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Studies of Electronic Structure of Saturated Organic Molecules

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The common effective Hamiltonian of the class of saturated hydrocarbons has been constructed and the expressions of density matrix (DM) elements for these systems have been obtained using the perturbation theory for DM. It has been shown that the transferrability of the characteristics of the electronic structure pertaining to identical atoms and bonds follows the transferrability of the elements of DM. The heteroatom influence on DM of saturated organic systems has been investigated.

1. INTRODUCTION

There are two aspects in dealing with a class of closely related objects: common features and unique properties of the individual representative. In the case of a class of chemical compounds, where the number of objects is infinite, their common properties become of great importance. Consequently, chemistry mainly deals with the common properties of the classes of molecules. In quantum theory the properties of a molecule are determined by its Hamiltonian. A class of molecules may be considered as a quantum mechanical object if there is a possibility to construct the common Hamiltonian and solve the common quantum mechanical problem. The purpose of our present work is to develop this approach for saturated organic molecules.

A common property, being the reason why the saturated organic molecules are characterized as a particular class of chemical compounds, is the structural similarity exhibited in tetrahedral surrounding of the carbon atoms. It might be expected that the common features of the electronic structure of the systems observed are related to the values not of the whole molecule but of the individual atoms and bonds. The basic characteristic of this kind is the mono-electron density matrix (DM) in the basis of localized AO. Therefore, the purpose stated above involves investigation of the properties of the Hamiltonian matrices, stating and solving the common quantum mechanical problem for the class of saturated organic molecules as well as analyzing the common expressions of DM elements and the related quantities.

II. A STUDY OF THE DENSITY MATRIX AND TOTAL ENERGY OF SATURATED HYDROCARBONS

The advantages of the sp^3-hybrid AO's (HAO's) for the investigation of the electronic structure of saturated hydrocarbons have been discussed at length in[1,2]. We have shown in ref. 3. that the effective hamiltonian matrix for any saturated hydrocarbon in this basis can be presented as a sum of the zero ($H_{(0)}$) and first order ($H_{(1)}$) matrices

$$H = H_{(0)} + H_{(1)} = \begin{Vmatrix} 0 & I \\ I & 0 \end{Vmatrix} + \begin{Vmatrix} A & B \\ \tilde{B} & C \end{Vmatrix}, \tag{1}$$

where I is the unit matrix, I, A, B and C are the n-dimensional matrices ($n = N/2$, N — the number of the basis functions). The transposed matrices are designated by ~. Matrix H is constructed using the numeration of basis functions (HAO), as shown in the example in Figure 1. In addition, it was assumed that the diagonal elements of matrix H equal zero and the neighbouring resonance integrals equal one. It should be noted that matrix $H_{(0)}$ contains elements corresponding to pairs of the overlapping of mutually directed orbitals and matrix $H_{(1)}$-elements corresponding to the non-neighbouring orbitals. The analysis of $H_{(1)}$ matrices for different hydrocarbons shows that blocks A, B and C have the same structures, in the sense that matrix elements such as k, l and n occur in the same positions. These elements, according to Figure 1 can be written as

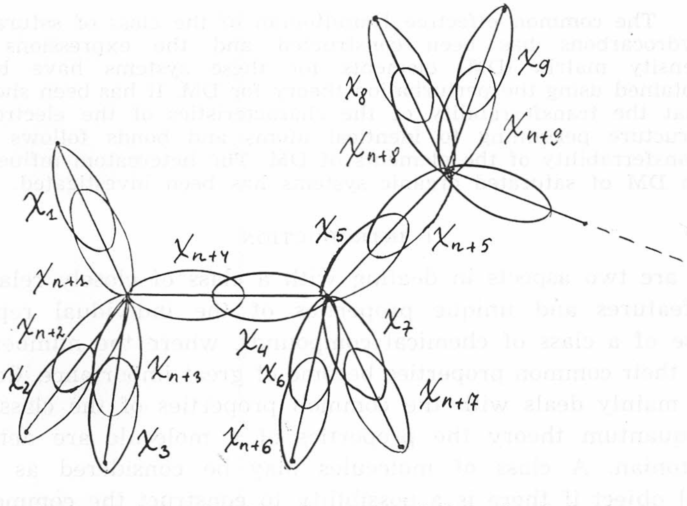

Figure 1. Numbering of the HAO's of a saturated molecule. 1s AO's of H atoms are designated in the same way as the sp^3-hybrid AO's of C atoms as all the diagonal elements in the matrix (1) are taken to be equal.

$$k = \langle y_{n+1} | H | y_{n+2} \rangle,\ l = \langle y_1 | H | y_2 \rangle,\ m = \langle y_1 | H | y_{n+2} \rangle \tag{2}$$

It should be noted that elements k and l are contained only in matrices A and C and element m, only in B. For instance, matrices A, B and C for nonbranched alkanes have on their main diagonals four-dimensional »connected« blocks. Thus, matrix A has the following form:

$$A = \begin{Vmatrix} 0 & l & l & l & t' & t'' & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ l & 0 & l & l & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ l & l & 0 & l & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ l & l & l & 0 & k & k & k & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & & & \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & & & \\ t' & \cdot & \cdot & k & 0 & k & k & \cdot & \cdot & \cdot & \cdot & \cdot \\ t'' & \cdot & \cdot & k & k & 0 & k & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & k & k & k & 0 & l & l & l & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & l & 0 & l & l & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \end{Vmatrix}, \tag{3}$$

where t', t'', ... are the matrix elements of the Hamiltonian between HAO's belonging to more distant atoms. Matrix C can be obtained from (3) by replacing l by k and vice versa, and matrix B by replacing l and k by m.

It should be noted that the modified atom — in the molecule (MAM) model developed in[1,2] is based on the asumption of equal electronegativity for HAO's of carbon and $1s$ — AO's of hydrogen atoms in alkanes. The good agreement of the results obtained in[1,2] with the experimental data justifies our assumption about the equality of all diagonal matrix elements of Hamiltonian (1). Likewise, the results of the works mentioned substantiate our estimations of the relative values of the non-diagonal Hamiltonian elements.

The possibility of represeting the Hamiltonian matrix of saturated hydrocarbons in the form (1) enables us to use the perturbation theory for DM[4] for the solution of the problem in question. Then the matrix of the residual (Y) charges (for this matrix the above mentioned perturbation theory is formulated) can take the form of the sum of the different order corrections containing the parameters included in perturbation matrix $H_{(1)}$. Matrix Y is connected with the DM represented in the HAO basis (P) by simple relation $Y = P — I$.

The expressions for DM of any saturated hydrocarbon with an accuracy of the second order members take the form

$$P = I + Y_{(0)} + Y_{(1)} + Y_{(2)}, \tag{4}$$

where

$$Y_{(0)} = \begin{Vmatrix} 0 & I \\ I & 0 \end{Vmatrix}, \quad Y_{(1)} = 1/2 \begin{Vmatrix} A—C & B—\hat{B} \\ \hat{B}—B & C—A \end{Vmatrix}, \quad Y_{(2)} = \begin{Vmatrix} L & M \\ \hat{M} & K \end{Vmatrix}, \tag{5}$$

and matrices L, M and K are connected with matrices A, B and C as follows

$$L = 1/4\,[CB + \hat{B}C — A\hat{B} — BA] — 1/8\,[(A — C), (B — \hat{B})]_{-},$$

$$K = —1/4\,[CB + \hat{B}C — A\hat{B} — BA] — 1/8\,[(A — C), B — \hat{B})]_{-}, \tag{6}$$

$$M = 1/4\,[[A, (A — C)]_{-} + \hat{B}^2 — B^2] — 1/8\,[(A — C)^2 — (B — \hat{B})^2],$$

the commutator of the matrices is designated by $[\ldots, \ldots]_{-}$. As it is seen from formula (5) for $Y_{(0)}$, the Hamiltonian structure for saturated hydrocarbons determines the existence of electron pairs localized on the bonds. It follows from (5) (6) that the expression for DM does not depend on the particular structure of matrices A, B and C. Such a result is determined by the fact that the structure of matrix $H_{(0)}$ is the same for all saturated hydrocarbons. Therefore, it is possible to state and solve the common problem for the total class of compounds in question. The DM elements analysis in ref. 3. shows that: a) the charge distribution in saturated hydrocarbons is homogeneous to the first order. The second order corrections to the populations of HAO's do not depend on the given molecule. Thus, the populations of the AO's of hydrogen atoms in all cases equal $1 - 3\,m\,\Delta$, and the populations of the sp^3- hybrid AO of carbon directed towards them equal $1 - 3\,m\,\Delta$, whereas the populations of the HAO of the C—C bonds equal one ($\Delta = 1/2 \cdot \cdot (l - k)$)[5,6] It justifies the presentation of the dipole moment of the saturated hydrocarbons molecule as a sum of the dipole moments of particular bonds; b) the bond orders between the mutually directed HAO's are equal to one with an accuracy of the first order members. The second order corrections are transferrable from one molecule to another. The bond orders corresponding to the pairs of non-neighbouring HAO's are determined both in the first and the second order by the magnitude of parameter Δ. These bond orders may be considered as a criterion of delocalization of the electrons in a molecule. It should be noted that the transferrability of DM elements follows from expression (6) and the common structure of blocks A, B and C.

The total energy equals[4]

$$E = \mathrm{sp}\,(PH) \tag{7}$$

The first three members of the total energy expansion into a series have the following form

$$E_{(0)} = 2n,\ E_{(1)} = 0,\ E_{(2)} = 1/4\, \Sigma\, [(A_{ik} - C_{ik})^2 + (B_{ik} - \hat{B}_{ik})^2] \tag{8}$$

Formula (8) states that the total energy zero order member of saturated hydrocarbon equals the sum of the individual bond contribution. The second order correction equals the sum of all pair-bond contributions. Therefore, the bond energies are additive and transferrable with the accuracy of the second order members.

III. HETEROATOM INFLUENCE ON DM OF SATURATED MOLECULES

The change in the Hamiltonian matrix under the influence of heteroatom X wil be modelled via a change of the diagonal matrix element $H_{11} = \alpha_x$, corresponding to AO $\varkappa_1$. It has been shown[6] that the parameter α_x for different substituents changes within fairly vide limits. Hence, α_x has been included into the zero-order Hamiltonian matrix of the substituted system

$$H_{(0)}^{(x)} = \begin{Vmatrix} h & I \\ I & 0 \end{Vmatrix}, \tag{9}$$

where the elements of block h equal $h_{ij} = \alpha_x\, \delta_{i1}\, \delta_{j1}$. We maintain that the first-order matrix $H_{(1)}$ for substituted system coincides with the corresponding matrix for hydrocarbon (formula (1)).

Let us consider the expression for DM elements for a system with Hamiltonian $H = H_{(0)}^{(x)} + H_{(1)}$. Matrix $Y_{(0)}^{(x)}$, irrespective of the structure of a given molecule, equals

$$Y_{(0)}^{(x)} = \left\| \begin{array}{cccccc|cccccc} cos\ \gamma & 0 & 0 & \cdot & \cdot & \cdot & sin\ \gamma & 0 & 0 & \cdot & \cdot & \cdot \\ 0 & 0 & 0 & \cdot & \cdot & \cdot & 0 & 1 & 0 & \cdot & \cdot & \cdot \\ 0 & 0 & 0 & \cdot & \cdot & \cdot & 0 & 0 & 1 & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \hline sin\ \gamma & 0 & 0 & \cdot & \cdot & \cdot & -cos\ \gamma & 0 & 0 & \cdot & \cdot & \cdot \\ 0 & 1 & 0 & \cdot & \cdot & \cdot & 0 & 0 & 0 & \cdot & \cdot & \cdot \\ 0 & 0 & 1 & \cdot & \cdot & \cdot & 0 & 0 & 0 & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 0 & 0 & \cdot & \cdot & \cdot \end{array} \right\| , \tag{10}$$

where

$$\gamma = arctg\, 2/\alpha_x,\ 0 \leq \gamma \leq (\pi/2)^6,\ \sin\gamma = \frac{2}{\sqrt{\alpha_x^2 + 4}},\ \cos\gamma = \frac{\alpha_x}{\sqrt{\alpha_x^2 + 4}} \tag{11}$$

Structure $Y_{(0)}^{(x)}$ reflects the local character of heteroatom influence on DM. It should be noted that the dependence of the $Y_{(0)}^{(x)}$ matrix elements on α_x, represented by formulae (10) and (11), coincides with the corresponding dependence of the two electron two-level system. The first order correction $Y_{(0)}^{(x)}$ can be presented as a sum

$$Y_{(1)}^{(x)} = Y_{(1)} + Y_{(1)}^{(x)} \tag{12}$$

where $Y_{(1)}$ is the part of DM correction which does not depend on α_x and is presented by formula (5). Matrix $Y_{(0)}^{(x)}$ is the part of correction $\overline{Y}_{(1)}^{(x)}$ corresponding to the heteroatom influence

$$\overline{Y}_{(1)}^{(x)} = \left\| \begin{array}{cc} R_{11} & R_{12} \\ R_{21} & R_{22} \end{array} \right\| \tag{13}$$

Matrix $\overline{Y}_{(1)}^{(x)}$ blocks have the following form

$$R_{st} = \left\| \begin{array}{ccccccc} 0 & r_{12}^{st} & r_{13}^{st} & \cdot & \cdot & \cdot \\ r_{21}^{st} & 0 & 0 & \cdot & \cdot & \cdot \\ r_{31}^{st} & 0 & 0 & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \end{array} \right\| \tag{14}$$

irrespective of the specific structure of blocks A, B and C. Matrix elements r_{1p}^{st}, r_{p1}^{st} are functions of α_x. Formulae (13) and (14) show that heteroatom X for a first approximation affects only the »bond« orders which include either the perturbed orbital, or the neighbouring one. On the other hand, heteroatom X does not effect the populations of HAO's. The populations change for more distant HAO's is described by the difference between the diagonal elements of the second-order corrections of substituted and not substituted systems

$$\overline{Y}^{(x)}_{(2)jj} = Y^{(x)}_{(2)jj} - Y_{(2)jj} = 1/4\,\{(A_{1j} - C_{1j})\,(B_{1j} - B_{j1}) -$$
$$- 2\,(A_{j1}\,B_{1j} + B_{j1}\,C_{1j}) \cdot f_1 + 2\,(A_{j1}\,B_{j1} + B_{1j}\,C_{j1}) \cdot f_2 - 4\,C_{j1}^2 \cdot f_3 +$$
$$+ [(B_{j1} + B_{1j})^2 - (A_{j1} - C_{j1})^2] \cdot f_4 + 2\,(A_{j1} - C_{j1})\,(B_{j1} + B_{1j}) \cdot f_5\}, \tag{15}$$

where

$$f_1 = \frac{1}{1 + \sin\gamma}, \; f_2 = \frac{\sin\gamma}{1 + \sin\gamma}, \; f_3 = \frac{\cos\gamma}{1 + \sin\gamma}, \; f_4 = \frac{\sin\gamma \cdot \cos\gamma}{1 + \sin\gamma}, \; f_5 = \frac{\cos^2\gamma}{1 + \sin\gamma},$$

$$f_5 = \frac{\cos^2\gamma}{1 + \sin\gamma}, \; j = 2, \dots n \tag{16}$$

Because of the function $f_1 \div f_5$ restriction (they are always less than 1 (Figure 2)), the correction $\overline{Y}_{(2)jj}^{(x)}$ at any α_x is a small value. Hence, the heteroatom influence in saturated systems has a local character for all substituents and all types of the hydrocarbon chain. This character is due to the pecularities of the Hamiltonian matrices structure which reveals itself in the »isolated« location of the large non-diagonal elements.

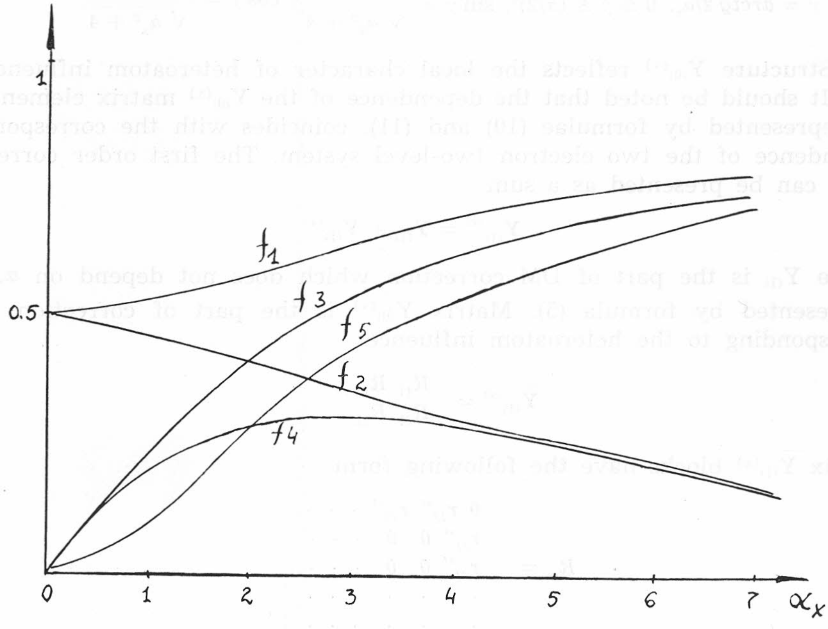

Figure 2. Dependence of functions $f_1 — f_5$ upon parameter α_x.

Corrections $\overline{Y}_{(2)ii}^{(x)}$ are alternating-sign quadratic functions of the non-diagonal matrix elements of the Hamiltonian of the system under analysis and they are determined exlusively by the Hamiltonian elements between HAO's localized on the bonds containing the perturbed HAO and the AO investigated. Therefore, the influence of heteroatom X on the population of the HAO in the epproximation used depends on the mutual arrangement of the above mentioned bonds and it does not depend on the remaining part of the molecule.

These conclusions are compatible with the results obtained in 3, where linear members of expansion of the corrections to DM in a series with respect to parameter α_x are investigated.

The relations between the elements of matrices A, B and C determine both the sign of the correction $\overline{Y}_{(2)jj}^{(x)}$ and the type of its dependence upon parameter α_x. In general, this dependence is complicated and difficult to analyze. Therefore, a study of formula (15) was made in two cases: a) when $A = C = 0$ and b) $B = 0$. It was shown that in the case (a), $\overline{Y}_{(2)jj}^{(x)} = 1/4 \, f_4 \, (B_{ij} + B_{j1})^2 > 0$ and the dependence of $\overline{Y}_{(2)ij}^{(x)}$ on α_x is not monotonic. When $\alpha_x \to \infty$, the correction $\overline{Y}_{(2)jj}^{(x)}$ tends to zero. In case (b), with regard to the smallness of the elements of matrix A—C[5,6], it can be shown that the correction to the population of HAO X_j is negative and increases uniformly with respect to the rise of α_x.

The results obtained can be used for the investigation of the character of inductive effect (IE) in saturated molecules. The analysis provided in[5,6] shows that the character of IE is determined by the sign of the correction to the population HAO $\varkappa_4 \overline{Y}_{(2)44}^{(x)}$: when $\overline{Y}_{(2)44}^{(x)} > 0$ we have the alternating IE character and when $\overline{Y}_{(2)44}^{(x)} < 0$ the IE character decreases uniformly. With regard to the interrelation discussed above between the sign $\overline{Y}_{(2)jj}^{(x)}$ and the type of $\overline{Y}_{(2)jj}^{(x)}$ dependence on α_x, it can be concluded that the alternating IE character is related to the non-monotonous $\overline{Y}_{(2)44}^{(x)}$ dependence on α_x while the decreasing IE character is related to the uniform $\overline{Y}_{(2)44}^{(x)}$ dependence upon α_x. The realization of either the first or the second case depends on the relations among the elements of matrices A, B and C. Therefore, on the basis of the interrelation obtained on the one hand and the positive experience of the application of the correlation analysis method, on the other hand, we may assume that the IE character decreases uniformly. We have to note that the correlation analysis method is based on the assumption of proportianality between the population change and the α_x value[7].

However, quantum mechanical calculations in[5,6] show a charge alternation. The reason for the charge alternation, as presented in[5], lies in the wrong parameterization which leads to erroneus relations between the individual matrix elements, corresponding to the non-neighbouring resonance integrals. As to the contribution of the electron, the donation effect of the atoms in alkanes is smaller[8] than the correction caused by IE.

IV. CONCLUSION

The general structure of the Hamiltonian matrices of saturated molecules allows construction of a common Hamiltonian and solution of the common quantum mechanical problem for the total class of given molecules. The transferrability of the electronic structure characteristic of atoms in similar chemical environments and similar chemical bonds, which is inherent in such systems, follows from the analysis of the common expressions obtained for the DM elements. The transferrability of the Hamiltonian matrix elements for saturated systems is born out by a comparison of the self-consistent fockian elements for different hydrocarbons in the basis of localized orbitals[9]. Whatever the structure of a particular molecule, the influence of the heteroatom on the electron density distribution in saturated molecules decreases rapidly and it is determined by the magnitude of overlapping of the mutually directed HAO's localized on the perturbed and considered bonds. The presence of the interrelation between the charge decrease character on the hydrocarbon chain and the type of their dependence upon the electronegativity of heteroatom makes it possible to conclude that the IE has a uniformly decreasing character.

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SAŽETAK

Proučavanje elektronske strukture zasićenih organskih molekula

V. Gineityte i D. Shatkovskaya

Korištenjem teorije simetrije konstruiran je efektivni hamiltonijan i matrica gustoće za klasu zasićenih organskih molekula. Razmatrana su njihova svojstva transferabilnosti.