butadiene is a somewhat more involved example as compared to benzene in two respects: First, this chain-like compound contains carbon atoms of different valencies, namely both mono- and di-valent ones. Second, the initially-double (C=C) bonds and the only initially-single (C-C) bond generally are characterized by distinct resonance parameters. Just the latter circumstance allows us to study the dependence of the actual shapes of GBOs upon the extent of conjugation of C=C bonds.

Let the relevant $2p_z$ AOs to be enumerated as shown in Fig. 2b. Further, resonance parameters B_{13} and B_{24} referring to C_1=C_3 and C_2=C_4 bonds will coincide with our energy unit as previously (i.e. $B_{13} = B_{24} = 1$). Meanwhile, the same parameter of the intervening (C_2-C_3) bond will be assumed to differ from the former one and will be denoted by γ.

The analogue of Eq.(26) for butadiene takes the form

$$\mathbf{B} = \begin{vmatrix} 1 & 0 \\ \gamma & 1 \end{vmatrix}, \quad \mathbf{BB}^+ = \begin{vmatrix} 1 & \gamma \\ \gamma & 1+\gamma^2 \end{vmatrix}. \tag{35}$$

The above-exhibited IFAM $\mathbf{BB}^+$ generally contains different diagonal elements 1 and $1+\gamma^2$, respectively. This implies dissimilar elementary fragments to reveal themselves in the symmetric butadiene. Moreover, an analogous asymmetry embraces also the respective $\varepsilon-$dependent basis orbitals. Indeed, the first GBO of butadiene $\varphi^*_{1(1)}(\varepsilon)$ attached to the terminal AO χ^*_1 possesses an additional tail over a single neighboring AO χ°_3 only whatever the parameter γ. The relevant expression follows from Eq.(14), viz.

$$\varphi^*_{1(1)}(\varepsilon) = \chi^*_1 + \frac{1}{\varepsilon}\chi^\circ_3. \tag{36}$$

This orbital represents the ethene-like fragment $C_1{=}C_3$. Meanwhile, the second GBO $\varphi^*_{2(2)}(\varepsilon)$ generally embraces two neighboring AOs χ°_3 and χ°_4 along with the principal orbital χ^*_2. Thus, from Eq.(15) we obtain

$$\varphi^*_{2(1+\gamma^2)}(\varepsilon) = \chi^*_2 + \frac{1}{\varepsilon}(\chi^\circ_4 + \gamma\chi^\circ_3). \tag{37}$$

It is seen that the shape of this GBO depends on the relative value of the resonance parameter γ and thereby on the extent of conjugation of C=C bonds. Let us consider this point in a more detail.

Let us assume for a moment that $\gamma = 0$. The increment of the AO χ°_3 vanishes in the GBO of Eq.(37) in this case and the very basis function then acquires a two-center form like that of Eq.(36), viz.

$$\varphi^*_{2(1)}(\varepsilon) = \chi^*_2 + \frac{1}{\varepsilon}\chi^\circ_4. \tag{38}$$

Thus, the two GBOs of a non-conjugated butadiene become similar and these represent the uniform C=C bonds. Accordingly, the off-diagonal element of the IFAM $\mathbf{BB}^+$ of Eq.(35) vanishes, whereas the diagonal elements become uniform and equal to 1. This allows us to accept the equalities $\varepsilon_1 = \varepsilon_2 = 1$ and $\varepsilon_3 = \varepsilon_4 = -1$ for occupied and for vacant MOs, respectively. As a result, the GBOs $\varphi^*_{1(1)}(\varepsilon)$ and $\varphi^*_{2(1)}(\varepsilon)$ of Eqs.(36) and (38) turn into simple bonding and antibonding combinations of pairs of AOs of respective C=C bonds, as it is the case in the standard PMO theory. Finally, the coefficients U_{im} may be assumed to take the following values

$$U_{11} = U_{21} = U_{12} = \frac{1}{\sqrt{2}}, \quad U_{22} = -\frac{1}{\sqrt{2}}. \tag{39}$$

In summary, the occupied MOs of our non-conjugated butadiene (ψ_1 and ψ_2) are expressible as follows

$$\psi_1 = \frac{1}{2}[\varphi^*_{1(1)}(1) + \varphi^*_{2(1)}(1)] = \frac{1}{2}[\chi^*_1 + \chi^\circ_3 + \chi^*_2 + \chi^\circ_4] \tag{40}$$

and

$$\psi_2 = \frac{1}{2}[\varphi^*_{1(1)}(1) - \varphi^*_{2(1)}(1)] = \frac{1}{2}[\chi^*_1 + \chi^\circ_3 - \chi^*_2 - \chi^\circ_4]. \tag{41}$$

These expressions also coincide with those resulting from the usual PMO theory [18,47].

Let us assume now that a certain small resonance parameter γ arises in our molecule. Emergence of an additional tail over the AO χ_3° in the GBO of Eq.(37) then appears to be the first sign of the starting conjugation. It is also seen that conjugation of two initially-double (C=C) bonds is an unilateral effect in the present approach. Indeed, only one of the two participating C=C bonds (namely C_2=C_4) 'extends its basis orbital' towards the another one (C_1=C_3) and, consequently, the overall model of butadiene gradually becomes asymmetric. It deserves mentioning in this context that asymmetric models of symmetric compounds is no novelty in organic chemistry. To illustrate this statement, we may recall, for example, the Clar's aromatic sextets for benzenoids [48] [A single aromatic sextet and a diene-like subsystem are then distinguished in naphthalene]. Two distinct localized molecular orbitals for the butadiene itself [38] serve as another example of asymmetric models.

Let us turn finally to the case of a strongly- conjugated butadiene, where $\gamma = 1$. The GBO of Eq.(37) then takes the form

$$\varphi^*_{2(2)}(\varepsilon) = \chi_2^* + \frac{1}{\varepsilon}(\chi_3^\circ + \chi_4^\circ) \tag{42}$$

and resembles a GBO of benzene shown in Eq.(27). This basis orbital represents a symmetric allyle fragment (C_3-C_2-C_4) in accordance with the expectation. Diagonal IFAM elements also differ one from another most significantly in this case and coincide with 1 and 2 for the ethene and allyle fragments, respectively. An analogous large extent of asymmetry may be then expected to refer to coefficients U_{1m} and U_{2m} within linear combinations of Eq.(12) for MOs ψ_m. On the other hand, symmetry of the final MO LCAO coefficients also is among natural anticipations. This implies asymmetric combinations of two distinct GBOs of Eqs.(36) and (42) to yield symmetric MOs of the strongly-conjugated butadiene after all. Let us dwell now just on this point.

As with any Hermitian (symmetric) $2 \times 2-$dimensional matrix, the eigenvectors of the matrix $\mathbf{BB}^+$ of Eq.(35) are expressible in terms of only two coefficients a and b (see e.g. [49]). For $\gamma = 1$, we then obtain

$$U_{11} = U_{22} = a = 0.526, \quad U_{21} = -U_{12} = b = 0.851. \tag{43}$$

As a result, the lowest occupied MO of the strongly-conjugated butadiene takes the form

$$\psi_1 = \frac{1}{\sqrt{2}}\{a[\chi_1^* + \frac{1}{\varepsilon_1}\chi_3^\circ] + b[\chi_2^* + \frac{1}{\varepsilon_1}(\chi_3^\circ + \chi_4^\circ)]\}, \tag{44}$$

where $\varepsilon_1 = 1.618$. It is seen that the weight of the GBO of the allyle fragment exceeds that of ethene in this MO in accordance with the higher value of the second diagonal element of the IFAM vs. the first one. Moreover, the predominant GBO of allyle proves to be localized mostly on its principal AO χ_2^* in this MO, as it was the case in the lowest occupied MO of benzene. As a result, the relevant overlap integral of the two GBOs is insignificant. For the HOMO of the strongly- conjugated butadiene ψ_2, we accordingly obtain

$$\psi_2 = \frac{1}{\sqrt{2}}\{-b[\chi_1^* + \frac{1}{\varepsilon_2}\chi_3^\circ] + a[\chi_2^* + \frac{1}{\varepsilon_2}(\chi_3^\circ + \chi_4^\circ)]\}, \tag{45}$$

where $\varepsilon_2 = 0.618$. As a result, the overlap integrals of the two GBOs is increased in this frontier MO. Moreover, the increment of ethene exceeds that of allyle in this case. Nevertheless, it is the GBO of allyle that determines the actual ratios between contributions of AOs χ_2^* and χ_4° in both MOs. Furthermore, the following relations may be easily proven, viz.

$$\frac{b}{\varepsilon_1} = a, \qquad \frac{a+b}{\varepsilon_1} = b, \qquad \frac{a}{\varepsilon_2} = b, \qquad \frac{a-b}{\varepsilon_2} = -a \tag{46}$$

that ensure the appropriate symmetry properties of the final MO LCAO coefficients. It also deserves mentioning here that $a/\sqrt{2}$ and $b/\sqrt{2}$ coincide with 0.372 and 0.602, i.e. with the standard MO LCAO coefficients of the strongly- conjugated butadiene [46, 47]. It is seen, therefore, that MOs of butadiene generally take the form of asymmetric linear combinations of two distinct adjusted GBOs representing dissimilar elementary fragments of this hydrocarbon, namely the ethene fragment and the allyle one.

3.3. The styrene (phenylethene) molecule

An asymmetric model for a symmetric compound (butadiene) has been discussed in the previous subsection. Now, we will have to do with an opposite case, i.e. with a model of a higher extent of symmetry vs. that of the molecule concerned. The latter will coincide with styrene (phenylethene), the $2p_z$ AOs of which will be enumerated as shown in Fig.2c. Choice of the principal set of AOs (i.e. of the subset $\{\chi^*\}$) also proves to be essential in this case. Indeed, the styrene system is characterized by distinct matrices $\mathbf{BB}^+$ and $\mathbf{B}^+\mathbf{B}$ in contrast to benzene and butadiene. As a result, an interchange of subsets $\{\chi^*\}$ and $\{\chi^\circ\}$ yields an alternative set of elementary fragments for styrene. In the present subsection, we will dwell exclusively on the choice exhibited in Fig.2c, which ensures the most symmetric set of fragments. The relevant IFAM $\mathbf{BB}^+$ is then as follows

$$\mathbf{BB}^+ = \begin{vmatrix} 2 & 1 & 1 & 1 \\ 1 & 2 & 1 & 0 \\ 1 & 1 & 2 & 1 \\ 1 & 0 & 1 & 2 \end{vmatrix} \tag{47}$$

and contains uniform diagonal elements equal to 2 as it was the case with benzene [see Eq.(26) for comparison]. The off-diagonal elements of the same matrix coincide with 1 except for zero elements in the position 2,4(4,2). This implies four similar allyl fragments to reveal themselves in styrene, namely C_7-C_1-C_5, C_5-C_2-C_6, C_6-C_3-C_7 and C_7-C_4-C_8. Moreover, these fragments are adjacent except for the second and the fourth ones. [The respective interfragmental graph then consists of two similar triangles 123 and 134 possessing a common edge 1-3, and vertices 2 and 4 take symmetric positions with respect to this edge]. Accordingly, four uniform three-center GBOs like those exhibited previously (see Eqs.(27) and (42)) participate in the relevant combinations of Eq.(12). Let these GBOs to be denoted by $\varphi^*_{1(2)}(\varepsilon)$, $\varphi^*_{2(2)}(\varepsilon)$, $\varphi^*_{3(2)}(\varepsilon)$ and $\varphi^*_{4(2)}(\varepsilon)$, where the subscript i of basis orbitals $\varphi^*_{i(2)}(\varepsilon)$ refers to AOs of the first subset. On the whole, the new representation of styrene in terms of four allyl fragments and/or of the above-specified four GBOs proves to be more symmetric as compared to the parent set of $2p_z$ AOs. Analysis of MOs of styrene may be carried out as previously. The increasing extent of delocalization of GBOs and thereby of their overlaps when passing from the lowest occupied MO to the highest one also may be concluded on the basis of Eqs. (27) and (42). Thus, we will confine ourselves here to the relevant results:

The lowest occupied MO (ψ_1) is representable as a bonding combination of the four GBOs, viz.

$$\psi_1 = \frac{1}{2}\{c[\varphi^*_{1(2)}(\varepsilon_1) + \varphi^*_{3(2)}(\varepsilon_1)] + d[\varphi^*_{2(2)}(\varepsilon_1) + \varphi^*_{4(2)}(\varepsilon_1)]\}, \tag{48}$$

where $c = 0.788, d = 0.615$ and $\varepsilon_1 = 2.136$. The GBOs of Eq.(48) are localized mostly on their principal AOs in this case. After substituting the relevant expressions for GBOs and summing up similar increments, we obtain

$$\psi_1 = \frac{1}{2}[c(\chi^*_1 + \chi^*_3) + d(\chi^*_2 + \chi^*_4) + \frac{c+d}{\varepsilon_1}(\chi^\circ_5 + \chi^\circ_6) + \frac{2c+d}{\varepsilon_1}\chi^\circ_7 + \frac{d}{\varepsilon_1}\chi^\circ_8], \tag{49}$$

or

$$\psi_1 = \frac{1}{2}[0.788(\chi^*_1 + \chi^*_3) + 0.615(\chi^*_2 + \chi^*_4) + 0.657(\chi^\circ_5 + \chi^\circ_6) + 1.026\chi^\circ_7 + 0.288\chi^\circ_8], \tag{50}$$

i.e. the standard form of the MO concerned. Uniform increments of $2p_z$ AOs χ_2^* and χ_4^* peculiar to this MO may be traced back to the above-discussed symmetry properties of the interfragmental graph of styrene. Furthermore, the highest value of the contribution of the AO χ_7° to the same MO may be accounted for by three participating GBOs, namely $\varphi_{1(2)}^*(\varepsilon_1)$, $\varphi_{3(2)}^*(\varepsilon_1)$ and $\varphi_{4(2)}^*(\varepsilon_1)$. Analogously, the coefficient at the AO χ_8° takes the smallest value because of a single contributing GBO $\varphi_{4(2)}^*(\varepsilon_1)$. It also deserves adding here that the relative values of increments of AOs χ_4^* and χ_8° are determined exclusively by the shape of the GMO of the relevant allyle ($\varphi_{4(2)}^*(\varepsilon)$) at the appropriate one-electron energy ($\varepsilon = \varepsilon_1$).

The next occupied MO of styrene (ψ_2) takes the form of an antisymmetric combination of only two GBOs $\varphi_{2(2)}^*(\varepsilon)$ and $\varphi_{4(2)}^*(\varepsilon)$, i.e.

$$\psi_2 = \frac{1}{2}[\varphi_{2(2)}^*(\varepsilon_2) - \varphi_{4(2)}^*(\varepsilon_2)]. \tag{51}$$

Moreover, the respective two allyl fragments (C_5-C_2-C_6 and C_7-C_4-C_8) possess no common carbon atoms and, consequently, the GBOs of Eq.(51) do not overlap one with another. It is no surprise in this connection that these fragments coincide with those embedded in styrene [16,17]. Accordingly, eigenvalue (ε_2) equals to $\sqrt{2}$ and thereby coincides with that of the lowest occupied MO of an isolated allyl [46]. Accordingly, the GBOs of Eq.(51) also take the form of the above-specified MO. Finally, invoking the expressions concerned allows the MO ψ_2 of styrene to be represented as follows

$$\psi_2 = \frac{1}{2}[(\chi_2^* - \chi_4^*) + \frac{1}{\sqrt{2}}(\chi_5^\circ + \chi_6^\circ - \chi_7^\circ - \chi_8^\circ)]. \tag{52}$$

It also deserves mentioning that the relative values of the MO LCAO coefficients of Eq.(52) are determined by the shape of the lowest occupied MO of an isolated allyl in this case.

The third occupied MO of styrene (ψ_3) takes the form of an antisymmetric combination of the remaining two GBOs, viz.

$$\psi_3 = \frac{1}{2}[\varphi_{1(2)}^*(\varepsilon_3) - \varphi_{3(2)}^*(\varepsilon_3)], \tag{53}$$

where $\varepsilon_3 = 1$. Equation (53) easily yields the following expression

$$\psi_3 = \frac{1}{2}[\chi_1^* + \chi_5^\circ - \chi_3^* - \chi_6^\circ], \tag{54}$$

which coincides with the standard MO LCAO form for the HOMO of benzene following from Eq.(32). It is evident that the 'external' allyle fragment C_7-C_4-C_8 does not participate in the formation of the MO ψ_3. That is why both the shape and the one-electron energy of this MO are transferable from benzene to styrene.

Finally, the HOMO of styrene (ψ_4) takes the form

$$\psi_4 = \frac{1}{2}\{d[\varphi^*_{1(2)}(\varepsilon_4) + \varphi^*_{3(2)}(\varepsilon_4)] - c[\varphi^*_{2(2)}(\varepsilon_4) + \varphi^*_{4(2)}(\varepsilon_4)]\}, \tag{55}$$

where coefficients c and d coincide with those of Eq.(48) and $\varepsilon_4 = 0.662$. Moreover, the adjacent GBOs of Eq.(55) overlap one with another most significantly. Thus, the MO ψ_4 may be concluded to be principally responsible for formation of the entire system of $\pi-$electrons in styrene. After substituting the relevant formulae for GBOs, we obtain

$$\psi_4 = \frac{1}{2}[0.615(\chi^*_1 + \chi^*_3) - 0.788(\chi^*_2 + \chi^*_4) - 0.261(\chi^\circ_5 + \chi^\circ_6) + 0.668\chi^\circ_7 - 1.190\chi^\circ_8], \tag{56}$$

The smallest absolute values of coefficients at AOs χ°_5 and χ°_6 in this MO may be accounted for by opposite signs of increments of participating GBOs in the linear combination of Eq.(55). In addition, the relative absolute values of contributions of AOs χ^*_4 and χ°_8 are determined exclusively by the shape of the GBO $\varphi^*_{4(2)}(\varepsilon_4)$ of the allyl fragment C_7-C_4-C_8 as it was the case with the MO ψ_1. Thus, the expectation about four similar allyl fragments revealing themselves in styrene is now supported by constitutions of the MOs of this AH.

4. Conclusions

The principal methodological achievements of the present study are as follows: i) A unified and energy-parameter-dependent representation is proposed for the whole set of MOs of any AH, viz. the so-called generalized MO (GMO); ii) GMOs of all AHs are shown to take a common form in the framework of the HMO theory; iii) The above-specified common GMO of AHs is represented as a linear combination of GMOs of elementary fragments contained within particular systems as shown in the principal expression of Eq.(10); iv) Individual MOs of a certain AH are demonstrated to follow from the above-mentioned general formula after substituting appropriate eigenvalues for the unspecified energy parameter.

As a result of application of the above-outlined methodology, the usual MOs (HMOs) of AHs prove to be expressed as linear combinations of adjusted MOs of elementary fragments. No small value condition is invoked in this approach for interfragmental interactions vs. intrafragmental ones. Moreover, the newly-derived expressions for HMOs of AHs turn into those of the PMO theory after imposing the above-specified condition. Thus, we have to do here with a generalization of the perturbation-theory-based expressions for MOs to the case of arbitrary values of intra- and interfragmental interactions.

Implications of the above-summarized achievements are as follows:

1. Three types of elementary fragments (namely, ethenes, allyls and trimethylenemethanes) are shown to reveal themselves in AHs. Moreover, the so-called adjacent fragments may be distinguished that always embrace a single common carbon atom. Thus, both elementary fragments and interfragmental bonds may be concluded to be uniform in all AHs. The overall situation here closely resembles that of alkanes, where five CH_n groups (n=0,1,2,3,4) were shown previously [40, 41] to play the role of elementary fragments. On this basis, the alternant hydrocarbons also may be regarded as a class of chemical compounds.

2. A new insight is given into the nature of the overall chemical bonding in AHs. Thus, the frontier MOs (especially the highest-occupied MO (HOMO)) are shown to consist of relatively extended and strongly-overlapping FOs and thereby to be responsible for the formation of the entire system of $\pi-$electrons in AHs. Meanwhile, the remaining MOs (including the lowest occupied ones) are made up of more compact and weakly-overlapping FOs, as it is the case with inner shell orbitals in general.

3. A new mental image is suggested for conjugation of initially-double (C=C) bonds. For example, formation of a strongly-conjugated butadiene system is shown to be accompanied by conversion of the usual two-center basis orbital of a single C=C bond (cf. the bond orbital of the PMO theory) into a three-center basis function, embracing also the adjacent carbon atom of the opposite C=C bond.

4. Basis orbitals of elementary fragments contained within the linear combinations for MOs of AHs are shown to be characterized by numerous common properties. In particular, orbitals of a bonding nature underly the expressions for occupied (bonding) MOs and vice versa. Moreover, a simple dependence is established between the shape of a certain basis orbital and the valency of the carbon atom the given orbital is attached to. These properties along with the very representability of MOs of AHs as linear combinations of those of elementary fragments replenish the overall system of general rules governing the electronic structures of these hydrocarbons.

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