Abstract
The article contains a summary of fundamentals of the perturbational non-canonical molecular orbital (PNCMO) theory formerly developed by the author. In some respects, the PNCMO theory is a generalization of the well-known simple PMO theory: First, the usual diagonalization problem (and/or the eigenvalue equation) for a certain model Hamiltonian matrix (H) is now replaced by two interrelated non-canonical one-electron problems, namely by the block-diagonalization problem for the matrix H following from the Brillouin theorem and determining non-canonical (localized) MOs (NCMOs) and by the commutation equation for the respective one-electron density matrix (charge-bond order (CBO)) matrix. Second, perturbative solutions of the above-specified alternative problems are sought in terms of entire submatrices (blocks) of the matrix H instead of usual matrix elements (e.g. of Coulomb and resonance parameters). Third, a generalized version of the perturbation theory (PT) is used in place of the standard Rayleigh-Schrödinger PT (RSPT), wherein non-commutative quantities stand for the usual (commutative) ones (cf. the so-called non-commutative RSPT (NCRSPT)). As a result, algebraic expressions are derived for the principal quantum-chemical characteristics (including the CBO matrix, the NCMO representation matrix and the total energy) that embrace definite classes of Hamiltonian matrices and thereby of molecules. To illustrate the point, saturated and conjugated hydrocarbons are taken as examples. Arguments are given that the PNCMO theory possibly forms the basis of a novel way of qualitative chemical thinking.

Introduction

The perturbational molecular orbital (PMO) theory [1-3] is among the most popular and efficient tools for evaluation of observed properties of molecules and for qualitative chemical thinking in general. As with any perturbative approach, the main advantage of the above-mentioned theory consists in a possibility of a direct comparison of two (or several) slightly different molecules or molecular systems, e.g. of a certain hydrocarbon and its heteroatom-containing derivative(s). In other words, application of the PMO theory allows our attention to be concentrated on consequences of an alteration in the structure of the system(s) under interest instead of properties of each molecule separately.

The PMO theory is commonly understood as a combination of the standard Rayleigh-Schrödinger perturbation theory (RSPT) [4, 5] and of the Hückel type
(and/or tight binding) approximation for Hamiltonian matrix elements (see e.g. [6-9]). In a broader sense, however, any perturbative solution of a secular (eigenvalue) equation for a Hückel type Hamiltonian matrix \( \mathbf{H} \) of molecule may be ascribed to the PMO theory along with the subsequent steps, e.g. derivation of the total energy and/or of the relevant charge-bond order (CBO) matrix using the eigenvectors and eigenvalues obtained. It is then no surprise that the results of the theory under discussion are usually interpreted in terms of individual orbitals (underlying the matrix \( \mathbf{H} \)) and their interactions, the latter often tending to replace the interatomic bonds in the qualitative chemical thinking.

For some specific series of molecules (e.g. polyenes), the Hückel type Hamiltonian matrices are known to take definite common forms. Accordingly, the so-called closed solutions of the relevant eigenvalue equations are obtainable that represent the entire series of the compounds concerned (see Ref.[9] for an overview). To a certain extent, the same refers also to the well-known alternant conjugated hydrocarbons. Indeed, the eigenvectors (MOs) and the eigenvalues of the relevant matrix \( \mathbf{H} \) are characterized by common properties found in quantum chemistry textbooks (see e.g. [8, 10, 11]). In the above-enumerated special cases, a subsequent employment of a perturbative approach really yields important general results, e.g. the famous rule of the alternating polarity ‘[12-15]. The overall potential of the usual PMO theory, however, is rather limited in respect of going beyond individual molecules and their pairs. The reason certainly lies in the nature of the secular (eigenvalue) equation itself that is designed to represent a single quantum mechanical system.

As is well-known, it is quite usual for chemists to think in terms of broad classes of compounds (e.g. alkanes, arenes, etc.), as well as of the so-called effects manifesting themselves in all representatives of a certain class (e.g. the inductive effect, conjugation of unsaturated fragments, etc.) [16-19]. In this connection, it seemed reasonable to look for a more general version of the PMO theory. To this end, alternative (the so-called non-canonical) one-electron problems have been taken as a basis instead of the secular (eigenvalue) equation, namely the commutation condition for the one-electron density matrix (DM) [14] and the (local) Brillouin theorem [20-24]. Perturbative solutions of these two problems in the framework of the Hückel type approximation resulted into a new version of the PMO theory called perturbational non-canonical MO (PNCMO) theory.

The above-mentioned two principal non-canonical one-electron problems are discussed below in a detail (Subsections 1.1 and 1.2). Let us only note here that the solutions of these problems proved to be obtainable for certain classes of Hamiltonian matrices in terms of entire submatrices (blocks) of the latter playing the role of multi-dimensional (and thereby non-commutative) parameters. The standard RSPT has been accordingly replaced by a certain generalized version of the perturbation theory, wherein non-commutative quantities stand instead of usual (commutative) ones [25, 26]. The relevant results have been consequently interpreted in terms of entire subsets of basis orbitals and the intersubset interaction. Thus, the PNCMO theory seems to offer a novel way of qualitative chemical thinking.

Despite the above-mentioned distinctive features of the generalized theory, a certain analogy between the latter and the usual PMO theory still remains, which is useful for understanding both the nature of the newly-introduced generalizations and the overall scheme of presentation chosen in this article. Before clarifying this
analogy, however, let us recall some well-known facts.

In its standard form \([4, 5]\), the RSPT is applicable to systems characterized by relatively large intervals between individual energy levels as compared to the extent of perturbation, usually referred to as the standard "perturbational" case (i). Meanwhile, the opposite extreme situation (embracing systems described by small or even zero inter-level energy intervals and known as a (quasi)degenerate case (ii)) needs a certain special treatment (namely, passing to linear combinations of (quasi)degenerate orbitals). If we take a simple two-level system at the Hückel level as an example, the above-mentioned cases (i) and (ii) are correspondingly characterized by small ratios \(\beta/(\alpha_1 - \alpha_2)\) and \((\alpha_1 - \alpha_2)/\beta\), where \(\alpha_1, \alpha_2\) and \(\beta\) stand for the Coulomb and resonance parameters, respectively.

The PNCMO theory overviewed in this article is constructed using the above-specified extreme two-level systems as prototypes. Thus, the standard (also alternatively called implicit) version of the theory (Sections 1 and 2) addresses systems representable by two weakly-interacting well-separated subsets of basis orbitals in analogy with the two-level system of the first type (i). Thereupon, the quasi-degenerate version of the PNCMO theory is overviewed in Section 3 that embraces systems described by two strongly-interacting subsets of orbitals.

1. The standard (implicit) form of the PNCMO theory

Let us consider a certain molecule or molecular system containing an even number of electrons \((2n)\). Let this system be represented by an orthogonal basis set \(\{\varphi\}\) (the case of a non-orthogonal basis set has been studied in Ref.\([27]\)). The total number of basis functions will be denoted by \(N\). It deserves an immediate emphasizing that neither the numbers \(n\) and \(N\), nor the nature of basis orbitals \(\{\varphi\}\) are specified at the present stage of our discussion.

Let us now introduce a certain zero order approximation for our system, wherein \(n\) basis orbitals of lowest one-electron energies are double-occupied, whilst the remaining \(s\) functions are vacant, where \(s = N - n\). Let these two types of orbitals be correspondingly denoted by \(\varphi_{(+)}^i\) and \(\varphi_{(-)}^l\), where \(i = 1, 2...n\) and \(l = n + 1, n + 2, ...N\). Since the occupation numbers of these basis orbitals are no longer equal to 2 and 0 after taking into account the perturbation (as discussed below), orbitals \(\varphi_{(+)}^i\) and \(\varphi_{(-)}^l\) will be referred to as initially-occupied and initially-vacant ones. Let the above-defined two types of orbitals be collected into separate \(n\)– and \(s\)–dimensional subsets denoted by \(\{\varphi_{(+)}\}\) and \(\{\varphi_{(-)}\}\), respectively. Another important property of our zero order approximation consists in absence of interactions between orbitals of different subsets. Meanwhile, interactions of the zero order magnitude are allowed inside subsets both \(\{\varphi_{(+)}\}\) and \(\{\varphi_{(-)}\}\). At the Hückel level, the interactions concerned coincide with respective resonance parameters.

Further, let us assume the above-specified zero order system to undergo a certain perturbation, generally embracing alterations in both Coulomb and resonance parameters including those of intra- and intersubset types. The newly-emerging interorbital interactions are supposed to be weak as compared to the energy gap between subsets \(\{\varphi_{(+)}\}\) and \(\{\varphi_{(-)}\}\). Finally, let our energy reference point be chosen in the middle of the above-mentioned gap. One-electron energies of orbitals \(\varphi_{(+)}^i\) and \(\varphi_{(-)}^l\) will be denoted by \(\varepsilon_{(+)}^i\) and \(\varepsilon_{(-)}^l\), respectively, where the minus sign in
front of $\varepsilon_{(-)l}$ is introduced for further convenience. Given that a negative energy unit is accepted as usual, energetic parameters both $\varepsilon_{(+)}i$ and $\varepsilon_{(-)l}$ take positive values, i.e. $\varepsilon_{(+)}i > 0$ and $\varepsilon_{(-)l} > 0$.

As a result, the total Hamiltonian matrix of our system ($H$) consists of the zero order member ($H(0)$) and of the first order one ($H(1)$), the former taking a block-diagonal form, viz.

$$H = H(0) + H(1) = \begin{pmatrix} E_{(+)} & 0 \\ 0 & -E_{(-)} \end{pmatrix} + Q \begin{pmatrix} T & R \\ R^+ & Q \end{pmatrix}. \quad (1.1)$$

Submatrices (blocks) $E_{(+)}$, $T$, $-E_{(-)}$, $Q$, and $R$ correspond here to individual subsets $\{\varphi_{(+)}\}$ and $\{\varphi_{(-)}\}$ and to their interaction, respectively, and correspondingly are $n \times n$- and $s \times s$-dimensional matrices. The superscript + represents here and below the Hermitian-conjugate (transposed) counterpart of the relevant matrix. Diagonal elements $E_{(+)}ii$ and $E_{(-)}ll$ of the zero order (sub)matrices $E_{(+)}$ and $E_{(-)}$ coincide with the above-introduced energetic parameters $\varepsilon_{(+)}i$ and $\varepsilon_{(-)l}$, respectively, whereas the off-diagonal ones $E_{(+)}ij$ ($i \neq j$) and $E_{(-)}lm$ ($m \neq l$) represent the zero order intrasubset interactions. Accordingly, $n \times n$- and $s \times s$-dimensional (sub)matrices $T$ and $Q$ contain certain corrections to the latter due to perturbation. Finally, newly-emerging intersubset interactions are included into the $n \times s$- and $s \times n$-dimensional (sub)matrices $R$ and $R^+$. As with numbers $n$ and $N$, the "internal" constitutions of (sub)matrices $E_{(+)}$, $T$, $E_{(-)}$, $Q$, and $R$ are not specified.

Consequently, Eq.(1.1) actually embraces a large class of specific Hamiltonian matrices and thereby a wide variety of underlying systems (although both $H$ and its blocks are referred to below as matrices for simplicity). It is also evident that the above-exhibited matrix $H$ is a generalization of a simple Hamiltonian matrix of a two-level two-electron system [28], viz.

$$h = h(0) + h(1) = \begin{pmatrix} \varepsilon_{(+)} & 0 \\ 0 & -\varepsilon_{(-)} \end{pmatrix} + \begin{pmatrix} \tau & \rho \\ \rho & \kappa \end{pmatrix}, \quad (1.2)$$

where $\varepsilon_{(+)} + \tau$, $-\varepsilon_{(-)} + \kappa$ and $\rho$ coincide with the usual Coulomb and resonance parameters, respectively. Accordingly, our principal condition about a weak intersubset interaction turns into that of a small ratio $\rho/(\varepsilon_{(+)} + \varepsilon_{(-)})$. In this connection, the $2\times2$-dimensional matrix $h$ may be called the prototype of the matrix $H$. It is also evident that the matrix $h$ refers to the usual "perturbational" case (i) of the Introduction that is characterized by a small resonance parameter as compared to the energy gap. Again, it is seen that passing from the simple $2\times2$-dimensional matrix $h$ of Eq.(1.2) to the multidimensional one ($H$ of Eq.(1.1)) is accompanied by replacing the usual (one-dimensional) parameters $(\varepsilon_{(+)}, \varepsilon_{(-)}, \tau, \kappa$ and $\rho)$ by multidimensional ones $(E_{(+)}$, $E_{(-)}$, $T$, $Q$, and $R$, respectively). Thus, we actually have to do here with a non-trivial generalization. It is then no surprise that this step has important consequences.

First of all, solution of the usual secular (eigenvalue) equation is no longer possible for the matrix $H$ [28]. This implies that neither the canonical MOs (CMOs) nor their one-electron energies may be derived and used as the principal quantum-chemical characteristic when describing the class of compounds embraced by the matrix $H$. Thus, we necessarily have to abandon the usual (canonical) MO method and turn to alternative (non-canonical) ones.
As opposed to the unique eigenvalue equation, various forms of the non-canonical one-electron problem are possible. The commutation equation [14] for the one-electron density matrix (DM) (Subsect. 1.1) was chosen as the principal problem in the PNCMO theory under discussion for the following reasons: First, the DM (and thereby the charge-bond order (CBO) matrix) is among the most fundamental unique quantum-chemical characteristics of molecule [29] describing the relevant charge distribution and related to numerous observed properties. Second, solution of the above-mentioned equation yields the CBO matrix \( \mathbf{P} \) directly without any reference to MOs and thereby allows us to study the relation between individual elements of the matrix \( \mathbf{P} \), on the one hand, and those of the respective Hamiltonian matrix \( \mathbf{H} \), on the other hand, i.e. between charge distribution and the structure of the given system. The third and the most important reason, however, is that the commutation equation for the DM proves to be solvable for the whole class of matrices embraced by Eq.(1.1) as discussed in the Subsection 1.1 in a detail.

An alternative non-canonical one-electron problem originates from the Brillouin theorem [20-24] and determines the so-called localized (non-canonical) MOs (LMOs) directly without invoking the usual canonical MOs (CMOs). This problem is a generalization of the eigenvalue equation for the prototypal matrix \( \mathbf{h} \) of Eq.(1.2) [28] to the case of multidimensional elements (Subsect. 1.2). Apart from solution of the commutation equation, the DM (CBO matrix) is also known to follow from the projector to the subspace of occupied one-electron states [29] including either CMOs or non-canonical MOs (NCMOs). Employment of just this fact allowed us to relate the overall charge (re)distribution to shapes (reshapings) of particular NCMOs (Subsect. 1.3). Finally, expressions for the total energy (Subsect. 1.4) also are obtainable using either the DM or NCMOs.

1.1. The direct way of derivation of the one-electron DM

The non-canonical one-electron problem for the DM (charge-bond order matrix) \( \mathbf{P} \) consists in solution of the following system of matrix equations [14, 30-34]

\[
[H, \mathbf{P}] = 0, \quad \mathbf{P}^2 = 2\mathbf{P}; \quad Tr\mathbf{P} = 2n,
\]

where \( \mathbf{H} \) is the initial Hamiltonian matrix coinciding with that of Eq.(1.1) in our case. Notations \([...,]_\cdot \) and \( Tr \) stand here and below for the commutator of matrices and for a Trace of the latter, respectively. The first relation of Eq.(1.1.1) (the commutation condition) is the main physical requirement determining the matrix \( \mathbf{P} \) [35] and resulting from the Dirac equation for the time-independent Hamiltonian [14]. The remaining relations are additional system-structure-independent restrictions following from the idempotence requirement \( (\mathbf{P}^2 = \mathbf{P}) \) for the projector \( \mathbf{P} = \mathbf{P}^2 \) [4, 29, 35] and from the charge conservation condition, respectively.

As opposed to the most well-known way of derivation of the CBO matrix \( \mathbf{P} \) on the basis of projector to the subspace of occupied one-electron (molecular) orbitals [29], the above-exhibited problem may be solved directly, i.e. without any reference to molecular orbitals (MOs). The solution concerned [36] was based on the following points: First, the CBO matrix \( \mathbf{P} \) has been sought in the form of power series

\[
\mathbf{P} = \sum_{k=0}^{\infty} \mathbf{P}(k) = \mathbf{P}(0) + \mathbf{P}(1) + \mathbf{P}(2) + \mathbf{P}(3)\ldots
\]
i.e. as a sum of increments \( (P_{(k)}) \) of increasing orders \((k)\) with respect to the first order Hamiltonian matrix \( H_{(1)} \) [Parameters contained within the latter and underlying the expansion should be specified in each particular case separately]. Second, both the total CBO matrix \( P \) and its individual increments \( P_{(k)}, k = 0, 1, 2, ... \) have been initially represented in terms of four submatrices (blocks) of appropriate dimensions (coinciding with those of blocks of matrices \( H, H_{(0)} \) and \( H_{(1)} \) of Eq.(1.1)), viz.

\[
P = \begin{pmatrix} P_{11} & P_{12} \\ P_{21} & P_{22} \end{pmatrix}, \quad P_{(k)} = \begin{pmatrix} P_{11}^{(k)} & P_{12}^{(k)} \\ P_{21}^{(k)} & P_{22}^{(k)} \end{pmatrix}, \tag{1.1.3}
\]

where the subscripts 11, 22 and 12(21) here and below refer to separate subsets of basis orbitals \( \{\varphi_+\} \) and \( \{\varphi_-\} \) and to their interaction, respectively. Accordingly, the blocks of the matrix \( P \) (i.e. \( P_{11}, P_{12}, P_{21} \) and \( P_{22} \)) also take the form of power series like that of Eq.(1.1.2). It deserves emphasising that no need arises here for specifying either the internal constitutions of the blocks concerned nor their dimensions \((n \text{ and } s)\) as it was the case with submatrices of the initial matrix \( H \) of Eq.(1.1). Quite the reverse, these blocks are considered as ”indivisible” elements of respective matrices. It should be kept in mind, however, that these are non-commutative quantities in contrast to usual (one-dimensional) matrix elements.

The above-specified form of the CBO matrix \( P \) has been subsequently substituted into the matrix problem of Eq.(1.1.1) and terms of each order \((k)\) separately have been collected (as is usual in perturbation approaches). As a result, the solution of Eq.(1.1.1) (i.e. the matrix \( P \)) has been obtained in terms of entire submatrices (blocks) of our matrix \( H \), i.e. via entire blocks \( E_+(1), E_-(1), T, R \) and \( Q \). Before passing to this solution, however, let us introduce some additional definitions and notations.

As is well-known, diagonal elements of any CBO matrix represent populations (occupation numbers) of the relevant basis orbitals. In our case, diagonal elements \( p_{11,i} \) and \( p_{22,ll} \) of submatrices (blocks) \( P_{11} \) and \( P_{22} \) yield occupation numbers of orbitals \( \varphi^{(+)}_i \) and \( \varphi^{(-)}_l \) belonging to subsets \( \{\varphi_+\} \) and \( \{\varphi_-\} \), respectively, where \( i = 1, 2, ... n \) and \( l = n+1, n+2, ... N \). Thus, the blocks \( P_{11} \) and \( P_{22} \) will be called the intrasubset population matrices and alternatively denoted by \( X_+ \) and \( X_- \). The relevant terms of the \( k \)th order will be accordingly designated by \( X_{(+)}^{(k)} \) and \( X_{(-)}^{(k)} \), respectively, so that the following relations are valid, viz.

\[
X_+ = \sum_{k=0}^{\infty} X_{(+)}^{(k)}, \quad X_- = \sum_{k=0}^{\infty} X_{(-)}^{(k)} \tag{1.1.4}
\]

Meanwhile, the off-diagonal (intersubset) blocks of our matrix \( P \) (i.e. \( P_{12} \) and \( P_{21} \)) represent bond orders between basis orbitals of opposite initial occupation, whereas the relevant blocks of the correction \( P_{(k)} \) (i.e. \( P_{12}^{(k)} \) and \( P_{21}^{(k)} \)) yield the increments of the \( k \)th order to the same quantities. Let us introduce the convenient designations \( -2G_{(k)} \) and \( -2G_{(k)}^+ \) for submatrices (blocks) \( P_{12}^{(k)} \) and \( P_{21}^{(k)} \), respectively, and note in advance that matrices \( G_{(k)} \) play an important role in the PNCMO theory. These are called below the intersubset coupling matrices (of the \( k \)th order). In the
above-defined terms, the standard form of the correction \( P_{(k)} \) is as follows

\[
P_{(k)} = \begin{pmatrix} X_{(+)}(k) & -2G_{(k)} \\ -2G_{(k)}^+ & X_{(-)}(k) \end{pmatrix}.
\] (1.1.5)

Let us now turn to particular values of the order parameter \((k)\).

The zero order member \((P_{(0)})\) of the power series of Eq.(1.1.2) follows from solution of the matrix problem shown in Eq.(1.1.1), where the zero order Hamiltonian matrix \((H_{(0)})\) stands instead of \(H\). As it may be easily shown, the matrix \(P_{(0)}\) of the following simple form

\[
P_{(0)} = \begin{pmatrix} 2I & 0 \\ 0 & 0 \end{pmatrix}
\] (1.1.6)

meets the relevant three equations, where \(I\) is an \(n\)–dimensional unit matrix. At the same time, \(P_{(0)}\) of Eq.(1.1.6) reflects the initial occupation numbers of our basis orbitals \(\varphi_{(+)}(i) = 1, 2, \ldots, n\) and \(\varphi_{(-)}(l) = n + 1, n + 2, \ldots, N\) equal to 2 and 0, respectively, and thereby corresponds to the ground state of our system. In terms of designations used in Eq. (1.1.5), we alternatively obtain that

\[
X_{(+)}^{(0)} = 2I, \quad X_{(-)}^{(0)} = 0, \quad G_{(0)} = 0.
\] (1.1.7)

Expressions for the subsequent members \(P_{(k)}, k = 1, 2, 3\ldots\) of the series concerned, however, take a much more involved form. In particular, the intersubset coupling matrices \(G_{(k)}\) \((k = 1, 2, 3\ldots)\) and thereby the off-diagonal blocks of any correction \(P_{(k)}(k = 1, 2, 3\ldots)\) are determined by the following matrix equations

\[
E_{(+)}G_{(k)} + G_{(k)}E_{(-)} + W_{(k)} = 0,
\] (1.1.8)

the last \(G_{(k)}\)-free terms of which are expressible via the relevant matrices of lower orders \((G_{(k-1)}, G_{(k-2)}, etc\)\), as well as via blocks \(T, R\) and \(Q\) of the first order Hamiltonian matrix \(H_{(1)}\) of Eq.(1.1) [37-40], e.g.

\[
W_{(1)} = R, \quad W_{(2)} = TG_{(1)} - G_{(1)}Q, \quad W_{(3)} = TG_{(2)} - G_{(2)}Q - (RG_{(1)}^+G_{(1)} + G_{(1)}G_{(1)}^+)R, \quad etc.
\] (1.1.9)

By contrast, the intrasubset population matrices of the \(k\)th order \((X_{(+)}^{(k)}\) and \(X_{(-)}^{(k)}\)) are representable algebraically via sums of products of matrices \(G_{(k)}\) of lower orders [37-40], e.g.

\[
X_{(+)}^{(1)} = X_{(-)}^{(1)} = 0, \quad X_{(+)}^{(2)} = -2G_{(1)}G_{(1)}^+, \quad X_{(-)}^{(2)} = 2G_{(1)}^+G_{(1)},
\]

\[
X_{(+)}^{(3)} = -2(G_{(1)}G_{(2)}^+ + G_{(2)}G_{(1)}^+), \quad X_{(-)}^{(3)} = 2(G_{(1)}^+G_{(2)} + G_{(2)}^+G_{(1)}), \quad etc.
\] (1.1.10)

Moreover, the relation

\[
TrX_{(+)}^{(k)} = -TrX_{(-)}^{(k)}
\] (1.1.11)

may be easily proven for any \(k\). This relation implies coincidence between the population lost by all orbitals of the subset \(\{\varphi_{(+)}\}\) and that acquired by all orbitals of its counterpart \(\{\varphi_{(-)}\}\) (or vice versa) within each order \(k\) separately due to the intersubset interaction. Thus, it may be interpreted as the charge conservation
condition for subsets \( \{ \varphi_+ \} \) and \( \{ \varphi_- \} \). An important implication of relations like those of Eq. (1.1.10) consists in representability of population alterations of basis orbitals \( \varphi_+ \) and \( \varphi_- \) (\( X^{(k)}_{(+)} \) and \( X^{(k)}_{(-)} \)) of each order \( k \) in the form of sums of increments of orbitals of the opposite subset \([37, 39, 41, 42]\), viz.

\[
X^{(k)}_{(+)} = - \sum_{m} x^{(k)}_{(+),i,(-)m}, \quad X^{(k)}_{(-)} = \sum_{j} x^{(k)}_{(-),l,(+)j}; \quad (1.1.12)
\]

where \( x^{(k)}_{(+),i,(-)m} \) (and \( x^{(k)}_{(-),l,(+)j} \)) are expressible as follows

\[
x^{(2)}_{(+),i,(-)m} = 2(G_{(1)im})^2, \quad x^{(3)}_{(+),i,(-)m} = 4G_{(1)im}G_{(2)im}, \quad (1.1.13)
\]

\[
x^{(4)}_{(+),i,(-)m} = 4G_{(1)im}G_{(3)im} + 2G_{(1)im}(G_{(1)}G_{(1)}G_{(1)})_{im} + 2(G_{(2)im})^2; \quad etc.
\]

and describe partial populations of the \( k \)th order transferred between individual orbitals of opposite subsets. Sums of Eq. (1.1.12) over \((-)m\) and over \((+)j\) embrace all initially-vacant orbitals \( \varphi_- m \) \( m = n + 1, n + 2, \ldots N \) and all initially-occupied ones \( \varphi_+ j \) \( j = 1, 2, \ldots n \), respectively. Moreover, it may be easily shown that

\[
x^{(k)}_{(+),i,(-)m} = x^{(k)}_{(-),m,(+)i} \quad (1.1.14)
\]

in accordance with the expectation. For total populations of orbitals \( \varphi_+ \) and \( \varphi_- \), we accordingly obtain

\[
X_{(+)} = 2 - \sum_{k=2}^{\infty} \sum_{m} x^{(k)}_{(+),i,(-)m} = 2 - \sum_{m} x_{(+),i,(-)m}, \quad (1.1.15)
\]

\[
X_{(-)} = \sum_{k=2}^{\infty} \sum_{j} x^{(k)}_{(-),l,(+)j} = \sum_{j} x_{(-),l,(+)j},
\]

where \( x_{(+),i,(-)m} \) and \( x_{(-),l,(+)j} \) are the overall partial populations transferred between the relevant pairs of orbitals [Note that Eq.(1.1.7) also is invoked here along with the first relation of Eq.(1.1.10)].

As is seen from the first relation of Eq.(1.1.13), the second order increment \( x^{(2)}_{(+),i,(-)m} \) to the partial population \( x_{(+),i,(-)m} \) transferred between orbitals \( \varphi_+ \) and \( \varphi_- \) is an \( a \) \( p r i o r i \) positive quantity. This implies that any initially-occupied orbital \( \varphi_+ \) loses its population due to perturbation in accordance with the expectation (the minus sign of Eq.(1.1.12) should be taken into consideration). Accordingly, any initially-vacant orbital \( \varphi_- \) acquires an additional population and this result also causes no surprise. Meanwhile, the signs of the relevant increments of higher orders \( x^{(3)}_{(+),i,(-)m}, x^{(4)}_{(+),i,(-)m}, \ldots \) cannot be established \( a \) \( p r i o r i \). Nevertheless, the expressions of Eq.(1.1.13) allow us to formulate the following rule: The increment \( x^{(k)}_{(+),i,(-)m} \) is a positive (negative) quantity, if the elements \( G_{(k-1)im}, G_{(k-2)im}, \ldots \) contained within the relevant definition are of the same (opposite) signs [41]. For example, \( x^{(3)}_{(+),i,(-)m} \) > 0, if both \( G_{(1)im} \) and \( G_{(2)im} \) are either of positive signs or of negative ones [Given that an element \( G_{(k)im} \) contains two additive components \( G_{(k)im}^{a} \) and \( G_{(k)im}^{b} \), coinciding (opposite) signs of the latter become
of importance in the formation of the absolute value of square \((G_{(k)im})^2\), e.g. of \((G_{(2)im})^2\). This rule forms the basis for conditions determining stabilization (destabilization) of a certain system due to perturbation (Subsect. 2.3).

As is seen from the above overview, the series of intersubset coupling matrices \(G_{(k)}, k = 1, 2, 3...\) prove to be the principal quantities of the present theory, and these are determined by matrix equations shown in Eq.(1.1.8). The latter are easily solvable and yield the usual "perturbational" fractions containing resonance parameters and energy differences in their numerators and denominators, respectively, under an assumption that \(n = s = 1\), i.e. in the particular case of one-dimensional parameters \(\varepsilon(\pm), \tau, \rho\) and \(\kappa\) instead of (sub)matrices \(E_{(\pm)}, T, R\) and \(Q\). Generally, however, we have to solve matrix equations of the following form

\[
AX + XB = aC, \quad (1.1.16)
\]

where \(X\) is the matrix being sought, \(A\) and \(B\) are known matrices and \(a\) is a constant. According to the theory of these equations [43], a unique solution exists under certain conditions imposed on matrices \(A\) and \(B\). Using the designations underlying Eq.(1.1.8), the solution concerned is representable in the form of the following integral [25, 36]

\[
G_{(k)} = \int_0^\infty \exp[E_{(+)}t]W_{(k)}\exp[E_{(-)}t]dt, \quad (1.1.17)
\]

which evidently yields no explicit expressions for matrices \(G_{(k)}\). In this connection, the present version of the PNCMO theory is called the implicit one. Nevertheless, explicit solutions are obtainable in some particular cases as discussed in Section 2 in a detail. Meanwhile, the present section is devoted to some relations between corrections \(P_{(k)}\), on the one hand, and other characteristics of the same systems, on the other hand, that have been found in the framework of the implicit form of the PNCMO theory.

As already mentioned, importance of the CBO matrix \(P\) as a quantum chemical characteristic is beyond any doubt. This matrix, however, yields the overall charge (re)distribution only, but not those of individual pairs of electrons. Meanwhile, just the shifts (displacements) of separate electron pairs form the basis of the qualitative chemical thinking (cf. the well-known 'curly arrow chemistry' (see e.g. [18])). Moreover, these pairs are assumed to be predominantly localized on individual chemical bonds and/or to build up the so-called lone electron pairs usually belonging to heteroatoms.

It is evident that squares of individual one-electron orbitals (MOs) may be expected to yield partial charge (re)distributions associated with separate electron pairs. The standard (canonical) MOs (CMOs), however, usually are delocalized over the whole system under study [4, 11] and thereby cannot be ascribed to individual chemical bonds. As a result, CMOs hardly are suitable for the above-specified purpose. Fortunately, one-electron orbitals as such are not unique (as opposed to the DM). This implies existence of other sets of MOs that offer a quantum chemical analogue of the above-described classical perspective on molecular systems. These alternative MOs are usually referred to as localized MOs(LMOs) and/or non-canonical...
MOs (NCMOs) [20-24, 44-46]. The most popular way of derivation of the latter consists in transforming the set of CMOs using various localization criteria [20, 47-50]. Again, NCMOs are also alternatively obtainable directly by invoking the Brillouin theorem [20-26, 28, 36, 51-55]. Just the latter approach is invoked below in this article for the following reasons: First, general expressions for NCMOs prove to be then obtainable for any system described by the Hamiltonian matrix $H$ of Eq.(1.1). Second, terms of the power series for the NCMO representation matrix are expressible in terms of entire blocks of the matrix $H$ and thereby these are directly comparable [36, 51, 52] to those for the matrix $P$ of Eqs.(1.1.6)-(1.1.10). Finally, zero order NCMOs may be chosen to coincide with individual basis orbitals. Consequently, changing extents of their subsequent delocalization due to perturbation are expected to reflect the classical shifts (displacements) of separate electron pairs. Thus, let us now turn to application of the Brillouin theorem to our Hamiltonian matrix of Eq.(1.1).

1.2. The block-diagonalization problem for the Hamiltonian matrix, and its perturbative solution

Among particular forms of the Brillouin theorem there is a zero value requirement for an off-diagonal element of the Fockian operator referring to an occupied and a vacant MO [11]. In its matrix form, this requirement resolves itself into the zero matrix condition for the occupied-vacant off-diagonal block (submatrix) of the total Fockian (or Hamiltonian) matrix in the basis of non-canonical MOs (NCMOs) being sought [21-23, 25-28, 36, 51-55].

Let us now dwell on the case of the Hamiltonian matrix $H$ of Eq.(1.1). Let us look for an unitary matrix $C$ that transforms the above-mentioned matrix $H$ into a block-diagonal form containing a direct sum of $n \times n$- and $s \times s$- dimensional submatrices $E_1$ and $E_2$, viz.

\[
H' = C^+ H C = \begin{pmatrix} E_1 & 0 \\ 0 & E_2 \end{pmatrix}.
\]  

Moreover, the unitarity condition of the following form

\[
C^+ C = I
\]  

ensures the orthogonality of NCMOs. It also deserves mention that Eq.(1.2.1) turns into the diagonality requirement under an assumption that $n = s = 1$ [28], i.e. for the two-electron prototype described by the matrix $h$ of Eq.(1.2). Further, our problem may be reformulated as follows

\[
HC = CE,
\]  

where $E$ stands for the total block-diagonal matrix of the right-hand side of Eq.(1.2.1). This alternative form, in turn, proves to be a generalization of the usual eigenvalue equation for the matrix $h$ to the case of multidimensional (non-commutative) elements. In this connection, the submatrices $E_1$ and $E_2$ of Eq.(1.2.1) may be conveniently called the eigenblocks of the matrix $H$ [28]. Accordingly, the problem of Eq.(1.2.3) will be referred to as the eigenblock equation for the same matrix.

As with basis orbitals $\{\varphi\}$, the NCMOs also may be collected into two subsets, viz. the $n$-dimensional subset of occupied NCMOs and the $s$-dimensional one of their vacant counterparts correspondingly denoted below by $\{\psi_1\}$ and $\{\psi_2\}$ [In some
cases, the subscripts (+) and (−) are more convenient and these are used instead of 1 and 2]. Accordingly, notations \(|\Psi_1\rangle >\) and \(|\Psi_2\rangle >\) will stand for respective ket-vectors (row-matrices). Passing from the initial basis set \(\{\varphi\}\) to that of NCMOs \(\{\psi\}\) will be then represented by the following relation

\[ |\Psi\rangle = |\Phi\rangle C \]  

(1.2.4)

where \(|\Psi\rangle >\) and \(|\Phi\rangle >\) are total row-matrices (ket-vectors) of NCMOs and of basis functions, respectively, i.e.

\[ |\Psi\rangle > = ||\Psi_1\rangle > |\Psi_2\rangle >> = ||\Psi_{(+)}\rangle >, \]

\[ |\Phi\rangle > = ||\Phi_1\rangle > |\Phi_2\rangle >> = ||\Phi_{(+)}\rangle >. \]  

(1.2.5)

As with the CBO matrix \(P\) (Subsect. 1.1), the transformation matrix \(C\) also has been sought in the form of four submatrices (blocks) \(C_{11}, C_{12}, C_{21}\) and \(C_{22}\) of appropriate dimensions, each of them consisting of sums over \(k\) of the relevant increments of the \(k\)th order \((C_{11}^{(k)}, C_{12}^{(k)}, C_{21}^{(k)}\) and \(C_{22}^{(k)}\), respectively). Moreover, the eigenblocks \(E_1\) and \(E_2\) also have been represented similarly [55], i.e.

\[ E_1 = \sum_{k=0}^{\infty} E_1^{(k)} \], \quad \[ E_2 = \sum_{k=0}^{\infty} E_2^{(k)} \]  

(1.2.6)

where \(E_1^{(k)}\) and \(E_2^{(k)}\) are the increments of the \(k\)th order. Since the zero order member \(H_{(0)}\) of our Hamiltonian matrix \(H\) of Eq.(1.1) complies with the block-diagonality condition from the outset, the following equalities

\[ C_{11}^{(0)} = C_{22}^{(0)} = I, \quad C_{12}^{(0)} = C_{21}^{(0)} = 0, \quad E_1^{(0)} = E_{(+)}^{(0)}, \quad E_2^{(0)} = -E_{(-)}^{(0)} \]  

(1.2.7)

may be accepted \textit{a priori} and and these imply coincidence of the total zero order matrix \(C_{(0)}\) with the unit matrix \(I\). Individual ket-vectors \(|\Psi_1\rangle >\) and \(|\Psi_2\rangle >\) take then the following form

\[ |\Psi_1\rangle > = |\Phi_1\rangle > \sum_{k=1}^{\infty} C_{11}^{(k)}, \quad |\Psi_2\rangle > = |\Phi_2\rangle > \sum_{k=1}^{\infty} C_{22}^{(k)} \]  

(1.2.8)

where

\[ C_{11} = I + \sum_{k=1}^{\infty} C_{11}^{(k)}, \quad C_{22} = I + \sum_{k=1}^{\infty} C_{22}^{(k)}, \quad C_{12} = \sum_{k=1}^{\infty} C_{12}^{(k)}, \quad C_{21} = \sum_{k=1}^{\infty} C_{21}^{(k)}. \]  

(1.2.9)

The expression of Eq.(1.2.8) is a generalization of the well-known LCAO form for the two MOs of our prototype described by the simple matrix \(h\) of Eq.(1.2), where submatrices of the matrix \(C\) stand instead of usual (one-dimensional) coefficients. It is also seen that (sub)matrices \(C_{12}\) and \(C_{21}\) represent the intersubset delocalization (intersubset tails) of NCMOs, whereas \(C_{11}\) and \(C_{22}\) reflect the consequent renormalization of the latter. In this connection, \(C_{11}\) and \(C_{22}\) are referred to below as renormalization matrices. Analogously, \(C_{11}^{(k)}\) and \(C_{22}^{(k)}\) are called renormalization matrices of the \(k\)th order. Finally, substituting Eq.(1.2.9) into Eq.(1.2.8) shows
that our NCMOs are of the basis-orbital-and-tail constitution. In other words, one-
to-one correspondence takes place between individual NCMOs $\psi_{1,i}$ ($\psi_{2,l}$) and
basis orbitals $\varphi_{(+i)}$ ($\varphi_{(-l)}$) so that delocalization of the former is a small correction only.
Thus, the assumption of Eq.(1.2.7) is equivalent to confinement to NCMOs of the
above-described particular structure. As a result, we largely reduce the extent of
ambiguity in determining NCMOs.

The very procedure of solution of the present matrix problem for NCMOs [36, 52] also closely resembles that for the CBO matrix $P$ (Subsect. 1.1): The above-
specified forms of matrices $C$ and $E$ have been substituted into Eqs.(1.2.1) and
(1.2.2) and terms of the same order ($k$) have been collected. Moreover, the similarity concerned embraces also the resulting matrices $C$ and $P$. This important and
somewhat surprising point deserves a more detailed discussion.

Comparative analysis of the two non-canonical problems [36, 52] showed that the
off-diagonal blocks of the correction $C_{(k)}$ (i.e. submatrices $C_{12}^{(k)}$ and $C_{21}^{(k)}$) actually
are determined by matrix equations of the form shown in Eq.(1.1.8), as it was the
case with the relevant blocks of the matrix $P$ (Subsect. 1.1). Moreover, equations
for blocks of the first and second orders (i.e. for $C_{12}^{(1)}$ and $C_{21}^{(1)}$, as well as for $C_{12}^{(2)}$
and $C_{21}^{(2)}$) contain the same $G_{(k)}$–free members $W_{(1)}$ and $W_{(2)}$ shown in Eq.(1.1.9).
Consequently, the off-diagonal blocks of corrections $C_{(1)}$ and $C_{(2)}$ are representable
via our former principal matrices $G_{(1)}$ and $G_{(2)}$, respectively, viz.

$$C_{12}^{(1)} = -C_{21}^{(1)+} = G_{(1)}, \quad C_{12}^{(2)} = -C_{21}^{(2)+} = G_{(2)}.$$  \hfill (1.2.10)

Analogously, diagonal blocks of the same corrections are expressible algebraically as follows

$$C_{11}^{(1)} = C_{22}^{(1)} = 0, \quad C_{11}^{(2)} = -\frac{1}{2}G_{(1)}G_{(1)}^+, \quad C_{22}^{(2)} = -\frac{1}{2}G_{(2)}G_{(2)}^+, \quad C_{11}^{(3)} = -\frac{1}{2}(G_{(1)}G_{(2)}^+ + G_{(2)}G_{(1)}^+), etc.$$  \hfill (1.2.11)

and these relations closely resemble their counterparts of Eq.(1.1.10) for $k \leq 3$.

These results evidently imply proportionality between respective submatrices of corrections $C_{(k)}$ and $P_{(k)}$ and thereby a high extent of similarity between entire
matrices $C$ and $P$. Consequently, both NCMOs (LMOs) and rows (columns) of the
CBO matrix are expected to be characterized by a similar dependence upon the
specific structure of the system under interest. On the same basis, both NCMOs
(LMOs) and the one-electron DM have been concluded to belong to the localized
way of describing electronic structures in general.

The above-described simple proportionalties between individual blocks of corrections $C_{(k)}$ and $P_{(k)}$, however, become replaced by more involved interdependences
with the growing value of the order parameter ($k$). The immediate reason for this
state of things is that the $G_{(k)}$–free terms of matrix equations of Eq. (1.1.8) determining the off-diagonal submatrices of matrices $C_{(k)}$ and $P_{(k)}$ are no longer uniform
for $k > 2$. For example, the equation for the submatrix $C_{12}^{(3)}$ contains the following
new matrix [52, 55]

$$\tilde{W}_{(3)} = TG_{(2)} - G_{(2)}Q - \frac{1}{2}(RG_{(1)}^+G_{(1)} + G_{(1)}G_{(1)}^+R + G_{(1)}RG_{(1)}^+)$$  \hfill (1.2.12)
instead of the former matrix \( W_3 \) of Eq.(1.1.9) and thereby yields another solution
denoted below by \( \tilde{G}_3 \). Nevertheless, matrices \( G_k \) and \( \tilde{G}_k \) prove to be interrelated
as discussed in the next Subsection. Before finishing the comparison of matrices \( C \)
and \( P \) it deserves mention that both the very fact of their similarity and the limited
extent of the latter may be easily understood by invoking the prototype of our systems
described by the \( 2 \times 2 \)-dimensional Hamiltonian matrix \( h \) of Eq.(1.2). Indeed,
the CBO matrix of this simple system (p) is determined by the shape of its only
occupied MO and, consequently, matrices \( c \) and \( p \) contain the same perturbational
degree and thereby are interrelated. To a certain extent, this interrelation is re-
tained also when passing to the case of two multidimensional interacting subsets
\( \{ \varphi_+ \} \) and \( \{ \varphi_- \} \).

Finally, the eigenblocks of the matrix \( H \) (\( E_1 \) and \( E_2 \)) also are expressible algebraically via entire matrices \( G_1 \), \( G_2 \) and \( \tilde{G}_3 \) as follows [55]

\[
E_1 = E_+ + T - \frac{1}{2}(RG_{(1)}^+ + G_{(1)}R^+ - \frac{1}{2}(RG_{(2)}^+ + G_{(2)}R^+ - \frac{1}{2}(RG_{(3)}^+ + \tilde{G}_3R^+)
- \frac{1}{8}(RG_{(1)}^+ G_{(1)}G_{(1)}^+ + G_{(1)}R^+G_{(1)}G_{(1)}^+ + G_{(1)}G_{(1)}^+R^+G_{(1)} + G_{(1)}G_{(1)}^+G_{(1)}G_{(1)}^+R^+)

E_2 = -E_- + Q + \frac{1}{2}(G_{(1)}^+R + R^+G_{(1)} - \frac{1}{2}(G_{(2)}^+R + R^+G_{(2)} - \frac{1}{2}(G_{(3)}^+R + R^+\tilde{G}_{(3)})
+ \frac{1}{8}(R^+G_{(1)}G_{(1)}^+G_{(1)} + G_{(1)}^+RG_{(1)}G_{(1)} + G_{(1)}^+G_{(1)}^+R^+G_{(1)} + G_{(1)}^+G_{(1)}G_{(1)}^+R^+)
\]

(1.2.13)

1.3. Interrelations between occupation numbers of basis orbitals and
delocalization coefficients of NCMOs

As already mentioned, matrices \( P \) and \( C \) contain information about the overall
charge (re)distribution and about that associated with individual electron pairs,
respectively. Again, the same matrices were shown to resemble one another in
the above subsection. This allows us to expect a certain interdependence to exist
between the above-mentioned two patterns of charge (re)distribution. Now, we will
turn to verification of this expectation.

It deserves an immediate emphasizing that the interrelation being sought is of a
non-trivial nature. Indeed, matrices \( P \) and \( C \) contain distinct submatrices \( G_{(k)} \) and
\( \tilde{G}_{(k)} \) for higher values of the order parameter (\( k \)) that are determined by different
matrix equations (Subsect. 1.2). Thus, we will invoke here an alternative (indirect)
way of derivation of the one-electron DM on the basis of projector to the subspace of
occupied one-electron orbitals (MOs). Instead of usual (canonical) MOs [29], however,
we will use the subset of occupied NCMOs \( \{ \psi_1 \} \) of subsection 1.2. Comparison
of expressions for the matrix \( P \) derived directly (as described in the subsection 1.1)
and indirectly (using NCMOs) is then expected to yield interrelations between sub-
matrices \( G_{(k)} \) and \( \tilde{G}_{(k)} \) for \( k=3,4,... \) and thereby between charge (re)distributions
under our interest.

Let us start with the general definition of the one-electron DM \( P(r | r') \) as a
projector [29] to the subset of occupied NCMOs \( \{ \psi_1 \} \), viz.

\[
P(r | r') = 2 |\psi_1(r)\rangle \langle \psi_1(r')|,
\]

(1.3.1)
where $|\Psi_1(r)\rangle$ and $\langle \Psi_1(r')|$ correspondingly stand for the ket-vector of occupied NCMOs and for the relevant bra-vector (i.e. row- and column matrices of the latter, respectively), whilst $r$ and $r'$ are vectors representing positions of an electron in the real space. After substituting the expressions like that of Eq.(1.2.8) into the right-hand side of Eq.(1.3.1), a new representation of the same DM $P(r | r')$ follows in terms of entire subsets (vectors) $|\Phi_1\rangle$ and $\langle \Phi_2|$ (or $|\Phi_{(+)}\rangle$ and $\langle \Phi_{(-)}|$), viz.

$$P(r | r') = \sum_{L,M=1}^{2} |\Phi_L(r)\rangle P_{LM} \langle \Phi_M(r')|,$$  

(1.3.2)

where $P_{LM}$ ($L = 1, 2; M = 1, 2$) are multidimensional elements (blocks) of the representation of the DM in terms of two subsets of basis functions $\{\varphi_1\}$ and $\{\varphi_2\}$ introduced in the subsection 1.1. The expression of Eq.(1.3.2) evidently is a matrix generalization of the well-known bilinear form of the DM in terms of individual basis functions [29]. At the same time, Eq.(1.3.2) yields the following formulae for $P_{LM}$ in terms of submatrices of the NCMO representation matrix $C$ of subsection 1.2, viz.

$$P_{11} = 2C_{11}C_{11}^+; \quad P_{22} = 2C_{21}C_{21}^+; \quad P_{12} = 2C_{11}C_{21}^+,$$  

(1.3.3)

where $C_{11}$ and $C_{21}$ are defined by Eqs.(1.2.8) and (1.2.9).

If we recall now that the one-electron DM $P(r | r')$ and thereby its particular representation in terms of subsets $\{\varphi_{(+)}\}$ and $\{\varphi_{(-)}\}$ are unique quantum chemical characteristics of molecules, the elements $P_{LM}$ of Eq.(1.3.2) necessarily coincide with submatrices of the CBO matrix $P$, i.e. $P_{11}$, $P_{22}$ and $P_{12}$ shown in the left-hand side of Eq.(1.1.3). The relations of Eq.(1.3.3) then form the basis of the indirect way of derivation of the matrix $P$. Moreover, the relevant results are expected to coincide with those obtained directly and described in the subsection 1.1. For $k=1$ and $k=2$, such a coincidence may be easily verified. Meanwhile, for higher values of the order parameter ($k$), the last relation of Eq.(1.3.3) yields non-trivial connections between pairs of matrices $G_{(k)}$ and $G_{(k)}$ [52]. For example, after substituting $-2G_{(3)}$ and

$$2[C_{21}^{(3)+} + C_{11}^{(2)+} C_{21}^{(1)+}] \equiv -2[C_{12}^{(3)} + C_{11}^{(2)} C_{12}^{(1)}]$$  

(1.3.4)

into the left- and right-hand sides of the above-mentioned relation, respectively, we obtain that

$$G_{(3)} = \tilde{G}_{(3)} - \frac{1}{2} G_{(1)} G_{(1)}^+ G_{(1)}.$$  

(1.3.5)

For $k=4$, an analogous procedure yields the following result

$$G_{(4)} = \tilde{G}_{(4)} - \frac{1}{2} (G_{(1)} G_{(1)}^+ G_{(2)} + G_{(1)} G_{(2)}^+ G_{(1)} + G_{(2)} G_{(1)}^+ G_{(1)}).$$  

(1.3.6)

Apart from the CBO matrix $P$ itself, the overall charge (re)distribution has been described in the Subsection 1.1 by a certain series of additional characteristics starting with the intrasubset population matrices $X_{(+)}$ and $X_{(-)}$ and their diagonal elements and ending with partial populations $x_{(+)}x_{(-)}$ transferred between separate pairs of basis orbitals $\varphi_{(+)}$ and $\varphi_{(-)}$. Thus, before turning to implications of the first two relations of Eq.(1.3.3), let us now introduce an analogous series of quantities representing the shapes (reshapings) of individual pairs of electrons. To
this end, let us take explicit expressions for an occupied NCMO \(\psi_{1,i}(\psi^{(+)}_i)\) and for a vacant one \(\psi_{2,l}(\psi^{(-)}_l)\) resulting from Eq.(1.2.8), viz.

\[
\psi^{(+)}_i = \sum_{(+)j} \varphi^{(+)}_j C_{11,ji} + \sum_{(-)m} \varphi^{(-)}_m C_{21,mi},
\]
\[
\psi^{(-)}_l = \sum_{(+)j} \varphi^{(+)}_j C_{12,jl} + \sum_{(-)m} \varphi^{(-)}_m C_{22,ml},
\]

(1.3.7)

where sums over \((+\rangle\rangle\) and \((-\rangle\rangle\) correspondingly embrace all orbitals of subsets \(\{\varphi^{(+)}\}\) and \(\{\varphi^{(-)}\}\) as previously. Let us now introduce the so-called partial (intersubset) delocalization coefficients of NCMOs \(\psi^{(+)}_i\) and \(\psi^{(-)}_l\) over particular basis orbitals \(\varphi^{(-)}_m\) and \(\varphi^{(+)}_j\), respectively [28]. Let these coefficients be correspondingly denoted by \(d^{(+)}_{i,(-)m}\) and \(d^{(-)}_{l,(+)}j\) and defined as follows

\[
d^{(+)}_{i,(-)m} = | C_{21,mi} |^2 = | G^{(+)}_{1} + G^{(+)}_{2} + G^{(+)}_{3} + \ldots |^2, \\
d^{(-)}_{l,(+)}j = | C_{12,jl} |^2 = | G^{(+)}_{1} + G^{(+)}_{2} + G^{(+)}_{3} + \ldots |^2.
\]

(1.3.8)

As is easily seen, the partial delocalization coefficients concerned also are expressible in the form of power series, i.e. as sums over parameter \(k\) of contributions \(d^{(+)}_{i,(-)m}\) and \(d^{(-)}_{l,(+)}j\), respectively; that, in turn, coincide one with another for the same pair of NCMOs (e.g. for \(\psi^{(+)}_i\) and \(\psi^{(-)}_m\)). We then obtain that

\[
d^{(k)}_{i,(-)m} = d^{(k)}_{i,(-)m}, \\
d^{(-)}_{l,(+)}j = d^{(-)}_{l,(+)}j.
\]

(1.3.9)

Further, let us define total delocalization coefficients of the same NCMOs \((D^{(+)}_i\) and \(D^{(-)}_l\) over basis orbitals of subsets \(\{\varphi^{(+)}\}\) and \(\{\varphi^{(-)}\}\), respectively, viz.

\[
D^{(+)}_i = \sum_{(-)m} d^{(+)}_{i,(-)m}, \\
D^{(-)}_l = \sum_{(+)} d^{(-)}_{l,(+)}j.
\]

(1.3.10)

Finally, complete delocalization coefficients of occupied NCMOs \(\{\psi^{(+)}\}\) and of vacant ones \(\{\psi^{(-)}\}\) will be defined as follows

\[
D^{(+)} = \sum_{(+)} D^{(+)}_i, \\
D^{(-)} = \sum_{(-)} D^{(-)}_l.
\]

(1.3.11)

Besides, substituting Eq.(1.3.10) into Eq.(1.3.11) and employment of Eq.(1.3.9) shows that \(D^{(+)}\) and \(D^{(-)}\) coincide one with another. Thus, the overall extent of delocalization of occupied NCMOs over the subset \(\{\varphi^{(-)}\}\) coincides with that of vacant NCMOs over \(\{\varphi^{(+)}\}\). [Note that such a ”symmetry” of MOs is peculiar to our prototype described by the Hamiltonian matrix \(\mathbf{h}\) of Eq.(1.2)].

Let us now introduce the so-called intersubset delocalization matrices \(\mathbf{D}^{(+)}\) and \(\mathbf{D}^{(-)}\) [52], viz.

\[
\mathbf{D}^{(+)} = C^{(+)}_{21} C_{21}, \\
\mathbf{D}^{(-)} = C^{(-)}_{12} C_{12},
\]

(1.3.12)

diagonal elements of the latter \((D^{(+)}_{ii})\) and \((D^{(-)}_{ll})\) coinciding with total delocalization coefficients of NCMOs \(\psi^{(+)}_i\) and \(\psi^{(-)}_l\) of Eq.(1.3.10). Meanwhile, traces of matrices \(\mathbf{D}^{(+)}\) and \(\mathbf{D}^{(-)}\) yield complete delocalization coefficients of Eq.(1.3.11) and

\[
\text{Tr}\mathbf{D}^{(+)} = \text{Tr}\mathbf{D}^{(-)} = D^{(+)} = D^{(-)}.
\]

(1.3.13)
If we substitute the power series for (sub)matrices $C_{21}$ and $C_{12}$ (Subsection 1.2) into the relations of Eq.(1.3.12), matrices $D_{(+)}$ and $D_{(-)}$ also become expressed in the form of an analogous series. The starting members of the latter are proportional to renormalization matrices of the same order, e.g.

$$
D_{(+)}^{(2)} = -2C_{11}^{(2)}, \quad D_{(+)}^{(3)} = -2C_{11}^{(3)}.
$$

(1.3.14)

Meanwhile, expressions for the next terms of the same series are of a somewhat more involved constitutions [52], e.g.

$$
D_{(+)}^{(4)} = -2C_{11}^{(4)} - (C_{11}^{(2)})^2.
$$

(1.3.15)

As already mentioned, our final step consists in employment of the first two relations of Eq.(1.3.3). The left-hand sides of these relations (i.e. $P_{11}$ and $P_{22}$) coincide with the intrasubset population matrices $X_{(+)}$ and $X_{(-)}$, respectively, as discussed above (subsection 1.1). Thus, the power series for the latter of Eqs.(1.1.4), (1.1.7) and (1.1.10) may be substituted into the relations concerned. The same refers also to the analogous series of Eqs.(1.2.9), (1.2.10) and (1.2.11) for (sub)matrices $C_{11}$ and $C_{21}$ contained within the right-hand sides of the same relations. Thereupon, interdependences between matrices $D_{(+)}^{(k)}(D_{(-)}^{(k)})$ and $C_{11}^{(k)}(C_{22}^{(k)})$ like those shown in Eqs.(1.3.14) and (1.3.15) should be invoked. We then obtain that

$$
X_{(+)}^{(k)} = -2D_{(+)}^{(k)}, \quad X_{(-)}^{(k)} = 2D_{(-)}^{(k)}
$$

(1.3.16)

for $k = 2, 3...$ Consequently, the total matrices $X_{(+)}(X_{(-)})$ and $D_{(+)}(D_{(-)})$ are interrelated as follows

$$
X_{(+)} = 2(I - D_{(+)}), \quad X_{(-)} = 2D_{(-)}.
$$

(1.3.17)

Thus, intrasubset population matrices prove to be proportional to the relevant intersubset delocalization matrices. For traces of matrices of the $k$th order we accordingly obtain

$$
TrX_{(+)}^{(k)} = -2TrD_{(+)}^{(k)}, \quad TrX_{(-)}^{(k)} = 2TrD_{(-)}^{(k)}
$$

(1.3.18)

and

$$
TrD_{(+)}^{(k)} = TrD_{(-)}^{(k)}
$$

(1.3.19)

is the analogue of Eq.(1.1.11) for the intersubset delocalization matrices. Meanwhile, traces of total matrices $X_{(+)}(X_{(-)})$ and $D_{(+)}(D_{(-)})$ meet the following relations

$$
TrX_{(+)} = 2(n - TrD_{(+)}), \quad TrX_{(-)} = 2TrD_{(-)}
$$

(1.3.20)

where the term $2n$ originates from the matrix $X_{(+)}^{(0)} = 2I$ of Eq.(1.1.7). [Note that the series for $D_{(+)}$ starts with the second order member $D_{(+)}^{(2)}$ of Eq.(1.3.14)]. Using Eq.(1.3.13) we then obtain that

$$
Tr(X_{(+)} + X_{(-)}) = TrP = 2n
$$

(1.3.21)

in accordance with the last relation of Eq.(1.1.1). Similarly, we may start with Eqs.(1.3.16) and (1.3.17) and turn to diagonal elements of matrices contained there. We then obtain

$$
X_{(+)}ii = 2(1 - D_{(+)}ii) \equiv 2(1 - D_{(+)}), \quad X_{(-)}ll = 2D_{(-)}ll \equiv 2D_{(-)}
$$

(1.3.22)
and

\[ X^{(k)}_{(+)|i} = -2D^{(k)}_{(+)|i} \equiv -2D^{(k)}_{(+)|i}, \quad X^{(k)}_{(-)|l} = 2D^{(k)}_{(-)|l} \equiv 2D^{(k)}_{(-)|l}, \]  \tag{1.3.23}

where \( D^{(+)}_{i} \) and \( D^{(-)}_{l} \) are total delocalization coefficients defined by Eq.\((1.3.10)\). These relations indicate that the actual population of any basis orbital \( \varphi^{(+)}_{i} \) (or \( \varphi^{(-)}_{m} \)) is determined only by the shape of a single NCMO, namely of the NCMO \( \psi^{(+)}_{i} \) (or \( \psi^{(-)}_{m} \)) associated with just the basis orbital concerned \([\text{One-to-one correspondence between basis orbitals and NCMOs should be recalled here (Subsect. 1.2)}\]). More precisely, the population of the given basis orbital lost (acquired) due to a certain interaction is proportional to the delocalization coefficient of the respective single NCMO (LMO) (and not to the sum of contributions of all occupied MOs as usual). This principal result forms the basis for interpretation of the overall charge (re)distribution in terms of displacements (shifts) of individual pairs of electrons. Another form of the same rule is as follows: The more delocalized the orbital \( \varphi^{(+)}_{i} \) becomes when building up the respective NCMO (LMO) \( \psi^{(+)}_{i} \), the more charge it loses and vice versa. This result may be also interpreted as a kind of simultaneous separability of both charge redistribution and delocalization into increments of separate pairs of electrons. Finally, invoking the expressions like those of Eqs.\((1.1.12)\) and \((1.3.10)\) for \( X^{(k)}_{(+)|i} \) (\( X^{(k)}_{(-)|l} \)) and \( D^{(k)}_{(+)|i} \) (\( D^{(k)}_{(-)|l} \)), respectively, yields proportionalities between the relevant partial increments, viz.

\[ x^{(k)}_{(+)|i,(-)|m} = 2d^{(k)}_{(+)|i,(-)|m}, \quad x^{(k)}_{(-)|l,(+)|j} = 2d^{(k)}_{(-)|l,(+)|j}. \]  \tag{1.3.24}

[The minus sign of Eq. \((1.1.12)\) is taken into consideration here]. Thus, the more population is transferred between orbitals \( \varphi^{(+)}_{i} \) and \( \varphi^{(-)}_{m} \), the larger is the partial delocalization coefficient of the NCMO (LMO) \( \psi^{(+)}_{i} \) over the same vacant basis function and vice versa. If we recall the definition of this coefficient as square of the relevant tail of the NCMO \( \psi^{(+)}_{i} \) (see Eq.\((1.3.8)\)), we may also conclude a more significant tail of this NCMO over the vacant orbital \( \varphi^{(-)}_{m} \) to correspond to a more efficient charge transfer between basis functions \( \varphi^{(+)}_{i} \) and \( \varphi^{(-)}_{m} \) and vice versa. Irrelevance of the intrasubset delocalization in the formation of charge redistributions also is among the conclusions. This result evidently causes no surprise. Immediate reasons why the respective terms vanish in the expressions for occupation numbers are clarified in Ref.[52]. It deserves mention finally that the relations of Eqs.\((1.3.22)\) and \((1.3.23)\) indicate both populations of basis orbitals and delocalization coefficients of NCMOs to be characterized by the same dependence upon the structure of the given system.

On the whole, the results of this subsection may be summarized as parallelism between charge (re)distribution and delocalization. Moreover, we obtain a certain quantum-chemical analogue of the Lewis perspective on charge (re)distribution \([56]\) and thereby of the 'curly arrow chemistry'\([18]\). Two differences between this analogue and its classical version deserve mention: First, NCMOs (LMOs) are not localized completely in contrast to the relevant classical model. Second, the approach suggested allows comparisons of relative extents of shifts (reshapings) of separate pairs of electrons for related compounds and/or for alternative routes of the same process. Just the second point may be regarded as an important advantage of the new approach over the classical one.
Finally, the principal result of this subsection may be alternatively formulated as a kind of one-orbital representation for populations lost (acquired) by individual basis orbitals. This state of things closely resembles the one-orbital representation of ionization potentials in the canonical MO method known as the Koopmans’ theorem [57]. If we recall that representations of this type are not achievable for ionization potentials and for charge (re)distributions in the NCMO and the CMO methods, respectively, the present results support the complementary nature of the above-mentioned principal approaches of quantum chemistry [58].

1.4. The principal relations concerning total energies

Total energies of molecules also rank among the most popular quantum-chemical characteristics. Moreover, these are comparable to experimental data even more directly, viz. to heats of formation and/or atomization.

As is well-known, total energies of molecules ($E$) usually are defined as sums of one-electron energies referring to occupied MOs (and/or of the relevant part of eigenvalues of the respective Hamiltonian matrix) multiplied by their occupation number 2 [1, 4, 13, 29]. As is seen from the above subsections 1.1 and 1.2, however, neither matrix equations for the DM of Eq.(1.1.1) nor the block-diagonalization problem of Eqs.(1.2.1) and (1.2.2) yield eigenvalues of particular Hamiltonian matrices. Thus, we need a more general definition of the total energy when looking for general expressions for the same quantity referring to the Hamiltonian matrix $H$ of Eq.(1.1). Fortunately, alternative definitions of this characteristic exist both in terms of the CBO matrix $P$ and via eigenblocks of the matrix $H$. These definitions correspondingly take the following forms [11, 14]

\[ E = Tr(PH) \]  \hspace{1cm} (1.4.1)

and

\[ E = 2TrE_1 = 2Tr\{C^+HC\}_{11}, \] \hspace{1cm} (1.4.2)

where $E_1$ is the $n \times n$—dimensional eigenblock of the Hamiltonian matrix referring to the subset of occupied NCMOs and the symbol $\{\ldots\}_{11}$ stands here for the submatrix of the matrix product $C^+HC$ taking the first diagonal position. It is evident that both Eq.(1.4.1) and (1.4.2) embrace the above-mentioned standard definition as a particular case [Note that matrices $P$ and $H$ take diagonal forms in the CMO basis. Moreover, diagonal elements of the former are 2 and 0 for occupied and vacant MOs]. It is also obvious that expressions for matrices $P$, $H$ and $E_1$ as sums over parameter $k$ of increments $P_k$, $H_k$ and $E_{1k}$ of Eqs.(1.1.2), (1.1) and (1.2.6), respectively, may be substituted into Eqs.(1.4.1) and (1.4.2). Collecting of terms of the same order $k$ within the right-hand sides of the latter relations then consequently yields the relevant power series for the energy $E$.

Instead, we will start with some general properties of the energy expansion. Let us note first that presence of the zero order member ($H_0$) and of the first order one ($H_1$) in our Hamiltonian matrix of Eq.(1.1) gives birth to two additive components [37] within any energy correction $E_k$, namely the $H_0$—containing component ($E^{(a)}_k$) and the $H_1$—containing one ($E^{(b)}_k$), viz.

\[ E_k = E^{(a)}_k + E^{(b)}_k. \]  \hspace{1cm} (1.4.3)
Given that the definition of Eq.(1.4.1) is used, the components concerned are expressible as follows

$$E^{(a)}_{(k)} = Tr(P^{(k)}_k H_{(0)}) , \quad E^{(b)}_{(k)} = Tr(P^{(k-1)}_{(k-1)} H_{(1)}) .$$

(1.4.4)

[An analogous partition of the right-hand side of Eq.(1.4.2) may be found in Ref.[52]]. Moreover, the above-exhibited components were shown to be interrelated as follows

$$(k - 1)E^{(b)}_{(k)} = -kE^{(a)}_{(k)}$$

(1.4.5)

for any $k$. This principal relation has been originally derived for $k \leq 4$ [37] by substituting into Eq.(1.4.4) the expressions for $P^{(k)}_k$ of Eqs.(1.1.5)-(1.1.10) followed by a definite algebraic procedure based on employment of Eq.(1.1.8). Later, the same result was rederived using Eq.(1.4.2) and verified for higher values of the order parameter $k$ [52]. Implications of Eq.(1.4.5) are as follows: First, this relation points to opposite signs of the components $E^{(a)}_{(k)}$ and $E^{(b)}_{(k)}$. Thus, the total $k$th order energy actually depends upon the difference between absolute values of these components. Second, the absolute value of $E^{(b)}_{(k)}$ is foreseen to exceed that of $E^{(a)}_{(k)}$ i.e. $|E^{(b)}_{(k)}| > |E^{(a)}_{(k)}|$. Consequently, it is the sign of $E^{(b)}_{(k)}$ that determines the actual sign of the total $k$th order energy $E_{(k)}$ and thereby its stabilizing or destabilizing nature. Thus, the $H_{(1)}$—containing component is expected to be the principal (decisive) one, whereas $E^{(a)}_{(k)}$ is likely to play a secondary role in the formation of the $k$th order energy $E_{(k)}$. The actual state of things, however, is somewhat more complicated as clarified below.

Let us note first that the relations of Eqs.(1.4.3) and (1.4.5) allow the total correction $E_{(k)}(k > 1)$ to be alternatively represented as follows

$$E_{(k)} = -\frac{1}{k - 1}E^{(a)}_{(k)} , \quad E_{(k)} = \frac{1}{k}E^{(b)}_{(k)}$$

(1.4.6)

and these expressions evidently are formally equivalent. Actually, however, the first relation of Eq.(1.4.6) yields chemically-meaningful formulae for the whole correction $E_{(k)}$ but not the second one. This circumstance, in turn, may be traced back to relative simplicity of the expression for $E^{(a)}_{(k)}$ itself vs. that for $E^{(b)}_{(k)}$, viz.

$$E^{(a)}_{(k)} = Tr[X^{(k)}_+ E_{(+)} - X^{(k)}_- E_{(-)}] ;$$

(1.4.7)

$$E^{(b)}_{(k)} = Tr[X^{(k-1)}_+ T + X^{(k-1)}_- Q] - 2Tr[G_{(k-1)}R^+ + G^+_{(k-1)} R] ,$$

(1.4.8)

where Eqs.(1.1) and (1.1.5) are correspondingly substituted for $H_{(0)}, H_{(1)}$ and $P^{(k-1)}_{(k-1)}$. As is easily seen, employment just of Eq.(1.4.7) along with the first relation of Eq.(1.4.6) yields a compact expression for the $k$th order energy ($E_{(k)}$) in terms of intrasubset population matrices of the same order only, viz.

$$E_{(k)} = -\frac{1}{k - 1}Tr[X^{(k)}_+ E_{(+)} - X^{(k)}_- E_{(-)}] .$$

(1.4.9)

After invoking proportionality between $X^{(k)}_+$ and $D^{(k)}_+$, as well as between $X^{(k)}_-$ and $D^{(k)}_-$ shown in Eq.(1.3.16), the above formula takes the following form

$$E_{(k)} = \frac{2}{k - 1}Tr[D^{(k)}_+ E_{(+)} + D^{(k)}_- E_{(-)}] ,$$

(1.4.10)
which points to a dependence of $\mathcal{E}_{(k)}$ upon the intersubset delocalization matrices $D_{(k)}^{(+)}$ and $D_{(k)}^{(-)}$. Hence, we obtain an analogue of the well-known intuition-based assumption about a relation between stabilization (or destabilization) of a certain system and the relevant extent of delocalization. By contrast, employment of Eq.(1.4.8) along with the second relation of Eq.(1.4.6) yields no simple interpretation of $\mathcal{E}_{(k)}$. More details concerning this intriguing situation may be found in the subsection 2.3.

The last and practically even more important implication of the relation of Eq.(1.4.5) consists in the possibility of summing up the components $E^{(+)}_{(k)}$ and $E^{(-)}_{(k)}$ within Eq.(1.4.3) so that the $k$th order energy $\mathcal{E}^{(k)}$ becomes expressible directly via the principal matrices $G^{(k)}$ and (sub)matrices (blocks) of our Hamiltonian matrix [37].

$$E^{(0)} = 2TrE^{(+)}$$
$$E^{(1)} = 2TrT$$
$$E^{(2)} = -2Tr(G_{(1)}R^+)$$
$$E^{(3)} = -2Tr(G_{(2)}R^+)$$
$$E^{(4)} = -2Tr(G_{(3)} + G_{(1)}G_{(1)}^+G_{(1)})R^+)$$
$$E^{(5)} = -2Tr(G_{(4)} + G_{(2)}G_{(1)}^+G_{(1)} + G_{(1)}G_{(2)} + G_{(1)}G_{(1)}^+G_{(2)})R^+)$$

(1.4.11)

[Derivations of $E^{(5)}$ and $E^{(6)}$ may be found in Refs.[38] and [40], respectively. The same expressions are obtainable also using Eq.(1.4.2) [52].] It is seen that the sum of zero and first order members of Eq.(1.4.11) coincides with the total energy of the subset of isolated occupied basis functions $\{\varphi^{(+)}\}$ in accordance with the expectation, whereas that of the remaining corrections describes stabilization (or destabilization) of the given system vs. the above-specified set. Comparison of the above-exhibited expressions to the usual perturbational formulae for energy corrections may be found in the subsection 2.3.

### 1.5. Indirect applications of the PNCMO theory

In this subsection, we are about to demonstrate that the actual scope of applicability of the above-described PNCMO theory is not limited to Hamiltonian matrices of Eq.(1.1) containing a zero order term $(H_{(0)})$ of the block-diagonal constitution.

Suppose that we start with a certain $N \times N$-dimensional Hamiltonian matrix $\tilde{H}$ that does not meet the above requirement. Let the orthogonal basis set underlying the matrix $\tilde{H}$ be denoted by $\{\chi\}$. Meanwhile, the total number of electrons coincides with $2n$ as previously.

Let us now assume that an unitary matrix $U$ is found that allows us to transform the matrix $\tilde{H}$ into the nearly block-diagonal form, viz.

$$U^+\tilde{H}U = H$$

(1.5.1)

where $H$ coincides with the Hamiltonian matrix of Eq.(1.1). It is evident that the above relation represents passing from our initial basis set $\{\chi\}$ to the former one $\{\varphi\}$. Employment of the standard PNCMO theory of subsections 1.1-1.4 to the transformed matrix $H$ allows us to find the relevant CBO matrix $P$ and the respective NCMO representation matrix $C$. The final step of the overall procedure then consists in retransforming the above-mentioned matrices $P$ and $C$ into the initial basis $\{\chi\}$ again by means of the following relations

$$\bar{P} = UPU^+$$
$$\bar{C} = UC$$

(1.5.2)
Let us recall now that the requirements underlying the standard PNCMO theory actually refer to constitution of the zero order Hamiltonian matrix $\hat{H}(0)$ only, viz. the latter should be of the block-diagonal constitution. Meanwhile, the first order member $\hat{H}(1)$ is free from additional conditions. Given that the initial matrix $\tilde{H}$ also consists of a zero order term ($\tilde{H}(0)$) and of the first order one ($\tilde{H}(1)$), i.e.

$$\tilde{H} = \tilde{H}(0) + \tilde{H}(1),$$

we may confine ourselves to finding an unitary matrix $U$ that transforms the zero order member $\tilde{H}(0)$ into a block-diagonal form shown in Eq.(1.1). As a result, we then arrive at the block-diagonalization problem for the matrix $\tilde{H}(0)$, viz.

$$U^+\tilde{H}(0)U = H(0) = \begin{bmatrix} E_+ & 0 \\ 0 & -E_- \end{bmatrix},$$

where $E_+$ and $E_-$ now play the role of the relevant eigenblocks. At the first sight, the problem of Eq.(1.5.4) resembles that of Eq.(1.2.1). Nevertheless, an important difference between these seemingly similar problems arises due to the zero order of the matrix concerned (i.e. of $\tilde{H}(0)$). Consequently, the problem of Eq.(1.5.4) cannot be solved perturbatively in contrast to that of Eq.(1.2.1). Fortunately, non-perturbative solutions of block-diagonalization problems also are possible in some cases as exemplified below (subsection 3.1). Given that such a solution is found and thereby the matrix $U$ is known, the remaining (first order) member of our initial Hamiltonian matrix ($\tilde{H}(1)$) may be transformed without any restriction using the following relation

$$U^+\tilde{H}(1)U = H(1).$$

Application of the above-formulated standard PNCMO theory to the sum $H(0) + H(1)$ then yields matrices $P$ and $C$ in the form of power series, individual members of which (i.e. $P(k)$ and $C(k)$) may be retransformed into the initial basis $\{\chi\}$ separately, i.e. on the basis of the following expressions

$$\tilde{P}(k) = UP(k)U^+, \quad \tilde{C}(k) = UC(k).$$

It deserves adding here that all relations concerning total energies and overviewed in the subsection 1.4 are invariant against unitary transformations of basis sets. This implies that energy components $\xi^{(a)}(k)$ and $\xi^{(b)}(k)$ may be derived either using the original relations of Eqs.(1.4.3)-(1.4.10) or their analogues containing members of the power series for matrices $\tilde{H}$ and $\tilde{P}$, i.e.

$$\xi^{(a)}(k) = Tr(\tilde{P}(k)\tilde{H}(0)), \quad \xi^{(b)}(k) = Tr(\tilde{P}(k-1)\tilde{H}(1)).$$

Analogously, the total correction $\xi(k)$ is alternatively representable as follows

$$\xi(k) = -\frac{1}{k-1}Tr(\tilde{P}(k)\tilde{H}(0)), \quad \xi(k) = \frac{1}{k}Tr(\tilde{P}(k-1)\tilde{H}(1)).$$

2. Particular cases of the PNCMO theory
In this Section, we will discuss two particular cases of the standard PNCMO theory of section 1 when explicit solutions may be obtained for principal matrix equations shown in Eq.(1.1.8). We start with the case of diagonal zero order matrices \( E(+) \) and \( E(-) \) of Eq.(1.1), when individual elements \( G_{(k)im} \) are expressible in terms of usual perturbational fractions (subsection 2.1). Properties of charge (re)distribution and delocalization referring just to this case are then discussed along with those of the relevant total energy (subsections 2.2 and 2.3, respectively). Thereupon, we turn to the case of matrices \( E(+) \) and \( E(-) \) proportional to the unit matrix \( (I) \) and discuss the consequent explicit expressions for entire principal matrices \( G_{(k)} \) along with the relevant implications (subsection 2.4).

2.1. The case of a diagonal zero order Hamiltonian matrix. Expressions for particular elements \( G_{(k)im} \) and their interpretation

The present subsection addresses the case of absence of the zero order intrasubset interactions in our system so that both inter- and intrasubset resonance parameters are of the first order magnitude. In other words, submatrices \( E(+) \) and \( E(-) \) of the zero order Hamiltonian matrix of Eq.(1.1) (and thereby the whole member \( H_{(0)} \)) are assumed to take diagonal forms, viz.

\[
E_{(+)} ij = \varepsilon_{(+)} i \delta_{ij}, \quad E_{(-)} lm = \varepsilon_{(-)} m \delta_{lm},
\]

(2.1.1)

where \( \varepsilon_{(+)} i \) and \( -\varepsilon_{(-)} m \) coincide with one-electron energies of basis orbitals \( \varphi_{(+)} i \) and \( \varphi_{(-)} m \), respectively (Section 1). Under the above condition, elements \( G_{(k)im} \) of matrices \( G_{(k)} \) are expressible in terms of the following fractions [27, 36]

\[
G_{(k)im} = -\frac{W_{(k)im}}{\varepsilon_{(+)} i + \varepsilon_{(-)} m},
\]

(2.1.2)

instead of the integral of Eq.(1.1.17). Using Eq.(1.1.9), we then obtain that

\[
G_{(1)im} = -\frac{R_{im}}{\varepsilon_{(+)} i + \varepsilon_{(-)} m},
\]

(2.1.3)

\[
G_{(2)im} = \frac{1}{\varepsilon_{(+)} i + \varepsilon_{(-)} m} \left\{ \sum_{(+)} j T_{ij} R_{jm} - \sum_{(-)} r R_{ir} Q_{rm} \frac{\varepsilon_{(+)} j + \varepsilon_{(-)} m}{\varepsilon_{(+)} i + \varepsilon_{(-)} r} \right\},
\]

(2.1.4)

whilst elements of higher orders take somewhat more cumbersome forms (see e.g.[59, 60]). Sums over \( (+) j \) and over \( (-) r \) correspondingly embrace here all orbitals of subsets \( \{ \varphi_{(+)} \} \) and \( \{ \varphi_{(+)} \} \) as previously. Let us turn now to interpretation of the above expressions.

Let us start with the first order element \( G_{(1)im} \). As is seen from Eq.(2.1.3), this element is proportional to the resonance parameter \( (R_{im}) \) between basis orbitals \( \varphi_{(+)} i \) and \( \varphi_{(-)} m \) and inversely proportional to the energy gap between the latter \( (\varepsilon_{(+)} i + \varepsilon_{(-)} m) \). The minus sign in front of \( \varepsilon_{(-)} m \) should be taken into consideration. Thus, the element \( G_{(1)im} \) represents the direct interaction between the orbitals concerned that is often alternatively called the through-space one. It is also evident that the element \( G_{(1)im} \) does not vanish if the orbitals concerned (i.e.
\( \varphi_{(+)} \) and \( \varphi_{(-)} \) are characterized by a non-zero resonance parameter. These orbitals are referred to below as neighboring ones. Meanwhile, the expression of Eq.(2.1.4) for the second order element \( G_{(2)im} \) is somewhat more involved and contains sums of products of pairs of mutually "connected" resonance parameters. Moreover, the remaining orbitals of the same system (i.e. \( \varphi_{(+)} \) and \( \varphi_{(-)} \)) also participate in the formation of the element \( G_{(2)im} \) and play the role of mediators in the second order interaction between orbitals \( \varphi_{(+)} \) and \( \varphi_{(-)} \). It is also seen that the orbitals \( \varphi_{(+)} \) and \( \varphi_{(-)} \) should overlap directly both with \( \varphi_{(+)} \) and with \( \varphi_{(-)} \) to be efficient mediators. In this connection \( G_{(2)im} \) has been interpreted as the indirect interaction between orbitals \( \varphi_{(+)} \) and \( \varphi_{(-)} \) through individual mediators. Similarly, the formula for the element \( G_{(3)im} \) [59, 60] contains sums of products of triplets of "connected" resonance parameters. Consequently, this element represents an analogous indirect interaction via pairs of mediators. Generally, the number of mediators coincides with \( k - 1 \) for an element \( G_{(k)im} \). Given that a certain diagonal element (say \( T_{ii} \)) takes a non-zero value, we accordingly have to do with the self-mediating effect of the orbital \( \varphi_{(+)} \).

Furthermore, an analogous interpretation may be easily extended also to elements of matrix products contained within definitions of intrasubset population matrices \( X_{(+)}^{(k)} \) and \( X_{(-)}^{(k)} \) of Eq.(1.1.10), e.g. \( G^{+} (1), G^{+} (2) \), etc. For example, the element \( (G^{+} (1))_{ij} \) is interpretable as the indirect interaction between basis orbitals \( \varphi_{(+)} \) and \( \varphi_{(+)} \), where orbitals of the opposite subset \( \varphi_{(-)} \) play the role of mediators.

Let us now formulate a general non-zero-value condition for indirect interorbital interactions [38, 61]. To this end, let us introduce the following explicit designations for resonance parameters contained within Eqs.(2.1.3) and (2.1.4), viz.

\[
T_{ij} = \langle \varphi_{(+)} | \hat{H} | \varphi_{(+)} \rangle, \quad R_{ir} = \langle \varphi_{(+)} | \hat{H} | \varphi_{(-)} \rangle, \quad (2.1.5) \\
Q_{rm} = \langle \varphi_{(-)} | \hat{H} | \varphi_{(-)} \rangle,
\]

where the orbitals concerned are shown inside the bra- and ket-vectors. The necessary condition for an element \( G_{(k)im} \) to take a non-zero value then consists in the presence of at least a single non-zero product of \( k \) "connected" resonance parameters in the system concerned, i.e.

\[
\langle \varphi_{(+)} | \hat{H} | \varphi_{1} \rangle < \varphi_{1} | \hat{H} | \varphi_{2} \rangle \ldots < \varphi_{k-2} | \hat{H} | \varphi_{k-1} \rangle < \varphi_{k-1} | \hat{H} | \varphi_{(-)} \rangle \neq 0, \quad (2.1.6)
\]

where the notations \( \varphi_{1}, \varphi_{2}, \ldots \varphi_{k-1} \) stand for mediating orbitals. In other words, presence of a chain-like set of \( k - 1 \) mediators in between the interacting orbitals \( \varphi_{(+)} \) and \( \varphi_{(-)} \) is required here. Given that the condition of Eq.(2.1.6) is met, we will say that in the given system there is a pathway of the \( k \)th order between orbitals \( \varphi_{(+)} \) and \( \varphi_{(-)} \). Moreover, additivity of the element \( G_{(k)im} \) with respect to contributions of individual pathways easily follows from expressions like that of Eq.(2.1.4). For an element of a matrix product like \( (G^{+} (1))_{ij} \), we accordingly have to do with a set of pathways between pairs of orbitals of the same subset (i.e. between \( \varphi_{(+)} \) and \( \varphi_{(+)} \)). It is also evident that increments of some pathways may cancel one another so that the indirect interaction concerned vanishes even if the relevant requirement of the form shown in Eq.(2.1.6) is met. That is why the conditions under discussion are of a necessary (but not sufficient) nature.

Finally, the well-known extinction of resonance parameters when the distance between the relevant orbitals grows [62] allows us to expect an analogous behaviour.
of interorbital interactions too. Nevertheless, indirect interactions of higher orders are likely to take significant values even for remote orbitals if the system concerned offers appropriate sets of mediators. Implications of Eq. (2.1.1) upon properties of charge (re)distribution and total energy are discussed in the next subsections (2.2 and 2.3).

2.2. Semilocal nature of charge (re)distribution and delocalization

This subsection addresses specific properties of charge (re)distribution and/or of delocalization for systems described by diagonal matrices $E_{(+)}$ and $E_{(-)}$ of Eq. (1.1).

As discussed already in the subsection 1.1, populations of basis orbitals $\varphi_+^{(i)}$ and $\varphi_-^{(i)}$ ($X_+^{(i)i}$ and $X_-^{(i)i}$) are expressible in terms of the relevant partial contributions ($x_+^{(i),i,-m}$ and $x_-^{(i),i,+j}$) referring to separate pairs of orbitals of opposite initial occupation (see Eq. (1.1.15)). These contributions, in turn, take the form of sums over the order parameter $(k)$ of increments $x_+^{(i),i,(-m)}$ and $x_-^{(i),i,+j}$. If we recall now the above-established proportionality between $x_+^{(i),i,(-m)}$ and the respective partial delocalization coefficient $d_+^{(k)}$ (see Eq. (1.3.24) along with the equalities shown in Eqs. (1.1.14) and (1.3.9)), we may actually confine ourselves to analysis of properties of increments $x_+^{(i),i,(-m)}$ of different orders $k$, i.e. of partial populations of the $k$th order transferred between orbitals $\varphi_+^{(i)}$ and $\varphi_-^{(-m)}$. To this end, the expressions for $G_{+}^{(k)mi}$ like those of Eq. (2.1.3) and (2.1.4) should be substituted into definitions of $x_+^{(i),i,(-m)}$ shown in Eq. (1.1.13).

Let us start with the increment of the second order $x_+^{(2)}$. As is seen from the first relation of Eq. (1.1.13), this increment is determined by square of the first order element $G_{+}^{(1)im}$ and thereby of the direct interaction between orbitals concerned (i.e. $\varphi_+^{(i)}$ and $\varphi_-^{(-m)}$). As with the above-specified interaction, the increment $x_+^{(2)}$ is then expected to take a non-zero value for neighboring pairs of basis orbitals only. Moreover, dependence of the increment concerned upon the mutual arrangement of only two orbitals in the real space is foreseen along with its rapid extinction when the distance between these orbitals increases. The a priori positive sign of $x_+^{(2)}$ (Subsection 1.1) also deserves recalling here. Consequently, the overall contribution of the second order to the population of an initially-occupied orbital $\varphi_+^{(i)}$ lost due to perturbation ($X_+^{(2)}$ of Eq. (1.1.12)) originates mainly from increments $x_+^{(2)}$ of the nearest-neighboring initially-vacant orbitals ($\varphi_-^{(-m)}$). The same evidently refers to the second order term ($D_+^{(2)}$) of the analogous power series for the delocalization coefficient ($D_+^{(2)}$) of the NCMO $\psi_+^{(+)}$ (Subsection 1.3), as well as to the relevant characteristics of initially-vacant orbitals. Moreover, transferability of contributions like $X_+^{(2)}$ and/or $X_-^{(2)}$ is predicted if the nearest neighborhoods of orbitals $\varphi_+^{(i)}$ and/or $\varphi_-^{(-m)}$ are similar.

The third order increment $x_+^{(3)}$ to the same partial transferred population ($x_+^{(i),i,(-m)}$) is determined by the product of elements $G_{+}^{(1)im}$ and $G_{+}^{(2)im}$ as the second expression of Eq. (1.1.13) shows. Consequently, the increment concerned does not vanish if the relevant orbitals $\varphi_+^{(i)}$ and $\varphi_-^{(-m)}$ interact both directly and indirectly by means of a single mediator and thereby these orbitals are both first-
and second-neighboring ones. In other words, at least a single trip of neighboring orbitals is required to ensure non-vanishing third order increments to charge (re)distribution and/or to delocalization. Moreover, additivity of these characteristics with respect to contributions of individual triplets of the above-specified type also is among anticipations. So far as the overall population of the orbital \( \varphi^{(+)}_i \) is concerned, the third order member of the relevant expansion \( \{X^{(3)}_{(+\cdot i\cdot)}\} \) depends upon a somewhat more extended neighborhood of the orbital under consideration as compared to the above-discussed second order term \( \{X^{(2)}_{(+\cdot i\cdot)}\} \). Moreover, the increment \( X^{(3)}_{(+\cdot i\cdot)} \) contributes to an increase (decrease) of the total population of the orbital \( \varphi^{(+)}_i \) if the direct and indirect interactions between the latter and the neighboring initially-vacant orbitals \( \varphi^{(-)}_m \) are of the same (opposite) signs (subsection 1.1).

Increments of higher orders to the partial transferred population \( x^{(+)}_{i\cdot(-\cdot m} \) also may be analyzed similarly. To be able to draw general conclusions regarding the increment \( x^{(k)}_{(+\cdot i\cdot(-\cdot m} \) of any order \( k \), let us recall the non-zero-value condition for elements \( G^{(k)}_{i\cdot m} \) in terms of pathways over basis orbitals (subsection 2.1) and note that cyclic (self-returning) pathways \([38]\) correspond to separate members of definitions of \( x^{(k)}_{(+\cdot i\cdot(-\cdot m} \) like those of Eq.(1.1.13). For example, a cyclic pathway of the \( k \)th order embracing orbitals \( \varphi^{(+)}_i \) and \( \varphi^{(-)}_m \) refers to the product \( G^{(k-1)}_{i\cdot m}G^{(1)}_{i\cdot m} \). The necessary condition for the increment \( x^{(k)}_{(+\cdot i\cdot(-\cdot m} \) to take a non-zero value then consists in the presence of at least a single pathway of the above-specified type in the system concerned. It is also evident that contributions of separate pathways to \( x^{(k)}_{(+\cdot i\cdot(-\cdot m} \) can cancel out one another. [Rules governing the signs of increments of different pathways have been formulated in Ref.[42]]. Finally, a cyclic pathway of the \( k \)th order embraces no more than \( k \) orbitals [Note that a certain orbital may be "visited" more than once in this pathway]. This implies that no more than \( k \) basis orbitals participate in the formation of the increment \( x^{(k)}_{(+\cdot i\cdot(-\cdot m} \).

In summary, the higher is the order parameter \( (k) \) of the given increment to the overall charge (re)distribution and/or delocalization, the more extended fragments of the system concerned are embraced by this increment. Again, convergence of the relevant power series \([58]\) ensures decrease of increments with increasing values of \( k \). Thus, a semilocal nature of both charge (re)distribution and delocalization may be finally concluded for all systems described by a diagonal zero order Hamiltonian matrix.

The results of this subsection have been successfully applied to systems consisting of weakly-interacting two-center chemical bonds and lone electron pairs. Bonding and antibonding orbitals of individual bonds along with those of lone pairs played the role of basis functions \( \{\varphi\} \) in this case. Accordingly, the weak interbond interaction allowed us to assume the diagonal constitutions of the relevant submatrices \( E^{(+)}_{i\cdot} \) and \( E^{(-)}_{i\cdot} \) of Eq.(1.1).

Heteroatom influence in substituted alkanes (the so-called inductive effect \([19]\)) has been studied \([63]\) in the first place. The above-discussed proportionalities between \( x^{(k)}_{(+\cdot i\cdot(-\cdot m} \) and \( d^{(k)}_{(+\cdot i\cdot(-\cdot m} \) along with other relations of subsection 1.3 formed the basis for two mutually equivalent interpretations of the effect concerned, namely in terms of a perturbed electron density distribution (as usual) and via changes in the degrees of delocalization of separate NCMOs and thereby of individual pairs of electrons. Moreover, the latter changes proved to be proportional to delocalization.
coefficients of NCMOs in the respective parent alkane. Finally, increments of the second order (i.e. $x^{(2)}_{(+i)(-m)}$ and $d^{(2)}_{(+i)(-m)}$) were shown to play the most important role in the formation of the electron density redistribution and/or reshaping of NCMOs due to emergence of a heteroatom. As a result, the short-range nature and other peculiarities of the inductive effect have been concluded to originate from a weak interbond delocalization in respective parent alkanes. Analogously, additivity of the total effect of two heteroatoms upon the hydrocarbon fragment has been revealed and traced back to the relevant additivity of delocalization. The general nature of the above-overviewed conclusions also deserves emphasizing, viz. these refer to any alkane and its derivative.

More subtle aspects of the heteroatom influence have been studied in Ref. [64], namely the so-called trans-effect revealing itself as non-equivalence of the cis- and trans-arranged $C_\beta-C_\gamma$ (or $C_\beta-H$) bonds with respect to the heteroatom-containing ($X-C_\alpha$) bond. The third order corrections to occupation numbers of basis orbitals proved to play the decisive role in this case. Moreover, contributions [63] and [64] provide us with a unified description of the inductive and trans-effects. Indeed, these two aspects of the heteroatom influence prove to be representable by members of different orders of the same power series.

In this context, investigation of non-additive effects of two substituents (inter-substituent interaction) in D,A-disubstituted benzenes [65] also deserves attention (D and A correspondingly stand here for an electron-donating substituent and for the electron-accepting one). The usual (canonical) MOs of benzene played the role of basis functions $\{\varphi\}$ here along with orbitals localized on individual substituents. The intersubstituent interaction was shown to manifest itself as two effects, viz. (i) as an alteration in the extent of the intramolecular charge transfer between an individual substituent and the phenyl ring owing to the indirect participation of orbitals of the another substituent and (ii) as an additional indirect charge transfer between substituents D and A by means of orbitals of the phenyl ring playing the role of mediators. Moreover, these two components of the intersubstituent interaction have been represented by terms of the fourth order of the expansion for the relevant CBO matrix $P$.

Therefore, classification of separate aspects of heteroatom influence proved to be possible on the basis of the order parameter ($k$) of the decisive terms of the power series applied. An analogous classification of chemical reactions also was among the achievements that are overviewed elsewhere in a detail [41, 42, 52, 66].

2.3. Interpretation of total energies as charge transfer energies. A new insight into the Dewar formula

Let us now discuss the implications of Eq.(2.1.1) upon the relevant total energy ($E$). To this end, let us return to general results of subsection 1.4 and employ our principal assumption of Eq.(2.1.1) in the expressions contained there.

The zero order member ($E_{(0)}$) of the power series for the total energy ($E$) follows directly from the first relation of Eq.(1.4.11) and coincides with the double sum of one-electron energies ($\varepsilon_{(+i)}^{(+)}$) of all initially-occupied orbitals $\varphi_{(+i)}^{(+)}$ and thereby with their total energy before the interaction in accordance with the expectation. Given that the actual one-electron energies of basis orbitals are entirely included into the
above-mentioned parameters $\varepsilon_{(\pm)i}$ so that diagonal elements $(T_{ii})$ of the matrix $T$
vanish (this always may be done without restrictions), a zero value follows from the second relation of Eq.(1.4.11) for the first order member of the same series ($E_{(1)}$) in accordance with original result of M. J. S. Dewar [13, 67, 68]. Thus, we may turn immediately to increments $E_{(k)}$ of higher orders ($k = 2, 3, 4...$).

As discussed already (Subsect. 1.4), each correction $E_{(k)}$ is representable as an algebraic sum of two components $E^{(\alpha)}_{(k)}$ and $E^{(\beta)}_{(k)}$ defined by Eqs.(1.4.3) and (1.4.4) and expressed as shown in Eqs.(1.4.7) and (1.4.8), respectively. Due to the diagonal constitution of our matrices $E_{(+)}$ and $E_{(-)}$ (see Eq.(2.1.1)), only diagonal elements of the intrasubset population matrices $X^{(k)}_{(+)}$ and $X^{(k)}_{(-)}$ actually contribute to the component $E^{(\alpha)}_{(k)}$ as Eq.(1.4.7) shows. As a result, this component depends only upon increments of the $k$th order to the populations of basis orbitals $(X^{(k)}_{(++)}$ and $X^{(k)}_{(--)})$. After representing the latter as sums of partial transferred populations of the respective order $k$ (see Eq.(1.1.12)) and invoking the relations of Eq.(1.1.14), we obtain the following formula for $E^{(\alpha)}_{(k)}$ [37], viz.

$$E^{(\alpha)}_{(k)} = -\sum_{(+i)(-m)} x^{(k)}_{(+i)(-m)} (\varepsilon_{(+)i} + \varepsilon_{(-)m}).$$

(2.3.1)

Thus, the component $E^{(\alpha)}_{(k)}$ is now expressible in terms of products of partial populations of the $k$th order transferred between orbitals of opposite initial occupation and energy intervals between the latter. Consequently, this component is interpretable as the charge transfer energy. The minus sign in front of the sum of Eq.(2.3.1) also has a clear meaning, namely it points to the destabilizing nature of $E^{(\alpha)}_{(k)}$, if $x^{(k)}_{(+i)(-m)}$ is a positive quantity and vice versa. [Note that $\varepsilon_{(+)i} > 0$ and $\varepsilon_{(-)m} > 0$ and thereby $\varepsilon_{(+)i} + \varepsilon_{(-)m} > 0$ in our negative energy units]. This result causes no surprise if we bear in mind that the positive sign of $x^{(k)}_{(+i)(-m)}$ implies a certain charge transfer from an orbital of the lower energy $(\varphi^{(+)i})$ to that of a higher energy $(\varphi^{(-)m})$.

Let us now turn to the remaining component of the $k$th order energy $(E^{(\beta)}_{(k)})$ defined by Eq.(1.4.8). Since diagonal elements of the matrix $Q$ also may be assumed to take zero values for analogous reasons, the expression of Eq.(1.4.8) consequently contains no increments of population alterations $X^{(k-1)}_{(++)}$ and $X^{(k-1)}_{(--)}$ in contrast to Eq.(1.4.7).

Hence, the component $E^{(\beta)}_{(k)}$ describes the effect of formation of bond orders between basis orbitals upon the $k$th order energy $(E_{(k)})$. It is also noteworthy that bond orders determining the component $E^{(\beta)}_{(k)}$ originate from members of the $(k - 1)$th order of the power series for the DM $P$. If we recall now that the intrasubset population matrices of the $k$th order (i.e. $X^{(k)}_{(+)}$ and $X^{(k)}_{(-)}$) are expressed in terms of products of the principal matrices of lower orders ($G_{(k-1)}, G_{(k-2)}, etc.$) that, in turn, represent intersubset bond orders being formed within previous terms of the same series (see Eq.(1.1.5)), the above-established interdependence between components $E^{(\alpha)}_{(k)}$ and $E^{(\beta)}_{(k)}$ shown in Eq.(1.4.5) causes no surprise. Moreover, charge redistribution of the $k$th order may be then considered as a consequence (or counter-effect) of formation of intersubset bond orders within terms of lower orders of the same series for the DM $P$. Thus, we have to do here with a certain gradual reorganization
of bonding, the energetic increments of which are interrelated and governed by Eq.(1.4.5). Furthermore, the above-drawn conclusions concerning the signs and absolute values of $E^{(\alpha)}_{(k)}$ and $E^{(\beta)}_{(k)}$ (subsection 1.4) allow us to expect that stabilization of our system vs. the set of isolated initially-occupied basis orbitals (if any) is entirely due to formation of new bond orders, and the subsequent charge redistribution actually reduces this stabilizing effect. Nevertheless, the absolute value of the total $k$th order energy ($E_{(k)}$) is proportional to that of the respective charge transfer energy $E^{(\alpha)}_{(k)}$ as the first relation of Eq.(1.4.6) indicates. Indeed, the minus signs of Eqs.(1.4.6) and (2.3.1) cancel out one another and we obtain [37]

$$E_{(k)} = \frac{1}{k-1} \sum_{(+i)(-m)} x_{(+i)(-m)}^{(k)} (\varepsilon_{(+i)} + \varepsilon_{(-m)}).$$  \hspace{1cm} (2.3.2)

On the basis of the above relation, an interpretation of the total $k$th order energy $E_{(k)}$ as the charge transfer energy also becomes acceptable (in spite of its somewhat oversimplified nature). This interpretation provides us with a quantum-chemical analogue of the intuition-based relation between stabilization and charge redistribution. If we recall now the interrelations between $x_{(+i)(-m)}^{(k)}$ and $d_{(+i)(-m)}^{(k)}$ shown in Eq.(1.3.24), we obtain that [52]

$$E_{(k)} = \frac{2}{k-1} \sum_{(+i)(-m)} d_{(+i)(-m)}^{(k)} (\varepsilon_{(+i)} + \varepsilon_{(-m)}).$$  \hspace{1cm} (2.3.3)

Thus, the $k$th order energy $E_{(k)}$ is alternatively interpretable as that of the delocalization of the initially-occupied basis orbitals over the initially-vacant ones, i.e. as the intersubset delocalization energy of all initially-localized pairs of electrons. Additivity of $E_{(k)}$ with respect to contributions of individual pairs of electrons also is easily seen from Eq.(2.3.3). Hence, the well-known intuition-based relation between delocalization and stabilization [16, 69] acquires a quantum-chemical support. It is also evident that Eq.(2.3.3) is a particular case of the relation of Eq.(1.4.10) referring to diagonal matrices $E_{(+)}$ and $E_{(-)}$.

As discussed in the subsection 1.1, the signs of partial transferred populations $x_{(+i)(-m)}^{(k)}$ depend upon those of elements $G_{(k)im}$ contained within the relevant definition of Eq.(1.1.13), the latter describing particular interorbital interactions in the present case (Subsection 2.1). The expression of Eq.(2.3.2) then allows us to formulate the rule governing the signs of energy corrections $E_{(k)}$ and thereby the nature of the respective effect. Thus, the a priori positive sign of any second order term $x_{(+i)(-m)}^{(2)}$ (Subsect. 1.1) indicates that the correction $E_{(2)}$ always is of stabilizing nature in accordance with the expectation. Meanwhile, the signs of the subsequent energy increments $E_{(k)}$, $k = 3, 4, ..$ depend upon those of the relevant partial transferred populations and thereby these are governed by the following rule: The correction $E_{(k)}$, $k = 3, 4, ..$ contributes to an additional stabilization (destabilization) of the given system (vs. the sum $E_{(0)} + E_{(1)}$), if the interorbital interactions concerned are of coinciding (opposite) signs for all (or almost all) pairs of orbitals $\varphi_{(+i)}$ and $\varphi_{(-m)}$. This rule will be referred to below as the sign consistence condition for interorbital interactions. Applications of the latter to chemical reactions are overviewed in Refs.[41, 52, 66].
As already mentioned, the vanishing correction $E_{(1)}$ is in line with the relevant result obtained by M.S.J.Dewar [13, 67, 68]. An analogous parallelism reveals itself also for higher values of the order parameter $k$. To show this, let us consider the second order term $E_{(2)}$ as an example. After substituting Eqs.(1.1.13) and (2.1.3) into Eq.(2.3.2) for $k = 2$, we obtain the following expression

$$E_{(2)}^{(D)} = 2 \sum_{(+i)(-m)} \frac{(R_{im})^2}{\varepsilon_{(+)}i + \varepsilon_{(-)}m} > 0,$$

(2.3.4)

which coincides with the usual perturbational formula for the second order energy $E_{(2)}$ originally applied to chemical problems by M.J.S. Dewar. [Just this fact is reflected by the superscript $(D)$]. Again, the above-discussed representation of any correction $E_{(k)}$ in terms of two components $E_{(k)}^{(\alpha)}$ and $E_{(k)}^{(\beta)}$ gives us a new insight into the content of the well-known formula of Eq.(2.3.4). Indeed, substituting Eqs.(1.1.13) and (2.1.3) into Eq.(2.3.1) shows that the absolute value of the negative second order charge transfer energy $E_{(2)}^{(\alpha)}$ coincides with that of $E_{(2)}^{(D)}$. At the same time, the remaining (positive) component $E_{(2)}^{(\beta)}$ is twice as large as $E_{(2)}^{(D)}$ as the second relation of Eq.(1.4.6) for $k = 2$ indicates. Thus, the stabilizing (positive) Dewar energy $E_{(2)}^{(D)}$ of Eq.(2.3.4) proves to be actually made up of a difference between the stabilization energy due to formation of intersubset bond orders ($E_{(2)}^{(\beta)}$) and the destabilization energy related to the consequent charge transfer and/or delocalization ($E_{(2)}^{(\alpha)}$) [Note that the above-mentioned newly-formed bond orders are contained within non-zero off-diagonal blocks of the matrix $P_{(1)}$ defined by Eq.(1.1.5)]. Accordingly, our previous expression for the second order energy $E_{(2)}$ shown in Eq.(1.4.11) proves to be a generalization of the Dewar formula to the case of intrasubset interactions (resonance parameters) of the zero order magnitude [70]. Evidently, the same refers even more to energy increments of Eq.(1.4.11) of higher orders ($k = 3, 4...$).

2.4. The case of uniform one-electron energies inside subsets of basis orbitals. Explicit formulae for entire matrices $G_{(k)}$

In addition to our previous assumption of Eq.(2.1.1), let the one-electron energies of all initially-occupied orbitals ($\varepsilon_{(+)}i, i = 1, 2, 3...$) and those of all initially-vacant ones ($\varepsilon_{(-)}m, m = n + 1, n + 2, ..N$) to take uniform values denoted by $\varepsilon_{(+)}$ and $\varepsilon_{(-)}$, respectively. After an appropriate choice of the energy unit, we may then accept the equality $\varepsilon_{(+)} = \varepsilon_{(-)} = 1$, the matrix form of which is as follows

$$E_{(+)} = E_{(-)} = I.$$

(2.4.1)

It is evident that Eq.(2.4.1) is a particular case of Eq.(2.1.1). This implies that all the above-overviewed implications of the latter (Subsections 2.1-2.3) automatically refer to the present case as well. In this connection, we concentrate ourselves here mostly on new (additional) implications of Eq.(2.4.1) vs. those of Eq.(2.1.1).

Let us start with the notation that our principal matrix equations shown in Eq.(1.1.8) may be solved algebraically under the condition of Eq.(2.4.1) [36] and,
consequently, the relevant matrices $G_{(k)}$ are expressible via entire blocks of our Hamiltonian matrix of Eq.(1.1), viz.

$$G_{(1)} = -\frac{1}{2}R, \quad G_{(2)} = \frac{1}{4}(TR - RQ), \text{etc.} \quad (2.4.2)$$

These matrices now correspondingly represent the direct intersubset interaction and the indirect one, wherein matrices $T$ and $Q$ describe the ”self-mediating effects” of subsets $\{\varphi_{(+)}\}$ and $\{\varphi_{(-)}\}$, respectively. Moreover, analogous expressions are easily obtainable for related characteristics, e.g. for the relevant CBO matrix $P$ and the NCMO representation matrix $C$. For example, the starting members of the series for the matrix $P$ follow from Eqs.(1.1.5)-(1.1.7) and (1.1.10) after employment of Eq.(2.4.2), e.g.

$$P_{(1)} = \begin{pmatrix} 0 & R \\ R^+ & 0 \end{pmatrix}, \quad P_{(2)} = \frac{1}{2} \begin{pmatrix} -RR^+ & RQ - QR \\ QR^+ - R^+T & R^+R \end{pmatrix}. \quad (2.4.3)$$

[Note that the zero order member $P_{(0)}$ is shown in Eq.(1.1.6)]. Similarly, the ket-vector of occupied NCMOs $|\Psi_1> \text{ (Subsection 1.2)}$ takes the following form

$$|\Psi_1> = |\Phi_1> (I - \frac{1}{8}RR^+) + \frac{1}{2} |\Phi_2> [R^+ + \frac{1}{2}(R^+T - QR^+)]. \quad (2.4.4)$$

It is easily seen that Eqs.(2.4.3) and (2.4.4) contain the same combinations of matrices $T, R$ and $Q$, namely $RR^+, R^+R, RQ - TR$, etc. This result serves as an additional illustration of the interdependence between matrices $P$ and $C$. Besides, these matrices are comparatively analyzed in Ref.[51] in a detail in connection with their relevance to alkanes.

Let us now dwell on implications of Eq.(2.4.1) upon the relevant total energies ($E$). After substituting Eq.(2.4.1) into Eqs.(1.4.9) and (1.4.10) and employment Eqs.(1.1.11), (1.3.11) and (1.3.19), respectively, we obtain

$$E_{(k)} = -\frac{2}{k - 1}TrX_{(+)}^{(k)} = \frac{4}{k - 1}TrD_{(+)}^{(k)} \equiv \frac{4}{k - 1}D_{(+)}, \quad (2.4.5)$$

i.e. the correction $E_{(k)}$ is now proportional to the complete delocalization coefficient ($D_{(+)}$) of occupied NCMOs $\{\psi_{(+)}\}$ defined by Eq.(1.3.11). An alternative form of Eq.(2.4.5) is as follows

$$E_{(k)} = -\frac{2}{k - 1} \sum_{(+i)} X_{(+ii)}^{(k)} = \frac{4}{k - 1} \sum_{(+i)} D_{(+ii)}^{(k)}. \quad (2.4.6)$$

Thus, the energy correction $E_{(k)}$ is expressible only via traces of matrices $X_{(+)}^{(k)}$ and/or $D_{(+)}^{(k)}$. After substituting the expressions for diagonal elements of these matrices $(X_{(+ii)}^{(k)}$ and $D_{(+ii)}^{(k)}$) in terms of the relevant partial increments as shown in Eqs.(1.1.12) and (1.3.10), we accordingly obtain that

$$E_{(k)} = \frac{2}{k - 1} \sum_{(+i)(-)m} x_{(+i)(-)m}^{(k)} = \frac{4}{k - 1} \sum_{(+i)(-)m} d_{(+i)(-)m}^{(k)}. \quad (2.4.7)$$
It is also evident that the same results are obtainable from Eqs. (2.3.2) and (2.3.3) after replacing all energy intervals $\varepsilon_{(+i)} + \varepsilon_{(-m)}$ by 2. Finally, a simple proportionality between matrices $G_{(1)}$ and $R$ seen from the first relation of Eq. (2.4.2) allows the corrections $E_k$ of Eq. (1.4.11) to be represented in terms of matrices $G_{(k)}$ only [38, 40], e.g.

$$E_2 = 4Tr(G_{(1)}G_{(1)}^{+}), \quad E_3 = 4Tr(G_{(2)}G_{(1)}^{+}),$$

$$E_4 = 4Tr[(G_{(3)} + G_{(1)}G_{(1)}^{+}G_{(1)})G_{(1)}^{+}],$$

$$E_5 = 4Tr[(G_{(4)} + 3G_{(2)}G_{(1)}^{+}G_{(1)})G_{(1)}^{+}],$$

Formulae of the above-exhibited type, however, proved to be somewhat cumbersome for practical applications. In this connection, alternative expressions for the same corrections $E_k$ have been derived, wherein the principal matrices of the right-hand sides of Eq. (2.4.8) of the highest order ($k$) have been eliminated. The derivations concerned [38, 40, 71] were based on recurrence relations for matrices $G_{(k)}$ following from Eqs. (1.1.8) and (1.1.9) under condition of Eq. (1.4.1), viz.

$$G_{(2)} = -\frac{1}{2}(TG_{(1)} - G_{(1)}Q), \quad G_{(3)} = -\frac{1}{2}(TG_{(2)} - G_{(2)}Q) - 2G_{(1)}G_{(1)}^{+}G_{(1)},$$

and on their subsequent employment to reformulate $Tr(G_{(3)}G_{(1)}^{+}), \quad Tr(G_{(4)}G_{(1)}^{+})$, etc. using cyclic transpositions of matrices inside the trace signs. We then obtain the following relations

$$Tr(G_{(3)}G_{(1)}^{+}) = Tr(G_{(2)}G_{(2)}^{+}) - 2Tr(G_{(1)}G_{(1)}^{+}G_{(1)}G_{(1)}^{+}),$$

$$Tr(G_{(4)}G_{(1)}^{+}) = Tr(G_{(3)}G_{(2)}^{+}) - 4Tr(G_{(2)}G_{(1)}^{+}G_{(1)}G_{(1)}^{+})$$

and alternative expressions for $E_4$ [71] and $E_5$ [38], viz.

$$E_4 = 4Tr(G_{(2)}G_{(2)}^{+}) - 4Tr(G_{(1)}G_{(1)}^{+}G_{(1)}G_{(1)}^{+}),$$

$$E_5 = 4Tr[(G_{(3)} - G_{(1)}G_{(1)}^{+}G_{(1)})G_{(2)}^{+}].$$

Besides, individual terms of the right-hand side of the above expression for $E_4$ contain positive-definite matrices $G_{(2)}G_{(2)}^{+}$ and $G_{(1)}G_{(1)}^{+}G_{(1)}G_{(1)}^{+}$. Note that any matrix product of the form $AA^{+}$ is a positive-definite matrix [72]. Consequently, the correction $E_4$ consists of a sum of a positive (stabilizing) and a negative (destabilizing) components in contrast to the $a priori$ positive second order energy $E_2$.

Corrections of even higher orders ($k = 6, 7, ..$) also may be derived similarly. For example, the sixth order energy $E_6$ takes the following form [40]

$$E_6 = 4Tr(G_{(3)}G_{(3)}^{+}) - 8Tr(G_{(1)}G_{(2)}^{+}G_{(1)}G_{(2)}^{+}) - 8Tr(G_{(1)}G_{(1)}^{+}G_{(1)}G_{(1)}^{+}G_{(1)}^{+}G_{(1)}).$$

The expressions of Eqs. (2.4.8), (2.4.11) and (2.4.12) have been successfully applied in studies of relative stabilities of linear and branched isomers of polyenes [73], as well as of individual Kekulé valence structures of benzenoids [38] and phenylenes [61].
3. An extension of the PNCMO theory to the case of two quasi-degenerate subsets of basis orbitals

The standard PNCMO theory of Section 1 was formulated for a nearly block-diagonal Hamiltonian matrix shown in Eq.(1.1) and referring to two weakly-interacting (well-separated) subsets of basis orbitals \{\varphi_{(+)}\} and \{\varphi_{(-)}\}. Now, we will turn to the opposite case, namely to systems characterized by a strong intersubset interaction as compared to the energy gap between orbitals of different subsets. Due to a prospective application of the results of the subsection 1.5, we will invoke the designations used there. Thus, let \{\chi\}, \{\chi_1\} and \{\chi_2\} stand for the $N \times N$-dimensional initial basis set and its subsets, respectively, the latter generally embracing different numbers of orbitals. The relevant total Hamiltonian matrix ($\tilde{H}$) will contain a zero order member ($\tilde{H}^{(0)}$) and a first order one ($\tilde{H}^{(1)}$) in accordance with Eq.(1.5.3). As opposed to the zero order term ($H^{(0)}$) of our former Hamiltonian matrix of Eq.(1.1), however, the present one ($\tilde{H}^{(0)}$) is assumed to take an anti-block-diagonal form, i.e.

$$
\tilde{H} = \tilde{H}^{(0)} + \tilde{H}^{(1)} = \begin{bmatrix}
0 & B^+ & 0 \\
B & A & M \\
0 & M^+ & F
\end{bmatrix},
$$

(3.1)

where the (sub)matrix $B$ embraces the most part of the intersubset interaction (specified below), whilst $A, F$ and $M$ stand for (sub)matrices of the first order magnitude vs. the former. Accordingly, the two-dimensional prototype of the matrix $\tilde{H}$ is as follows

$$
\tilde{h} = \tilde{h}^{(0)} + \tilde{h}^{(1)} = \begin{bmatrix}
0 & \beta \\
\beta & 0
\end{bmatrix} + \begin{bmatrix}
\alpha & \mu \\
\mu & \phi
\end{bmatrix},
$$

(3.2)

and represents a two-level system characterized by a large resonance parameter ($\beta + \mu$) vs. the difference in the Coulomb ones ($\alpha - \phi$), i.e. a system of the second type (ii) of the Introduction. Again, two quasi-degenerate energy levels underly the simple matrix $\tilde{h}$. In this connection, systems embraced by the matrix $\tilde{H}$ of Eq.(3.1) are referred to below as those of two quasi-degenerate subsets of basis orbitals. Now, let us turn to derivation of the CBO matrix $\tilde{P}$ and of the NCMO representation matrix $\tilde{C}$ corresponding to the above-specified systems.

3.1. General results for any pair of quasi-degenerate subsets

As with the application of the usual RSPT to the simple matrix $\tilde{h}$ of Eq.(3.2), we expect to get rid of the quasi-degeneracy between subsets $\{\chi_1\}$ and $\{\chi_2\}$ by finding an appropriate unitary transformation of the basis set. As discussed in the Subsection 1.5, we may confine ourselves to block-diagonalization of the zero order member $\tilde{H}^{(0)}$ in accordance with Eq.(1.5.4). Non-perturbative solution of the block-diagonalization problem for the matrix $\tilde{H}^{(0)}$ of Eq.(3.1) is described in Ref.[53] in a detail along with conditions imposed on the matrix $B$. Two alternative forms of the transformation matrix $U$ have been derived in this study, viz.

$$
U = \frac{1}{\sqrt{2}} \begin{bmatrix}
1 & KB \\
B^+K & -I
\end{bmatrix}, \quad U = \frac{1}{\sqrt{2}} \begin{bmatrix}
1 & BL \\
LB^+ & -I
\end{bmatrix},
$$

(3.1.1)
where $\mathbf{K} \mathbf{B} = \mathbf{B} \mathbf{L}$ and $\mathbf{K}$ and $\mathbf{L}$ are Hermitian matrices defined as follows

$$
\mathbf{K} = (\mathbf{B} \mathbf{B}^+)^{-1/2}, \quad \mathbf{L} = (\mathbf{B}^+ \mathbf{B})^{-1/2}.
$$

(3.1.2)

The eigenblocks of the matrix $\tilde{\mathbf{H}}(0)$, in turn, coincide with the inverse counterparts of matrices $\mathbf{K}$ and $\mathbf{L}$, viz.

$$
\mathbf{E}_+ = \mathbf{K}^{-1} = (\mathbf{B} \mathbf{B}^+)^{1/2}, \quad \mathbf{E}_- = \mathbf{L}^{-1} = (\mathbf{B}^+ \mathbf{B})^{1/2}.
$$

(3.1.3)

Our next step consists in application of the matrix $\mathbf{U}$ of Eq.(3.1.1) to transform the first order member $\tilde{\mathbf{H}}(1)$ of Eq.(3.1) in accordance with Eq.(1.5.5). The resulting total Hamiltonian matrix then resembles that of Eq.(1.1), where submatrices of the new first order member $\mathbf{H}(1)$ are expressible via those of $\tilde{\mathbf{H}}(1)$ of Eq.(3.1) as follows

$$
\mathbf{T} = \frac{1}{2} \left[ (\mathbf{A} + \mathbf{B} \mathbf{L} \mathbf{F} \mathbf{L}^* \mathbf{B}^*) + (\mathbf{B} \mathbf{L} \mathbf{M}^* \mathbf{L}^* \mathbf{M}^*) \right],
$$

$$
\mathbf{Q} = \frac{1}{2} \left[ (\mathbf{F} + \mathbf{L} \mathbf{F}^* \mathbf{A} \mathbf{B}^*) - (\mathbf{M}^* \mathbf{L} \mathbf{B} + \mathbf{L} \mathbf{B}^* \mathbf{M}) \right],
$$

$$
\mathbf{R} = \frac{1}{2} \left[ (\mathbf{A} \mathbf{B} \mathbf{L} - \mathbf{B} \mathbf{L} \mathbf{F}) + (\mathbf{B} \mathbf{L} \mathbf{M}^* \mathbf{L}^* \mathbf{M}) \right].
$$

(3.1.4)

[The second expression of Eq.(3.1.1) is used here]. Consequently, the standard PNCMO theory of Section 1 may be applied to find formulae for separate members ($\mathbf{P}(k)$ and $\mathbf{C}(k)$, $k = 0, 1, 2, ..$) of power series for matrices $\mathbf{P}$ and $\mathbf{C}$. Due to the generally non-diagonal constitution of (sub)matrices $\mathbf{K}$ and $\mathbf{L}$ and thereby of eigenblocks $\mathbf{E}_+$ and $\mathbf{E}_-$ (see Eq.(3.1.3)), the implicit form of the PNCMO theory should be invoked here. In other words, matrix equations of Eq.(1.1.8) should be solved for any order parameter ($k$), where $\mathbf{K}^{-1}$ and $\mathbf{L}^{-1}$ stand for $\mathbf{E}_+$ and $\mathbf{E}_-$, respectively. For example, the first order matrix $\mathbf{G}(1)$ is obtainable from solution of the following equation

$$
\mathbf{G}(1) \mathbf{K} + \mathbf{L} \mathbf{G}(1) + \mathbf{K} \mathbf{R} \mathbf{L} = \mathbf{0},
$$

(3.1.5)

where the (sub)matrix $\mathbf{R}$ is shown in the last relation of Eq.(3.1.4). The final step of the overall procedure consists in retransforming the CBO matrix $\mathbf{P}$ and the NCMO representation matrix $\mathbf{C}$ obtained into the basis $\{\chi\}$ again.

As discussed already, each member of the expansions concerned (i.e. $\mathbf{P}(k)$ and $\mathbf{C}(k)$) may be retransformed separately as shown in Eq.(1.5.6). For example, retransformation of the zero order member $\mathbf{P}_0$ of Eq.(1.1.6) of the expansion for the CBO matrix $\mathbf{P}$ by means of Eqs.(3.1.1) and (1.5.6) yields the following result

$$
\tilde{\mathbf{P}}_0 = \begin{bmatrix} \mathbf{I} & \mathbf{K} \mathbf{B} \\ \mathbf{B}^+ \mathbf{K} & \mathbf{I} \end{bmatrix}, \quad \tilde{\mathbf{P}}_0 = \begin{bmatrix} \mathbf{I} & \mathbf{B}^+ \mathbf{L} \\ \mathbf{L} \mathbf{B}^+ & \mathbf{I} \end{bmatrix}.
$$

(3.1.6)

The above-exhibited matrix coincides with the CBO matrix of alternant hydrocarbons derived in Ref.[74] using the known constitution of their canonical MOs. Such a coincidence causes no surprise if we bear in mind that these hydrocarbons are among systems embraced by the zero order matrix $\tilde{\mathbf{H}}(0)$ of Eq.(3.1) as discussed in the next subsection. Accordingly, the zero order member ($\mathbf{C}_0$) of the relevant
expansion for the NCMO representation matrix \( \tilde{C} \) follows after retransforming the matrix \( \tilde{C}_{(0)} = I \) (subsection 1.2) and takes the form [53]

\[
\tilde{C}_{(0)} = \frac{1}{\sqrt{2}} \begin{vmatrix} I & KB \\ B+K & -I \end{vmatrix}, \quad \tilde{C}_{(0)} = \frac{1}{\sqrt{2}} \begin{vmatrix} I & BL \\ LB+ & -I \end{vmatrix}.
\]

(3.1.7)

Comparison of Eqs. (3.1.6) and (3.1.7) indicates a high extent of similarity between zero order members of the two expansions (as it was the case with the CBO matrix and the NCMO representation matrix of Section 1). In particular, columns of the matrix \( \tilde{P}_{(0)} \) coincide with coefficients occupied NCMOs to within the factor \( 1/\sqrt{2} \). A similar result has been obtained also in Ref.[75]. Analogously, the relevant members of higher orders (\( \tilde{P}_{(k)} \) and \( \tilde{C}_{(k)} \), \( k = 1, 2, .. \)) result after applying the matrix \( U \) of Eq.(3.1.1) to respective corrections \( P_{(k)} \) and \( C_{(k)} \), of subsections 1.1 and 1.2.

Let us concentrate ourselves here mostly on the CBO matrix \( \tilde{P} \). As is seen from Eq.(1.1.5), the \( k \)th order member (\( P_{(k)} \)) of the series to be retransformed is representable as a sum of two components denoted below by \( P^{(g)}_{(k)} \) and \( P^{(x)}_{(k)} \) and correspondingly containing the intersubset coupling matrices (\( G_{(k)} \)) and the intrasubset population matrices (\( X_{(+)}^{(k)} \) and \( X_{(-)}^{(k)} \)), viz.

\[
P_{(k)} = P^{(g)}_{(k)} + P^{(x)}_{(k)},
\]

(3.1.8)

where

\[
P^{(g)}_{(k)} = \begin{vmatrix} 0 & -2G_{(k)} \\ -2G_{(k)} & 0 \end{vmatrix}, \quad P^{(x)}_{(k)} = \begin{vmatrix} X_{(+)}^{(k)} & 0 \\ 0 & X_{(-)}^{(k)} \end{vmatrix}.
\]

(3.1.9)

It is evident that each of the components \( \tilde{P}^{(g)}_{(k)} \) and \( \tilde{P}^{(x)}_{(k)} \) also may be retransformed separately. Moreover, the resulting total correction \( \tilde{P}_{(k)} \) accordingly consists of a sum of two retransformed components as follows

\[
\tilde{P}_{(k)} = \tilde{P}^{(g)}_{(k)} + \tilde{P}^{(x)}_{(k)}.
\]

(3.1.10)

where

\[
\tilde{P}^{(g)}_{(k)} = UP^{(g)}_{(k)}U^+, \quad \tilde{P}^{(x)}_{(k)} = UP^{(x)}_{(k)}U^+.
\]

(3.1.11)

Let us now introduce the following designations for individual submatrices (blocks) of the retransformed matrices \( \tilde{P}^{(g)}_{(k)} \) and \( \tilde{P}^{(x)}_{(k)} \), viz.

\[
\tilde{P}^{(g)}_{(k)} = \begin{vmatrix} Y_{(k)} & V_{(k)} \\ V^+_{(k)} & Z_{(k)} \end{vmatrix}, \quad \tilde{P}^{(x)}_{(k)} = \begin{vmatrix} S_{(k)} & J_{(k)} \\ J^+_{(k)} & N_{(k)} \end{vmatrix}.
\]

(3.1.12)

As shown in Refs.[54, 76], submatrices \( Y_{(k)} \) and \( Z_{(k)} \) of the component \( \tilde{P}^{(g)}_{(k)} \) are expressible as follows

\[
Y_{(k)} = -BLG^+_{(k)} - G_{(k)}LB^+, \quad Z_{(k)} = G^+_{(k)}BL + LB^+G_{(k)}
\]

(3.1.13)

and interrelated as exhibited below

\[
Y_{(k)} = -BLZ_{(k)}LB^+.
\]

(3.1.14)
Analogously, the remaining submatrix $V_{(k)}$ of the same component $\tilde{P}^{(g)}_{(k)}$ is representable via a skew-symmetric matrix $\Delta_{(k)}$, viz.

$$V_{(k)} = -BL\Delta_{(k)},$$  \hspace{1cm} (3.1.15)$$

where

$$\Delta_{(k)} = -\Delta^+_{(k)} = G^+_{(k)}BL - LB^+G_{(k)}.$$  \hspace{1cm} (3.1.16)$$

Meanwhile, submatrices of the intra-subset- population- matrices-containing component $\tilde{P}^{(a)}_{(k)}$ take the following form

$$S_{(k)} = \frac{1}{2}(X_{(+)}^{(k)} + BLX_{(-)}^{(k)}LB^+),$$  \hspace{1cm} (3.1.17)$$

$$N_{(k)} = \frac{1}{2}(X_{(-)}^{(k)} + LB^+X_{(+)}^{(k)}BL),$$  \hspace{1cm} (3.1.18)$$

$$J_{(k)} = -\frac{1}{2}BL(X_{(-)}^{(k)} - LB^+X_{(+)}^{(k)}BL) = -\frac{1}{2}(BLX_{(-)}^{(k)} - X_{(+)}^{(k)}BL).$$  \hspace{1cm} (3.1.19)$$

Finally, the component $\tilde{P}^{(a)}_{(k)}$ vanishes for $k = 1$ due to the first relation of Eq.(1.1.10) and we obtain that

$$\tilde{P}^{(a)}_{(1)} = Y_{(1)}^{\top} V^{(1)}_{(1)} Z^{(1)}_{(1)},$$  \hspace{1cm} (3.1.20)$$

where $Y_{(1)}$, $Z_{(1)}$ and $V_{(1)}$ are defined by Eqs.(3.1.13)-(3.1.16). For comparison, the first order member ($\tilde{C}^{(1)}_{(1)}$) of the expansion for the retransformed NCMO representation matrix ($\tilde{C}$) is as follows

$$\tilde{C}^{(1)} = \frac{1}{\sqrt{2}} \left| \begin{array}{cc} -BLG^+_{(1)} & G_{(1)} \\ G^+_{(1)} & LB^+G_{(1)} \end{array} \right|,$$  \hspace{1cm} (3.1.21)$$

and the extent of its similarity to $\tilde{P}^{(a)}_{(1)}$ is much lower (as compared to that between matrices $\tilde{P}^{(a)}_{(0)}$ and $\tilde{C}^{(a)}_{(0)}$ of Eqs.(3.1.6) and (3.1.7)). The same refers even more to corrections $\tilde{P}^{(a)}_{(k)}$ and $\tilde{C}^{(a)}_{(k)}$ of higher orders ($k = 2, 3, ..$). Nevertheless, certain relations have been established between these corrections [54].

Let us now turn to power series for total energies of systems described by the Hamiltonian matrix of Eq.(3.1). Thus, the zero order member of this series ($\mathcal{E}_{(0)}$) takes the following form [53]

$$\mathcal{E}_{(0)} = 2TrK^{-1} = 2Tr[(BB^+)^{1/2}].$$  \hspace{1cm} (3.1.22)$$

Further, the relevant first order term $\mathcal{E}_{(1)}$ follows from the second relation of Eq.(1.4.11) after substituting the first formula of Eq.(3.1.4) and is expressible as follows

$$\mathcal{E}_{(1)} = 2TrT = Tr[A + F + BLM^+ + LB^+M],$$  \hspace{1cm} (3.1.23)$$

where the cyclic transposition of matrices inside the trace sign is used. This correction generally does not vanish due to non-zero values of diagonal elements of the matrix $T$ defined by Eq.(3.1.4). Moreover, the first order energy $\mathcal{E}_{(1)}$ of Eq.(3.1.23) actually coincides with $\mathcal{E}_{(1)}^{(g)}$ (see Eqs.(1.4.4) and (1.5.7)), whereas $\mathcal{E}_{(1)}^{(a)}$ vanishes due
to the skew-symmetric nature of the matrix $\Delta_{(1)}$ defined by Eq.(3.1.16). Thus, the expression of Eq.(3.1.23) is alternatively obtainable by substituting matrices $\widetilde{H}_{(1)}$ of Eq.(3.1) and $\widetilde{P}_{(0)}$ of Eq.(3.1.6) into the second relation of Eq.(1.5.7).

Members of higher orders of the same expansion ($\mathcal{E}_{(k)}$, $k = 2, 3, \ldots$) also may be derived analogously using any of the relations shown in Eq.(1.5.8). Since the matrix $\widetilde{H}_{(0)}$ of Eq.(3.1) is of a more simple constitution as compared to $\widetilde{H}_{(1)}$, employment of the first relation of Eq.(1.5.8) proves to be more convenient for this purpose and, consequently, a more compact formula for $\mathcal{E}_{(k)}$ follows. Indeed, only the off-diagonal blocks of the correction $\widetilde{P}_{(k)}$ (i.e. (sub)matrices $V_{(k)}$ and $J_{(k)}$) are able to contribute to the component $\mathcal{E}_{(k)}^{(a)}$ (the first relation of Eq.(1.5.8) is based on). Moreover, the actual contributions of (sub)matrices $V_{(k)}$ vanish because of the skew-symmetric nature of (sub)matrices $\Delta_{(k)}$ of Eq.(3.1.16) as it was the case with the $V_{(1)}$–related increment of the first order energy. The final formula for the $k$th order energy is then as follows

$$\mathcal{E}_{(k)} = -\frac{1}{k-1}Tr(J_{(k)}B^+ + J_{(k)}^+B), \quad k = 2, 3, \ldots$$

(3.1.24)

and contains the (sub)matrices $J_{(k)}$ only. Thus, the correction $\mathcal{E}_{(k)}$ proves to be expressible via alterations in the intersubset bond orders caused by the (sub)matrices $J_{(k)}$. If we bear in mind that (sub)matrices $V_{(k)}$ also generally yield non-zero increments to individual bond orders as demonstrated in Ref.[76], the above outcome seems to be somewhat unexpected. The overall situation here, however, closely resembles that described in the subsections 1.4 and 2.3. In particular, other submatrices of corrections $\widetilde{P}_{(k)}$ of Eq.(3.1.12) also participate in the formation of the $k$th order energy, namely of the relevant $\beta$–component ($\mathcal{E}_{(k)}^{(b)}$). To illustrate this point, let us dwell on components $\mathcal{E}_{(2)}^{(a)}$ and $\mathcal{E}_{(2)}^{(b)}$ of the second order energy $\mathcal{E}_{(2)}$. Thus, substituting matrices $\widetilde{H}_{(1)}$ and $\widetilde{P}_{(1)}$ of Eqs.(3.1) and (3.1.20) into the definition of $\mathcal{E}_{(2)}^{(b)}$ shown in Eq.(1.5.7) yields the following result

$$\mathcal{E}_{(2)}^{(b)} = Tr[Y_{(1)}A + Z_{(1)}F + V_{(1)}M^+ + V_{(1)}^+M].$$

(3.1.25)

It is seen that the $\beta$–component of the second order energy generally contains all submatrices of the correction $\widetilde{P}_{(1)}$ of Eq.(3.1.20) and thereby it is related to the overall primary effect of our perturbation upon charge and bond order distribution. Meanwhile, the relevant $\alpha$–component takes the form

$$\mathcal{E}_{(2)}^{(a)} = Tr(J_{(2)}B^+ + J_{(2)}^+B)$$

(3.1.26)

and contains the (sub)matrix $J_{(2)}$ only in accordance with Eq.(3.1.24). If we recall now opposite signs of components $\mathcal{E}_{(2)}^{(a)}$ and $\mathcal{E}_{(2)}^{(b)}$ along with the relation $| \mathcal{E}_{(2)}^{(b)} | > | \mathcal{E}_{(2)}^{(a)} |$ of subsection 1.4, we arrive at a conclusion that only a part of the overall secondary energetic effect of the perturbation $\widetilde{H}_{(1)}$ (namely, the increment of $J_{(2)}$–dependent alterations in the intersubset bond orders) is actually subtracted from the total primary effect when building up the correction $\mathcal{E}_{(2)}$. A more detailed illustration of these results is given below (Subsection 3.2).
Now, we are about to consider some particular cases of the matrix \( \wt{H} \) of Eq.(3.1) and draw more specific conclusions concerning charge and bond order (re)distributions and energy alterations due to perturbation.

3.2. Specific results for alternant conjugated hydrocarbons and their derivatives

As already mentioned, alternant conjugated hydrocarbons are among systems underlying the anti-block-diagonal zero order matrix \( \wt{H}_0 \) of Eq.(3.1). The present subsection addresses just these compounds and the relevant specific perturbation matrices.

As is well-known, the concept of alternant hydrocarbons (AHs) arises in the framework of the simple Hückel model of \( \pi \)-electron systems [6, 7, 10, 11, 62]. Thus, let us start with this model, wherein the \( 2p_z \) AOs of carbon atoms play the role of initial orbitals \( \{ \chi \} \). Moreover, resonance parameters between AOs of chemically-bound pairs of atoms only are taken into consideration here. An AH is then defined as a system, the atoms(AOs) of which are divisible into two types (subsets) of the so-called starred and unstarred atoms (AOs) so that no chemical bonds are present between atoms (AOs) of the same type (subset). Under an appropriate numbering of AOs, the above-mentioned subsets coincide with the former subsets \( \{ \chi_1 \} \) and \( \{ \chi_2 \} \) (Subsect. 3.1). It is then evident that the common Hückel type Hamiltonian matrix of AHs takes an anti-block-diagonal form coinciding with that of the zero order term of Eq.(3.1). Suppose that resonance parameters of all chemical bonds take the same value (\( \beta \)) in addition and the latter plays the role of our energy unit, i.e. the equality \( \beta = 1 \) is accepted. Similarly, Coulomb parameters of all AOs also are assumed to take the same value (\( \alpha \)) that serves as an energy reference point, i.e. \( \alpha = 0 \). Consequently, non-zero elements of the (sub)matrix \( B \) refer to chemical bonds only and equal to 1. Moreover, formulae of Eqs.(3.1.6) and (3.1.7) reflect the common CBO matrix of AHs and the relevant NCMO representation matrix that have been comparatively analyzed in Ref.[53] in a detail. Finally, the zero order energy \( \mathcal{E}_0 \) of Eq.(3.1.22) coincides with the total \( \pi \)-electron energy of AHs.

Accordingly, the total Hamiltonian matrix of Eq.(3.1) embraces perturbed analogues (derivatives) of AHs. Corrections \( \wt{P}_k \) defined by Eqs.(3.1.10)-(3.1.19) then describe charge and bond order redistribution due to perturbation. In particular, elements of the correction \( \wt{P}_{(1)} \) of Eq.(3.1.20) yield the classical polarizabilities of AHs. Indeed, they are known to be definable in terms of derivatives of elements of the CBO matrix of the perturbed system with respect to separate elements of the perturbation matrix [10, 12, 13, 62]. Hence, polarizabilities of the atom-atom and atom-bond type result from the following derivatives

\[
\begin{align*}
\pi_{ii} &= \frac{\partial Y_{(1)ii}}{\partial A_{ii}}, & \pi_{ij} &= \frac{\partial Y_{(1)ii}}{\partial A_{jj}}, & \pi_{pj} &= \frac{\partial Z_{(1)pp}}{\partial A_{jj}}, & \pi_{ip,j} &= \frac{\partial V_{(1)ip}}{\partial A_{jj}},
\end{align*}
\]

(3.2.1)

where the subscripts \( i \) and \( j \) belong to the first subset \( \{ \chi_1 \} \), whereas \( p \) refers to the second one \( \{ \chi_2 \} \). Besides, \( \pi_{ii} \) is usually called the self-polarizability of the \( i \)th atom (AO). As is well-known, perturbations of AHs are traditionally classified into those associated with Coulomb and resonance parameters of \( 2p_z \) AOs. In this connection, two particular first order matrices (\( \wt{H}_{(1)} \)) have been distinguished and studied separately in Ref.[54], viz. a block-diagonal matrix (\( \wt{H}_{(1)}^{(bd)} \)) corresponding to
\[ M = M^+ = 0 \] and an anti-block-diagonal one \( \tilde{H}^{(bd)}_{(1)} \) containing zero matrices instead of both \( A \) and \( F \), i.e.

\[
\tilde{H}^{(bd)}_{(1)} = \begin{bmatrix} A & 0 \\ 0 & F \end{bmatrix}, \quad \tilde{H}^{(ab)}_{(1)} = \begin{bmatrix} 0 & M \\ M^+ & 0 \end{bmatrix}.
\] (3.2.2)

It is evident that the first perturbation matrix \( \tilde{H}^{(bd)}_{(1)} \) embraces alterations both in Coulomb parameters and in the resonance ones inside subsets of either starred or unstarred AOs. Meanwhile, the second matrix \( \tilde{H}^{(ab)}_{(1)} \) refers to changes in resonance parameters of the intersubset type so that the relevant total matrix \( \tilde{H} \) remains to be of anti-block-diagonal constitution.

To overview the relevant results, let us start with the perturbation matrix \( \tilde{H}^{(bd)}_{(1)} \).

The equality \( M = M^+ = 0 \) allowed us to derive the following relations

\[
G^{(bd)+}BL = LB^+G^{(bd)}_{(1)}, \quad BLG^{(bd)+}_{(1)} = C^{(bd)}_{(1)}LB^+,
\] (3.2.3)

where the relevant matrices are denoted here and below by an additional superscript \((bd)\). The above relations, in turn, ensure vanishing matrices \( \Delta^{(bd)}_{(1)} \) and \( V^{(bd)}_{(1)} \) of Eqs.(3.1.15) and (3.1.16) so that the resulting first order correction \( \tilde{P}^{(bd)}_{(1)} \) of Eq.(3.2.20) also is a block-diagonal matrix, viz.

\[
\tilde{P}^{(bd)}_{(1)} = \begin{bmatrix} Y^{(bd)}_{(1)} & 0 \\ 0 & Z^{(bd)}_{(1)} \end{bmatrix}.
\] (3.2.4)

It is seen that the perturbation \( \tilde{H}^{(bd)}_{(1)} \) exerts influence upon populations of basis orbitals and upon intrasubset bond orders within the first order approximation. Meanwhile, bond orders of the intersubset type are not influenced by this perturbation. This result may be regarded as the matrix generalization of the known zero values for polarizabilities of AHs of the atom-bond type \( (\pi_{ip,j}) \) [12]. Further, the submatrices \( Y^{(bd)}_{(1)} \) and \( Z^{(bd)}_{(1)} \) were shown to meet the following matrix equations

\[
K Y^{(bd)}_{(1)} + Y^{(bd)}_{(1)} K = KAK - K^2BFB^+K^2,
\]

\[
L Z^{(bd)}_{(1)} + Z^{(bd)}_{(1)} L = LFL - L^2B^+ABL^2
\] (3.2.5)

that belong to the type shown in Eq.(1.1.16). Consequently, (sub)matrices \( Y^{(bd)}_{(1)} \) and \( Z^{(bd)}_{(1)} \) are expressible in the form of an integral like that of Eq.(1.1.17). The latter allows us to establish the signs of polarizabilities of the atom-atom type \( (\pi_{ij} \text{ and } \pi_{pj}) \) of Eq.(3.2.1)). As a result, we obtain a new integral representation for the classical polarizabilities of AHs, as well as a simple (re)derivation [54] of the well-known rule of the alternating polarity [12-15].

Similarly, the first order correction \( \tilde{C}^{(bd)}_{(1)} \) to the NCMO representation matrix \( \tilde{C}^{(bd)}_{(1)} \) results from Eq.(3.1.21) after employment of Eq.(3.2.3). This correction also is representable in terms of matrices \( Y^{(bd)}_{(1)} \) and \( Z^{(bd)}_{(1)} \), viz.

\[
\tilde{C}^{(bd)}_{(1)} = \frac{1}{2\sqrt{2}} \begin{bmatrix} Y^{(bd)}_{(1)} & -Y^{(bd)}_{(1)} BL \\ Z^{(bd)}_{(1)} LB^+ & Z^{(bd)}_{(1)} \end{bmatrix}.
\] (3.2.6)
This result forms the basis for interdependence [54] between charge and bond order redistribution in AHs due to the perturbation concerned, on the one hand, and the respective reshaping of NCMOs (LMOs), on the other hand.

For the anti-block-diagonal matrix \( \tilde{H}^{(ab)}_{(1)} \), the analogues of Eqs.(3.2.3) and (3.2.5) are as follows

\[
BLG_{(1)}^{(ab)+} = -G_{(1)}^{(ab)+}LB^+, \quad G_{(1)}^{(ab)+}BL = -LB^+G_{(1)}^{(ab)}, \quad (3.2.7)
\]

\[
\tilde{P}^{(ab)}_{(1)} = \begin{vmatrix} 0 & V^{(ab)}_{(1)} \\ V^{(ab)+}_{(1)} & 0 \end{vmatrix}, \quad (3.2.8)
\]

and

\[
L\Delta_{(1)}^{(ab)} + \Delta^{(ab)}_{(1)}L = L(M^+BL - LB^+M)L, \quad (3.2.9)
\]

where matrices \( \Delta_{(1)}^{(ab)} \) and \( V^{(ab)}_{(1)} \) are interrelated as shown in Eq. (3.1.15). As is seen from comparison of Eqs.(3.2.4) and (3.2.8), the corrections \( \tilde{P}^{(bd)}_{(1)} \) and \( \tilde{P}^{(ab)}_{(1)} \) are of opposite constitutions as it is the case with the respective perturbation matrices shown in Eq.(3.2.2).

The second order corrections \( \tilde{P}^{(bd)}_{(2)} \) and \( \tilde{P}^{(ab)}_{(2)} \) corresponding to the perturbation matrices \( \tilde{H}^{(bd)}_{(1)} \) and \( \tilde{H}^{(ab)}_{(1)} \), respectively, accordingly follow from Eqs.(3.1.10) and (3.1.12). The relevant comparative analysis [76] showed that both corrections are of the same constitution, namely of the anti-block-diagonal one, viz.

\[
\tilde{P}^{(bd)}_{(2)} = \begin{vmatrix} 0 & V^{(bd)}_{(2)} + J^{(bd)}_{(2)} \\ V^{(bd)+}_{(2)} + J^{(bd)+}_{(2)} & 0 \end{vmatrix}, \quad \tilde{P}^{(ab)}_{(2)} = \begin{vmatrix} 0 & V^{(ab)}_{(2)} + J^{(ab)}_{(2)} \\ V^{(ab)+}_{(2)} + J^{(ab)+}_{(2)} & 0 \end{vmatrix}, \quad (3.2.10)
\]

where submatrices \( V^{(bd)}_{(2)} \) and \( V^{(ab)}_{(2)} \) are proportional to respective skew-symmetric matrices \( \Delta^{(bd)}_{(2)} \) and \( \Delta^{(ab)}_{(2)} \), the latter being determined by matrix equations like that of Eq.(3.2.9). Again, submatrices \( J^{(bd)}_{(2)} \) and \( J^{(ab)}_{(2)} \) of Eq.(3.2.10) are representable algebraically as follows [76]

\[
J^{(bd)}_{(2)} = -2BLG_{(1)}^{(bd)+}G_{(1)}^{(bd)} = -\frac{1}{2}(V^{(bd)}_{(1)})^2BL = -\frac{1}{2}BL(Z^{(bd)}_{(1)})^2, \quad (3.2.11)
\]

\[
J^{(ab)}_{(2)} = -2BLG_{(1)}^{(ab)+}G_{(1)}^{(ab)} = -\frac{1}{2}BL\Delta_{(1)}^{(ab)}\Delta^{(ab)+}_{(1)} = -\frac{1}{2}V^{(ab)}_{(1)}V^{(ab)+}_{(1)}BL.
\]

Let us now turn to total energies of AHs and their derivatives. As already mentioned, the parent AHs are characterized by the zero order energy \( \mathcal{E}_0 \) of Eq.(3.1.22). The first order corrections to the latter due to perturbations \( \tilde{H}^{(bd)}_{(1)} \) and \( \tilde{H}^{(ab)}_{(1)} \) follow from Eq.(3.1.23) under assumptions that \( M = M^+ = 0 \) and \( A = F = 0 \), respectively. The resulting simple formulae for \( \mathcal{E}^{(bd)}_{(1)} \) and \( \mathcal{E}^{(ab)}_{(1)} \) coincide with respective classical analogues in accordance with the expectation. For example, the equality \( \mathcal{E}^{(bd)}_{(1)loc} = \alpha \) follows for a local perturbation (\( \alpha \)) of a certain Coulomb parameter, e.g. of the AO \( \chi_{1,1} \) (\( A_{11} = \alpha \)). Similarly, \( \mathcal{E}^{(ab)}_{(1)loc} = 2\rho_{mn}\mu \) results for a local perturbation of an intersubset resonance parameter, say, of that between AOs \( \chi_{1,m} \) and \( \chi_{2,n} \).
where \( m_n = \mu \), where \( p_{mn} \) stands for the bond order between the AOs concerned in the parent AH. Further, the relevant corrections of the second order (\( \mathcal{E}^{(bd)}_{(2)} \) and \( \mathcal{E}^{(ab)}_{(2)} \)) consist of \( \alpha \)– and \( \beta \)–components as discussed in the above subsection, i.e.

\[
\mathcal{E}^{(bd)}_{(2)} = \mathcal{E}^{(bd,\alpha)}_{(2)} + \mathcal{E}^{(bd,\beta)}_{(2)}, \quad \mathcal{E}^{(ab)}_{(2)} = \mathcal{E}^{(ab,\alpha)}_{(2)} + \mathcal{E}^{(ab,\beta)}_{(2)},
\]

where terms of the right-hand sides of the above relations result from Eq.(3.1.26) and (3.1.25), viz.

\[
\mathcal{E}^{(bd,\alpha)}_{(2)} = Tr[J^{(bd)}_{(2)} B^+ + J^{(bd)}_{(2)} B], \quad \mathcal{E}^{(bd,\beta)}_{(2)} = Tr[Y^{(bd)}_{(1)} A + Z^{(bd)}_{(1)} F]
\]

and

\[
\mathcal{E}^{(ab,\alpha)}_{(2)} = Tr[J^{(ab)}_{(2)} B^+ + J^{(ab)}_{(2)} B], \quad \mathcal{E}^{(ab,\beta)}_{(2)} = Tr[V^{(ab)}_{(1)} M^+ + V^{(ab)}_{(1)} M].
\]

To discuss these components in a more detail, let us start with the block-diagonal perturbation matrix \( \mathcal{H}^{(bd)}_{(1)} \). It is seen that the component \( \mathcal{E}^{(bd,\beta)}_{(2)} \) generally embraces the first order corrections both to populations of AOs and to intrasubset bond orders. For the above-specified local alteration in the Coulomb parameter of the AO \( \chi_{1,1} \) \( (A_{11} = \alpha) \), however, only a single element of the submatrix \( Y^{(bd)}_{(1)} \) remains, i.e.

\[
\mathcal{E}^{(bd,\beta)}_{(2)loc} = Y^{(bd)}_{(1)11} \alpha = \pi_{11} \alpha^2,
\]

where \( \pi_{11} \) is the self-polarizability of the AO under perturbation defined as shown in Eq.(3.2.1). Thus, the component \( \mathcal{E}^{(bd,\beta)}_{(2)loc} \) is proportional to the population \( (Y^{(bd)}_{(1)11}) \) acquired by the AO \( \chi_{1,1} \) due to the given perturbation and, consequently, it may be traced back to lowering of the one-electron energy of electrons acquired by the AO \( \chi_{1,1} \). It is no surprise that this primary energetic effect of our local perturbation \( (A_{11} = \alpha) \) is stabilizing for \( \alpha > 0 \) [The \textit{a priori} positive sign of any self-polarizability (in our negative energy units) should be kept in mind here]. Finally, the effect concerned is twice as large as the relevant total correction \( \mathcal{E}^{(bd)}_{(2)loc} \) equal to \( \pi_{11} \alpha^2 / 2 \) \[62\].

The \( \alpha \)–component of the same second order correction consists of a sum of increments of individual carbon-carbon bonds as the first relation of Eq.(3.2.13) indicates [One-to-one correspondence between non-zero elements of the (sub)matrix \( B \) and chemical bonds should be recalled here]. Moreover, each of these increments is proportional to the respective element of the (sub)matrix \( J^{(bd)}_{(2)} \). For the local perturbation \( (A_{11} = \alpha) \), the (sub)matrix \( J^{(bd)}_{(2)} \) was shown to give rise mostly to lowering of orders of bonds attached to the site (AO) of perturbation \( (\chi_{1,1}) \) \[76\]. Thus, the above-concluded primary stabilization of the system due to concentration of population on the perturbed AO \( (\chi_{1,1}) \) becomes reduced twice because of the secondary weakening of the neighboring bonds originating from the (sub)matrix \( J^{(bd)}_{(2)} \). [The latter, however, is not the only contributor to orders of individual bonds: The (sub)matrix \( V^{(bd)}_{(2)} \) also gives rise to some alterations \[76\], but their total energetic effect vanishes].

Before passing to components of the correction \( \mathcal{E}^{(ab)}_{(2)} \) referring to the anti-block-diagonal perturbation \( \mathcal{H}^{(ab)}_{(1)} \), let us distinguish two possible types of elements of the
matrix $\mathbf{M}$, namely (i) elements representing (positive or negative) alterations in resonance parameters of the former chemical bonds and (ii) elements referring to formation of new weak bonds between AOs of different subsets. Let us assume for simplicity that our perturbation matrix $\tilde{\mathbf{H}}_{(1)}^{(ab)}$ contains only some positive elements of the second type, i.e. some new bonds are formed inside our AH. The component $E_{(2)}^{(ab,\beta)}$ of Eq.(3.2.14) then represents the overall primary stabilization of the system due to emergence of these new bonds that is twice as large as the relevant total correction $E_{(2)}^{(ab)}$. For example, formation of a single bond $\text{C}_m-\text{C}_n$ is accompanied by the following energy increment

$$E_{(2)\text{loc}}^{(ab,\beta)} = 2V_{(1)mn}^{(ab)} = 2\pi_{mn,mn}^{2},$$

(3.2.16)

where $\pi_{mn,mn}$ is the self-polarizability of the bond concerned. Accordingly, the component $E_{(2)}^{(ab,\alpha)}$ of Eq.(3.2.14) consists of increments of "initial" carbon-carbon bonds as it was the case with $E_{(2)}^{(bd,\alpha)}$ of Eq.(3.2.13). Thus, $E_{(2)}^{(ab,\alpha)}$ describes the secondary destabilizing effect of the same perturbation upon orders of the already-existing bonds. Analysis of some specific examples [76] showed that the secondary effect consists in a predominant weakening of the former bonds in the nearest neighborhood of the newly-emerging bond $\text{C}_m-\text{C}_n$. In other words, formation of new bonds necessarily is accompanied by weakening of already-existing bonds in accordance with the classical concept of the limited valence. The above-described redistribution of bond orders has been called the rebonding effect in Ref.[77]. Studies of more involved perturbations in AHs may be found in Refs.[78,79].

3.3. The case of separate pairs of strongly-interacting basis orbitals. Application to alkanes and their derivatives

Perturbation matrices of two particular types (see Eq.(3.2.2)) have been discussed in the above subsection 3.2. Let us now return again to the most general initial Hamiltonian matrix of quasi-degenerated systems shown in Eq. (3.1) and introduce some simplifications into the zero order member of the latter ($\tilde{\mathbf{H}}_{(0)}$). Meanwhile, the first order term will now contain four non-zero submatrices $\mathbf{A}$, $\mathbf{F}$ and $\mathbf{M}$, as shown in Eq.(3.1).

Let us start with an assumption that the total number of basis orbitals of our system ($N$) coincides with that of electrons ($2n$) and thereby takes an even value. Further, each subset ($\{\chi_1\}$ and $\{\chi_2\}$) will contain the same number of orbitals equal to $n$. Most importantly, orbitals of different subsets are now assumed to interact predominantly in pairs. In other words, any orbital of the first subset (say, $\chi_{1,i}$) is supposed to interact significantly only with a single orbital of the second subset. Let the latter to acquire the number $n+i$ and to be denoted by $\chi_{2,n+i}$. Resonance parameters inside the above-specified pairs of strongly-interacting orbitals $\chi_{1,i}$ and $\chi_{2,n+i}$ then consequently take relatively large values as compared to the remaining resonance parameters. Under the above-accepted numbering of basis orbitals, these significant parameters occupy diagonal positions in the relevant (sub)matrix $\mathbf{B}$. Let us assume finally that differences between these parameters (if any) are of the first order magnitude so that these may be incorporated into diagonal elements of the (sub)matrix $\mathbf{M}$. Given that the averaged value of the
above-specified large parameters is chosen as an energy unit, we ultimately arrive at the following simple relation

\[ B = B^+ = I. \quad (3.3.1) \]

Substituting Eq.(3.3.1) into Eq.(3.1) shows that the resulting total Hamiltonian matrix describes a set of \( n \) weakly-interacting two-level systems, each of them being represented by a matrix \( \hat{h} \) of Eq.(3.2). It is also evident that a slightly heteropolar (or almost homopolar) two-center chemical bond may be ascribed to each individual two-level system of the above-mentioned type. Thus, we actually have to do here with a set of \( n \) weakly-interacting almost homopolar bonds. Let the latter to acquire the numbers \( I = 1, 2, 3..n \). Accordingly, the bond between orbitals \( \chi_{1,i} \) and \( \chi_{2,n+i} \) will be referred to as the \( I \)th bond. Systems under present discussion may be primarily exemplified by saturated hydrocarbons (alkanes) represented in the basis of \( sp^3 \)-hybrid AOs (HAOs) of carbon atoms and 1s AOs of hydrogen atoms. Pairs of orbitals pertinent to individual C–C and C–H bonds coincide with the strongly-interacting ones in this case \[80\]. Indeed, resonance parameters inside pairs of AOs(HAOs) pertinent to any C–C and C–H bond are of much higher absolute values in alkanes as compared to the remaining resonance parameters as the relevant estimations show. Moreover, Coulomb parameters of all basis orbitals are of close values in these systems. Derivatives of alkanes containing slightly more electronegative heteroatoms also are embraced by the Hamiltonian matrix concerned.

Let us now turn to the overview of the relevant results. First, substituting Eq.(3.3.1) into Eq.(3.1.1) yields the following simple transformation matrix

\[
U' = \frac{1}{\sqrt{2}} \begin{bmatrix} I & I \\ I & -I \end{bmatrix}, \quad (3.3.2)
\]

which represents passing to bonding and antibonding combinations of orbitals of individual bonds, usually referred to as bond orbitals (BOs) [The superscript \( t \) is used here and below to distinguish the case concerned from that of subsection 3.1]. Analogously, employment of Eq.(3.3.1) within Eq.(3.1.2) ensures coincidence of matrices both \( K \) and \( L \) with the unit matrix (I). Moreover, the same refers to the eigenblocks \( E_{(+)} \) and \( E_{(-)} \) defined by Eq.(3.1.3), i.e. \( E_{(+)} = E_{(-)} = I \). The latter result, in turn, is nothing more than the assumption of Eq.(2.4.1). Consequently, the explicit matrix form of the PNCMO theory of subsection 2.4 proves to be applicable in the present case along with the relevant implications exhibited in Eqs.(2.4.2)-(2.4.9), where

\[
T = \frac{1}{2} [(A + F) + (M^+ + M)], \quad Q = \frac{1}{2} [(A + F) - (M^+ + M)], \quad R = \frac{1}{2} [(A - F) + (M^+ - M)]. \quad (3.3.3)
\]

[The above relations also easily result from those of Eq.(3.1.4) after employment of Eq.(3.3.1)]. It is evident that the afore-defined BOs take the role of our principal basis functions \( \{\varphi\} \) (Sections 1 and 2).

Let us now consider members of the power series for the relevant retransformed CBO matrix \( \tilde{P}' \). As is seen from Eqs.(3.1.6) and (3.1.12)-(3.1.20), substituting the unit matrix (I) for matrices \( B, K \) and \( L \) yields significant simplifications of the
relevant expressions: First, the zero order term of the expansion concerned \( \tilde{P}'(0) \) now consists of unit matrices as it was the case with the transformation matrix of Eq.(3.3.2), viz.

\[
\tilde{P}'(0) = \begin{bmatrix} I & I \\ I & I \end{bmatrix}.
\] (3.3.4)

This result indicates uniform values (equal to 1) both of populations of basis functions \( \{ \chi \} \) and of all bond orders inside the strongly-interacting pairs of orbitals \( \chi_{1,i} \) and \( \chi_{2,n,i} \) within the zero order approximation. Second, a single (sub)matrix (denoted below by \( \Pi(k) \)) arises instead of the former two different (sub)matrices \( Y_{(k)} \) and \( Z_{(k)} \) of Eq.(3.1.13) within diagonal positions of the first component \( \tilde{P}'(0) \) of the \( k \)th order correction \( \tilde{P}'_{(k)} \). Moreover, this new (sub)matrix is proportional to the symmetric part \( \left( G'_{(k)} \right) \) of the relevant principal matrix \( G'_{(k)} \). Analogously, the present version \( \left( V'_{(k)} \right) \) of the former (sub)matrix \( V_{(k)} \) of Eqs.(3.1.15) and (3.1.16) is proportional to the skew-symmetric part \( \left( G'^{\circ}_{(k)} \right) \) of the same matrix \( G'^{\circ}_{(k)} \). Further, the former (sub)matrices \( S_{(k)} \) and \( N_{(k)} \) of the remaining component \( \tilde{P}'_{(k)} \) defined by Eqs.(3.1.17) and (3.1.18) now turn into a single matrix denoted below by \( \Lambda_{(k)} \). Moreover, the latter becomes expressible via the intrasubset population matrices only and/or in terms of intersubset delocalization matrices (relations of Eq.(1.3.16) should be invoked in this case). The same refers also to the present analogue of the submatrix \( J_{(k)} \). We then obtain that

\[
\tilde{P}'_{(1)} = \begin{bmatrix} \Pi_{(1)} & 2G'^{\circ}_{(1)} \\ -2G'^{\circ}_{(1)} & -\Pi_{(1)} \end{bmatrix}
\] (3.3.5)

and

\[
\tilde{P}'_{(k)} = \begin{bmatrix} \Lambda_{(k)} + \Pi_{(k)} & J_{(k)} + 2G'^{\circ}_{(k)} \\ J_{(k)} - 2G'^{\circ}_{(k)} & \Lambda_{(k)} - \Pi_{(k)} \end{bmatrix}
\] (3.3.6)

for \( k = 1 \) and \( k = 2, 3, \ldots \), respectively, where

\[
\Pi_{(k)} = -2G'^{\circ}_{(k)}, \quad k = 1, 2, 3, \ldots
\] (3.3.7)

\[
\Lambda_{(k)} = \frac{1}{2}(X_{(+)}^{(k)} + X_{(-)}^{(k)}) = -(D_{(+)}^{(k)} - D_{(-)}^{(k)}),
\] (3.3.8)

\[
J_{(k)} = \frac{1}{2}(X_{(+)}^{(k)} - X_{(-)}^{(k)}) = -(D_{(+)}^{(k)} + D_{(-)}^{(k)}),
\] (3.3.9)

and

\[
G'^{\circ}_{(k)} = \frac{1}{2}(G'_{(1)} + G'^{\circ}_{(1)}), \quad G'^{\circ}_{(1)} = \frac{1}{2}(G'_{(1)} - G'^{\circ}_{(1)}).
\] (3.3.10)

Let us now discuss the role of the above-enumerated (sub)matrices in the formation of charge and bond order redistribution due to perturbation in the system(s) concerned. As is seen from Eqs.(3.3.5) and (3.3.6), the (sub)matrices \( \Pi_{(k)} \), \( k = 1, 2, 3, \ldots \) yield dipole-like contributions \( \pm \Pi_{(k)ii} \) to populations of strongly-interacting orbitals \( \chi_{1,i} \) and \( \chi_{2,n+i} \). In this connection, \( \Pi_{(k)} \), \( k = 1, 2, 3, \ldots \) have been called the (inrabond) polarization matrices of the \( k \)th order [80]. On the basis of Eqs.(2.4.2),
(3.3.3) and (3.3.10), the first two representatives of the series of matrices \( \Pi_{(k)} \) are expressible as follows

\[
\Pi_{(1)} = \frac{1}{2} (A - F), \quad \Pi_{(2)} = \frac{1}{4} (FM + M^+F - AM^+-MA).
\] 

(3.3.11)

The first relation of Eq.(3.3.11) indicates that diagonal elements \( \Pi_{(1)ii} \) of the (sub)matrix \( \Pi_{(1)} \) are determined by local differences in Coulomb parameters of orbitals \( \chi_{1,i} \) and \( \chi_{2,n+i} \) in accordance with the expectation. At the same time, the right relation points to a non-local origin of the second order dipoles \( \pm \Pi_{(2)ii} \). Finally, an evident connection deserves mention between intrabond polarization and the rule of the alternating polarity. Indeed, (sub)matrices \( Y^{(bd)}_{(1)} \) and \( Z^{(bd)}_{(1)} \) of Eq.(3.2.4) yield the above-mentioned rule as discussed in the subsection 3.2. Again, the same (sub)matrices are the prototypes of the polarization matrix \( \Pi_{(1)} \).

By contrast, (sub)matrices \( A_{(k)} \) of Eq.(3.3.8) yield uniform contributions to populations of the same orbitals \( \chi_{1,i} \) and \( \chi_{2,n+i} \). Moreover, the sum \( X_{(+)ii}^{(k)} + X_{(-)ii}^{(k)} \) contained within the definition of the diagonal element \( A_{(k)ii} \) coincides with the total population of the \( k \)th order lost (acquired) by the \( I \)th bond due to perturbation that, in turn, is devided equally among orbitals \( \chi_{1,i} \) and \( \chi_{2,n+i} \). Thus, (sub)matrices \( A_{(k)} \) describe redistribution (transfer) of population among our bonds and these have been referred to [80] as the charge transfer matrices.

Let us now turn to alterations in bond orders inside pairs of strongly-interacting orbitals \( \chi_{1,i} \) and \( \chi_{2,n+i} \) (alternatively called below the "internal" bond orders) resulting from diagonal elements of the off-diagonal blocks of corrections \( \tilde{P}'_{(k)} \) of Eqs.(3.3.5) and (3.3.6). It is evident that skew-symmetric (sub)matrices \( 2G'_{(k)} \) yield zero contributions to these bond orders in contrast to the former matrices \( V_{(k)} \) (Subsect. 3.2). Consequently, diagonal elements \( J_{(k)ii} \) of (sub)matrices \( J_{(k)}, k = 2, 3, \ldots \) are now the only contributors to the "internal" bond orders. Moreover, these decisive elements are expressible either in terms of population alterations of the same (i.e. \( k \)th) order referring to the BOs of the given bond \( (\varphi_{(+)i} \) and \( \varphi_{(-)i} \)) or via the respective corrections to delocalization coefficients of NCMOs \( \psi_{(+)}^i \) and \( \psi_{(-)}^i \) as Eq.(3.3.9) shows, viz.

\[
J_{(k)ii} = \frac{1}{2}(X_{(+)}^{(k)ii} - X_{(-)}^{(k)ii}) = -(D_{(+)ii}^{(k)} + D_{(-)ii}^{(k)}).
\] 

(3.3.12)

As is seen from the above formula, a negative sign of the element \( J_{(k)ii} \) and thereby lowering of the order of the \( I \)th bond unambiguously follows if the relevant increments to delocalization coefficients of both NCMOs attached to the given bond \( (\psi_{(-)}^i \) and \( \psi_{(+)}^i \)) are positive quantities and vice versa. In other words, we actually arrive at a local relation between the alteration in the order of the \( I \)th bond and additional (de)localization of respective two NCMOs. Alternatively, a negative sign of the element \( J_{(k)ii} \) is ensured if the BBO \( \varphi_{(+)}^i \) of the given bond loses its population whilst the relevant ABO \( \varphi_{(-)}^i \) acquires it so that \( X_{(+)}^{(k)ii} < 0 \) and \( X_{(-)}^{(k)ii} > 0 \). This conclusion evidently is not surprising.

Let us recall now that intrasubset population matrices of any order \( k \) (i.e. \( X_{(+)}^{(k)} \) and \( X_{(-)}^{(k)} \)) are representable via the intersubset coupling matrices of lower orders, viz. \( G_{(k-1)}, G_{(k-2)}, \ldots \), (see Eq.(1.1.10)), the latter determining the relevant corrections to intersubset bond orders between BBOs and ABOs as Eq.(1.1.5) indicates. This
implies that the extent of the alteration in the "internal" bond order of the $I$th bond depends upon orders of "external" bonds formed by its BOs $\varphi_{(+)}i$ and $\varphi_{(-)}i$ with other basis orbitals ($\varphi_{(+)}j, j \neq i$ and $\varphi_{(-)}l, l \neq i$) within previous terms of the power series. Moreover, the stronger these "external" bonds become, the more the "internal" bond order is altered. Thus, we now arrive at explicit interdependences between the "internal" and "external" bond orders.

For illustration, let us consider the most important contributors to the "internal" bond orders, viz. the diagonal elements $(J_{(2)ii})$ of the second order matrix $J_{(2)}$. After invoking the expressions for $X_{(+)}^{(2)}$ and $X_{(-)}^{(2)}$ shown in Eq.(1.1.10) and substituting them into Eq. (3.3.12), we obtain that

$$J_{(2)ii} = -\left[ \sum_{m} (G_{(1)im})^2 + \sum_{j} (G_{(1)ji})^2 \right] < 0 \quad (3.3.13)$$

i.e. any element $J_{(2)ii}$ is an a priori negative quantity. Thus, bond orders inside pairs of strongly-interacting orbitals $\chi_{1,i}$ and $\chi_{2,n+i}$ are unambiguously predicted to be reduced to within the second order terms inclusive. It is also seen that lowering of the order of the $I$th bond is proportional to the sum of squares of orders of "external" bonds that are formed by its orbitals $\varphi_{(+)}i$ and $\varphi_{(-)}i$ with BOs of other bonds. The negative sign of $J_{(2)ii}$ may be also alternatively traced back to the fact that BBOs always loose their population, whereas ABOs acquire it for $k = 2$ (Subsect. 1.1). Therefore, the rebonding effect (introduced in the subsection 3.2) now acquires a more rigorous form.

Finally, the relevant total energy is worth some discussion. Thus, substituting Eq.(3.3.1) into Eq.(3.1.22) shows that the zero order term $\mathcal{E}_{(0)}$ now coincides with $2n$, i.e. with the total energy of $n$ isolated homopolar bonds. This result evidently causes no surprise. Similarly, from Eq.(3.1.23), we obtain

$$\mathcal{E}_{(1)} = Tr[A + F + 2M]. \quad (3.3.14)$$

Thus, the first order correction $\mathcal{E}_{(1)}$ represents the energetic effect of deviation of the actual bonds of our system from uniform homopolar ones. The present analogue of Eq.(3.1.24), in turn, takes the following simple form

$$\mathcal{E}_{(k)} = -\frac{2}{k-1}TrJ_{(k)}, \quad k = 2, 3, . . . \quad (3.3.15)$$

Thus, the energy correction of any order $(k)$ is now proportional to the sum of alterations in the "internal" bond orders. The same evidently refers also to the relevant $\alpha-$component $(\mathcal{E}_{(k)}^{(\alpha)})$. Hence, we actually arrive at a new interpretation of the principal relation of Eq.(1.4.5), wherein alterations in the "internal" bond orders play the role of the former charge transfer (Subsection 2.3). Emergence of such an alternative is not surprising if we recall the direct relation between elements $J_{(k)ii}$ and changes in populations of BOs $\varphi_{(+)}i$ and $\varphi_{(-)}i$ seen from Eq.(3.3.12). It should be kept in mind, however, that the $\beta-$component of the same energy correction also generally embraces populations of basis orbitals along with the "external" bond orders. For example, the present form of Eq.(3.1.25) is as follows

$$\mathcal{E}_{(2)}^{(\beta)} = Tr[\Pi_{(1)}(A - F)] + 2Tr[G_{(1)}^{(0)}(M^+ - M)] \quad (3.3.16)$$

and contains the intrabond dipoles $\pm \Pi_{(1)ii}$. 45
3.4. Systems consisting of uniform homopolar bonds. An analogue of the classical concept of conjugation

The last and the simplest case of quasi-degenerate systems (discussed below) corresponds to combination of the principal assumption of the above subsection shown in Eq. (3.3.1) and of the anti-block-diagonal first order matrix \( \tilde{H}^{(ab)}_{(1)} \) of Eq. (3.2.2). In other words, we will now consider alternant systems representable by the following total Hamiltonian matrix

\[
\tilde{H}(c) = \tilde{H}'_0 + \tilde{H}^{(ab)}_{(1)} = \begin{pmatrix}
0 & I & 0 \\
I & 0 & M \\
M^T & 0 & 0
\end{pmatrix} 
\]

resulting from that of the above subsection under an assumption of vanishing submatrices A and F. The results under present interest also are easily obtainable from those of subsection 3.3 under employment of the equality \( A = F = 0 \). The reason why this specific case is distinguished and discussed separately lies in its relevance to an important and wide class of chemical compounds, viz. to acyclic conjugated hydrocarbons [The superscript \( (c) \) of the left-hand side of Eq. (3.4.1) is used just in this connection]. Thus, let us start with the perturbational perspective on these popular compounds in the framework of the Hückel type approximation.

Suppose that a certain conjugated hydrocarbon contains two types of uniform bonds, namely strong double (C=C) bonds and weak single (C−C) ones so that resonance parameters of the former exceed significantly those of the latter in the basis of \( 2p_z \) AOs of carbon atoms. Moreover, let our hydrocarbon have an even number of carbon atoms that will be denoted by \( 2n \) as previously. The \( 2p_z \) AOs of these atoms will then compose our \( 2n \times 2n \)-dimensional basis set \( \{ \chi \} \). It is also assumed that our hydrocarbon contains no adjacent double bonds and no cycles having an odd number of carbon atoms. Evidently, this model primarily refers to acyclic polyenes [40, 58, 73, 77]. Nevertheless, it has been applied recently also to individual Kekulé valence structures of related (poly)cyclic compounds [38, 61].

Further, let our hydrocarbon contain exactly \( n \) double (C=C) bonds. Given that the basis orbitals \( \{ \chi \} \) are enumerated as described in the above subsection (i.e. the AOs belonging to the \( I \)th C=C bond acquire the numbers \( i \) and \( n+i \)), the system concerned may be considered as a set of \( n \) weakly-interacting C=C bonds, where the single (C−C) bonds serve as a means of this interaction.

Let us assume finally that Coulomb parameters of all AOs \( \{ \chi \} \) are uniform and coincide with our energy reference point. This evidently implies zero diagonal elements of the relevant Hamiltonian matrix. Similarly, uniform values of resonance parameters of all C=C bonds will serve as the energy unit. These parameters will be entirely included into the zero order member of our Hamiltonian matrix. Meanwhile, resonance parameters of single (C−C) bonds will be incorporated into the relevant first order member. We then immediately arrive at the Hamiltonian matrix of Eq. (3.4.1), where \( n \times n \)-dimensional (sub)matrices I and M correspondingly embrace resonance parameters of C=C and C−C bonds. It is also evident that diagonal elements of the (sub)matrix M take zero values, i.e. \( M_{ii} = 0 \) for any \( i \). At the same time, non-zero off-diagonal elements of the same matrix \( M_{ij} \neq 0 (i \neq j) \) refer to C−C bonds. Otherwise, these elements vanish.

Let us now dwell on some general properties of hydrocarbons represented by the Hamiltonian matrix \( \tilde{H}^{(c)} \) of Eq. (3.4.1). To this end, let us employ the equality
$A = F = 0$ within the principal relations of the above subsection. In particular, from both the last relation of Eq.(3.3.3) and the first formula of Eq.(2.4.2) it follows that the first order matrix $G^{(c)}_{(1)}$ is of the skew-symmetric nature. Moreover, the same may be easily shown to refer also to the relevant principal matrices $(G^{(c)}_{(k)})$ of higher orders ($k = 2, 3...$). In summary, we obtain that

$$G^{(c)+}_{(k)} = -G^{(c)}_{(k)}, \quad k = 1, 2, 3... \tag{3.4.2}$$

Let us now turn to implications of the above result. Thus, employment of Eq.(3.4.2) within Eq.(1.1.10) followed by invoking Eq.(1.3.16) yields the result exhibited below

$$X^{(k,c)}_{(+)} = -X^{(k,c)}_{(-)}, \quad D^{(k,c)}_{(+)} = D^{(k,c)}_{(-)} \tag{3.4.3}$$

instead of the former coincidences of traces of analogous matrices (see Eqs.(1.1.11) and (1.3.13)). On the basis of Eq.(3.4.3) one can immediately conclude that

$$X^{(k,c)}_{(+\textit{ii})} = -X^{(k,c)}_{(-\textit{ii})}, \quad D^{(k,c)}_{(+\textit{ii})} = D^{(k,c)}_{(-\textit{ii})} \tag{3.4.4}$$

for any $k$ and for any $i$. The first relation of Eq.(3.4.4) shows that the population of the $k$th order lost by the BBO $\varphi_{(+i)}$ of the $I$th C=C bond coincides with that acquired by the respective ABO $\varphi_{(-i)}$ or vice versa (the latter case is allowed for $k = 3, 4, ..$ only (Subsection 1.1)). Consequently, the double (C=C) bonds of conjugated hydrocarbons ultimately take (loose) no population and this result causes little surprise. Analogously, the second relation of Eq.(3.4.4) indicates that total delocalization coefficients of NCMOs $\psi_{(+i)}$ and $\psi_{(-i)}$ of the same C=C bond are uniform.

Let us now turn to the relevant CBO matrix $\tilde{P}^{(c)}_{(c)}$. It is evident that the zero order member $\tilde{P}^{(c)}_{(0)}$ of the power series concerned coincides with that of the above subsection, i.e. with $\tilde{P}^{(c)}_{(0)}$ of Eq.(3.3.4). As a result, interpretation of the latter (subsection 3.3) may be straightforwardly transferred to $\tilde{P}^{(c)}_{(0)}$. Further, from Eqs.(3.3.8) and (3.4.3) it follows that (sub)matrices $\Lambda^{(c)}_{(k)}$, $k = 2, 3..$ vanish within any subsequent correction $\tilde{P}^{(c)}_{(k)}$ in accordance with the above-mentioned zero charge redistribution among C=C bonds. Moreover, the same refers also to the symmetric parts $(G^{(c)*}_{(k)})$ of the principal matrices $G^{(c)}_{(k)}$ and thereby to polarization matrices $\Pi^{(c)}_{(k)}$ defined by Eq.(3.3.7). The overall result is then as follows

$$\Lambda^{(c)}_{(k)} = \Pi^{(c)}_{(k)} = 0, \quad k = 1, 2, 3.. \tag{3.4.5}$$

and ensures coincidence of the ultimate occupation numbers of AOs $\{\chi\}$ with the relevant zero order increments (equal to 1). At the same time, the result of Eq.(3.4.5) indicates the anti-block-diagonal constitution of any correction $\tilde{P}^{(c)}_{(k)}$. The principal (sub)matrix $J^{(c)}_{(k)}$ contained within the off-diagonal blocks of this correction, in turn, results from Eq.(3.3.9) after employment of Eqs.(3.4.3) and (3.4.4). We then obtain that

$$J^{(c)}_{(k)} = X^{(k,c)}_{(+)} = -2D^{(k,c)}_{(+)} , \quad J^{(c)}_{(k\textit{ii})} = X^{(k,c)}_{(+\textit{ii})} = -2D^{(k,c)}_{(+\textit{ii})}. \tag{3.4.6}$$
It also deserves mention that the former skew-symmetric part \( \mathbf{G}^c_{(k)} \) of the matrix \( \mathbf{G}_{(k)} \) of Eq.(3.3.5) now coincides with the total matrix \( \mathbf{G}^{(c)}_{(k)} \). Collecting the above-overviewed results followed by invoking Eq.(1.1.10) then yields the final expression for the correction \( \mathbf{P}^{(c)}_{(k)} \), viz.

\[
\mathbf{P}^{(c)}_{(k)} = \begin{vmatrix} 0 & \Omega_{(k)} \ \\
\Omega_{(k)}^T & 0 \end{vmatrix}, \quad k = 1, 2, 3, \ldots
\]  

(3.4.7)

where

\[
\Omega_{(k)} = \mathbf{J}^{(c)}_{(k)} + 2\mathbf{G}^{(c)}_{(k)}
\]  

(3.4.8)

and

\[
\mathbf{J}^{(c)}_{(1)} = 0, \quad \mathbf{J}^{(c)}_{(2)} = 2(\mathbf{G}^{(c)}_{(1)})^2, \quad \mathbf{J}^{(c)}_{(3)} = 2(\mathbf{G}^{(c)}_{(1)}\mathbf{G}^{(c)}_{(2)} + \mathbf{G}^{(c)}_{(2)}\mathbf{G}^{(c)}_{(1)}), \quad \mathbf{J}^{(c)}_{(4)} = -2(\mathbf{G}^{(c)}_{(1)}\mathbf{G}^{(c)}_{(3)} + \mathbf{G}^{(c)}_{(3)}\mathbf{G}^{(c)}_{(1)}) + 2(\mathbf{G}^{(c)}_{(2)})^2 - 2(\mathbf{G}^{(c)}_{(1)})^4, \text{etc.}
\]  

(3.4.9)

It is evident that most of comments of the above subsection (3.3) concerning the former matrices \( \mathbf{J}_{(k)} \) of Eq.(3.3.9) are directly transferable to the present matrices \( \mathbf{J}^{(c)}_{(k)} \). In this connection, we will concentrate our attention here mostly on specific points referring to the case of conjugated hydrocarbons:

1) The orders of C=C bonds in a certain conjugated hydrocarbon are determined by diagonal elements \( \Omega_{(k)ii} \) of matrices \( \Omega_{(k)} \), whereas those of C–C bonds follow from the relevant off-diagonal elements \( \Omega_{(k)ij}, i \neq j \). Thus, matrices \( \Omega_{(k)} \) actually represent redistribution of bond orders (rebonding) due to conjugation of C=C bonds. In this connection, \( \Omega_{(k)} \) has been called the rebonding matrix of the \( k \)th order. It also deserves mention that \( \Omega_{(k)} \) are now the only non-zero submatrices inside members of the power series for the CBO matrix \( \mathbf{P}^{(c)} \).

2) The rebonding effect in conjugated hydrocarbons manifests itself as an interdependence between orders of the newly-formed C–C bonds and alterations in the orders of the "initial" C=C bonds. In particular, the (negative) second order correction to the order of the \( I \)th C=C bond (determined by the element \( J^{(c)}_{(2)ii} \)) was shown to depend upon the sum of squares of first order increments to orders of the adjacent C–C bonds. [This relation is based on the one-to-one correspondence between non-zero elements of the matrix \( \mathbf{G}^{(c)}_{(1)} \) and C–C bonds [73]].

3) An alteration in the order of the \( I \)th C=C bond proves to be directly related to the respective change of population of its bonding orbital \( \varphi_{(+i)} \) and this relation is valid for each \( k \) separately as Eq.(3.4.6) indicates. Moreover, the same alteration is proportional to the relevant increment to the delocalization coefficient of the occupied NCMO of the same C=C bond \( \psi_{(+i)} \). Thus, weakening of a certain C=C bond necessarily is accompanied by an additional delocalization of the respective single pair of electrons and vice versa.

Let us now turn to the relevant energy expansion. The zero order member of the latter \( \{\mathcal{E}^{(c)}_{(0)}\} \) coincides with \( 2n \) as previously (Subsection 3.3), whereas \( \mathcal{E}^{(c)}_{(1)} \) takes a zero value due to vanishing diagonal elements of matrices \( \mathbf{A}, \mathbf{F} \) and \( \mathbf{M} \). Furthermore, components of terms of higher orders of the energy expansion are easily obtainable.
by substituting Eqs.(3.4.1) and (3.4.7) into Eq.(1.5.7), and these are expressible as follows

\[ E^{(\alpha,c)}_{(k)} = 2Tr \Omega_{(k)} = 2Tr J^{(c)}_{(k)}, \]
\[ E^{(\beta,c)}_{(2)} = 2Tr [\Omega_{(k-1)} M^+] = 2Tr [(J^{(c)}_{(k-1)} + 2G^{(c)}_{(k-1)}) M^+]. \]  

It is seen that the \( \alpha \)-component of the \( k \)th order energy \( E^{(\alpha,c)}_{(k)} \) is proportional to the sum of respective corrections to orders of C=C bonds in a full agreement with the results of the above subsection. In contrast to the previous relation of Eq.(3.3.16), however, the \( \beta \)-component \( E^{(\beta,c)}_{(2)} \) now contains only the sum of \( (k - 1) \)th order increments to orders of C−C bonds [One-to-one correspondence between non-zero elements of the submatrix \( M \) and C−C bonds should be recalled here]. Hence, the components \( E^{(\beta,c)}_{(k)} \) and \( E^{(\alpha,c)}_{(k)} \) represent the energetic increments of two principal aspects of the rebonding effect, namely of formation of C−C bonds and of the consequent alterations in the orders of C=C bonds, respectively. The relation of Eq.(1.4.5) then indicates an interdependence between absolute values of these energetic increments and their opposite signs. In other words, new (i.e. C−C) bonds may be formed only at the expense of the already-existing bonds. This principal result may be regarded as a quantum-chemical justification of the classical concept of the limited valence for conjugated hydrocarbons. Finally, the total correction \( E^{(c)}_{(k)} \) now represents the ultimate energetic yield of the above-mentioned two interdependent aspects of bond order redistribution and has been accordingly called the \( k \)th order rebonding energy.

Proportionality of the total correction \( E^{(c)}_{(k)} \) to \( Tr J^{(c)}_{(k)} \) and thereby to the sum of alterations of the \( k \)th order in the orders of C=C bonds follows directly from Eq.(3.3.15). Moreover, the same correction \( E^{(c)}_{(k)} \) is now representable as a sum of the relevant energetic increments associated with formation of C−C bonds. Analogous two alternative forms of the total rebonding energy \( E^{(c)}_{(k)} \) also are possible, viz.

\[ E^{(c)} = \sum_{k=2}^{\infty} \frac{2}{1-k} Tr J^{(c)}_{(k)}, \quad E^{(c)} = \sum_{k=2}^{\infty} \frac{2}{k} Tr (\Omega_{(k-1)} M^+) \]  

and exhibit additivity with respect to individual contributors (i.e. C=C and C−C bonds, respectively). Besides, employment of the expression for \( J^{(c)}_{(k)} \) in terms of the matrix \( D_{(+)}^{(k)} \) shown in Eq.(3.4.6) yields the earlier-discussed formula for \( E^{(c)}_{(k)} \) of Eq.(2.4.5) in accordance with the expectation. Thus, the rebonding energy actually coincides with the total delocalization energy inside the subset \{\( \phi^{(+)} \)\} of initially-occupied orbitals of C=C bonds.

It is seen, therefore, that the rebonding effect is the only factor determining both the CBO matrix and the total energy of conjugated hydrocarbons consisting of uniform C=C bonds connected by uniform C−C bonds. Moreover, the above-established weakening of the former bonds due to formation of the latter is in line with the observed trends in bond lengths of acyclic conjugated hydrocarbons [81]. These results allow us to conclude that the rebonding effect is the quantum-chemical analogue of the classical concept of conjugation. The dual nature of the effect also is among the conclusions, i.e. it may be considered either as an interaction between C=C bonds or as a sum of the relevant intrabond effects.
REFERENCES

1. M.J.S. Dewar, and R.C. Dougherty, *The PMO Theory of Organic Chemistry* (Plenum Press, New York, 1975).
2. D.-K. Seo, G. Papoian and R. Hoffmann, Int. J. Quant Chem. 77, 408 (2000).
3. L. Rincon, J. Mol. Struct. (Theochem) 731, 213 (2005).
4. L. Zülicke, *Quantenchemie, Bd.1, Grundlagen und Allgemeine Methoden* (Deutscher Verlag der Wissenschaften, Berlin, 1973).
5. L.D. Landau, E.M. Lifshits, *Quantum Mechanics. The Non-relativistic Theory* (Nauka, Moscow, 1974).
6. E. Hückel, Z. Phys. 70, 204 (1931).
7. E. Hückel, Z. Phys. 76, 628 (1932).
8. A. Streitwieser, Jr., *Molecular Orbital Theory* (John Wiley & Sons, New York, 1961).
9. W. Kutzelnigg, J. Comput. Chem. 28, 25 (2007).
10. C.A. Coulson, B.O’Leary and R.B. Mallion, *Hückel Theory for Organic Chemistry* (Academic Press, London, 1978).
11. S. Huzinaga, *The MO Method* (Mir, Moscow, 1983) [in Russian].
12. C.A. Coulson and H.C. Longuet-Higgins, Proc. Roy. Soc. (London) A192, 16 (1947); A193, 447 (1948).
13. M.J.S. Dewar, *The Molecular Orbital Theory of Organic Chemistry* (McGraw-Hill, New York, 1969).
14. M.M. Mestechkin, *The Density Matrix Method in Quantum Chemistry* (Naukova Dumka, Kiev, 1977) [in Russian].
15. I. Gutman, Z. Naturforsch 36A, 1112 (1981).
16. J. March, *Advanced Organic Chemistry, Reactions, Mechanisms and Structure* (Wiley Interscience, New York, 1985).
17. F.A. Carroll, *Perspectives on Structure and Mechanism in Organic Chemistry* (Brooks/Cole, Pacific Grove, CA, 1998).
18. M. Edenborough, *Organic Reaction Mechanisms. A Step by Step Approach* (Taylor and Francis, London, 1999).
19. A.N. Vereshtchagin, *The Inductive Effect* (Nauka, Moscow, 1987) [in Russian].
20. O. Chalvet (Ed.), *Localization and Delocalization in Quantum Chemistry, Atoms and Molecules in the Ground State*, Vol.1 (Reidel, Dordrecht, 1975).
21. I. Mayer, Chem. Phys. Lett. 89, 390 (1982).
22. P.R. Surjan, I. Mayer, and M. Ketesz, J. Chem. Phys. 77, 2454 (1982).
23. I. Mayer, and P.R Surjan, J. Chem. Phys. 80, 5649 (1984).
24. J.P. Daudey, Chem. Phys. Lett. 24, 574 (1974).
25. V. Gineityte, Int. J. Quant. Chem. 68, 119 (1998).
26. V. Gineityte, Lith. J. Phys. 44, 219 (2004).
27. V. Gineityte, Int. J. Quant. Chem. 72, 559 (1999).
28. V. Gineityte, J. Mol. Struct. (Theochem), 333, 297 (1995).
29. R. McWeeny, *Methods in Molecular Quantum Mechanics*, 2nd. ed. (Academic Press, London, 1992).
30. M.M. Mestechkin, Teoretich. Eksperim. Khim. 4, 154 (1968).
31. M. Mestechkin, Int. J. Quant. Chem. 15, 601 (1979).
32. M.M. Mestechkin, Teoretitch. Eksperim. Khim. 12, 739 (1976).
33. L. Cohen and C. Frischberg, J. Chem. Phys. 65, 4234 (1976).
34. M. Simonetta and E. Gianinetti, In: Molecular Orbitals in Chemistry, Physics and Biology, Eds. P.-O. Löwdin, B. Pullman (Academic, New York, London, 1964), pp. 83-112.
35. R. McWeeny, Phys. Rev. 126, 1028 (1962).
36. V. Gineityte, J. Mol. Struct. (Theochem) 343, 183 (1995).
37. V. Gineityte, J. Mol. Struct. (Theochem) 585, 15 (2002).
38. V. Gineityte, MATCH Commun. Math. Comput. Chem. 72, 39 (2014).
39. V. Gineityte, Int. J. Quant. Chem. 94, 302 (2003).
40. V. Gineityte, On Relative Stabilities of Distinct Polyenes. An Extension of the Concept of Conjugated Paths ArXiv (2015) https://arxiv.org/abs/1501.04734.
41. V. Gineityte, Z. Naturforsch. 64A, 132 (2009).
42. V. Gineityte, Int. J. Chem. Model. 4, 189 (2012).
43. P. Lankaster, Theory of Matrices (Academic Press, New York, 1969).
44. F. Jensen, Introduction to Computational Chemistry, 2nd. ed. (John Wiley & Sons, 2007).
45. S. Liu, J.M. Perez-Jorda and W. Yang, J. Chem. Phys. 112, 1634 (2000).
46. Z. Szekeress and P.R. Surjan, Chem. Phys. Lett. 369, 125 (2003).
47. S.F. Boys, Rev. Mod. Phys. 32, 296 (1960).
48. C. Edmiston and K. Ruedenberg, Rev. Mod. Phys. 34, 457 (1963).
49. C. Edmiston and K. Ruedenberg, J. Chem. Phys. 43, s97 (1965).
50. J. Pipek and P.G. Mezey, J. Chem. Phys. 90, 4916 (1989).
51. V. Gineityte, J. Mol. Struct. (Theochem), 288, 111 (1993).
52. V. Gineityte, Lith. J. Phys. 51, 107 (2011).
53. V. Gineityte, Int. J. Quant. Chem. 101, 274 (2005).
54. V. Gineityte, Int. J. Quant. Chem. 105, 232 (2005).
55. V. Gineityte, Lith. J. Phys. 42, 397 (2002).
56. G.N. Lewis, J. Amer. Chem. Soc. 38, 762 (1916).
57. T.C. Koopmans, Physica, 1, 104 (1934).
58. V. Gineityte, J. Mol. Struct. (Theochem) 487, 231 (1999).
59. V. Gineityte, J. Mol. Struct. (Theochem) 680, 199 (2004).
60. V. Gineityte, Int. J. Quant. Chem. 108, 1141 (2008).
61. V. Gineityte, Monatsh. Chem., (2018). https://doi.org/10.1007/s00706-017-2133-3
62. R. Zahradnik, R. Polak, Elements of Quantum Chemistry (Plenum Press, New York, 1980).
63. V. Gineityte, J. Mol. Struct. (Theochem) 364, 85 (1996).
64. V. Gineityte, J. Mol. Struct. (Theochem) 532, 257 (2000).
65. V. Gineityte, J. Mol. Struct. (Theochem) 546, 107 (2001).
66. V. Gineityte, Quasi-classical Alternatives in Quantum Chemistry, ArXiv (2014) https://arxiv.org/abs/1402.6268.
67. M.J.S. Dewar, R. Pettit, J. Chem. Soc. 1625 (1954).
68. M.J.S. Dewar, J. Amer. Chem. Soc. 106, 669 (1984).
69. V.F.Traven, Electronic Structure and Properties of Organic Molecules (Khimia, Moscow, 1989) [in Russian].
70. V. Gineityte, Int. J. Quant. Chem. **77**, 534 (2000).
71. V. Gineityte, Int. J. Chem. Model. **5**, 99 (2013).
72. R. A. Horn and C.R. Johnson, *Matrix Analysis* (Cambridge Univ. Press, Cambridge, 1986).
73. V. Gineityte, Monatsh. Chem. **147**, 1303 (2016).
74. G.G. Hall, Proc. Roy. Soc. (London), **A229**, 251 (1955).
75. A.V. Luzanov, J. Structural Chemistry, **21**, 703 (1981).
76. V. Gineityte, Int. J. Quant. Chem. **106**, 2145 (2006).
77. V. Gineityte, J. Mol. Struct. (Theochem) **497**, 83 (2000).
78. V. Gineityte, Croat. Chem. Acta **81**, 487 (2008).
79. V. Gineityte, Croat. Chem. Acta **86**, 171 (2013).
80. V. Gineityte, J. Mol. Struct. (Theochem) **430**, 97 (1998).
81. B. Milian-Medina, J. Gierschner, WIREs Comput. Mol. Sci. **2**, 513 (2012).