

INTRABOND EFFECTS CAUSED BY INTERBOND INTERACTION IN SATURATED ORGANIC MOLECULES

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Abstract

The paper is devoted to further development of the perturbative version of the non-canonical method of molecular orbitals overviewed recently (V.Gineityte, Lith.J.Phys., 44, 219 (2004)) and called the PNCMO theory. General expressions are derived for the common one-electron density matrix of saturated organic molecules in the basis of $1s_H$ AOs of hydrogen atoms and sp^3 - hybrid AOs of the remaining atoms and for respective total energies. Explicit algebraic representations are obtained for intrabond effects taking place in the above-specified systems due to interbond interaction. The concepts of homolytic and heterolytic predissociation of bonds are introduced to describe these effects. Interdependences are demonstrated between increments of various intra- and interbond effects to the total energy of the systems under study. Moreover, the final stabilization energy of the system vs. the respective set of isolated bonds and lone electron pairs is shown to result from a certain 'balance' between increments of opposite signs. In particular, the stabilizing contributions of newly- formed bond orders between orbitals of different bonds due to their interaction are shown to be necessarily accompanied by destabilizing increments of intrabond type that are traced back to the homo- and heterolytic predissociation of bonds. The results obtained are compared to those of particular cases studied previously.

Key words: Non-canonical method of molecular orbitals, one-electron density matrix, total energy of molecule, perturbation theory

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1. INTRODUCTION

Electronic structures of molecules are most commonly studied in terms of delocalized molecular orbitals (MOs) resulting from the canonical Hartree-Fock (HF) equation [1-3]. Since the MOs are usually sought in the form of linear combination of certain basis functions (e.g. atomic orbitals (AOs)), the canonical HF equation resolves itself into diagonalization problem for the Fockian matrix. The well-known Rayleigh-Schrödinger perturbation theory (RSPT) [2,4] is among popular approximate methods used to obtain the solution. Given that the Fockian matrices are additionally replaced by respective Hückel model Hamiltonian matrices and the self-consistent nature of the HF equation is ignored, application of the RSPT yields general algebraic results embracing entire series of the so-called related molecules. This qualitative approach to electronic structures of molecules is usually referred to as the perturbative MO (PMO) theory [5].

The canonical HF equation, however, is not the only possible form of one-electron problems for molecules. Moreover, various representations of an alternative (non-canonical) one-electron problem are possible [1,2].

As delocalized MOs are more easily obtainable from the canonical HF equation, the non-canonical one-electron problem is usually adapted [6] to look for orbitals localized mostly on separate fragments of molecule (Orbitals of this type are more closely related to chemical concepts of bonds, lone electron pairs, etc. [6-8]).

In this context, the Brillouin theorem [1,6] is of particular interest. Indeed, applications of this theorem is equivalent to solution of the non-canonical HF equation as shown in [1]. On the other hand, the Brillouin theorem yields a new and more general matrix problem after turning to matrix representation [9-15], namely the block-diagonalization problem for the Fockian matrix or for its approximations including the Hückel model Hamiltonian matrix. Moreover, this problem proved to be solvable in terms of entire submatrices (blocks) of the initial matrix without specifying either the internal constitutions or dimensions of these blocks [12-15]. To this end, a special formalism of the perturbation theory was developed that was called the non-commutative RSPT (NCRSPT) [15,16]. Application of the latter actually resulted into general expressions for non-canonical MOs (NCMOs) in the form of linear combinations of two subsets of basis functions with matrix coefficients [17].

The one-electron density matrix (DM) also is among the most fundamental characteristics of molecule describing charge distribution and related to numerous observed properties [2,3]. A general perturbative expression for this matrix was shown to be obtainable on the basis of projector to the entire subset of occupied NCMOs [17]. Moreover, the same power series for the DM may be derived directly from solution of the so-called commutation equation by means of the NCRSPT [14]. For the total energy of molecule ε , an analogous power series [18,19] followed from the relation of this characteristic to the DM \mathbf{P} ($\varepsilon = \text{Trace}(\mathbf{P}\mathbf{H})$, where \mathbf{H} is the Hamiltonian matrix). These results and their applications have been overviewed recently in Ref.[16]. The approach under discussion was called there the perturbative NCMO (PNCMO) theory of molecules.

An important feature of this new theory consists in the fact that no explicit definition of the principal basis set was required when deriving its principal expressions [14]. The only condition imposed on this basis was the possibility of revealing two subsets of basis functions within the set $\{\varphi\}$ so that the energy differences between orbitals of different subsets exceed considerably the intersubset interactions (resonance parameters) and one of these subset is initially-occupied in addition. As it turned out later [16], orbitals localized on separate fragments of the system(s) under study usually meet this requirement. In the case of saturated organic molecules, the above-specified orbitals coincide with bond orbitals (BOs) defined as eigenfunctions of separate two-dimensional Hamiltonian matrix blocks associated with pairs of atomic or hybrid orbitals pertinent to the same bond. It is also worth mentioning here that neither AOs nor hybrid AOs (HAOs) meet the above-specified requirements.

Given that BOs are chosen to play the role of basis functions in the PNCMO theory, the resulting characteristics of electronic structures (viz. the NCMO representation matrix, the DM and the total energy) are expressed in terms of certain principal matrices $\mathbf{G}_{(k)}$ ($k = 1, 2, 3..$) describing the direct (through-space) and in-

direct (through-bond) interactions of these orbitals [14]. These expressions allowed us to reveal the role of various interbond interactions in the formation of the actual electronic structure(s) of the system(s) under study.

Bond orbitals, however, are not the optimum basis functions in respect of describing the influence of interbond interactions upon internal characteristics of separate bonds, e.g. bond orders, bond dipole moments, etc. Moreover, the alternative representation of the DM in the basis of AOs and/or HAOs (usually referred to as the charge- bond order matrix) describes the intrabond characteristics in a far more convenient way [20-24] as compared to the above-discussed matrix in the basis of BOs.

Recent investigations of charge- bond order matrices of some particular systems showed that the interbond interactions give rise to definite intrabond effects [20, 21, 23]. These may be exemplified by the so-called rebonding effect [23] taking place in hydrocarbons and involving reduction of internal bond orders of separate bonds due to interbond interaction so that the extent of lowering is proportional to sums of squares of newly-formed bond orders between orbitals of the bond under consideration and those of other bonds. Moreover, the intrabond effects under discussion were shown to play an important role in chemical reactions [25, 26]. In this context, derivation of expressions for intrabond effects as general as it is possible becomes of importance.

It should be noted that retransformation of the results of the PNCMO theory into the AO (HAO) basis underlying the above-expected derivation is not a trivial problem. The point is that BOs are defined in terms of local pairs of AOs (HAOs), whereas members of the power series of the PNCMO theory are expressed in terms of entire submatrices (blocks) of the initial Hamiltonian matrix [16]. That is why we had to confine ourselves to local retransformation matrices in Ref.[21,24].

In this paper, we are about to suggest a retransformation procedure of a quite general scope of applicability that refers to any saturated molecule and embraces also the particular types of hydrocarbons studied before [20,22]. On this basis, we expect to be able to introduce some new concepts concerning intrabond effects in saturated organic molecules, as well as to consider the results obtained previously [20-23] from a more general point of view.

The scheme of the paper is as follows:

We start with the common Hückel model Hamiltonian matrix of saturated molecules represented in the basis of HAOs and/or AOs. To be able to apply the expressions of the PNCMO theory, we transform this matrix into the basis of BOs and discuss the resulting one-electron DM $\tilde{\mathbf{P}}$ (Section 2). Thereupon, members of the power series for the matrix $\tilde{\mathbf{P}}$ are retransformed into the HAO(AO) basis again and the intrabond effects following from the charge- bond order matrix \mathbf{P} are analyzed (Section 3). Section 4 is devoted to the analogous consideration of the total energy.

2. THE ONE-ELECTRON DENSITY MATRIX OF SATURATED ORGANIC MOLECULES IN THE BASIS OF BOND ORBITALS

Let us start with specifying of the systems under study. The term 'saturated organic molecules' used throughout this article embraces systems containing more or less localized two-center chemical bonds and lone electron pairs. The more precise

definition consists in the first order magnitude of the non-neighboring resonance parameters vs. those between strongly-overlapping (neighboring) pairs of orbitals [13, 27-32] in the initial basis of $1s_H$ AOs of hydrogen atoms and sp^3 -hybrid AOs (HAOs) of the remaining atoms. For simplicity let us call them both the HAO basis.

Let our basis set of HAOs $\{\chi\}$ to contain an even total number of orbitals ($2N$), where N stands for the number of bonds and lone electron pairs. In the latter case, an even total number of basis orbitals may be ensured by introducing respective faked antibonding orbitals [14]. These additional orbitals are presumed to be situated at sufficiently high one-electron energies so as to exert no influence upon final results.

Let the $2N$ -dimensional basis set $\{\chi\}$ to be divided into two N -dimensional subsets $\{\chi'\}$ and $\{\chi''\}$ so that the strongly overlapping pairs of the neighboring orbitals find themselves in the different subsets. Furthermore, let us enumerate the basis functions in such a way that the neighboring pairs of orbitals acquire the coupled numbers i and $N+i$. Finally, orbitals described by larger absolute values of Coulomb parameters (α) will be included into the first subset.

The common Hückel model Hamiltonian matrix of saturated molecules may be then presented as a sum of zero order ($\mathbf{H}_{(0)}$) and first order terms ($\mathbf{H}_{(1)}$), viz.

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

where submatrices correspond to subsets $\{\chi'\}$ and $\{\chi''\}$, and to their interaction. In particular, submatrices $\mathbf{A}_{(0)}$, $\mathbf{C}_{(0)}$ and $\mathbf{B}_{(0)}$ of the zero order term $\mathbf{H}_{(0)}$ are of diagonal constitution consisting of Coulomb parameters of HAOs χ'_i and χ''_{N+i} ($\mathbf{A}_{(0)ii} = \alpha_{I1}$, $\mathbf{C}_{(0)ii} = \alpha_{I2}$) and of resonance parameters between the latter ($\mathbf{B}_{(0)ii} = \beta_I$). Submatrices $\mathbf{A}_{(1)}$, $\mathbf{C}_{(1)}$ and $\mathbf{B}_{(1)}$ of the first order term $\mathbf{H}_{(1)}$ are square matrices of arbitrary structure. The superscript $+$ is used here and below for Hermitian-conjugate (transposed) matrices.

The energy reference point and the energy unit will be assumed to be chosen so that the above-enumerated parameters (α_{I1} , α_{I2} and β_I) take positive values for any bond and the inequality $\alpha_{I1} \geq \alpha_{I2}$ is valid (A negative energy unit is assumed to be actually accepted). Inasmuch as the Coulomb and the intrabond resonance parameters always may be entirely included into the zero order matrix $\mathbf{H}_{(0)}$, the diagonal elements of the first order submatrices $\mathbf{A}_{(1)}$, $\mathbf{C}_{(1)}$ and $\mathbf{B}_{(1)}$ will be supposed to take zero values, i.e. $\mathbf{A}_{(1)ii} = \mathbf{C}_{(1)ii} = \mathbf{B}_{(1)ii} = 0$ for any i .

Let us define now the bonding and antibonding BOs of the I -th bond as eigenfunctions of the respective two-dimensional Hamiltonian matrix block in the basis $\{\chi'_i, \chi''_{N+i}\}$, i.e.

$$\varphi_{(+i)} = z_I \chi'_i + v_I \chi''_{N+i}, \quad \varphi_{(-i)} = v_I \chi'_i - z_I \chi''_{N+i}, \quad (2)$$

where the expressions for coefficients z_I and v_I take the form [31]

$$z_I = \cos\left(\frac{\gamma_I}{2}\right), \quad v_I = \sin\left(\frac{\gamma_I}{2}\right) \quad (3)$$

and

$$\gamma_I = \arctan \left[\frac{2\beta_I}{\alpha_{I1} - \alpha_{I2}} \right], \quad 0 \leq \gamma_I \leq \frac{\pi}{2}. \quad (4)$$

As a result, passing from the basis of HAOs $\{\chi\}$ to that of BOs $\{\varphi\}$ will be described by the following unitary (and Hermitian) matrix

$$\mathbf{U} = \mathbf{U}^+ = \begin{vmatrix} \mathbf{Z} & \mathbf{V} \\ \mathbf{V} & -\mathbf{Z} \end{vmatrix}, \quad (5)$$

where \mathbf{Z} and \mathbf{V} are N -dimensional diagonal submatrices consisting of coefficients z_I and v_I of Eq.(3), respectively. The transformed Hamiltonian matrix $\tilde{\mathbf{H}}$ takes then the form

$$\tilde{\mathbf{H}} = \mathbf{U}^+ \mathbf{H} \mathbf{U} = \mathbf{U}^+ \mathbf{H}_{(0)} \mathbf{U} + \mathbf{U}^+ \mathbf{H}_{(1)} \mathbf{U} = \tilde{\mathbf{H}}_{(0)} + \tilde{\mathbf{H}}_{(1)} \quad (6)$$

and contains a diagonal zero order member $\tilde{\mathbf{H}}_{(0)}$. As a result, the total matrix $\tilde{\mathbf{H}}$ meets the requirements of the PNCMO theory [14,16]. This, in turn, allows us to invoke the expressions for the relevant one-electron DM $\tilde{\mathbf{P}}$ derived in Ref.[14] in the form of power series. The corrections $\tilde{\mathbf{P}}_{(k)}$ of this series also are expressible in terms of four submatrices, viz.

$$\tilde{\mathbf{P}}_{(k)} = \begin{vmatrix} \tilde{\mathbf{Q}}_{(k)+} & -2\mathbf{G}_{(k)} \\ -2\mathbf{G}_{(k)}^+ & \tilde{\mathbf{Q}}_{(k)-} \end{vmatrix}, \quad (7)$$

where k here and below stands for the order parameter. The blocks $\tilde{\mathbf{Q}}_{(k)+}$ and $\tilde{\mathbf{Q}}_{(k)-}$ correspond here to N -dimensional subspaces of bonding BOs (BBOs) and of antibonding BOs (ABOs), respectively, and determine the k -th order increments to occupation numbers of these orbitals along with intrasubspace bond orders.

The submatrices $-2\mathbf{G}_{(k)}$ ($k = 1, 2, \dots$) taking the off-diagonal positions within the correction $\tilde{\mathbf{P}}_{(k)}$ coincide with the principal matrices of the PNCMO theory (Section 1) up to the factor -2 . At the same time, these determine the k -th order increments to the intersubspace bond orders referring to pairs of BOs of opposite initial occupation.

The zero order member $\tilde{\mathbf{P}}_{(0)}$ of the power series for the DM $\tilde{\mathbf{P}}$ takes a diagonal form containing the initial occupation numbers of BOs. These coincide with 2 and 0 for BBOs and ABOs, respectively. Hence, the submatrix $\tilde{\mathbf{Q}}_{(0)+} = 2\mathbf{I}$ is the only non-zero block of the matrix $\tilde{\mathbf{P}}_{(0)}$.

Separate elements ($G_{(k)il}$) of the principal matrices $\mathbf{G}_{(k)}$ were shown to be expressible algebraically [14] provided that a zero order member of diagonal constitution may be revealed in the total Hamiltonian matrix of the system(s) under study. Our matrix of Eq.(6) corresponds to just this case and thereby the expressions for $G_{(k)il}$ of Ref. [14] may be invoked here.

Let the one-electron energies of BBOs and of ABOs taking the diagonal positions within the matrix $\tilde{\mathbf{H}}_{(0)}$, to be denoted by $E_{(+i)}$ and $E_{(-l)}$, respectively. The expressions for elements $G_{(1)il}$ and $G_{(2)il}$ take then the form

$$G_{(1)il} = - \frac{\langle \varphi_{(+i)} | \hat{H} | \varphi_{(-l)} \rangle}{E_{(+i)} - E_{(-l)}}, \quad (8)$$

$$G_{(2)il} = \frac{1}{E_{(+i)} - E_{(-l)}} \left[\sum_m^{BBOs} \frac{\langle \varphi_{(+i)} | \hat{H} | \varphi_{(+m)} \rangle \langle \varphi_{(+m)} | \hat{H} | \varphi_{(-l)} \rangle}{E_{(+m)} - E_{(-l)}} - \sum_r^{ABOs} \frac{\langle \varphi_{(+i)} | \hat{H} | \varphi_{(-r)} \rangle \langle \varphi_{(-r)} | \hat{H} | \varphi_{(-l)} \rangle}{E_{(+i)} - E_{(-r)}} \right], \quad (9)$$

where the numerators of fractions contain resonance parameters between BOs indicated within the bra- and ket-vectors.

Elements $G_{(1)il}$ of Eq.(8) have been interpreted as direct (through-space) interactions between BOs $\varphi_{(+i)}$ and $\varphi_{(-l)}$. Accordingly, $G_{(2)il}$ of Eq.(9) represent indirect (through-bond) interactions of the same BOs, where both BBOs ($\varphi_{(+m)}$) and ABOs ($\varphi_{(-r)}$) of other bonds are able to play the role of mediators.

Finally, the diagonal elements $G_{(1)ii}$ and $G_{(2)ii}$ deserve a separate discussion. Thus, the above-introduced definition of BOs ensures zero values for intrabond resonance parameters $\langle \varphi_{(+i)} | \hat{H} | \varphi_{(-i)} \rangle$ and thereby for first order elements $G_{(1)ii}$. The second order element $G_{(2)ii}$, in turn, describes the indirect intrabond interaction between BOs of the I-th bond by means of orbitals of other bonds that will be referred to as the intrabond coupling for simplicity. As it is seen from Eq.(7), the intrabond coupling $G_{(2)ii}$ determines the bond order between BOs $\varphi_{(+i)}$ and $\varphi_{(-i)}$ of the I-th bond due to interbond interaction.

Let us turn now to submatrices $\tilde{\mathbf{Q}}_{(k)+}$ and $\tilde{\mathbf{Q}}_{(k)-}$ of Eq.(7). For the first order correction $\tilde{\mathbf{P}}_{(1)}$, the relevant blocks $\tilde{\mathbf{Q}}_{(1)+}$ and $\tilde{\mathbf{Q}}_{(1)-}$ coincide with zero matrices [14], whereas those corresponding to higher values of the order parameter are expressible in terms of products of the principal matrices $\mathbf{G}_{(k)}$ of lower orders. In particular, the most important second order corrections $\tilde{\mathbf{Q}}_{(2)+}$ and $\tilde{\mathbf{Q}}_{(2)-}$ take the form

$$\tilde{\mathbf{Q}}_{(2)+} = -2\mathbf{G}_{(1)}\mathbf{G}_{(1)}^+, \quad \tilde{\mathbf{Q}}_{(2)-} = 2\mathbf{G}_{(1)}^+\mathbf{G}_{(1)}. \quad (10)$$

These relations imply the following explicit forms for alterations in occupation numbers of the BBO $\varphi_{(+i)}$ and of the ABO $\varphi_{(-i)}$ of the I-th bond against their initial values (equal to 2 and 0, respectively), viz.

$$\begin{aligned} X_{(+i)} &\approx \tilde{Q}_{(2)+,ii} = -2 \sum_p^{ABOs} (G_{(1)ip})^2, \\ X_{(-i)} &\approx \tilde{Q}_{(2)-,ii} = 2 \sum_m^{BBOs} (G_{(1)mi})^2. \end{aligned} \quad (11)$$

The above expressions evidently correspond to confinement to second order corrections. In the framework of this approximation, alterations in occupation numbers of BOs prove to be determined by squares of direct interactions between BOs of the bond under consideration and those of other bonds, the latter contributing additive increments to both $X_{(+i)}$ and $X_{(-i)}$. From Eq.(11) it follows also that the initially-occupied BO $\varphi_{(+i)}$ always loses some population, whilst the initially- vacant BO $\varphi_{(-i)}$ acquires it as a consequence of the interbond interaction. Finally, the alterations in occupation numbers of BOs shown in Eq.(11) may be traced back to emergence of

bond orders of intersubspace type within the first order matrix $\tilde{\mathbf{P}}_{(1)}$ (Note that the latter are determined by elements of matrices $-2\mathbf{G}_{(1)}$ as Eq.(7) indicates).

Now, no more is required as to retransform the matrix $\tilde{\mathbf{P}}$ defined by Eqs.(7)-(11) into the HAO basis again. This procedure is performed in the next Section.

3. ANALYSIS OF THE RETRANSFORMED ONE-ELECTRON DENSITY MATRIX. THE PRINCIPAL INTRABOND EFFECTS IN SATURATED MOLECULES

It is evident that each correction $\tilde{\mathbf{P}}_{(k)}$ of the DM $\tilde{\mathbf{P}}$ may be retransformed into the basis $\{\chi\}$ separately using the matrix \mathbf{U} of Eq.(5), viz.

$$\mathbf{P}_{(k)} = \mathbf{U}\tilde{\mathbf{P}}_{(k)}\mathbf{U}^+. \quad (12)$$

Substituting Eqs.(5) and (7) into Eq.(12) yields the following expression for the k -th order correction $\mathbf{P}_{(k)}$ of the charge- bond order matrix \mathbf{P}

$$\mathbf{P}_{(k)} = \begin{vmatrix} \mathbf{T}'_{(k)} + \mathbf{\Pi}'_{(k)} & \mathbf{\Omega}_{(k)} + \mathbf{\Lambda}_{(k)} \\ \mathbf{\Omega}_{(k)}^+ + \mathbf{\Lambda}_{(k)}^+ & \mathbf{T}''_{(k)} + \mathbf{\Pi}''_{(k)} \end{vmatrix}, \quad (13)$$

where the $N \times N$ -dimensional submatrices of the right-hand side take the form

$$\mathbf{T}'_{(k)} = \mathbf{Z}\tilde{\mathbf{Q}}_{(k)+}\mathbf{Z} + \mathbf{V}\tilde{\mathbf{Q}}_{(k)-}\mathbf{V}, \quad \mathbf{T}''_{(k)} = \mathbf{V}\tilde{\mathbf{Q}}_{(k)+}\mathbf{V} + \mathbf{Z}\tilde{\mathbf{Q}}_{(k)-}\mathbf{Z}, \quad (14)$$

$$\mathbf{\Pi}'_{(k)} = -2(\mathbf{V}\mathbf{G}_{(k)}^+\mathbf{Z} + \mathbf{Z}\mathbf{G}_{(k)}\mathbf{V}), \quad \mathbf{\Pi}''_{(k)} = 2(\mathbf{Z}\mathbf{G}_{(k)}^+\mathbf{V} + \mathbf{V}\mathbf{G}_{(k)}\mathbf{Z}), \quad (15)$$

and

$$\mathbf{\Omega}_{(k)} = \mathbf{Z}\tilde{\mathbf{Q}}_{(k)+}\mathbf{V} - \mathbf{V}\tilde{\mathbf{Q}}_{(k)-}\mathbf{Z}, \quad \mathbf{\Lambda}_{(k)} = 2(\mathbf{Z}\mathbf{G}_{(k)}\mathbf{Z} - \mathbf{V}\mathbf{G}_{(k)}^+\mathbf{V}). \quad (16)$$

The intrabond characteristics (i.e. the occupation numbers of HAOs and the neighboring bond orders) evidently are determined by diagonal elements of submatrices of matrices $\mathbf{P}_{(k)}$. The latter, in turn, imbibe the interbond interactions $G_{(1)il}$ and $G_{(2)il}$ as Eqs.(10), (11) and (13)-(16) indicate. This offers us a possibility of revealing the intrabond effects caused by the interbond interaction in the general case without specifying the structure of the molecule under study.

The diagonal constitution of matrices \mathbf{Z} and \mathbf{V} allows us to conclude immediately that diagonal elements of submatrices $\mathbf{T}'_{(k)}$ and $\mathbf{T}''_{(k)}$, as well as those of $\mathbf{\Omega}_{(k)}$ are determined by corrections to occupation numbers of BOs ($\tilde{Q}_{(k)+,ii}$ and $\tilde{Q}_{(k)-,ii}$), whilst the analogous elements of the remaining submatrices ($\mathbf{\Pi}'_{(k)}$, $\mathbf{\Pi}''_{(k)}$ and $\mathbf{\Lambda}_{(k)}$) are proportional to respective intrabond interactions of BOs ($G_{(k)ii}$).

Let us dwell now on consideration of the I-th bond and confine ourselves to the second order increments. Let us define the following new characteristics of this bond

$$\Delta X_{(2)I} = \tilde{Q}_{(2)+,ii} + \tilde{Q}_{(2)-,ii} \quad (17)$$

$$\Delta R_{(2)I} = \tilde{Q}_{(2)+,ii} - \tilde{Q}_{(2)-,ii} \quad (18)$$

The term $\Delta X_{(2)I}$ represents the total population lost (acquired) by the I-th bond owing to interbond interaction. This characteristic actually consists of difference between absolute values of population lost by the BBO $\varphi_{(+)i}$ and of that acquired

by the ABO $\varphi_{(-)i}$. Again, the increment $\Delta R_{(2)I}$ is determined by the sum of the same absolute values and thereby describes the total redistributed population referring to the I-th bond. It is seen that negative contributions to $\Delta R_{(2)I}$ arise owing to both the additional occupation of the ABO $\varphi_{(-)i}$ and the partial deoccupation of the BBO $\varphi_{(+)i}$ as Eq.(11) indicates. Hence, a negative sign of the total redistributed population $\Delta R_{(2)I}$ follows. Along with the above-discussed characteristics $\Delta X_{(2)I}$ and $\Delta R_{(2)I}$, our bond also is represented by respective diagonal elements of matrices $\mathbf{\Pi}'_{(k)}$, $\mathbf{\Pi}''_{(k)}$ and $\mathbf{\Lambda}_{(k)}$. For $k = 1$, these elements vanish owing to zero direct intrabond interaction $G_{(1)ii}$. This implies that the relevant second order increments ($\Pi'_{(2)ii}$, $\Pi''_{(2)ii}$ and $\Lambda_{(2)ii}$) should be considered that are determined by the intrabond coupling $G_{(2)ii}$.

Let us replace now the diagonal elements of matrices \mathbf{Z} and \mathbf{V} of Eqs.(14)-(16) by coefficients z_I and v_I of Eq.(3). For the zero order increments to characteristics of the I-th bond, we then obtain

$$T'_{(0)ii}(T''_{(0)ii}) = 1 \pm \cos \gamma_I, \quad \Omega_{(0)ii} = \sin \gamma_I. \quad (19)$$

The relevant first order corrections prove to yield no contributions to characteristics under study, whilst the second order increments are as follows

$$T'_{(2)ii}(T''_{(2)ii}) = \frac{1}{2}\Delta X_{(2)I} \pm \frac{1}{2}\Delta R_{(2)I} \cos \gamma_I, \quad (20)$$

$$\Omega_{(2)ii} = \frac{1}{2}\Delta R_{(2)I} \sin \gamma_I, \quad (21)$$

$$\Pi'_{(2)ii}(\Pi''_{(2)ii}) = \mp 2G_{(2)ii} \sin \gamma_I, \quad (22)$$

$$\Lambda_{(2)ii} = 2G_{(2)ii} \cos \gamma_I \quad (23)$$

where the upper signs of the right-hand sides of Eqs.(20) and (22) correspond to matrices denoted by the superscript ' , whilst the lower ones refer to matrices supplemented with the superscript ". The definitions of Eqs.(17) and (18) also are invoked when deriving Eqs.(20)-(23).

Let us turn now to interpretation of these expressions. Let us start with the zero order increments. The zero order dipole-like increment $\pm \cos \gamma_I$ to populations of HAOs χ'_i and χ''_{N+i} resulting from elements $T'_{(0)ii}$ and $T''_{(0)ii}$ of Eq.(19) is inherent in the bond under consideration whatever the structure of the whole molecule (γ_I is defined by Eq.(4)). This dipole coincides with the respective value for an isolated bond. Hence, it may be called the primary dipole moment of the I-th bond [21]. In accordance with the expectation, the population of the HAO χ'_i of the more electronegative atom becomes increased, whereas that of the HAO χ''_{N+i} is accordingly reduced as compared to 1. Similarly, the increment $\sin \gamma_I$ following from the element $\Omega_{(0)ii}$ may be referred to as the primary bond order of the I-th bond.

Alterations in occupation numbers of HAOs as well as in intramolecular bond orders due to interbond interaction are determined by second order contributions as the above-derived expressions indicate. Thus, let us consider these terms in a more detail.

Let us start with diagonal elements of matrices $\mathbf{T}'_{(k)}$ and $\mathbf{T}''_{(k)}$ defined by Eq.(20). It was mentioned already that these elements originate from redistribution of population among BOs. In addition, the sum of these elements equal to

$$T'_{(2)ii} + T''_{(2)ii} = \Delta X_{(2)I} \quad (24)$$

coincides with the total lost (acquired) population of the I-th bond. Consequently, the elements $T'_{(2)ii}$ and $T''_{(2)ii}$ describe the actual way of distribution of the lost (acquired) population of the I-th bond among the two HAOs. It is no surprise in this connection that the expressions for these elements contain uniform increments ($\frac{1}{2}\Delta X_{(2)I}$) equal to a half of the total population lost (acquired) by this bond and a dipole-like increment ($\pm d_{(2)I}$), where

$$d_{(2)I} = \frac{1}{2}\Delta R_{(2)I} \cos \gamma_I. \quad (25)$$

It is seen that this dipole depends on the total redistributed population $\Delta R_{(2)I}$ and vanishes for homopolar bonds described by uniform Coulomb parameters (Given that $\alpha_{I1} = \alpha_{I2}$, $\gamma_I = \frac{\pi}{2}$ and $\cos \gamma_I = 0$). Moreover, the *a priori* negative sign of $d_{(2)I}$ for any I follows from the negative sign of $\Delta R_{(2)I}$. This implies that the HAO χ'_i pertinent to the more electronegative atom loses its population owing to formation of the dipole $\pm d_{(2)I}$, whereas the HAO χ''_{N+i} acquires an additional population. Therefore, the primary dipole moment of the I-th bond becomes reduced after 'embedding' this bond into any molecule. In this connection, the term $\pm d_{(2)I}$ has been called the depolarization dipole moment [21].

Opposite orientations of the primary dipole and of the depolarization one may be easily accounted for by shapes of BOs $\varphi_{(+)i}$ and $\varphi_{(-)i}$. Thus, the shape of the BBO $\varphi_{(+)i}$ of Eq.(2) ensures the primary reduction of population of the HAO χ'_i when this BO is deoccupied. Accordingly, the additional population acquired by the ABO $\varphi_{(-)i}$ becomes localized mainly on the HAO χ''_{N+i} . Both of these effects evidently contribute to reduction of the primary dipole moment of our bond.

The diagonal element $\Omega_{(2)ii}$ of the matrix $\Omega_{(2)}$ shown in Eq.(21) represents the second order increment to the internal bond order of the I-th bond and also is determined by the total redistributed population $\Delta R_{(2)I}$. The negative sign of the latter implies reduction of the primary bond order under influence of the interbond charge redistribution. This result also causes no surprise if we recall an additional occupation of the antibonding BO $\varphi_{(-)i}$ and a certain deoccupation of the bonding BO $\varphi_{(+)i}$ underlying the total redistributed population $\Delta R_{(2)I}$.

It is seen, therefore, that two interdependent intrabond effects originate from charge redistribution among BOs, namely the depolarization of an initially-heteropolar bond and the related reduction of the internal bond order. In the case of an initially-homopolar bond, lowering of the internal bond order only is observed. The above-mentioned simultaneous effects evidently reflect a trend towards a homolytic dissociation of the given bond after including it into the molecule under study. In this connection, the term 'the homolytic predissociation' will be used to refer to these interdependent effects.

Let us turn now to the remaining second order increments shown in Eqs.(22) and (23) and determined by the intrabond coupling $G_{(2)ii}$. The sign of the latter cannot be established *a priori* (i.e. without specifying the structure of the system) in contrast to population alterations of BOs. The same refers also to the sign of the secondary dipole moment ($\pm p_{(2)I}$) resulting from the elements $\Pi'_{(2)ii}$ and $\Pi''_{(2)ii}$ of Eq.(22) and defined as follows

$$p_{(2)I} = -2G_{(2)ii} \sin \gamma_I. \quad (26)$$

Nevertheless, an interdependence is evident between the sign of this dipole and that of the related alteration in the bond order of the I-th bond described by the increment $\Lambda_{(2)ii}$ of Eq.(23). Moreover, reduction of the bond order (predissociation) is expected to take place for a negative value of the intrabond coupling ($G_{(2)ii}$), and this effect is predicted to be accompanied by emergence of a positive dipole ($p_{(2)I} > 0$) (Just this fact makes the term 'the polarization dipole moment' used to refer to the increment $\pm p_{(2)I}$ [21] even more appropriate). Inasmuch as the total dipole moment of our bond grows in this case, we have actually to do here with the trend towards a heterolytic dissociation or, more conveniently, with the heterolytic predissociation of an initially heteropolar bond.

The case of an initially homopolar bond deserves a separate consideration in this respect. Indeed, formation of a non-zero secondary dipole ($\pm p_{(2)I}$) due to intrabond coupling is possible also for the above-specified bond. In particular, dipole moments of this type were shown to be responsible for the secondary (induced) dipoles of C-C(C-H) bonds under influence of a heteroatom-containing bond [21]. Emergence of such a secondary dipole, however, is not accompanied by reduction of the internal bond order ($\Lambda_{(2)ii} = 0$ in this case). Hence, the secondary polarization of homopolar bonds does not imply their heterolytic predissociation. In other terms, the heterolytic predissociation is among consequences of interbond interaction only so far as the initially heteropolar bond are concerned.

The additive nature of increments representing the homo- and heterolytic predissociations of bonds also is among the conclusions of this section.

4. CONTRIBUTIONS OF INTRABOND EFFECTS TO TOTAL ENERGIES OF SATURATED ORGANIC MOLECULES

In this Section, we will look for alterations in total energies representing the homo- and heterolytic predissociation of bonds. In this connection, we start with an overview of the general results of the PNCMO theory concerning total energy [16,18,19].

As it was mentioned already (Section 1), the total energy of the system(s) under study (ε) has been expressed in the form of power series in the framework of the PNCMO theory. Moreover, any correction of this series ($\varepsilon_{(k)}$) was shown to consist of a sum of two interrelated components ($\varepsilon_{(k)}^{(\alpha)}$ and $\varepsilon_{(k)}^{(\beta)}$) defined as follows

$$\varepsilon_{(k)}^{(\alpha)} = \text{Trace}(\mathbf{P}_{(k)}\mathbf{H}_{(0)}), \quad \varepsilon_{(k)}^{(\beta)} = \text{Trace}(\mathbf{P}_{(k-1)}\mathbf{H}_{(1)}). \quad (27)$$

The above-mentioned relation takes the form

$$(k-1)\varepsilon_{(k)}^{(\beta)} = -k\varepsilon_{(k)}^{(\alpha)}. \quad (28)$$

Opposite signs of both components result from this principal relation along with the following inequality for their absolute values

$$\left| \varepsilon_{(k)}^{(\beta)} \right| > \left| \varepsilon_{(k)}^{(\alpha)} \right|. \quad (29)$$

The possibility of expressing the total correction $\varepsilon_{(k)}$ in terms of either $\varepsilon_{(k)}^{(\alpha)}$ or $\varepsilon_{(k)}^{(\beta)}$ also is evident from the above results, viz.

$$\varepsilon_{(k)} = -\frac{1}{k-1}\varepsilon_{(k)}^{(\alpha)}, \quad \varepsilon_{(k)} = \frac{1}{k}\varepsilon_{(k)}^{(\beta)}. \quad (30)$$

Finally, stabilization of the system due to interaction (the latter is assumed to be contained within the first order Hamiltonian matrix $\mathbf{H}_{(1)}$) was shown to be determined by the second order correction $\varepsilon_{(2)}$. Given that a negative energy unit is accepted, the above statement along with Eq.(30) resolves itself into the following relations

$$\Delta\varepsilon_{stab} = \varepsilon_{(2)} = \varepsilon_{(k)}^{(\alpha)} + \varepsilon_{(k)}^{(\beta)} = -\varepsilon_{(k)}^{(\alpha)} > 0, \quad \varepsilon_{(k)}^{(\alpha)} < 0, \quad \varepsilon_{(k)}^{(\beta)} = -2\varepsilon_{(k)}^{(\alpha)} > 0, \quad (31)$$

where $\Delta\varepsilon_{stab}$ stands for the stabilization energy.

As with other expressions of the PNCMO theory, the relations of Eqs.(27)-(31) originally refer to the basis of BOs. In contrast to the power series for the DM, however, Eqs.(27)-(31) are invariant against an unitary transformation of the basis set. That is why the labels $\tilde{}$ used in Eqs.(6) and (7) for characteristics represented in the basis of BOs are omitted here.

The above-discussed invariance of Eqs.(27)-(31) allows us to substitute the corrections $\mathbf{P}_{(k)}$ of Eqs.(13)-(16) along with the zero and first order members of the initial Hamiltonian matrix of Eq.(1) directly into Eq.(27). As a result, we are able to derive the expressions for both the total corrections $\varepsilon_{(k)}$ and their separate components $\varepsilon_{(k)}^{(\alpha)}$ and $\varepsilon_{(k)}^{(\beta)}$ in terms of characteristics of our system(s) represented in the basis of HAOs $\{\chi\}$. For the zero and first order members, the result is as follows

$$\varepsilon_{(0)} = \varepsilon_{(0)}^{(\alpha)} = \sum_I \varepsilon_{(0)I}^{(\alpha)}, \quad \varepsilon_{(1)} = 0, \quad (32)$$

where $\varepsilon_{(0)I}^{(\alpha)}$ is the primary energy of the I-th bond, viz.

$$\varepsilon_{(0)I}^{(\alpha)} = (\alpha_{I1} + \alpha_{I2}) + (\alpha_{I1} - \alpha_{I2}) \cos \gamma_I + 2\beta_I \sin \gamma_I. \quad (33)$$

Let us turn now to the second order energy $\varepsilon_{(2)}$ responsible for stabilization of our system vs. the set of isolated bonds and lone electron pairs. Let us start with a brief discussion of its separate components $\varepsilon_{(2)}^{(\alpha)}$ and $\varepsilon_{(2)}^{(\beta)}$.

Thus, zero values of diagonal elements of submatrices $\mathbf{A}_{(1)}$, $\mathbf{B}_{(1)}$ and $\mathbf{C}_{(1)}$ of Eq.(1) ensure zero contributions to the correction $\varepsilon_{(2)}^{(\beta)}$ originating both from the internal bond orders and from the populations of HAOs. This implies the component $\varepsilon_{(2)}^{(\beta)}$ to be determined by non-neighboring bond orders that are formed between pairs of HAOs of different bonds due to their interaction. Hence, the increment $\varepsilon_{(2)}^{(\beta)}$ will be called the interbond component of the second order energy.

Again, the diagonal constitution of submatrices $\mathbf{A}_{(0)}$, $\mathbf{B}_{(0)}$ and $\mathbf{C}_{(0)}$ of the zero order Hamiltonian matrix $\mathbf{H}_{(0)}$ of Eq.(1) ensures the dependence of the remaining component $\varepsilon_{(2)}^{(\alpha)}$ of the correction $\varepsilon_{(2)}$ exclusively on intrabond characteristics. In this connection, the increment $\varepsilon_{(2)}^{(\alpha)}$ will be referred to as the intrabond component of the second order correction to the total energy.

Let us turn now to the principal relations shown in Eqs.(28)-(31). From Eq.(31) it follows that the absolute value of $\varepsilon_{(2)}^{(\beta)}$ exceeds twice the relevant value of $\varepsilon_{(2)}^{(\alpha)}$. Hence, stabilization of the whole system vs. the set of isolated bonds and lone pairs proves to be actually determined by the interbond component $\varepsilon_{(2)}^{(\beta)}$ of the second order energy $\varepsilon_{(2)}$ and thereby only by newly-formed bond orders between pairs of HAOs

of different bonds due to their interaction. Furthermore, the opposite signs of $\varepsilon_{(2)}^{(\alpha)}$ and $\varepsilon_{(2)}^{(\beta)}$ seen from Eq.(28) and (31) allow us then to expect that the above-specified stabilization necessarily is accompanied by intrabond destabilization. Finally, the larger is the total extent of destabilization of bonds, the more stabilized the system actually becomes due to the interbond interaction.

In this connection, let us consider the intrabond component $\varepsilon_{(2)}^{(\alpha)}$ in a more detail. It is evident that the relevant expression may be presented as a sum of partial increments of separate bonds as shown in Eq.(32), where

$$\begin{aligned} \varepsilon_{(2)I}^{(\alpha)} = & \frac{1}{2}(\alpha_{I1} + \alpha_{I2})\Delta X_{(2)I} + \frac{1}{2}(\alpha_{I1} - \alpha_{I2})\Delta R_{(2)I} \cos \gamma_I + \beta_I \Delta R_{(2)I} \sin \gamma_I \\ & - 2(\alpha_{I1} - \alpha_{I2})G_{(2)ii} \sin \gamma_I + 4\beta_I G_{(2)ii} \cos \gamma_I \end{aligned} \quad (34)$$

describes the destabilization energy of the I-th bond. Three types of increments are present in Eq.(34): The first $\Delta X_{(2)I}$ -containing term describes the effect of charge redistribution among separate bonds and lone electron pairs of our system upon the energy of the I-th bond. The subsequent two $\Delta R_{(2)I}$ -containing increments of the same relation represent the contribution of the homolytic predissociation of the I-th bond to the same energy. Finally, the last two ($G_{(2)ii}$ -containing) terms may be accordingly traced back to the heterolytic predissociation of the same bond.

Before passing to the more detailed analysis of these increments, let us note that the last two terms of the right-hand side of Eq.(34) actually cancel out each other. To show this, the alternative form of Eq.(4), namely

$$(\alpha_{I1} - \alpha_{I2}) \sin \gamma_I = 2\beta_I \cos \gamma_I \quad (35)$$

should be substituted into Eq.(34).

We may conclude on this basis that the heterolytic predissociation is an energy-free effect in the framework of the Hückel model. This result causes no surprise if we recall that electrostatic forces are not considered explicitly in this model (just these forces are expected to protect the bonds from the heterolytic dissociation).

The total intrabond component $\varepsilon_{(2)}^{(\alpha)}$ of the second order correction $\varepsilon_{(2)}$ takes then the following final form

$$\begin{aligned} \varepsilon_{(2)}^{(\alpha)} = & \sum_I \frac{1}{2}(\alpha_{I1} + \alpha_{I2})\Delta X_{(2)I} + \sum_I \left[\frac{1}{2}(\alpha_{I1} - \alpha_{I2}) \cos \gamma_I \right. \\ & \left. + \beta_I \sin \gamma_I \right] \Delta R_{(2)I} \end{aligned} \quad (36)$$

and contains two principal contributions describing the total effects of charge redistribution among bonds and of their homolytic predissociation, respectively. These contributions are likely to be of opposite signs within the total intrabond energy $\varepsilon_{(2)}^{(\alpha)}$ as it was the case with the intra- and interbond components within the total second order energy $\varepsilon_{(2)}$ (see Eq.(31)).

Indeed, the inequalities $\alpha_{I1} \geq \alpha_{I2} > 0$ and $\beta_I > 0$ accepted in Section 2 and the *a priori* negative sign of any redistributed population $\Delta R_{(2)I}$ ensure the negative sign of the second sum of Eq.(36). Hence, the homolytic predissociation always contributes to the destabilizing nature of the total intrabond component $\varepsilon_{(2)}^{(\alpha)}$ in accordance with the expectation. So far as the first sum of Eq.(36) is concerned, it

is likely to take a positive value and thereby to yield a certain stabilizing increment to the total intrabond energy $\varepsilon_{(2)}^{(\alpha)}$.

The latter anticipation is based on the following points. First, negative (lost) populations ($\Delta X_{(2)I} < 0$) correspond to electron-donating bonds and positive (acquired) populations ($\Delta X_{(2)I} > 0$) refer to electron-accepting bonds in the first sum of Eq.(36). Second, the electron-donating bonds usually are those described by lower mean values of Coulomb parameters, whereas the electron-accepting bonds coincide with those represented by higher mean values of the same parameters. This allows us to expect that the total positive increment of electron-accepting bonds to the first sum of Eq.(36) exceeds the absolute value of the total negative increment of the electron-donating bonds and thereby the sum under discussion takes a positive value. In other terms, charge is usually transferred from bonds that are built up of orbitals of a lower average electronegativity to those formed by HAOs of higher electronegativity and thereby a certain stabilization of the system is expected to result (In the case of two interacting bonds (1 and 2), this conclusion may be easily verified by invoking the equality $\Delta X_{(2)1} = -\Delta X_{(2)2}$ based on the charge conservation condition). It should be mentioned finally that the negative sign of the total intrabond component $\varepsilon_{(2)}^{(\alpha)}$ implies that the increment of the homolytic predissociation predominates over that of interbond charge redistribution in Eq.(36). Hence, the intrabond destabilization may be largely traced back to the homolytic predissociation.

It is seen, therefore, that the constitution of the total energy of saturated organic molecules reflects interdependences between inter- and intrabond effects. Moreover, the final stabilization energy of the system vs. the set of isolated bonds and lone electron pairs is a result of a certain 'balance' between positive and negative increments. In other terms, any of the effects under study causes the respective counter-effect upon the total energy:

First, formation of new non-neighboring bond orders between HAOs of different bonds due to interbond interaction gives rise to stabilization of the system. This interbond effect, however, necessarily causes a definite intrabond destabilization that reduces twice the 'original' stabilizing increment of non-neighboring bond orders. Second, the above-mentioned destabilization is primarily due to the homolytic predissociation of bonds. To ensure the latter, however, a certain redistribution of population necessarily takes place among bonds. As a result, the actual extent of intrabond destabilization also becomes somewhat reduced against its original value.

5. COMPARISON OF THE RESULTS OBTAINED TO THOSE OF PREVIOUS STUDIES. CONCLUDING REMARKS

1. The retransformation procedure suggested in this paper is applied to the total one-electron density matrix of saturated organic molecules and not to its separate submatrices as it was the case in Refs. [21,24]. Consequently, the total charge-bond order matrix of these systems is obtained in the present study in contrast to expressions for individual occupation numbers of HAOs derived previously [21]. This allows us to consider alterations in both occupation numbers and bond orders caused by the interbond interaction and to introduce the concepts of homo- and heterolytic predissociation of bonds. Moreover, a certain analogy may be traced between the latter concepts and those used when discussing alterations in internuclear distances due to perturbation [33].

2. The initial Hamiltonian matrix of the present study (see Eq.(1)) is a generalization of that of hydrocarbons [20,22] to the case of non-uniform Coulomb parameters and of dissimilar intrabond resonance parameters. The same evidently refers to corresponding results too. In particular, the matrix $\mathbf{\Omega}_{(2)}$ defined by Eq.(16) proves to be a generalization of the rebonding matrix of Ref.[23]. It is no surprise in this connection that the homolytic predissociation of bonds defined in the present study embraces the rebonding effect of Ref.[23], the latter consisting in reduction of the neighboring bond orders in hydrocarbons due to formation of non-neighboring bond orders.

3. Comparison of the results of the present study to those of Refs. [20,22,23] shows that passing from hydrocarbons to heteroatom- containing systems is accompanied by emergence of an alternative way of (pre)dissociation of bonds, namely of the heterolytic (pre)dissociation. This result evidently is not unexpected as the heterolytic dissociation is peculiar to heteroatom- containing (heteropolar) bonds. Redistribution of population among separate bonds (interbond charge transfer) in heteroatom- containing systems following from our study also causes no surprise.

4. The expression for the intrabond component ($\varepsilon_{(2)}^{(\alpha)}$) of the second order energy ($\varepsilon_{(2)}$) derived in this paper and shown in Eq.(36) is an alternative form of Eq.(40) of Ref. [18] representing the same energy increment in terms of charge redistribution among separate bond orbitals. Passing from this previous result to that of Eq.(36) actually corresponds to reformulating of charge redistribution among BOs in terms of contributions of separate bonds. In this context, cancellation of the $G_{(2)ii}$ -containing terms when deriving Eq.(36) from Eq.(34) is a natural course of things.

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