

Application of the non-canonical method of molecular orbitals for investigation of electronic structures of conjugated hydrocarbons

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Abstract

The article contains an investigation of applicability to conjugated hydrocarbons of the non-canonical method of molecular orbitals (NCMO method) developed previously for saturated organic molecules (V. Gineityte, *J. Mol. Struct. (Theochem)* 343 (1995) 183; 430 (1998) 97) and based on the direct obtaining of localized MOs (LMOs) and of the one-electron density matrix (DM) in the form of two interrelated power series. Convergence of these series is expected to be slower for conjugated hydrocarbons as compared to their saturated analogues. In this connection, the third and fourth order terms of the power series for the DM absent in the previous articles were derived, and the particular case of an alternant hydrocarbon was studied in a detail. In contrast to saturated hydrocarbons, considerable differences in the rates of convergence of the power series for the DM prove to be peculiar to conjugated molecules. Thus, the convergence rate of power series for linear polyenes decreases gradually when the chain length increases. Again, turning from linear to cyclic constitution of the chain leads to drastic reduction of the convergence rate. These results along with the interdependence between power series for LMOs and for the DM allowed us to compare the extents of localizability of one-electron orbitals and thereby the nature of chemical bonds in conjugated and saturated hydrocarbons. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Saturated and conjugated hydrocarbons are usually considered as separate classes of molecules in the classical chemistry [1,2]. This point of view is evidently based on an assumption about distinct or even contrasting peculiarities of their chemical constitution [2–4]. Thus, localized two-electron bonds are assumed to be inherent in saturated hydrocarbons (alkanes). Alternatively, a system of more or less

delocalized bonds is expected to be present in conjugated molecules.

The aforementioned qualitative differences, however, contradict themselves almost completely when turning to quantum chemistry. This trend may be traced back to application of the same methods when studying representatives of both classes.

The most popular approach of quantum chemistry is based on the solution of the canonical Hartree–Fock (HF) equation [5–7]. The matrix form of this problem consists in diagonalization of the Fockian matrix, and the relevant solutions (eigenvectors of this matrix) coincide with the delocalized molecular orbitals (MOs) usually referred to as the canonical MOs

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(CMOs). In this connection, studies of electronic structures of molecules are usually carried out in terms of delocalized MOs, and this refers to both saturated and conjugated hydrocarbons.

In spite of feasibility of obtaining various types of localized MOs (LMOs) by transforming the set of occupied CMOs on the basis of various localization criteria [4,6], the influence of the delocalized approach discussed before on the whole theoretical chemistry was quite significant. In particular, the emphasis of theoretical investigations was largely replaced on similarity between saturated and non-cyclic (aliphatic) conjugated hydrocarbons. Moreover, resonance parameters between two sp^3 -hybrid atomic orbitals (AOs) of the same carbon atom in a saturated ($-CH_2-$) group was shown to play an analogous role [8] as those between the initially-double bonds in conjugated hydrocarbons. In this connection, even the concept of σ -conjugation in alkanes has been suggested [8]. Such a common point of view to both types of molecules was borne out by experimental facts. In particular, photoelectron spectra (ionization potentials) of both chains exhibit a similar behavior when the number of carbon atoms grows [9–11].

It is no surprise in this situation that the classical concept of localized bonds has been even considered as superfluous. Thus, localization of electrons belonging to separate bonds was called “an illusion” in Ref. [8]. The greater popularity of the a posteriori ways of obtaining LMOs by transforming the sets of CMOs [4,6] also contributed to the opinion described before. Indeed, the sets of LMOs when obtained from CMOs seem to be of a subsidiary nature.

Such an attitude towards the concept of localized and/or delocalized bonds, however, is likely to change if we turn to the direct (non-canonical) way of obtaining LMOs on the basis of the Brillouin theorem [12–23]. The block-diagonalization problem for the Fockian or Hückel type Hamiltonian matrix H should be solved in this case, and it may be traced back to the non-canonical HF equation [7].

The actual solutions of the block-diagonalization problem for saturated organic molecules in general [17,18,20] and for alkanes in particular [15,16,19] have been obtained by means of certain type of perturbation theory in the form of power series. As a result, the relevant expressions for LMOs have been derived without invoking the concept of delocalized MOs.

Moreover, the respective one-electron density matrix (DM) P and thereby the total energy E also may be obtained directly either on the basis of LMOs [23] or by means of solution of the commutation equation for matrices H and P [17]. Consequently, it is the concept of delocalized MOs that seems to be superfluous when applying the non-canonical MO (NCMO) method.

In this context, the question arises whether or not the above-described non-canonical approach may be extended to conjugated hydrocarbons. Given that the answer is affirmative, a more general viewpoint to the nature of chemical bonds in conjugated and saturated hydrocarbons and thereby to similarity and differences of electronic structures of these molecules seems to be feasible. Just these possibilities are explored in this article. Investigation of applicability of the NCMO approach to conjugated hydrocarbons is essential also for development of the method itself. Indeed, simplicity of the Hückel-type Hamiltonian matrices of conjugated hydrocarbons allows us to illustrate the rather abstract results of Refs. [15–22].

The non-canonical one-electron problems were solved in Refs. [15–23] for Hückel-type Hamiltonian matrices of quite general forms. In particular, the common Hamiltonian matrix of alkanes in the basis of sp^3 -hybrid AOs (HAOs) of carbon atoms and $1s_H$ AOs of hydrogen atoms [16,19] was actually based on the only assumption that the system under study contains a set of isolated bonds to within the zero-order approximation. The aliphatic conjugated hydrocarbons also may be considered as consisting of the respective sets of slightly interacting $C=C$ bonds. Inasmuch as no explicit form of the basis orbitals is required when constructing the model Hamiltonian matrix of Refs. [16,19], the above-described non-canonical approach seems to be applicable to conjugated hydrocarbons as well, provided the relevant power series converge. Hence, it is the rate of convergence of the series that becomes the main question here.

The block-diagonalization problem for the matrix H and the commutation equation for matrices H and P were shown to be closely interrelated [17]. Moreover, the power series for the LMO representation matrix and for the DM have been expressed in terms of the same principal submatrices. Hence, both power series may be expected to converge (or diverge) simultaneously.

In contrast to LMOs, the DMs of conjugated molecules obtained on the basis of power series may be directly compared to respective exact matrices in the framework of the Hückel model. Thus, we will confine ourselves in this article to investigation of the power series for the DMs of conjugated hydrocarbons. It should be also noted here that convergence of the power series for the DM of certain molecule and thereby for its LMO representation matrix implies that LMOs of the bond-orbital-and-tail structure may be obtained for this molecule [15,17] (bond orbitals refer here to the initially-isolated bonds).

Further, we will study the case of the largest interbond interaction (coinciding with the intrabond one) and thereby of the slowest rate of convergence of power series. Given that conjugated hydrocarbons are described by uniform resonance parameters β corresponding to all neighboring pairs of $2p_z$ AOs, the difference between one-electron energies referring to bonding and antibonding combinations of pairs of these AOs equals to 2β . Again, the resonance parameter corresponding to bonding and antibonding orbitals of two conjugated bonds coincides with $1/2\beta$. As a result, the usual ratio of the perturbation theory “(resonance parameter)/(energy difference)” becomes equal to $1/4 = 0.25$. For saturated hydrocarbons this ratio does not exceed 0.1 [19] (Such a small value is because of the fact that interbond resonance parameters are estimated to be considerably smaller vs. the intrabond ones in the HAO basis). Hence, slower convergence of the power series under discussion may be expected for conjugated hydrocarbons vs. that of saturated ones.

In this connection, we start with derivation of the third- and fourth-order terms of the power series for the one-electron DM and total energy that are absent in Refs. [15–23]. (Section 2). Thereupon, we turn to the alternant model relevant to conjugated hydrocarbons (Section 3). And finally, we examine the rate of convergence of the power series for DMs of particular conjugated hydrocarbons (Section 4).

2. Algebraic expressions for the common DM and the total energy of hydrocarbons to within the fourth order terms inclusive

Let us consider a saturated or a conjugated

hydrocarbon containing n C–C (C–H) or n C=C bonds, respectively. Let us assume that our molecule may be considered as consisting of isolated bonds to within the zero-order approximation. Moreover, these bonds will be described by uniform Coulomb parameters α and uniform resonance parameters β taken equal to 0 and 1, respectively, for convenience.

Let the initial $2n$ -dimensional basis set $\{\chi\}$ consisting of n HAOs along with 1_{SH} AOs or of n $2p_z$ AOs to be divided into two n -dimensional subsets $\{\chi'\}$ and $\{\chi''\}$ so that orbitals belonging to the same bond find themselves in the different subsets. Further, let us enumerate the basis functions in such a way that the orbitals belonging to the same bond acquire the coupled numbers i and $n+i$. As a result, the following $2n \times 2n$ -dimensional Hamiltonian matrix may be constructed for any hydrocarbon [18,21]

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

where I is the n -dimensional unit matrix and A , B and C are $n \times n$ -dimensional submatrices. The zero order term $H_{(0)}$ of Eq. (1) contains the resonance parameter $\beta = 1$ in the positions $(i, n+i)$, whereas the first order term $H_{(1)}$ involves the interbond resonance parameters. The superscript “+” designates the transposed matrix.

The DM (bond order matrix) P corresponding to the Hamiltonian matrix H of Eq. (1) may be expressed in the form of power series

$$P = \sum_{k=0}^{\infty} P_{(k)} \quad (2)$$

The first three members of this series ($k = 0, 1, 2$) have been obtained in Ref. [19] in terms of two principal matrices $G_{(1)}$ and $G_{(2)}$ defined as follows. These members take the form

$$P_{(k)} = \begin{vmatrix} T_{(k)} + \Pi_{(k)} & M_{(k)} + 2G_{(k)}^{\circ} \\ M_{(k)}^+ + 2G_{(k)}^{\circ+} & T_{(k)} - \Pi_{(k)} \end{vmatrix} \quad (3)$$

where

$$\Pi_{(k)} = -2G_{(k)}^* \quad (4)$$

$$T_{(0)} = I, \quad T_{(1)} = 0, \quad T_{(2)} = [G_{(1)}^+, G_{(1)}]_- \quad (5)$$

$$M_{(0)} = I, \quad M_{(1)} = 0, \quad M_{(2)} = -[G_{(1)}, G_{(1)}^+]_+ \quad (6)$$

The notations $[\cdot, \cdot]_-$ and $[\cdot, \cdot]_+$ stand for the commutator and anticommutator of matrices, respectively, whilst the superscripts * and ° designate the symmetric and skew-symmetric parts of matrices $G_{(k)}$ defined as follows [24]:

$$G_{(k)}^* = \frac{1}{2}(G_{(k)} + G_{(k)}^+), \quad G_{(k)}^\circ = \frac{1}{2}(G_{(k)} - G_{(k)}^+) \quad (7)$$

For hydrocarbons, the principal matrices $G_{(k)}$ take the form [17,19]

$$G_{(k)} = -\frac{1}{2}V_{(k)} \quad (8)$$

where

$$V_{(0)} = 0, \quad V_{(1)} = R, \quad V_{(2)} = SG_{(1)} - G_{(1)}Q \quad (9)$$

and the matrices S , R and Q are related to A , B and C as follows:

$$\begin{aligned} S &= \frac{1}{2}[(A + C) + (B + B^+)], \\ Q &= \frac{1}{2}[(A + C) - (B + B^+)], \\ R &= \frac{1}{2}[(A - C) - (B - B^+)] \end{aligned} \quad (10)$$

The third and fourth order terms of Eq. (2) also may be obtained as described in Refs. [17,19]. To this end, the relevant members of the power series for the DM P' in the basis of bond orbitals (BOs) should be derived in terms of matrices $G_{(3)}$ and $G_{(4)}$. Thereupon, the corrections $P'_{(3)}$ and $P'_{(4)}$ should be retransformed into the basis of HAOs and $1s_H$ AOs or $2p_z$ AOs as discussed in Ref. [19]. The bonding (antibonding) BOs are assumed here to be defined as normalized sums (differences) of basis orbitals (HAOs) belonging to the same bond.

As a result, the expressions for $P_{(k)}$ ($k = 3, 4$) also take the form of Eq. (3), where the matrices $\Pi_{(k)}$ ($k = 3, 4$) are expressed in terms of $G_{(k)}^*$ ($k = 3, 4$) as shown in Eq. (4), whilst the matrices $T_{(k)}$ and $M_{(k)}$

($k = 3, 4$) are

$$T_{(3)} = [G_{(1)}^+, G_{(2)}]_- + [G_{(2)}^+, G_{(1)}]_- \quad (11)$$

$$\begin{aligned} T_{(4)} &= [G_{(1)}^+, G_{(3)}]_- + [G_{(3)}^+, G_{(1)}]_- + [G_{(2)}^+, G_{(2)}]_- \\ &\quad + (G_{(1)}^+ G_{(1)} G_{(1)}^+ G_{(1)} - G_{(1)} G_{(1)}^+ G_{(1)} G_{(1)}^+) \end{aligned} \quad (12)$$

$$M_{(3)} = -[G_{(1)}^+, G_{(2)}]_+ - [G_{(2)}^+, G_{(1)}]_+ \quad (13)$$

$$\begin{aligned} M_{(4)} &= -[G_{(1)}^+, G_{(3)}]_+ - [G_{(3)}^+, G_{(1)}]_+ - [G_{(2)}^+, G_{(2)}]_+ \\ &\quad - (G_{(1)}^+ G_{(1)} G_{(1)}^+ G_{(1)} + G_{(1)} G_{(1)}^+ G_{(1)} G_{(1)}^+) \end{aligned} \quad (14)$$

The new principal matrices $G_{(k)}$ ($k = 3, 4$) may be expressed as follows:

$$G_{(k)} = -\frac{1}{2}(V_{(k)} - L_{(k)}), \quad (k = 3, 4) \quad (15)$$

where

$$V_{(k)} = SG_{(k-1)} - G_{(k-1)}Q \quad (16)$$

and

$$L_{(3)} = -4G_{(1)}G_{(1)}^+G_{(1)} \quad (17)$$

$$L_{(4)} = -2(G_{(1)}G_{(1)}^+G_{(2)} + 2G_{(1)}G_{(2)}^+G_{(1)} + G_{(2)}G_{(1)}^+G_{(1)}) \quad (18)$$

The total energy of any hydrocarbon may be defined as follows [25]:

$$E = \text{Spur}(PH) \quad (19)$$

Substituting Eqs. (1) and (2) into Eq. (19) yields the expression for the k -th order correction $E_{(k)}$ to the total energy

$$E_{(k)} = \text{Spur}(P_{(k)}H_{(0)}) + \text{Spur}(P_{(k-1)}H_{(1)}) \quad (20)$$

In particular, the zero order term $E_{(0)}$ is

$$E_{(0)} = \text{Spur}(P_{(0)}H_{(0)}) = 2n \quad (21)$$

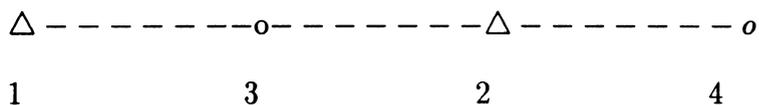
and contains the sum of energies of n isolated bonds.

3. The particular case of alternant hydrocarbons

In contrast to saturated molecules, the majority of

$$P_{14} = -0,438(-0,448)$$

$$P_{13} = 0,898(0,895), \quad P_{23} = 0,438(0,448)$$



$$P_{15} = -0,375(-0,388)$$

$$P_{14} = 0,860(0,871), \quad P_{24} = 0,500(0,486) \quad P_{25} = 0,781(0,784)$$



$$P_{34} = -0.078(-0.084)$$

$$P_{16} = 0.297(0.300)$$

Fig. 1. Diagram representing the numerical values of bond orders in the butadiene and hexatriene molecules estimated on the basis of power series derived in this paper and the respective exact values in the framework of the Hückel model (within parantheses). Basis orbitals belonging to subsets $\{\chi'\}$ and $\{\chi''\}$ are designated by Δ and \circ , respectively.

conjugated hydrocarbons may be considered as alternant systems. In the framework of the alternant model, resonance parameters between the nearest neighboring $2p_z$ AOs only should be taken into consideration.

The aforementioned numbering of basis orbitals (Section 2) allows the subsets $\{\chi'\}$ and $\{\chi''\}$ to be considered as coinciding with the two subsets of basis orbitals distinguished within the basis sets of alternant hydrocarbons [7,26,27] so that the intra-subset resonance parameters take zero values. In terms of submatrices of Eq. (1) this requirement

takes the form

$$A = C = 0 \quad (22)$$

Thus, let us consider the particular case described by Eq. (22) within the expressions for the DM P and the total energy E .

From Eq. (10) it follows that R becomes a skew-symmetric (skew-Hermitian) matrix in this case, i.e. $R^+ = -R$. Moreover, the same is true for the matrix $G_{(1)}$ defined by Eq. (8), viz. $G_{(1)}^+ = -G_{(1)}$. In contrast, the remaining matrices of Eq. (10) (S and Q) are symmetric (Hermitian) matrices.

The second order matrices $V_{(2)}$ and $G_{(2)}$ defined by Eqs. (8) and (9) also become skew-symmetric (skew-Hermitian) matrices. This implies that $G_{(2)}^* = 0$ and $\Pi_{(2)} = T_{(2)} = 0$ for any alternant hydrocarbon (see Eqs. (4) and (5)).

Similar consideration of the subsequent terms ($k = 3, 4$) allows us to conclude that all matrices $G_{(k)}$, $k = 1, 2, 3, 4$ are skew symmetric (skew-Hermitian) matrices, i.e.

$$G_{(k)}^+ = -G_{(k)}, \quad G_{(k)} = G_{(k)}^\circ, \\ G_{(k)}^* = 0, \quad k = 1, 2, 3, 4 \quad (23)$$

and

$$\Pi_{(k)} = T_{(k)} = 0, \quad k = 1, 2, 3, 4. \quad (24)$$

In contrast, the matrices $M_{(k)}$ are symmetric (Hermitian) matrices, i.e. $M_{(k)} = M_{(k)}^*$. Using Eq. (23) the latter may be expressed as follows:

$$M_{(2)}^* = 2(G_{(1)}^\circ)^2 \quad (25)$$

$$M_{(3)}^* = 2[G_{(1)}^\circ, G_{(2)}^\circ]_+ \quad (26)$$

$$M_{(4)}^* = 2[G_{(1)}^\circ, G_{(3)}^\circ]_+ + 2(G_{(2)}^\circ)^2 - 2(G_{(1)}^\circ)^4 \quad (27)$$

On the whole, the DM of an alternant hydrocarbon consists of the corrections of the form

$$P_{(0)} = \begin{vmatrix} I & I \\ I & I \end{vmatrix}, \\ P_{(k)} = \begin{vmatrix} 0 & M_{(k)}^* + 2G_{(k)}^\circ \\ M_{(k)}^* - 2G_{(k)}^\circ & 0 \end{vmatrix} \quad (28)$$

$$k = 1, \dots, 4.$$

It is seen that the matrices $M_{(k)}^*$ stand for the symmetric parts of the off-diagonal blocks of the corrections $P_{(k)}$, $k = 1, 2, 3, 4$, whilst $2G_{(k)}^\circ$ play the role of the respective skew-symmetric parts. It is also seen that the diagonal elements of the correction $P_{(k)}$ (population alterations) are equal to zero as it was established previously for alternant hydrocarbons by invoking other approaches [7,26,27].

Inasmuch as $G_{(k)ii}^\circ = 0$ for any i , the neighboring bond orders of alternant hydrocarbons are defined by

diagonal elements $M_{(k)ii}^*$ of matrices $M_{(k)}^*$ shown in Eqs. (25)–(27).

After substituting Eq. (28) into Eq. (20) we obtain the correction $E_{(k)}$

$$E_{(k)} = 2\text{Spur}M_{(k)} + 2\text{Spur}(G_{(k-1)}^\circ K^\circ) \\ + \text{Spur}(M_{(k-1)}^* J^*) \quad (29)$$

where the following notations are introduced

$$K^\circ = B^+ - B \quad (30)$$

$$J^* = B^+ + B. \quad (31)$$

Hence, we have derived the expressions for the DM P and the total energy E of an alternant hydrocarbon.

4. Convergence of the power series for the DM and total energy of simplest alternant conjugated hydrocarbons

Let us start with the butadiene molecule. Numbering of the relevant four $2p_z$ AOs is shown in Fig. 1. The resonance parameters for the initially-double bonds (1,3) and (2,4) are included into the zero-order Hamiltonian matrix of Eq. (1), whilst that for the initially-single bond (2,3) is incorporated into the first order matrix $H_{(1)}$. It is evident that Eq. (22) holds true in this case. The matrices B , J^* and K° for the butadiene molecule (the latter two being defined by Eqs. (30) and (31) are

$$B = \begin{vmatrix} 0 & 0 \\ 1 & 0 \end{vmatrix}, \quad J^* = \begin{vmatrix} 0 & 1 \\ 1 & 0 \end{vmatrix}, \quad K^\circ = \begin{vmatrix} 0 & 1 \\ -1 & 0 \end{vmatrix} \quad (32)$$

The principal matrices $G_{(k)} = G_{(k)}^\circ$ ($k = 1, 2, 3, 4$) become

$$G_{(1)}^\circ = -\frac{1}{4}K^\circ, \quad G_{(2)}^\circ = 0, \quad (33)$$

$$G_{(3)}^\circ = \frac{1}{32}K^\circ = -\frac{1}{8}G_{(1)}^\circ, \quad G_{(4)}^\circ = 0$$

whilst the matrices $M_{(k)} = M_{(k)}^*$ ($k = 2, 3, 4$), are

$$M_{(2)} = -\frac{1}{8}I, \quad M_{(3)} = 0, \quad M_{(4)} = \frac{3}{128}I \quad (34)$$

where $I = I^{(2)}$ is the two-dimensional unit matrix.

As a result, the following expression for the total

DM P of butadiene may be obtained

$$P = \begin{vmatrix} I & I \\ I & I \end{vmatrix} - \frac{1}{2} \begin{vmatrix} 0 & K \\ -K & 0 \end{vmatrix} - \frac{1}{8} \begin{vmatrix} 0 & I \\ I & 0 \end{vmatrix} \\ + \frac{1}{16} \begin{vmatrix} 0 & K \\ -K & 0 \end{vmatrix} + \frac{3}{128} \begin{vmatrix} 0 & I \\ I & 0 \end{vmatrix} + \dots \quad (35)$$

It is seen that the bond orders P_{13} and P_{24} for the initially-double bonds are determined by even corrections $P_{(0)}$, $P_{(2)}$ and $P_{(4)}$, whilst those for the initially single bond (P_{23}) along with the remaining bond order (P_{14}) are conditioned by the odd corrections $P_{(1)}$ and $P_{(3)}$. It is also seen that the relation $P_{23} = -P_{14}$ holds true for the butadiene molecule. Numerical values of the bond orders following from Eq. (35) are displayed in Fig. 1 along with the respective exact values for butadiene in the framework of the simple Hückel model. It is seen that deviations do not exceed 0.01.

For the total energy E the relevant four terms of power series are

$$E_{(0)} = 4, \quad E_{(1)} = E_{(3)} = 0, \quad E_{(2)} = \frac{1}{2}, \\ E_{(4)} = -\frac{1}{32} \quad (36)$$

and the total energy is $E = 4,469$. The respective exact value is $\tilde{E} = 4,472$ for comparison.

It may be concluded, therefore, that the power series for the DM and total energy of butadiene converges fairly well in the case of uniform resonance parameters. All the more so it may be expected to converge when the resonance parameters of the initially double bonds exceed that for the initially single bond.

Let us turn now to the analogous model of the hexatriene molecule. The analogues of matrices shown in Eq. (32) are

$$B = \begin{vmatrix} 0 & 0 & 0 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{vmatrix}, \quad J^* = \begin{vmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{vmatrix}, \\ K^\circ = \begin{vmatrix} 0 & 1 & 0 \\ -1 & 0 & 1 \\ 0 & -1 & 0 \end{vmatrix}. \quad (37)$$

The principal matrices $G_{(k)}$ of the hexatriene molecule take the form

$$G_{(1)} = -\frac{1}{4}K^\circ, \quad G_{(2)} = \frac{1}{8} \begin{vmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ -1 & 0 & 0 \end{vmatrix}, \quad (38)$$

$$G_{(3)} = \frac{1}{32}K^\circ = -\frac{1}{8}G_{(1)}, \quad G_{(4)} = -\frac{1}{4}G_{(2)}.$$

And finally, the matrices $M_{(k)}$ ($k = 2,3,4$) are

$$M_{(2)} = \frac{1}{8} \begin{vmatrix} -1 & 0 & 1 \\ 0 & -2 & 0 \\ 1 & 0 & -1 \end{vmatrix}, \quad M_{(3)} = \frac{1}{16}J^*, \\ M_{(4)} = -\frac{1}{64} \begin{vmatrix} 1 & 0 & 1 \\ 0 & -2 & 0 \\ 1 & 0 & 1 \end{vmatrix}. \quad (39)$$

As a result, the power series for the DM P like that of Eq. (35) yields the bond orders for hexatriene displayed in Fig. 1. These also are compared to the relevant exact values. It is seen that deviations from the exact values are somewhat larger as compared to those of butadiene, although the convergence of the power series is beyond any doubt. The respective corrections to the total energy are

$$E_{(0)} = 6, \quad E_{(2)} = 1, \quad E_{(1)} = E_{(3)} = E_{(4)} = 0 \quad (40)$$

and build up the total energy of hexatriene equal to $E = 7,000$, whilst the exact value is $\tilde{E} = 6,989$.

The somewhat slower convergence of the power series for hexatriene may be related to the non-zero matrix $G_{(2)}$ of this molecule. To define a quantitative measure of the matrix $G_{(2)}$ against $G_{(1)}$, the Euclidean norms [28] of matrices $G_{(k)}$ denoted by $g_{(k)}$ may be used. These are defined as follows:

$$g_{(k)} = \left(\sum_{ij} |G_{(k)ij}|^2 \right)^{1/2}. \quad (41)$$

Using Eqs. (38) and (41) in the case of hexatriene we obtain

$$g_{(1)} = \frac{\sqrt{4}}{4} = 0.5, \quad g_{(2)} = \frac{\sqrt{2}}{8} = 0.177 \quad (42)$$

and the ratio $\eta = g_{(2)}/g_{(1)} = 0.354$. For the butadiene molecule the analogous ratio equals to zero as $G_{(2)} = 0$.

In this context, any linear polyene containing n initially double bonds deserves attention. In this case the equality $G_{(1)} = -1/4K^\circ$ follows where

$$K^\circ = \begin{vmatrix} 0 & 1 & 0 & 0 & \dots \\ -1 & 0 & 1 & 0 & \dots \\ 0 & -1 & 0 & 1 & \dots \\ 0 & 0 & -1 & 0 & \dots \\ \dots & \dots & \dots & \dots & \dots \end{vmatrix} \quad (43)$$

Accordingly, the matrix $G_{(2)}$ for polyene is

$$G_{(2)} = \frac{1}{8} \begin{vmatrix} 0 & 0 & 1 & 0 & 0 & 0 & 0 & \dots \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & \dots \\ -1 & 0 & 0 & 0 & 1 & 0 & 0 & \dots \\ 0 & -1 & 0 & 0 & 0 & 1 & 0 & \dots \\ 0 & 0 & -1 & 0 & 0 & 0 & 1 & \dots \\ \dots & \dots \end{vmatrix} \quad (44)$$

The relevant Euclidean norms $g_{(1)}$ and $g_{(2)}$ may be expressed as follows:

$$g_{(1)} = \frac{\sqrt{2(n-1)}}{4}, \quad g_{(2)} = \frac{\sqrt{2(n-2)}}{8} \quad (45)$$

and their ratio is

$$\eta = \frac{g_{(2)}}{g_{(1)}} = \frac{1}{2} \sqrt{\frac{n-2}{n-1}} \quad (46)$$

As it is seen from Eq. (46), the ratio η increases from 0 to 1/2 when the number of the initially-double bonds grows (1/2 corresponds to the case $n \rightarrow \infty$). Therefore, the rate of convergence decreases when the chain becomes longer. The reason for this tendency is because of the following reason: The longer the chain becomes, the more non-zero indirect interactions between bond orbitals arise (Elements of the matrix $G_{(2)}$ are known to describe indirect (through-bond) interactions of bond orbitals [17]). In contrast, the slower convergence of power series for longer chains established previously indicates that the

localized approach in general becomes less adequate for these systems.

In this context, the benzene molecule also seems to be of interest, as entirely delocalized bonds are assumed to be inherent there [1–3]. The relevant matrices B , J^* and K° are

$$B = \begin{vmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{vmatrix}, \quad J^* = \begin{vmatrix} 0 & 1 & 1 \\ 1 & 0 & 1 \\ 1 & 1 & 0 \end{vmatrix}, \quad (47)$$

$$K^\circ = \begin{vmatrix} 0 & 1 & -1 \\ -1 & 0 & 1 \\ 1 & -1 & 0 \end{vmatrix}$$

whilst the matrices $G_{(1)}$, $G_{(2)}$, $M_{(2)}$ and $M_{(3)}$ take the form

$$G_{(1)} = -\frac{1}{4}K, \quad G_{(2)} = \frac{1}{2}G_{(1)}, \quad (48)$$

$$M_{(2)} = M_{(3)} = \frac{1}{8} \begin{vmatrix} -2 & 1 & 1 \\ 1 & -2 & 1 \\ 1 & 1 & -2 \end{vmatrix}$$

The Euclidean norms of matrices $G_{(1)}$ and $G_{(2)}$ for the benzene molecule along with their ratio η are

$$g_{(1)} = 0.612, \quad g_{(2)} = 0.306, \quad \eta = 0.500 \quad (49)$$

and the relevant power series is unlikely to converge. This implies that the localized approach is inadequate for the benzene molecule. This fact may be related to the cyclic structure of this molecule. A more detailed study of this point shows that the cyclic structure of the benzene molecule offers more mediators for indirect interactions of bond orbitals. As a result, more non-zero elements arise within the matrix $G_{(2)}$, and the norm of this matrix increases. This result is in line with the fact that no LMOs of the bond-orbital-and-tail structure may be obtained for the benzene molecule [4,27].

5. Conclusions

The following conclusions may be drawn:

1. The non-canonical MO method developed previously for investigation of electronic structures

of saturated organic molecules may be extended also to certain types of conjugated hydrocarbons, in particular to sufficiently short non-cyclic polyene chains. This result implies that LMOs of the bond-orbital-and-tail structure exist for these chains. Hence, there are no fundamental (qualitative) differences in the nature of chemical bonds of linear conjugated chains and of alkanes. In this connection, common peculiarities of electronic structures of these molecules discussed in Ref. [8] acquire an additional support. In contrast, the majority of conclusions of Ref. [19] concerning the electronic structures of alkanes (e.g. additivity of the total energy to within the second order terms inclusive, the relation of the total energy to the so-called rebonding effect, etc.) may be extended to short non-cyclic polyene chains as well. Moreover, the same is likely to be true also for the main peculiarities of the heteroatom influence [20].

2. The above-drawn conclusions, however, refer neither to long polyene chains nor to cyclic conjugated hydrocarbons. Hence, NCMOs of the bond-orbital-and-tail structure are unlikely to exist for these molecules, and this implies a quite different nature of chemical bonds in these systems.
3. On the whole, considerable individual differences in the extents of validity of the NCMO approach and thereby of localizability of one-electron orbitals for separate representatives of the class of conjugated hydrocarbons may be concluded. This peculiarity may be traced back to the slower convergence of the power series for the DM of conjugated hydrocarbons originating from the smaller alterations in the values of resonance parameters along the conjugated chain as compared to the saturated one.
4. A qualitative measure of localizability of one-electron orbitals may be defined in terms of the Euclidean norms of the principal matrices $G_{(1)}$ and $G_{(2)}$ [17]. The ratio between these norms reflecting the rate of convergence of the power series for LMOs and DM, proves to be determined by the relative number of indirect interbond interactions vs. the direct ones.
5. The results of this article also contribute to comparative analysis of the NCMO and CMO methods and thereby of the localized and delocalized approaches to electronic structures of mole-

cules, and the following conclusions may be drawn here:

1. These approaches are equivalent in the sense that both CMOs and NCMOs may be obtained directly without invoking the alternative concept.
2. Application of the CMO approach allows us to reveal differences in one-electron energy spectra of molecules but not those between the extents of localizability of one-electron orbitals. The NCMO method makes an opposite case in this respect. As a result, these methods may be considered as complementary approaches, and neither localized nor delocalized MOs are superfluous.
3. In contrast to the most popular CMO method being adequate for any molecule, adequacy of the NCMO approach is not evident “a priori”. In this context, the CMO method may be considered as the most appropriate way of investigation of various classes of molecules on the unified basis. Alternatively, the NCMO method seems to be the most suitable approach for investigation of differences in electronic structures of individual molecules, in particular in the extents of localizability of one-electron orbitals. In this respect, the NCMO method is more closely related to the concept of chemical classification of molecules as compared to the CMO approach.
6. The extent of localizability of one-electron orbitals related to the convergence rate of the power series in the framework of the NCMO approach may be regarded as the quantum chemical analogue of the classical concept of localized and/or delocalized bonds which forms the basis of the chemical classification of molecules.

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