The rebonding effect in hydrocarbons as a quantum-chemical analogue of the classical concept of conjugation

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Abstract

It is shown that the only non-zero submatrix of the bond-order matrix of aliphatic conjugated hydrocarbons (polyenes) describes the so-called rebonding effect manifesting itself as a redistribution of bond orders between various pairs of $2p_z$ AOs when building up the molecule. Rules governing both the rebonding effect and its consequences upon the total energy are formulated in an explicit algebraic form. Arguments are given for the conclusion that the rebonding effect is the quantum-chemical analogue of the classical concept of conjugation. In addition, the results allowed us to substantiate the concept of the classical chemistry about the limited valency of carbon atoms in molecules and the additive models for conjugation energy. A rather involved (dual) nature of the conjugation effect is demonstrated. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Bond-order matrix; Aliphatic conjugated hydrocarbons; Total energies; Alternant hydrocarbons

1. Introduction

Simple and general rules governing the mutual influence of effective atoms and/or bonds in molecules are known to form the basis of the classical theoretical chemistry [1,2]. In some cases, these rules are alternatively called effects.

Application of the concept of an effect implies that certain common consequences are anticipated in similar constitutional situations whatever the details of the structure of the particular compound. The inductive effect of heteroatom describing the influence of the latter upon the remaining fragment of a saturated organic molecule [3] may be mentioned here as an example. The well-known short range nature of this effect serves to illustrate the above-mentioned common consequences.

Establishing of quantum-chemical analogues for classical effects makes an important task. Two ends may be achieved after solving this problem, namely substantiation of implicit postulates underlying the effect under study [4] and discovering new features of the effect itself. In particular, the quantum-chemical analogue of the inductive effect found in Ref. [4] allowed the additive components of the heteroatom influence to be derived explicitly. It should be mentioned here that simplicity and general nature are among the most desired features of the quantum-chemical analogues being sought.

Conjugation of two coplanar unsaturated fragments (or of a lone electron pair and an unsaturated group) [1,2,5] is also among the most popular classical effects. An additional overlap of $2p_z$ AOs of the neighboring fragments owing to the formally single bond in

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between them is usually considered as the origin of this effect. Additional stabilization of the whole molecule versus the set of isolated fragments along with shortening of the initially single bond are the main common consequences of conjugation [2]. Characteristic changes in the relevant UV [6,7] and photoelectron spectra [8] also may be mentioned here.

Linear and branched unsaturated hydrocarbons (polyenes) are a particular type of conjugated molecules. On the whole, conjugation of C=C bonds may be described by relatively small consequences to the so-called collective properties of molecules [2], e.g. to total energies, bond lengths, etc. Indeed, stabilization energies of polyenes [9] are known to be small as compared to the total sum of bond energies [10]. Moreover, this additional contribution to the total energy may be expressed as a sum of modified increments of separate C=C bonds [10]. So far as the internuclear distances are concerned [5], the initially-double bonds remain considerably shorter as compared to the initially-single bonds, although the former are lengthened and the latter are shortened versus the relevant values for the isolated C=C and C–C bonds, respectively.

Thus, the main aim of this paper is to discover the quantum chemical analogue of conjugation in hydrocarbons and to study the principal features of this effect.

As discussed previously [4], application of the Hückel type models for molecules under study is the most promising way of expressing the consequences of the classical effects in terms of quantum chemistry. The point is that the common model Hamiltonian matrices may be constructed for the entire classes of molecules in the framework of just the above-mentioned model. This possibility, in turn, allows common expressions to be obtained for the relevant one-electron density matrices (DMs) in the form of power series. Application of these expressions ensure the simplicity and the general nature of quantum-chemical analogues being sought.

Aliphatic conjugated hydrocarbons are among the molecules, the above-described quantum-chemical approach is applicable to [11]. Moreover, the common Hückel type Hamiltonian matrix initially constructed for alkanes [12–16], and thereby the respective expressions for the one-electron DM proved to be appropriate for conjugated hydrocarbons as well,

although the rate of convergence of the power series for the DM was slower in the latter case [11].

Studies of the above-mentioned DM to within the second-order terms inclusive [16] showed that separate building blocks (submatrices) may be revealed in this matrix, each of them describing certain type of intramolecular interaction. Quantum chemical analogue of conjugation also is likely to be among these submatrices. However, we cannot confine ourselves to the second-order terms of the power series for the DM, when studying the conjugated hydrocarbons [11]. Thus, submatrices of the third- and fourth-order corrections also should be taken into consideration.

As it was shown previously [11], the number of non-zero submatrices of the DM becomes largely reduced if we turn to alternant hydrocarbons. On the other hand, the conjugation effect is evidently relevant also to this type of molecules. Hence, the quantum-chemical analogue of conjugation is likely to be found among non-zero blocks of the DM just of alternant hydrocarbons. In this connection, the above-mentioned particular case is studied in this paper.

Thus, in Section 2, we start with the exploration of the DM of alternant conjugated hydrocarbons to within the fourth-order terms inclusive. Later, in Section 3, the main features of the conjugation energy are discussed.

2. Redistribution of bond orders when building up a conjugated hydrocarbon. The rebonding effect

Let us consider an alternant conjugated hydrocarbon containing n initially-double (C=C) bonds.

All the $2p_z$ AOs of carbon atoms will be described by the uniform Coulomb parameters α taken to be equal to zero for the sake of convenience. Let us also assume that our molecule consists of isolated C=C bonds to within the zero-order approximation [11]. In this connection, resonance parameters β referring to the initially-double bonds and taken equal to one are included into the zero-order Hamiltonian matrix $H_{(0)}$. On the other hand, resonance parameters of the initially-single (C–C) bonds also are assumed to be equal to one, but are incorporated into the first-order Hamiltonian matrix $H_{(1)}$ as in Ref. [11].

Let the $2n$-dimensional basis set $\{\chi\}$ consisting of $2p_z$ AOs to be divided into two n-dimensional subsets $\{\chi'\}$ and $\{\chi''\}$ so that orbitals belonging to the same initially-double bond find themselves in different subsets. Furthermore, let us enumerate the basis functions in such a way that orbitals belonging to the same C=C bond acquire the coupled numbers i and $n + i$. Such a numbering of basis orbitals allows the subsets $\{\chi'\}$ and $\{\chi''\}$ to be considered as coinciding with the two subsets of orbitals usually distinguished within the basis sets of alternant hydrocarbons [17–19].

As a result, the following $2n \times 2n$-dimensional Hamiltonian matrix may be constructed for the alternant hydrocarbons [11]

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

where I is an n-dimensional unit matrix representing the resonance parameters $\beta = 1$ corresponding to the C=C bonds and taking the positions $(i, n + i)$, and B is an $n \times n$-dimensional block (submatrix) containing the resonance parameters referring to the initially-single (C–C) bonds. The superscript ' + ' of Eq. (1) designates the transposed matrix.

As it was shown in Refs. [11–16], the DM (bond-order matrix) P corresponding to the Hamiltonian matrix H of Eq. (1) may be expressed in the form of power series with respect to parameters included in the first-order matrix $H_{(1)}$, i.e.

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

and the corrections $P_{(k)}$ are of the following constitution [11]

$$P_{(0)} = \begin{vmatrix} I & I \\ I & I \end{vmatrix}, \qquad P_{(k)} = \begin{vmatrix} 0 & \Omega_{(k)} \\ \Omega_{(k)}^+ & 0 \end{vmatrix}, \qquad k = 1, 2... \qquad (3)$$

The $n \times n$-dimensional off-diagonal block $\Omega_{(k)}$ specified below proves to be the only non-zero submatrix of the correction $P_{(k)}$ of alternant hydrocarbons. Thus, it is the matrix $\Omega_{(k)}$ that is likely to represent the quantum-chemical analogue of conjugation.

As with any matrix [20], the matrix $\Omega_{(k)}$ may be expressed in the form of a sum of its symmetric part

$M_{(k)}^*$ and of its skew-symmetric part $\Gamma_{(k)}^o$, viz.

$$\Omega_{(k)} = M_{(k)}^* + \Gamma_{(k)}^o. \qquad (4)$$

The superscripts * and ^{o} here and further designate symmetric and skew-symmetric matrices. The symmetric parts $M_{(k)}^*$ of matrices $\Omega_{(k)}$ of alternant hydrocarbons take the form [11]

$$M_{(0)}^* = I, \qquad M_{(1)}^* = 0, \qquad M_{(2)}^* = 2(G_{(1)}^o)^2,$$

$$M_{(3)}^* = 2[G_{(1)}^o, G_{(2)}^o]_+, \qquad (5)$$

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

where the notation $[...,...]_+$ stands for an anti-commutator of matrices. The principal $n \times n$-dimensional matrices $G_{(k)}^0 (k = 0, 1, 2, 3)$, in turn, have been expressed as follows:

$$G_{(0)}^o = 0, \qquad G_{(1)}^o = -\frac{1}{2}R^o,$$

$$G_{(2)}^o = -\frac{1}{2}(S^*G_{(1)}^o - G_{(1)}^o Q^*), \qquad (6)$$

$$G_{(3)}^o = -\frac{1}{2}(S^*G_{(2)}^o - G_{(2)}^o Q^*) + 2(G_{(1)}^o)^3.$$

The matrices R^o, S^* and Q^* arising from Eq. (6) are related to submatrices B and B^+ of the initial matrix H of Eq. (1). Let us define the following matrices for convenience:

$$K^o = B^+ - B, \qquad J^* = B^+ + B. \qquad (7)$$

The matrices R^o, S^* and Q^* are

$$S^* = -Q^* = \frac{1}{2}J^*, \qquad R^o = \frac{1}{2}K^o. \qquad (8)$$

The skew-symmetric parts $\Gamma_{(k)}^o$ of matrices $\Omega_{(k)}$, in turn, are proportional to the respective principal matrices $G_{(k)}^o$, viz.

$$\Gamma_{(k)}^o = 2G_{(k)}^o. \qquad (9)$$

Let us now turn to the interpretation of matrices $\Omega_{(k)}$. The zero-order correction $P_{(0)}$ defined in Eq. (3) consists of four unit matrices. As a result, uniform occupation numbers of basis orbitals and uniform bond orders between pairs of basis functions (χ_i' and χ_{n+i}'') corresponding to the initially-double (C=C) bonds both equal to one follow to within the zero-order approximation (Note that the bond orders

referring to the C=C bonds take the diagonal positions of the off-diagonal blocks of the corrections $P_{(k)}$).

Inasmuch as $\Gamma^o_{(k)ii} = 0$ for any i, diagonal elements of submatrices $\Omega_{(k)}$ coincide with those of their symmetric parts $M^*_{(k)}$, i.e. $\Omega_{(k)ii} = M^*_{(k)ii}$. Hence, the kth-order corrections to the bond orders between pairs of basis orbitals χ'_i and χ''_{n+i} are determined by the respective diagonal elements of the matrix $M^*_{(k)}$.

Let the bond orders of the initially-double (C=C) bonds to be called the neighboring bond orders, whereas the remaining bond orders (including those of the initially-single bonds) are referred to as the non-neighboring bond orders.

From the definition of matrices $M^*_{(k)}$ shown in Eq. (5), it follows that diagonal elements $M^*_{(k)ii}$ are conditioned by certain combinations of elements of matrices $G^o_{(k-1)}, G^o_{(k-2)}$, etc. The latter, in turn, are known to describe the respective corrections to the bond orders between bonding and antibonding bond orbitals (BOs) [15,21] of different initially-double bonds (the BOs are defined as normalized sums and differences between pairs of AOs χ'_i and χ''_{n+i}). This implies that the kth-order corrections to the neighboring bond orders are actually made up of the $(k-1)$th and lower-order corrections to the non neighboring bond orders. Thus, the neighboring and the non-neighboring bond orders prove to be inter-related, viz. the larger are the latter within previous corrections $P_{(k-1)}, P_{(k-2)}$, etc., the more the former are altered within the subsequent correction $P_{(k)}$. Let us discuss this point in more detail.

The equality $M^*_{(1)} = 0$ seen from Eq. (5) yields zero values for the first-order corrections to the neighboring bond orders of any hydrocarbon, whilst the non-neighboring bond orders between bonding BOs (BBOs) and antibonding BOs (ABOs) belonging to different C=C bonds are represented by elements of the principal matrix $G^o_{(1)}$. These elements, in turn, determine the second-order corrections to the neighboring bond orders. Indeed, from Eq. (5) it follows that:

$$M^*_{(2)ii} = \Omega_{(2)ii} = -2\sum_j (G^o_{(1)ij})^2 < 0 \tag{10}$$

and this expression serves to bear out the above statement. It is seen that alteration (lowering) of the neighboring bond order of the Ith C=C bond is proportional to sum of squares of the first-order increments to the non-neighboring bond orders formed by the BBO of

the Ith bond with ABOs of other C=C bonds. Similarly, the third-order corrections to the neighboring bond orders prove to be determined by first- and second-order corrections to the non-neighboring bond orders, etc.

It is seen, therefore, that redistribution of bond orders actually takes place when building up a hydrocarbon, and it may be called the rebonding effect. In this connection, the matrix $\Omega_{(k)}$ may be interpreted as the kth-order rebonding matrix. Substituting Eq. (3) into Eq. (2) allows the total DM to presented in the form

$$P = \begin{vmatrix} I & \Omega \\ \Omega^+ & I \end{vmatrix} \tag{11}$$

where

$$\Omega = I + \sum_{k=1}^{\infty} \Omega_{(k)} \tag{12}$$

is the total rebonding matrix expressed in the form of a power series.

The above-established meaning of the matrix Ω supports our expectation that the rebonding effect is the quantum-chemical analogue of conjugation. Indeed, lowering of the neighboring bond orders along with the emergence of the non-neighboring bond orders is in line with the observed lenghtening of the initially-double bonds and shortening of the initially-single bonds owing to conjugation [5] (Section 1).

3. Peculiarities of the rebonding energy of alternant hydrocarbons

The total energy of any system follows from the general relation [22]

$$E = \text{Spur}(PH). \tag{13}$$

Substituting Eqs. (1) and (2) into Eq. (13) yields a power series for the energy E of an alternant hydrocarbon, i.e.

$$E = \sum_{k=0}^{\infty} E_{(k)}. \tag{14}$$

The zero-order term of Eq. (14) ($E_{(0)} = 2n$) describes the sum of energies of n isolated C=C bonds [16]. Other corrections $E_{(k)}(k \geq 1)$ take the form

$$E_{(k)} = 2\text{Spur}M^*_{(k)} + 2\text{Spur}(\Omega_{(k-1)}B^+). \tag{15}$$

The first increment of Eq. (15) is proportional to the sum of the kth-order corrections to the neighboring bond orders, whereas the second one involves the $(k-1)$th order rebonding matrix $\Omega_{(k-1)}$. It should be also noted here that diagonal elements of the latter, i.e. $\Omega_{(k-1)ii} = M^*_{(k-1)ii}$ do not contribute to the correction $E_{(k)}$, as diagonal elements of matrices B and B^+ usually take zero values [11] (this is because of the close values of the neighboring resonance parameters that may be entirely included into the zero-order Hamiltonian matrix shown in Eq. (1)). Moreover, the matrices B and B^+ contain elements equal to one only in the positions corresponding to the initially-single bonds in conjugated hydrocarbons [11]. This implies that only the non-neighboring bond orders referring to the initially-single bonds contribute to the second term of Eq. (15). Hence, the correction $E_{(k)}$ may be called the kth-order rebonding energy and denoted by $E_{(k)\mathrm{reb}}$.

Furthermore, the kth-order rebonding energy may be rewritten in the form

$$E_{(k)\mathrm{reb}} = E'_{(k)\mathrm{reb}} + E''_{(k)\mathrm{reb}} \qquad (16)$$

where

$$E'_{(k)\mathrm{reb}} = 2\mathrm{Spur}M^*_{(k)} \qquad (17)$$

$$E''_{(k)\mathrm{reb}} = 2\mathrm{Spur}(G^o_{(k-1)}K^o) + \mathrm{Spur}(M^*_{(k-1)}J^*). \qquad (18)$$

The second part of the rebonding energy ($E''_{(k)\mathrm{reb}}$) is rewritten here into a more "symmetrized" form being more convenient for further derivations. The matrices K^o and J^* are defined in Eq. (7).

It is seen that alternations in the total energy originating from the kth-order corrections to the neighboring bond orders and from the $(k-1)$th-order corrections to the non-neighboring bond orders are being summed up within the correction $E_{(k)\mathrm{reb}}$. This result describes how the rebonding effect manifests itself within the total energy.

As the kth-order corrections to the neighboring bond orders are conditioned by the $(k-1)$th-order corrections to the non-neighboring bond orders (Section 2), certain interrelations may be expected between the relevant increments to the correction $E_{(k)\mathrm{reb}}$ defined by Eqs. (17) and (18).

To find these relations, let us start with the second-order terms ($k=2$) (The first-order correction $E_{(1)}$ to

the total energy E takes a zero value provided that the neighboring resonance parameters are entirely included into the zero-order Hamiltonian matrix and Spur $J^* = 0$). As is seen from Eq. (10), $M^*_{(2)ii} < 0$ and $E'_{(2)\mathrm{reb}} < 0$ in β units. This implies that lowering of the neighboring bond orders leads to certain destabilization of the system. On the other hand, if we substitute the equalities $M^*_{(1)} = 0$ and $K^o = -4G^o_{(1)}$ into Eq. (18) for $k=2$, the expression for $E''_{(k)\mathrm{reb}}$ of the form

$$E''_{(2)\mathrm{reb}} = -4\mathrm{Spur}M^*_{(2)} \qquad (19)$$

results, where the definition of the matrix $M^*_{(2)}$ is also used. This part of the correction $E_{(2)\mathrm{reb}}$ is positive in β units and causes certain stabilization of the whole system.

Comparison of Eqs. (17) and (19) shows that

$$E''_{(2)\mathrm{reb}} = -2E'_{(2)\mathrm{reb}} \qquad (20)$$

for any alternant hydrocarbon. Thus, the two increments to the second-order rebonding energy are interdependent. Moreover, the stabilization energy of an alternant hydrocarbon due to the formation of the non-neighboring bond orders exceeds twice the respective destabilizing effect caused by alternations in the neighboring bond orders.

Using Eqs. (16), (17) and (19), the total second-order rebonding energy may be represented in the form

$$E_{(2)\mathrm{reb}} = -2\mathrm{Spur}M^*_{(2)} = -2\mathrm{Spur}\Omega_{(2)} > 0 \qquad (21)$$

and proves to be positive in β units.

Let us turn now to the third-order correction. After substituting $-4G^o_{(1)}$ for K^0 and using the definition of the matrix $M^*_{(3)}$ shown in Eq. (5), the first $G^o_{(k-1)}$-containing term of Eq. (18) for $k=3$ yields $-2\mathrm{Spur}M^*_{(3)}$. The second $M^*_{(k-1)}$-containing increment of the correction $E''_{(3)\mathrm{reb}}$ may be reformulated on the basis of the two alternative expressions for the matrix J^*, namely

$$J^* = 2S^*, \qquad J^* = -2Q^* \qquad (22)$$

where the latter results from Eq. (8). In addition, the term $SG_{(1)} - G_{(1)}Q$ arising after the application of Eq. (22) should be replaced by $-2G_{(2)}$ in accordance with Eq. (6). We then obtain

$$\mathrm{Spur}(M^*_{(2)}J^*) = -\mathrm{Spur}M^*_{(3)}. \qquad (23)$$

As a result, the correction $E''_{(3)\text{reb}}$ is

$$E''_{(3)\text{reb}} = -3\text{Spur}M^*_{(3)} \qquad (24)$$

and the total third-order rebonding energy equals to

$$E_{(3)\text{reb}} = -\text{Spur}M^*_{(3)} = -\text{Spur}\Omega_{(3)}. \qquad (25)$$

Comparison of Eq. (17) for $k = 3$ to Eq. (25) shows that

$$E''_{(3)\text{reb}} = -\frac{3}{2}E'_{(3)\text{reb}}. \qquad (26)$$

The relations of Eqs. (25) and (26) evidently are the third-order analogues of Eqs. (20) and (21), respectively. It is seen that the two parts of the third-order rebonding energy also are interdependent as it was the case with $E'_{(2)\text{reb}}$ and $E''_{(2)\text{reb}}$, only the ratio between the third-order increments differs from that for the second-order corrections. Opposite signs of $E'_{(3)\text{reb}}$ and $E''_{(3)\text{reb}}$ also are noteworthy.

Similar relations may be obtained for the fourth-order corrections as well, although a more involved procedure is required to derive them. Thus, the fourth-order analogue of Eq. (23) is

$$\text{Spur}(M^*_{(3)}J^*) = -8\text{Spur}(G^o_{(2)})^2 \qquad (27)$$

where the definition of the matrix $M^*_{(3)}$ is used, and $-4G^o_{(2)}$ is substituted for $[G^o_{(1)}, J^*]_+$ in accordance with Eqs. (6) and (22). Using the relation $K^o = -4G^o_{(1)}$, the following expression for the total fourth-order rebonding energy may be derived

$$E_{(4)\text{reb}} = -4\text{Spur}\{(G^o_{(2)})^2 + (G^o_{(1)})^4\}. \qquad (28)$$

Let us introduce the designation

$$V_{(3)} = S^*G^o_{(2)} - G^o_{(2)}Q^* = \frac{1}{2}[G^o_{(2)}, J^*]_+ \qquad (29)$$

and note that the matrix $V_{(3)}$ is contained within the matrix $G_{(3)}$ as it is seen from Eq. (6). As a result, an alternative expression for $\text{Spur}(M^*_{(3)}J^*)$ may be obtained, i.e.

$$\text{Spur}(M^*_{(3)}J^*) = 4\text{Spur}(G^o_{(1)}V_{(3)}). \qquad (30)$$

Furthermore, the following relation:

$$\text{Spur}(G^o_{(1)}V_{(3)}) = -2\text{Spur}(G^o_{(1)}G^o_{(3)}) + 4\text{Spur}(G^o_{(1)})^4 \qquad (31)$$

proves to be useful here (definitions of matrices $G_{(3)}$

and $V_{(3)}$ shown in Eqs. (6) and (29) should be used when deriving this relation).

On the basis of Eqs. (27) and (30), it follows that

$$\text{Spur}(G^o_{(1)}V_{(3)}) = -2\text{Spur}(G^o_{(2)})^2. \qquad (32)$$

Again, Eqs. (31) and (32) may be considered as an alternative expression for $\text{Spur}(G^o_{(1)}V_{(3)})$. Taking the right-hand sides of these relations, we obtain

$$\text{Spur}(G^o_{(1)}G^o_{(3)}) = 2\text{Spur}(G^o_{(1)})^4 + \text{Spur}(G^o_{(2)})^2. \qquad (33)$$

Using Eq. (33), the *Spur* of the matrix $M^*_{(4)}$ may be represented in the form

$$\text{Spur}M^*_{(4)} = 6\text{Spur}\{(G^o_{(1)})^4 + (G^o_{(2)})^2\}. \qquad (34)$$

Eq. (34) may be used for remaking the expression for $E_{(4)\text{reb}}$ shown in Eq. (28). As a result, we obtain

$$E_{(4)\text{reb}} = -\frac{2}{3}\text{Spur}M^*_{(4)} = -\frac{2}{3}\text{Spur}\Omega_{(4)}. \qquad (35)$$

On the other hand, Eqs. (16), (17) and (35) yield

$$E''_{(4)\text{reb}} = -\frac{8}{3}\text{Spur}M^*_{(4)} = -\frac{8}{3}\text{Spur}\Omega_{(4)} \qquad (36)$$

and

$$E''_{(4)} = -\frac{4}{3}E'_{(4)\text{reb}}. \qquad (37)$$

Therefore, interrelations between the neighboring and the non-neighboring bond orders (Section 2) prove to be accompanied by certain molecular-structure-independent ratios between the respective increments to the total energy.

Comparison of Eqs. (20), (26) and (37) allows us to expect that the relation of the form

$$E''_{(k)\text{reb}} = -\frac{k}{k-1}E'_{(k)\text{reb}} \qquad (38)$$

holds true for any k. This relation yields some essential features of the rebonding effect:

1. From Eq. (38) it follows that $E''_{(k)\text{reb}} \rightarrow E'_{(k)\text{reb}}$ if $k \rightarrow \infty$. This result implies a mutual compensation of both increments to the rebonding energy when the order of the correction grows. Hence, the power series for the total energy is likely to converge rapidly even if sufficiently large non-neighboring bond orders arise within the correction $P_{(k)}$ (this is the case only for polyenes as shown in Ref. [11]).

2. The relation shown in Eq. (38) allows the total kth-order correction $E_{(k)\mathrm{reb}}$ to be rewritten either in terms of $M_{(k)}^*$ as shown in Eqs. (21), (25) and (35) or in terms of $(\Omega_{(k-1)}B^+)$. As a result, two alternative forms of the total rebonding energy E_{reb} become possible, namely

$$E_{\mathrm{reb}} = \sum_{k=2}^{\infty} \frac{1}{(1-k)} E'_{(k)\mathrm{reb}} = \sum_{k=2}^{\infty} \frac{2}{(1-k)} \mathrm{Spur} M_{(k)}^*$$

(39)

and

$$E_{\mathrm{reb}} = \sum_{k=2}^{\infty} \frac{1}{k} E''_{(k)\mathrm{reb}} = \sum_{k=2}^{\infty} \frac{2}{k} \mathrm{Spur}(\Omega_{(k-1)}B^+). \quad (40)$$

Hence, the total rebonding energy may be interpreted either as an interbond interaction energy related to the formation of the non-neighboring bond orders or as the energy describing the respective intrabond effects.

3. Using Eq. (39) allows the total rebonding energy E_{reb} to be represented in the form

$$E_{\mathrm{reb}} = \sum_{I=1}^{n} E_{\mathrm{reb}(I)}$$

(41)

where

$$E_{\mathrm{reb}(I)} = \sum_{k=2}^{\infty} \frac{2}{(1-k)} \mathrm{Spur} M_{(k)ii}^*$$

(42)

is the increment of the Ith C=C bond.

It is seen that the total rebonding energy of an alternant hydrocarbon is additive with respect to increments of particular initially-double (C=C) bonds. Moreover, each of these increments depends only on corrections to the neighboring bond order of the bond under consideration. This conclusion is in line with the fact that the observed conjugation energies of polyenes are expressible as sums of modified increments of separate C=C bonds [10].

4. Eqs. (15–18) may be substituted with Eq. (38) and the following interrelation results:

$$\mathrm{Spur}\,\Omega_{(k)} = \left(\frac{1}{k} - 1\right)\mathrm{Spur}(\Omega_{(k-1)}B^+)$$

(43)

which may be interpreted as a conservation condition for bond orders. Indeed, this relation indicates

that the sum of the kth-order corrections to the neighboring bond orders is proportional to the sum of the $(k-1)$th-order corrections to the non-neighboring bond orders corresponding to the initially-single bonds.

Hence, the non-neighboring bond orders may be formed at the expense of the neighboring bond orders, and vice versa. This result may be considered as the quantum-chemical analogue of the classical concept of limited valency of carbon atoms in molecules [23].

4. Conclusion

The results of this paper allow us to conclude that the rebonding effect is the quantum-chemical analogue of conjugation in hydrocarbons. The main arguments for this conclusion are as follows:

1. The rebonding matrix is the only non-zero submatrix of the DM of alternant hydrocarbons, and the total energy of these systems coincides with the rebonding energy.
2. Alterations in bond orders due to rebonding are in line with respective changes of bond lengths owing to conjugation.
3. Rules governing the rebonding effect are common to any aliphatic hydrocarbon. Just the same is known to be the case with rules governing conjugation.
4. Consequences of the rebonding effect being represented in terms of power series are small. This conclusion coincides with the observed insignificant changes in lengths of the C–C and C=C bonds versus their standard values [5] and with small conjugation energies as compared to total sum of bond energies [10].

The above-drawn conclusion about the quantum-chemical analogue of conjugation allowed us to formulate the principal features of the effect in an explicit mathematical form. The following aspects may be mentioned here:

1. The bond orders arising between AOs of different C=C bonds within the $(k-1)$th-order correction $P_{(k-1)}$ to the bond-order matrix P and alternations of bond orders inside the C=C bonds within the subsequent correction $P_{(k)}$ are interrelated as

described by the conservation condition for bond orders shown in Eq. (43).

2. Within the *k*th-order correction to the total (rebonding) energy, additive contributions of opposite signs correspond to the above-mentioned two types of alterations in bond orders.

3. The two increments to the *k*th-order rebonding energy are described by molecular-structure-independent but *k*-dependent ratios.

4. Two alternative representations of the total (rebonding) energy are possible, viz. the representation in terms of newly-formed bond orders between AOs of different C=C bonds and that in terms of alterations of bond orders inside the C=C bonds.

5. The total (rebonding) energy is additive with respect to increments of particular C=C bonds.

The results of the paper contribute to the substantiation of the concept of limited valency of carbon atoms being among the principal postulates of the classical chemistry, as well as of additive models for conjugation energy [10]. Moreover, the obtained results indicate a dual nature of conjugation, i.e. it may be considered either as an interbond interaction or as an intrabond effect.

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