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Spectral Meaning of Coefficients Within the Adjacency Matrix Eigenfunctions of Chemical Graphs of Alkanes

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Adjacency matrix (***AM***) eigenfunctions of isospectral chemical graphs of alkanes (C_nH_{2n+2}), in terms of atoms (G^{a}_{Ch}) and bonds (G^{b}_{Ch}), have been studied. The two eigenfunctions Φ_i and Ψ_i of the ***AM***s $\boldsymbol{A}(G^{a}_{Ch})$ and $\boldsymbol{A}(G^{b}_{Ch})$ referring to the same eigenvalue ε_i have been expressed in terms of a common set of n principal coefficients, each associated with a definite carbon atom. As a result, functions Φ_i and Ψ_i proved to be of common global constitution. Interrelations between the local structures of functions Φ_i and Ψ_i have been also established. These results have been used to substantiate a hypothesis concerning the spectral meaning of coefficients within eigenfuctions Φ_i of matrices $\boldsymbol{A}(G^{a}_{Ch})$. These coefficients are assumed to determine the extents of participation of individual atoms in the ionization of a molecule from the energy level ε_i, although no direct link seems to be present between the ***AM***s $\boldsymbol{A}(G^{a}_{Ch})$ and the respective hamiltonian matrices.

INTRODUCTION

Spectral characteristics of molecules are commonly expected to be determined by the electronic structure of the given system defined in terms of orbitals and their interactions. In this connection, quantum-mechanical methods are usually used for interpretation of molecular spectra.[1]

In the case of photoelectron spectra it is the canonical MO method and the Koopmans theorem that form the basis of most theoretical investigations.[1–3] According to this theorem, the ionization potentials of molecules are related to eigenvalues of the respective one-electron Hamiltonian (Fockian) matrices. Then, the coefficients of the eigenfunctions of these matrices determine the relative extents of participation of separate basis orbitals in ionization of the molecule from the respective energy level ε_i.

An alternative definition of molecular structure is used in classical chemistry, which is based on both types of atoms involved within the given compound and the way the atoms are bound together.[4] It is just these aspects of the structure that are represented in chemical formulas. It is noteworthy that no internal structure of atoms is considered explicitly in classical chemistry.

Chemical formulas form the basis of clasification for the immense amount of information both on the observed properties of isolated molecules[5,6] and on chemical reactions.[7] In this context, studies of relations between spectral characteristics of molecules and peculiarities of their chemical formulas are of interest.

The π-electron subspectra of conjugated hydrocarbons seem to be the only example when the relation to chemical structure of the respective C-skeleton proves to be rather simple.[8] Indeed, one-to-one correspondence between $2p_z$ AOs and carbon atoms takes place in this case and the relevant Hueckel Hamiltonian matrices $\boldsymbol{H}$ linearly depend on the adjacency matrices (***AM***s) $\boldsymbol{A}(\mathrm{G})$ of graphs G, the latter describing the respective C-skeletons, *i.e.*

$$\boldsymbol{H} = \alpha \boldsymbol{I} + \beta \boldsymbol{A}(\mathrm{G}) \tag{1}$$

where $\boldsymbol{I}$ is the unit matrix and α and β are energy constants equal to the average Coulomb and resonance integrals, respectively. As a result, coefficients of eigenfunctions of the ***AM***s $\boldsymbol{A}(\mathrm{G})$ describe the relative extents of participation both of individual $2p_z$ AOs and of separate carbon atoms in ionization of the molecule.

The problem, however, becomes more involved when turning to other types of molecules. This may be illustrated by the results of Ref. 9, where the high-energy bands (HEB) in the photoelectron spectra of alkanes[10] located in the range 17–26 eV have been related to centain subspectra of chemical graphs. Indeed, the graphs of alkanes determining the Hamiltonian matrices used in Ref. 9 do not coincide with the usual chemical graphs in terms of atoms. Let us discuss this point in more detail.

The simplest one-parameter Hueckel type Hamiltonian matrix $\boldsymbol{H}$ in the basis of bonding bond orbitals (BOs) has been used to describe the HEBs of alkanes.[9,11,12] The mean value of interactions (resonanace integrals) between BOs of the nearest (geminal) bonds plays the role of the only parameter β in this case, and the average value of the BO energy stands for parameter α. As a result, a linear dependence, like that shown in Eq. (1), takes place between matrices $\boldsymbol{H}$ and the respective ***AM***s $\boldsymbol{A}(\mathrm{G_H})$. Graphs $\mathrm{G_H}$ (Figure 1) have been named Hamiltonian matrix graphs.[9]

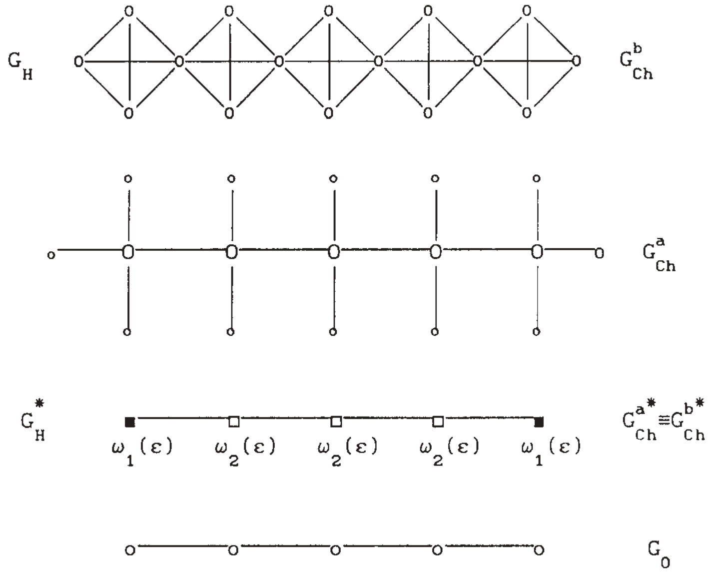

Figure 1. The Hamiltonian matrix graph of *n*-pentane (G_H), the relevant chemical graphs in terms of atoms (G^a_{Ch}) and bonds (G^b_{Ch}), as well as their common reduced form denoted by an asterisk. The simple chain (G_0) is also shown.

Since one-to-one correspondence between BOs and chemical bonds takes place in alkanes, matrix $\boldsymbol{A}(G_H)$ represents the adjacencies of both BOs and bonds. To distinguish these alternatives, chemical graphs in terms of bonds (G^b_{Ch}) formally coinciding with respective graphs G_H have been introduced.[9] Then, coefficients C_{ki} of eigenfunctions Ψ_i of the ***AM***s $\boldsymbol{A}(G_H) \equiv \boldsymbol{A}(G^b_{Ch})$ determine the extents of participation of separate BOs(bonds) in ionization of the molecule.

The relation of graphs G^b_{Ch} to the usual graphs of alkanes in terms of atoms (G^a_{Ch}) (Figure 1) has been established[9] by invoking the so-called line graphs.[13] It has been also shown that the two graphs G^a_{Ch} and G^b_{Ch} are isospectral (except for an additional system-structure-independent eigenvalue of the ***AM***s $\boldsymbol{A}(G^a_{Ch})$ *vs.* $\boldsymbol{A}(G^b_{Ch})$) if the appropriate diagonal elements of the ***AM*** $\boldsymbol{A}(G^a_{Ch})$ are used. These elements proved to be equal to 0 and 3 for mono- and four-valent vertices of graphs G^a_{Ch} associated with hydrogen and carbon atoms, respectively.

However, no direct link seems to be present between the ***AM***s $\boldsymbol{A}(G^a_{Ch})$ and the respective matrices $\boldsymbol{H}$ largely because of their different dimensions. In this connection, establishing the relation between atoms underlying the ***AM***s $\boldsymbol{A}(G^a_{Ch})$ and AOs also is faced with difficulties.

Nevertheless, coincidence of the system-structure-dependent subspectra of graphs $G_H \equiv G^b_{Ch}$ and G^a_{Ch} allowed us to relate the HEBs of alkanes to the respective subspectra of ***AM***s $\boldsymbol{A}(\mathrm{G}^{\mathrm{a}}_{\mathrm{Ch}})$. Moreover, peculiarities of the HEBs have been successfully interpreted in terms of those of graphs $\mathrm{G}^{\mathrm{a}}_{\mathrm{Ch}}$.[9] In this context, the question arises about the meaning of coefficients D_{mi} of eigenfunctions Ψ_i of the ***AM***s $\boldsymbol{A}(\mathrm{G}^{\mathrm{a}}_{\mathrm{Ch}})$.

It is quite natural to assume that these coefficients determine the extents of participation of separate atoms in ionization of the molecule. For the above-discussed reasons, however, such an assumption is not trivial and it should be subtantiated. An indirect way of doing this seems to be the most promising one.

Thus, let us suppose that the suggested interpretation is adequate. Then, certain interrelations between the sets of coefficients $\{C_{ki}\}$ and $\{D_{mi}\}$ and thereby between the eigenfunctions Ψ_i and Φ_i are feasible. Furthermore, relations of both local and global nature may be expected here.

Indeed, participation of certain chemical bond in ionization of the molecule is likely to be directly related to those of the two involved atoms and *vice versa*. This implies interdependences between local structures of eigenfunctions Ψ_i and Φ_i.

Furthermore, the extents of participation of separate $CH_2(CH_3)$-groups in ionization of the molecule may be expected to be proportional to those of respective full subgraphs (tetrahedrons) of graphs $\mathrm{G}^{\mathrm{b}}_{\mathrm{Ch}}$, and this is due to the one-to-one correspondence between these elementary units. Accordingly, some common global structure might be inherent in eigenfunctions Ψ_i and Φ_i of the ***AM***s $\boldsymbol{A}(\mathrm{G_H}) \equiv \boldsymbol{A}(\mathrm{G}^{\mathrm{b}}_{\mathrm{Ch}})$ and $\boldsymbol{A}(\mathrm{G}^{\mathrm{a}}_{\mathrm{Ch}})$.

Therefore, revealing of the above-anticipated interrelations between the eigenfunction of the ***AM***s $\boldsymbol{A}(\mathrm{G}^{\mathrm{a}}_{\mathrm{Ch}})$ and $\boldsymbol{A}(\mathrm{G}^{\mathrm{b}}_{\mathrm{Ch}})$ of chemical graphs of alkanes is the main aim of this paper.

To compare the global structures of eigenfunctions, reduction of secular equations for the ***AM***s $\boldsymbol{A}(\mathrm{G}^{\mathrm{a}}_{\mathrm{Ch}})$ and $\boldsymbol{A}(\mathrm{G}^{\mathrm{b}}_{\mathrm{Ch}})$ of alkanes (C_nH_{2n+2}) into n-dimensional effective problems[9,14–16] will be used. The most general way of the procedure analogous to that suggested in Ref. 15 is described in Section 2. Section 3 is devoted to interrelations between the eigenfunctions being sought. Particular graphs are studied in Section 4.

THE GENERAL WAY OF REDUCING THE SECULAR PROBLEMS FOR THE AMs OF CHEMICAL GRAPHS OF ALKANES (C_nH_{2n+2}) INTO n-DIMENSIONAL PROBLEMS

Let us consider the eigenvalue equations

$$\boldsymbol{A}(\mathrm{G_H})\boldsymbol{C} = \varepsilon \mathrm{C}, \qquad \boldsymbol{A}(\mathrm{G}^{\mathrm{b}}_{\mathrm{Ch}})\boldsymbol{C} = \varepsilon \boldsymbol{C} \tag{2}$$

$$\boldsymbol{A}(\mathrm{G}^{\mathrm{a}}_{\mathrm{Ch}})\boldsymbol{D} = \varepsilon \boldsymbol{D} \tag{3}$$

where the two relations of Eq. (2) are identical. Moreover, the same designation ε is used in Eqs. (2) and (3) in connection with isospectrality of graphs G^{a}_{Ch} and G^{b}_{Ch} Ref. 9 (Section 1).

Let us start with reduction of the eigenvalue problem of Eq. (2). The most general procedure essentially consists in forming the variable $Z = 2^{1/2}(C_a+C_b+C_c+C_d)/\varepsilon$ for each subgraph of graphs $G_H \equiv G^{b}_{Ch}$ (tetrahedron) containing vertices a, b, c and d and in formulating the system of effective equations for n variables $\{Z_k\}$ $k = 1, 2... n$. In contrast to the procedure of Ref. 9, turning to variables $\{Z_k\}$ may be carried out for any type of graphs $G_H \equiv G^{b}_{Ch}$.

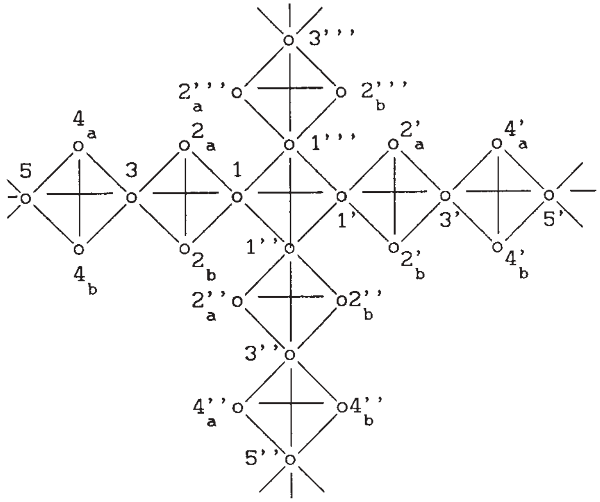

Figure 2. Numbering of vertices in a branched graph G^{b}_{Ch}.

To demonstrate this, let us start with a branched fragment of our graphs shown in Figure 2. Let C_{1j} ($j = 1, 2, 3, 4$) stand for C_1, $C_{1'}$, $C_{1''}$ and $C_{1'''}$, whereas C_{2j} will designate C_2, $C_{2'}$, $C_{2''}$ and $C_{2'''}$, *etc.* The equality $C_{pja} = C_{pjb} \equiv C_{pj}$ for any even p and thereby for all pairs of three-valent vertices of graphs $G_H \equiv G^{b}_{Ch}$ will be accepted. This requirement is equivalent to elimination of the subspace which is antisymmetric with respect to transposition $a \Leftrightarrow b$.[9] Like in previous contributions,[9,14–16] the diagonal elements of the initial ***AM***s $\boldsymbol{A}(G^{b}_{Ch})$ and $\boldsymbol{A}(G_H)$ will be taken equal to 1. Let us define variables $\{Z_k\}$ as follows

$$Z_1 = (2^{1/2}/\varepsilon)\sum_{j=1}^{4} C_{1j}; \qquad Z_{2j} = (2^{1/2}/\varepsilon)\ [C_{1j} + 2C_{2j} + C_{3j}];$$
$$Z_{4j} = (2^{1/2}/\varepsilon)[C_{3j} + 2C_{4j} + C_{5j}],\ etc. \tag{4}$$

Taking the four secular equations for vertices 1j (j = 1, 2, 3, 4), and summing them up over j, we obtain

$$\sum_{j=1}^{4} \mathrm{C}_{3j} + 2\sum_{j=1}^{4} C_{2j} + 4\sum_{j=1}^{4} C_{1j} = \varepsilon\sum_{j=1}^{4} C_{1j} \,. \tag{5}$$

After employment of Eq. (4), the effective equation for variable Z_1 results from Eq. (5), *i.e.*

$$\sum_{j=1}^{4} Z_{2j} + 3Z_1 = \varepsilon Z_1 \,. \tag{6}$$

The case of branching at the tertiary carbon atom follows from the above-outlined procedure if we assume that

$$\mathrm{C}_{2'''} = \mathrm{C}_{3'''} = \ldots = 0 \,. \tag{7}$$

Indeed, the initial secular equation for the three-valent vertex 1''' yields the equality

$$\mathrm{C}_{1'''} = 2^{-1/2} Z_1 \tag{8}$$

which, in turn, may be substituted into the relevant form of Eq. (6), *viz.*

$$\sum_{j=1}^{3} Z_{2j} + (2^{1/2}/\varepsilon)\mathrm{C}_{1'''} + 3Z_1 = \varepsilon \mathrm{Z}_1 \,. \tag{9}$$

As a result, the respective effective secular equation follows, *i.e.*

$$\sum_{j=1}^{3} Z_{2j} + (3 + 1/\varepsilon)Z_1 = \varepsilon \mathrm{Z}_1 \,. \tag{10}$$

If the requirement that

$$\mathrm{C}_{2''} = \mathrm{C}_{3''} = \ldots = 0 \tag{11}$$

is added to Eq. (7), we analogously obtain

$$\sum_{j=1}^{2} Z_{2j} + (3 + 2/\varepsilon)Z_1 = \varepsilon \mathrm{Z}_1 \tag{12}$$

and this effective equation evidently corresponds to an internal full subgraph within graphs $\mathrm{G_H} \equiv \mathrm{G}^{\mathrm{b}}_{\mathrm{Ch}}$ of normal alkanes. It may be easily proven that similar equations refer to full subgraphs within any non-branched fragment of graphs $\mathrm{G}^{\mathrm{b}}_{\mathrm{Ch}} \equiv \mathrm{G_H}$. For a terminal subgraph, it follows that

$$Z_2 + (3 + 3/\varepsilon)Z_1 = \varepsilon \mathrm{Z}_1 \tag{13}$$

whilst for methane, we obtain

$$(3 + 4/\varepsilon)Z_1 = \varepsilon Z_1 \ . \tag{14}$$

The n equations like those shown in Eqs. (6), (10), (12)–(14) for each particular graph $\mathrm{G_H} \equiv \mathrm{G}^{\mathrm{b}}_{\mathrm{Ch}}$ may be collected into an effective secular problem for the respective n-dimensional reduced ***AM*** $\boldsymbol{A}(\mathrm{G}^{*}_{\mathrm{H}}) \equiv \boldsymbol{A}(\mathrm{G}^{\mathrm{b}*}_{\mathrm{Ch}})$. The reformulated secular problems of Eq. (2) become

$$\boldsymbol{A}(\mathrm{G}^{*}{}_{\mathrm{H}})\boldsymbol{Z} = \varepsilon \boldsymbol{Z}, \qquad \boldsymbol{A}(\mathrm{G}^{\mathrm{b}*}_{\mathrm{Ch}})\boldsymbol{Z} = \varepsilon \boldsymbol{Z} \tag{15}$$

where $\boldsymbol{Z}$ is an n-dimensional column-matrix consisting of coefficients $\{Z_{\mathrm{k}}\}$, and $\mathrm{G}^{*}_{\mathrm{H}} \equiv \mathrm{G}^{\mathrm{b}*}_{\mathrm{Ch}}$ are the respective reduced graphs containing n vertices (Figure 1).

From the structure of the new equations in terms of n variables $\{Z_k\}$, it follows that the reduced matrices $\mathrm{A}(\mathrm{G}^{*}_{\mathrm{H}}) \equiv \mathrm{A}(\mathrm{G}^{\mathrm{b}*}_{\mathrm{Ch}})$ contain non-zero off-diagonal elements equal to 1 in positions $(k, k{+}1)$ corresponding to the next-nearest pairs of vertices. As a result, the arrangement of edges within the reduced graphs $\mathrm{G}^{*}_{\mathrm{H}} \equiv \mathrm{G}^{\mathrm{b}*}_{\mathrm{Ch}}$ coincides with that of the simple chain G_0 (Figure 1).

Again, the diagonal elements $\omega_v(\varepsilon)$ of the ***AM***s $\boldsymbol{A}(\mathrm{G}^{*}_{\mathrm{H}}) \equiv \boldsymbol{A}(\mathrm{G}^{\mathrm{b}*}_{\mathrm{Ch}})$ depend on both the energy variable ε and valency v of the respective vertex of the reduced graph

$$\omega_v(\varepsilon) = 3 + (4 - v)/\varepsilon \ . \tag{16}$$

Equation (4) contains expressions for $\{Z_k\}$ in terms of $\{C_k\}$. On the other hand, the initial set of coefficients $\{C_k\}$ may be expressed in terms of new variables $\{Z_k\}$. To this end, let us start with the initial secular equation for vertex $1j$ (Figure 2)

$$C_{3j} + 2C_{2j} + \sum_{m=1}^{4} C_{1m} = \varepsilon \mathrm{C}_{1j} \tag{17}$$

and invoke the definitions of Z_1 and Z_{2j} of Eq. (4). After substituting the latter into Eq. (17), we obtain

$$C_{1j} = 2^{-1/2}\,\varepsilon(Z_1 + Z_{2j})/(\varepsilon + 1) \ . \tag{18}$$

Analogously, from the initial secular equation for C_{2j}, the expression for the latter is

$$C_{2j} = 2^{-1/2}\,Z_{2j} \ . \tag{19}$$

It may be easily proven that

$$C_{3j} = 2^{-1/2}\,\varepsilon(Z_{2j} + Z_{4j})/(\varepsilon + 1);\ C_{4j}{=}2^{-1/2}Z_{4j},\ \mathit{etc.} \tag{20}$$

for the remaining part of graph $G_H \equiv C^{b}_{Ch}$ shown in Figure 2. Moreover, similar relations may be obtained for any three- (see Eq. (8)) and for any four-valent vertex of graphs G^{b}_{Ch}, *i.e.*

$$C_{(3)k} = 2^{-1/2} Z_k, \qquad C_{(6)k,k+1} = 2^{-1/2}\, \varepsilon (Z_k + Z_{k+1})/(\varepsilon + 1) \tag{21}$$

where $(3)k$ stands for a three-valent vertex belonging to the k-th tetrahedron and $(6)k$, $k+1$ describes a six-valent vertex belonging to both the k-th and $(k+1)$-th tetrahedrons.

Given that the k-th tetrahedron contains two three-valent vertices, the equality $C_{(3)ka} = C_{(3)kb}$ may be used and we then obtain

$$Z_{(3)k} = 2^{1/2} C_{(3)k} = 2^{-1/2}\, (C_{(3)ka} + C_{(3)kb})\ . \tag{22}$$

Therefore, the above-outlined reduction may be considered as a generalization of that developed in Ref. 9 for normal alkanes where turning to normalized sums of coefficients referring to BOs of geminal pairs of C–H bonds was used.

Let us discuss now the secular problem of Eq. (3). This problem may be easily reduced into an n-dimensional one.[9] To do this, it is no more required to eliminate coefficients $\{D_{(1)k}\}$ at the mono-valent vertices of graphs G^{a}_{Ch} (hydrogen atoms) from the initial secular problem of Eq. (3). Because of zero values of the diagonal elements of matrix $A(G^{a}_{Ch})$ corresponding to hydrogen atoms, expressions of the form

$$D_{(1)k} = D_{(4)k}/\varepsilon \tag{23}$$

are to be substituted into equations for the four-valent vertices and an n-dimensional problem

$$\boldsymbol{A}(G^{a*}_{Ch}) \boldsymbol{D}_{(4)} = \varepsilon \boldsymbol{D}_{(4)} \tag{24}$$

results, where $\boldsymbol{D}_{(4)}$ is an n-dimensional column-matrix containing the n coefficients of Eq. (3) referring to four-valent vertices (carbon atoms). Moreover, the elements of the new matrix $\boldsymbol{A}(G^{a*}_{Ch})$ coincide with those of $\boldsymbol{A}(G^{b*}_{Ch})$ of Eq. (16). This conclusion, in turn, allows us to accept the equalities

$$D_{(4)i} = Z_i \quad \text{and} \quad D_{(4)ki} = Z_{ki} \tag{25}$$

for any eigenvalue ε_i. The principal result of Eq. (25) forms the basis of comparative analysis of eigenfunctions Φ_i and Ψ_i.

INTERRELATIONS BETWEEN EIGENFUNCTIONS Φ_i AND Ψ_i, AND INTERPRETATION OF THEIR COEFFICIENTS

Let us start with eigenfunctions of the AMs of graphs $G_H \equiv G^{b}_{Ch}$. In the general case shown in Figure 2, an eigenfunction Ψ may be written in the form

$$\Psi = \sum_{j=1}^{4} \, [C_{1j}\chi_{j1} + C_{2j}(\chi_{j2a}+\chi_{j2b}) + C_{3j}\chi_{j3} + C_{4j}(\chi_{j4a} + \chi_{j4b}) + \ldots] \qquad (26)$$

where χ stand for bond orbitals. If we substitute the expressions of Eq. (21) and collect terms containing particular variables Z_k, the eigenfunction Ψ_i corresponding to the eigenvalue ε_i may be represented as a linear combination of n ε_i-dependent local-structure-determined basis orbitals $\eta_k(\varepsilon_i)$ with coefficients Z_{ki} resulting from Eq. (15), *i.e.*

$$\Psi_i = \sum_{k=1}^{n} \, \eta_k(\varepsilon_i)\, Z_{ki} \ . \qquad (27)$$

For the branched graph of Figure 2, the following expressions for orbitals $\eta_k(\varepsilon)$ result

$$\eta_{(4)1}(\varepsilon) = [2^{-1/2}\,\varepsilon/(\varepsilon + 1)] \sum_{j=1}^{4} \chi_{j1} \qquad (28)$$

and

$$\eta_{(2)2j}(\varepsilon) \ = \ 2^{-1/2} \ \{(\chi_{j2a} + \chi_{j2b}) + [\varepsilon/(\varepsilon + 1)](\chi_{j1} + \chi_{j3})\} \ . \qquad (29)$$

The orbitals of Eqs. (28) and (29) refer to variables Z_1 and Z_{2j} and thereby to the four-and two-valent vertices of the reduced graphs. A function like that of Eq. (29) has been obtained in Ref. 9 for normal alkanes. Analogously, the orbitals

$$\eta_{(3)1}(\varepsilon) \ = \ 2^{-1/2} \ \{[\varepsilon/(\varepsilon + 1)]\sum_{j=1}^{3} \ \chi_{j1} + \chi_{1'''}\} \qquad (30)$$

$$\eta_{(1)1}(\varepsilon) \ = \ 2^{-1/2} \ \{[\varepsilon/(\varepsilon + 1)] \ \chi_1 + \chi_{1'} + \chi_{1''} + \chi_{1'''}\} \qquad (31)$$

result instead of Eq. (28) for tertiary and terminal carbon atoms, respectively, and thereby for three- and mono-valent vertices of reduced graphs. It is seen that the orbitals defined by Eqs. (28)–(31) are localized on the four BOs of the respective full subgraph (tetrahedron) only.

The procedure of reducing graph G^{a}_{Ch} into G^{a*}_{Ch} shows that the eigenfunction Φ_i of the ***AM*** $\boldsymbol{A}(G^{a}_{Ch})$ may be represented in the form

$$\Phi_i = \sum_{k=1}^{n} \, \mu_k(\varepsilon_i)\, D_{(4)ki} \qquad (32)$$

where

$$\mu_k(\varepsilon) = \lambda_{(4)k} + (1/\varepsilon) \sum_{m=1}^{r} \lambda_{(1)km} \tag{33}$$

are ε-dependent basis orbitals, each of them pertinent to a definite CH_r-group. Unspecified basis functions corresponding to carbon and hydrogen atoms ($\lambda_{(4)k}$ and $\lambda_{(1)km}$) are introduced in Eq. (33). The sum of Eq. (33) embraces the hydrogen atoms adjacent to the k-th carbon atom.

Comparing Eqs. (27) and (32) and taking into account the equality of Eq. (25) shows that eigenfunctions Ψ_i and Φ_i referring to eigenvalue ε_i contain the same n coefficients $Z_{ki} \equiv D_{(4)ki}$. This set of n principal coefficients, in turn, may be regarded as describing the global structure of an eigenfunction. Hence, functions Ψ_i and Φ_i may be taken to be of the common global structure.

Let us turn now to the local structures of eigenfunctions Ψ_i and Φ_i.

Equations (21) and (23) along with Eq. (25) allow us to conclude that the coefficients of both matrices C and D of the initial secular problems of Eqs. (2) and (3) have been actually expressed in terms of the same n principal coefficients $\{D_{(4)k}\}$, $k = 1, 2...n$ at the carbon atoms within the usual chemical graphs G^{a}_{Ch}. Moreover, these expressions contain relations of local nature. Thus, the coefficient $D_{(1)k}$ referring to a mono-valent vertex of a graph G^{a}_{Ch} (a hydrogen atom) attached to the k-th four-valent vertex (k-th carbon atom) is proportional to the only coefficient $D_{(4)k}$ as shown in Eq. (23). On the other hand, it follows from Eq. (21) and the equality of Eq. (25) that any coefficient $C_{(3)k}$ corresponding to a three-valent vertex of graphs $G^{b}_{Ch} \equiv G_H$ (to a C–H bond) is proportional to the respective coefficient $D_{(4)k}$ at the carbon atom of this bond, whereas the coefficient $C_{(6)k,k+1}$ referring to a six-valent vertex of graphs $G^{b}_{Ch} \equiv G_H$ (to a C–C bond) is proportional to the sum of coefficients $D_{(4)k}$ and $D_{(4)k+1}$ at the two carbon atoms making up this bond. The above-discussed proportionalities are displayed in Figure 3.

Therefore, the local structures of eigenfunctions Ψ_i and Φ_i referring to the same eigenvalue ε_i are interrelated.

Let us suppose now that coefficients $D_{(1)ki}$ and $D_{(4)ki}$ of Eq. (3) determine the relative extents of participation of hydrogen and carbon atoms, respectively, in ionization of the molecule from the energy level ε_i. Then, the above results imply that the extent of participation of any bond in ionization of the molecule is directly related to those of two involved atoms. Alternatively, the extent of participation of an atom appears to be determined by those of bonds attached to this atom.

Indeed, it follows from the definition of coefficients $\{Z_k\}$ given by Eq. (4) and coincidence between Z_k and $D_{(4)k}$ that the extent of participation of a carbon atom in ionization of the molecule is proportional to the sum of amplitudes determining the extents of participation of the four attached bonds

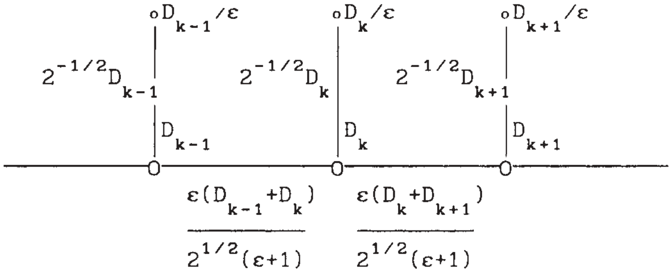

Figure 3. Amplitudes associated with the relative extents of participation of separate atoms and bonds of an alkane in ionization of the molecule (D_k stands for $D_{(4)k}$ for any k).

(Contributions of atoms and bonds should be defined as squares of the relevant coefficients. In this context, interrelations between amplitudes associated with the extents of participation and not between the extents themselves are noteworthy). Again, the extent of participation of a hydrogen atom is proportional to that of the respective H–C bond in accordance with the expectation.

Furthermore, the above-mentioned proportionalities contain the same factors for both carbon and hydrogen atoms. Thus, let $R_{(4)ki}$ stand for the sum of amplitudes referring to the four bonds attached to the k-th carbon atom. Then, from Eqs. (4) and (25) it follows that

$$R_{(4)ki} = 2^{-1/2}\,\varepsilon_i D_{(4)ki} \tag{34}$$

whilst for a hydrogen atom from Eqs. (19) and (23), we obtain

$$R_{(1)ki} = 2^{-1/2}\,\varepsilon_i D_{(1)ki} \tag{35}$$

where $R_{(1)ki} = C_{(3)ki}$ is the amplitude describing the extent of participation of a C–H bond.

Therefore, interpretation of coefficients $D_{(4)ki}$ and $D_{(1)k}$ as describing the extents of participation of separate atoms in ionization of the molecule leads to consequences expected in the Introduction.

STUDIES OF PARTICULAR EXAMPLES

Let us consider the structures of eigenfunctions Ψ_i and Φ_i of the AMs of graphs $G_H \equiv G^b_{Ch}$ of particular alkanes in this Section. The most illustrative examples of these graphs will be studied here, and these have been chosen so as to be able to represent the principal coefficients $Z_{ki} \equiv D_{(4)ki}$ in a simple algebraic form. As a result, the structures of eigenfunctions Ψ_i and Φ_i may be easily predicted on the basis of Eqs. (27) and (32).

A general remark should be made here:

Coefficients $Z_{ki} \equiv D_{(4)ki}$ standing within Eqs. (27) and (32) correspond to the n-dimensional secular problem shown in Eqs. (15) and (24) and are assumed to be normalized accordingly. After returning to the initial $(3n+1)$- and $(3n+2)$-dimensional bases $\{\chi\}$ and $\{\lambda\}$ within the expressions for eigenfunctions Ψ_i and Φ_i, respectively, the sets of n principal coefficients become renormalized within each of these functions separately. As a result, the final eigenfunctions meet the relations

$$D_{(4)ki}/R_{(4)ki} = D_{(1)ki}/R_{(1)ki} \tag{36}$$

instead of those of Eqs. (34) and (35).

Let us start with the first representative of the series C_nH_{2n+2}, *i.e.* with the methane molecule. The respective reduced graphs $G_{H}^{*} \equiv G_{Ch}^{b*} \equiv G_{Ch}^{a*}$ contain a single vertex described by the diagonal element of the AM equal to $\omega_0 = 3 + 4/\varepsilon$. Since only the eigenvalue $\varepsilon = 4$ corresponds to the HEB of methane,[9] the equality $\omega_0 = 4$ results in this case.

The only eigenfunction Φ of the ***AM A***(G_{Ch}^{a}) of methane associated with the HEB involves a single orbital $\mu(\varepsilon)$ defined by Eq. (33)

$$\mu(\varepsilon) = N(\varepsilon)\ [\lambda_{(4)} + (1/\varepsilon)\sum_{m=1}^{4} \lambda_{(1)\mathrm{m}}] \tag{37}$$

where $N(\varepsilon)$ is an ε-dependent normalization constant. For $\varepsilon = 4$, $N(\varepsilon) = 2/(5)^{1/2}$ and the eigenfunction Φ becomes

$$\Phi = [(1/2)\,(5)^{-1/2}]\ [4\lambda_{(4)} + \sum_{m=1}^{4} \lambda_{(1)\mathrm{m}}]\ . \tag{38}$$

The respective totally-symmetric eigenfunction $\Psi \equiv \eta_s$ of the ***AM A***$(G_H) \equiv$ ***A***(G_{Ch}^{b}) consists of the normalized sum of four BOs χ_j

$$\Psi = \eta_s = (1/2)\sum_{j=1}^{4} \chi_j\ . \tag{39}$$

From Eq. (39) it follows that each C–H bond takes an equal part in the ionization of methane from the energy level ε related to the HEB. Alternatively, Eq. (38) indicates that the amplitude associated with participation of the four-valent carbon atom is four times larger than that referring to a mono-valent hydrogen atom. These results are entirely consistent with each other. The equality of Eq. (36) may be easily proven for methane molecule.

Let us turn now to ethane. Since the reduced graphs $G_{H}^{*} \equiv G_{Ch}^{b*} \equiv G_{Ch}^{a*}$ of this molecule contain two mono-valent vertices, both described by the ***AM*** element $\omega_1(\varepsilon)$ of Eq. (16), the reduced secular problem resembles a two-level problem involving similar Coulomb integrals.

In this connection, the two eigenfunctions $\Phi_{(+)}$ and $\Phi_{(-)}$ of the ***AM*** $\boldsymbol{A}(\mathrm{G}^{\mathrm{a}}_{\mathrm{Ch}})$ of ethane resemble the normalized sum and difference, respectively, of two basis functions $\mu_1(\varepsilon)$ and $\mu_2(\varepsilon)$ defined by Eq. (33). The relevant eigenvalues are $\varepsilon_{(+)} = 4.65$ and $\varepsilon_{(-)} = 3$ (Note that the resonance parameter β describing the interaction between pairs of geminal bonds in alkanes is negative,[11,12] and $\varepsilon_{(+)} > \varepsilon_{(-)} > 0$ in β units).

After substituting these eigenvalues for ε of Eq. (33) and normalization, eigenfunctions $\Phi_{(+)}$ and $\Phi_{(-)}$ take the form

$$\Phi_{(+)} = (2.28)^{-1/2}\left\{\left[\lambda'_{(4)} + (1/4.65)\sum_{m'=1}^{3}\lambda_{(1)m'}\right] + \left[\lambda''_{(4)} + (1/4.65)\sum_{m''=1}^{3}\lambda_{(1)m''}\right]\right\}$$

$$\Phi_{(-)} = (3/8)^{1/2}\left\{\left[\lambda'_{(4)} + (1/3)\sum_{m'=1}^{3}\lambda_{(1)m'}\right] - \left[\lambda''_{(4)} + (1/3)\sum_{m''=1}^{3}\lambda_{(1)m''}\right]\right\} \qquad (40)$$

where the basis functions λ, referring to the first and second CH_3-group, are denoted by ' and '', respectively. It is seen that an increased contribution of hydrogen atoms relative to those of carbon atoms proves to be peculiar to function $\Phi_{(-)}$, as compared to $\Phi_{(+)}$.

The respective eigenfunctions $\Psi_{(+)}$ and $\Psi_{(-)}$ of the ***AM*** $\boldsymbol{A}(\mathrm{G}_{\mathrm{H}}) \equiv \boldsymbol{A}(\mathrm{G}^{\mathrm{b}}_{\mathrm{Ch}})$ of ethane may be approximately expressed as the normalized sum and difference, respectively, of two η_s-like basis functions shown in Eq. (39) relative to the two carbon atoms.[9] Let us denote the BOs pertinent to the C–C and C–H bonds by $\chi_{(\mathrm{C-H})}$ and $\chi_{(\mathrm{C-H})'}$ respectively. Then, eigenfunctions $\Psi_{(+)}$ and $\Psi_{(-)}$ may be approximately expressed in terms of these BOs in the form

$$\Psi_{(+)} \approx (10^{-1/2}\left\{\sum_{i'=1}^{3}\chi_{(\mathrm{C-H})i'} + 2\chi_{(\mathrm{C-C})} + \sum_{i''=1}^{3}\chi_{(\mathrm{C-H})i''}\right\}$$

$$\Psi_{(-)} \approx (6)^{-1/2}\left\{\sum_{i'=1}^{3}\chi_{(\mathrm{C-H})i'} - \sum_{i''=1}^{3}\chi_{(\mathrm{C-H})i''}\right\} \qquad (41)$$

where the subscripts i' and i'' refer to BO of the firs and second CH_3-groups, respectively.

It is seen that the contribution of the basis function $\chi_{(\mathrm{C-C})}$ referring to the C–C bond is relatively increased within function $\Psi_{(+)}$ and it turns to zero within function $\Psi_{(-)}$. This, in turn, implies an increased contribution of orbitals $\chi_{(\mathrm{C-H})}$ pertinent to C–H bonds within eigenfunction $\Psi_{(-)}$, as compared to $\Psi_{(+)}$. Hence, interpretations of coefficients of the eigenfunctions of the ***AM***s $\boldsymbol{A}(\mathrm{G}^{\mathrm{a}}_{\mathrm{Ch}})$ and $\boldsymbol{A}(\mathrm{G}^{\mathrm{b}}_{\mathrm{Ch}})$ are in line with each other for the ethane molecule as well.

Let us discuss now the general case of normal alkanes. The n energy levels of these molecules associated with the HEB have been established to be situated inside the band limits $\Delta\varepsilon = (2; 5.37)$, and no local (out-of-band) states emerge in this case.[9,14] Then, the principal coefficients $Z_{ki} \equiv D_{(4)ki}$ may be approximately described[9,14] by those of the sin-like eigenfunctions of the ***AM***s $\boldsymbol{A}(\mathrm{G}_0)$ of the simple chain G_0.[17]

Let us confine ourselves to the lowest and highest MOs of the HEB of normal alkanes. In accordance with the above-mentioned sin-like global structure of the eigenfunctions, the lowest MO is characterized by uniform (positive) signs of the principal coefficients $Z_k \equiv D_{(4)k}$ along the chain (k = 1, 2...n), and the relevant eigenfunctions of the ***AM***s $\boldsymbol{A}(\mathrm{G_H}) \equiv \boldsymbol{A}(\mathrm{G}^{\mathrm{b}}_{\mathrm{Ch}})$ and A($\mathrm{G}^{\mathrm{a}}_{\mathrm{Ch}}$) may be referred to as $\Psi_{(++)}$ and $\Phi_{(++)}$, respectively. Again, the highest MO of the HEB contains alternating signs of coefficients $Z_k \equiv D_{(4)k}$ and the relevant eigenfunctions may be conveniently designated by $\Psi_{(+-)}$ and $\Phi_{(+-)}$.

Analogously to functions $\Phi_{(+)}$ and $\Phi_{(-)}$ of the ethane molecule, the eigenvalues corresponding to the above-discussed eigenfunctions $\Phi_{(++)}$ and $\Phi_{(+-)}$ meet the inequality $\varepsilon_{(++)} > \varepsilon_{(+-)} > 0$. Hence, functions $\Phi_{(+-)}$ contain relatively increased contributions of hydrogen atoms relative to those of carbon atoms in accordance with the $1/\varepsilon$-like form of the dependence of the coefficients at the basis functions $\lambda_{(1)km}$, as shown in Eq. (33). On the other hand, it is the eigenfunction $\Psi_{(+-)}$ that is characterized by a larger contribution of BOs $\chi_{(\mathrm{C-H})}$, as compared to the eigenfunction $\Psi_{(++)}$, in connection with the cancellation of the relevant contributions of the BOs $\chi_{(\mathrm{C-C})}$ within function $\Psi_{(+-)}$ due to opposite signs of the neighboring pairs of coefficients Z_k and Z_{k+1}.

Therefore, the analysis of particular examples shows that interpretations of coefficients of the adjacency matrix eigenfunctions Φ_i and Ψ_i as determining the relative extents of participation of individual atoms and bonds, respectively, in ionization of the molecule lead to mutually consistent conclusions.

CONCLUDING REMARKS

Coefficients of the eigenfunctions of the ***AM***s $\boldsymbol{A}(\mathrm{G}^{\mathrm{a}}_{\mathrm{Ch}})$ of chemical graphs of alkanes in terms of atoms have been assumed to determine the extents of participation of individual atoms in ionization of the molecule. This interpretation is borne out by both the interrelations between the local structures and the common global structure of the eigenfunctions Ψ_i and Φ_i established in this paper. In particular, the above-mentioned features of the eigenfunctions imply that participation of an atom in ionization of the molecule is determined by those of bonds attached to this atom and vice versa, which result is in line with the expectation. Analysis of particular examples also supports the above-discussed spectral meaning of coefficients within the adjacency matrix eigenfunctions.

It is noteworthy that no need arises for specifying the internal structure of atoms and/or bonds themselves when establishing the extents of their participation in ionization of the molecule on the basis of the adjacency matrix coefficients. Hence, the relation of the high-energy band within the photoelectron spectra of alkanes to the definite subspectra of the usual chemical graphs G^{a}_{Ch} may be regarded as an application of the classical chemical concepts to the investigation of the spectral characteristics of molecules.

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SAŽETAK

Spektralni značaj koeficijenata u vlastitim funkcijama matrice susjedstva izvedenih iz kemijskih grafova alkana

Viktorija Gineityte

Proučene vlastite funkcije izospektralnih matrica susjedstva izvedenih iz reprezentacija alkana (C_nH_{2n+2}) preko atoma (G^a_{Ch}) odnosno veza (G^b_{Ch}). Vlastite funkcije Φ_i i Ψ_i dviju matrica susjedstva $\boldsymbol{A}(G^a_{Ch})$ odnosno $\boldsymbol{A}(G^b_{Ch})$, kojima je pridružena ista vlastita vrijednost ε_i, izražene su preko zajedničkog skupa od n glavnih koeficijenata, od kojih se svaki odnosi na po jedan ugljikov atom. Time je dokazano da funkcije Φ_i i Ψ_i imaju zajedničku globalnu strukturu. Uspostavljen je i odnos između lokalnih struktura funkcija Φ_i i Ψ_i. Taj rezultat podupire pretpostavku o spektralnom značaju koeficijenata u vlastitim funkcijama Φ_i matrica $\boldsymbol{A}(G^a_{Ch})$. Za te se koeficijente pretpostavlja da određuju sudjelovanje pojedinih atoma u ionizaciji molekule premda, izgleda, ne postoji izravna veza između matrice susjedstva $\boldsymbol{A}(G^a_{Ch})$ i matrice hamiltoniana.