

# Second-Order Effects in the Hückel Model of Perturbed Alternant Hydrocarbons and Their Coincidence for Specific One- and Two-Center Perturbations

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**ABSTRACT:** Explicit algebraic expressions are derived and analyzed for the second-order corrections to the charge-bond order (CBO) matrix of perturbed alternant hydrocarbons (PAHs) in terms of entire blocks of the common Hamiltonian matrix of parent AHs in the framework of the simple Hückel model. The derivation is based on the direct means of solution of the commutation equation for the one-electron density matrix by means of passing to the basis of noncanonical molecular orbitals of parent AHs followed by application of the noncommutative Rayleigh–Schrödinger perturbation theory and retransformation of the results into the initial basis of  $2p_z$  AOs of carbon atoms. The second-order corrections obtained are shown to determine alterations in bond orders between chemically bound pairs of atoms under influence of the most popular types of perturbation, viz. changes in the Coulomb parameter(s) and emergence of new intermolecular resonance parameter(s). The same corrections are also demonstrated to play an important role in the formation of stabilization energies of PAHs vs. those of parent AHs. On this basis, an additional insight is given into the content of the classical formulae for total energies of PAHs in terms of self-polarizabilities of atoms and bonds, viz. an energy correction is shown to be made up of a difference between the primary stabilizing contribution of perturbation (which is twice as large as the final stabilization energy) and the destabilizing increment related to weakening of remaining chemical bonds. A detailed comparison of CBO matrices and stabilization energies is made for compounds originating from the same parent hydrocarbon (R) after perturbation of the Coulomb parameter of a certain AO  $\chi_r$  and after building up a composite AH R–R' by formation of a new bond between AOs  $\chi_r$  and  $\chi'_r$  of two identical AHs R and R' (e.g., pyridine and biphenyl). The first-order corrections to CBO matrices of these systems are shown to be expressible in terms of the same submatrices, whereas the respective

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second-order corrections contain coinciding submatrices referring to parent fragments R and R'. As a result, coincidences are established (i) between the self-polarizability of the  $r$ th atom of the parent AH R and that of the bond between atoms  $r$  and  $r'$  of the composite AH R–R', (ii) between alterations in orders of chemical bonds due to both types of perturbation, and (iii) between stabilization energies referring to a single fragment R or R' under an assumption of coinciding perturbation parameters. On this basis, a nontrivial and intriguing similarity is concluded between respective electronic structures in general. Finally, two particular second-order effects are revealed for the same systems, viz. a destabilizing effect related mostly to a local weakening of bonds at the site of perturbation and an energy-free effect manifesting itself as emergence of changes in all bond orders of alternating nature. © 2006 Wiley Periodicals, Inc. Int J Quantum Chem 106: 2145–2160, 2006

**Key words:** alternant conjugated hydrocarbons; charge-bond order matrix; stabilization energy; pyridine; biphenyl

## 1. Introduction

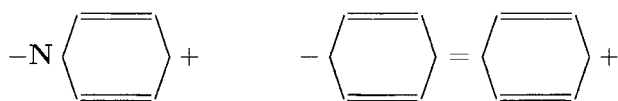
Common peculiarities of electronic structures of different molecules are among facts of particular interest in quantum chemistry. This refers especially to non-trivial examples of similarity of electronic structures embracing compounds of essentially distinct chemical constitution. Accordingly, specific concepts are usually introduced to distinguish these groups of molecules. For example, the concepts of isoconjugated systems [1] and of isospectral graphs [2–4] may be mentioned.

The well-known conjugated alternant hydrocarbons (AHs) [1, 4–8] also rank among systems of the above-described type. Indeed, electronic structures of these molecules are characterized by numerous common peculiarities that can be represented in the form of general rules in the framework of the simple Hückel model. The principal classical results for these hydrocarbons [9–12] refer to constitutions of their usual (canonical) molecular orbitals (MOs) along with the relevant one-electron energies and to related charge-bond order (CBO) matrices. Recent results concerning common properties of noncanonical MOs of AHs [13] may also be added here.

Numerous organic compounds are known to be representable as perturbed alternant hydrocarbons (PAHs) [1, 14]. Two types of perturbations are usually distinguished, viz. small alterations in Coulomb parameters (the so-called one-center perturbations) and changes in resonance parameters (two-center perturbations). Perturbations of the former type serve to describe aromatic heterocycles (e.g., pyridine), where alteration(s) in Coulomb parameters correspond to the site(s) of substitution. Again, two-center perturbations represent breaking and/or formation of new bonds inside and/or between AHs. Continuing interest in electronic structures of

PAHs is due to their applicability as model systems when studying various aspects of chemical reactions. In particular, the results concerning alterations in total energies of AHs due to perturbation form the basis of the popular PMO theory of chemical reactivity [1]. These alterations, in turn, are expressible in terms of polarizabilities of various types (e.g., atom–atom, atom–bond) following from the first-order corrections to CBO matrices of parent AHs.

It should be mentioned immediately that the overall constitution of the first-order correction to the CBO matrix depends essentially on the nature of perturbation [15]. In particular, one-center perturbations are known to give rise to alterations in occupation numbers of all  $2p_z$  AOs in accordance with the famous rule of alternating polarity [5, 6, 9–12, 15, 16]. In the case of a two-center perturbation, the alternant nature of the resulting PAH and thereby the uniform charge distribution may be preserved (cf. perturbations of the so-called intersubset type [15]). Hence, at least two different classes of compounds seem to originate from the single class of AHs. Nevertheless, there are grounds to expect a certain extent of nontrivial similarity between electronic structures of the above-discussed two types of PAHs. This refers especially to pairs of compounds originating from the same parent AH (R) after perturbing the Coulomb parameter of a certain AO  $\chi_r$  and after building up a composite AH R–R' by formation of a new bond between AOs  $\chi_r$  and  $\chi_{r'}$  of two identical AHs R and R' (cf. pyridine and biphenyl). Indeed, consideration of constitutions of additional resonance structures of these PAHs promotes an expectation about similar alterations in the orders of chemical bonds to emerge in these two types of systems. As for instance, *para*-quinoidal structures of pyridine and biphenyl (cf. the so-called Zwitterion [1, 17]) may be mentioned (Scheme 1).



**SCHEME 1.** Para-quinoidal structures of pyridine and biphenyl.

The well-studied first-order correction  $\mathbf{P}_{(1)}$  to the common CBO matrix of PAHs  $\mathbf{P}$  does not contribute to alterations in bond orders referring to actual chemical bonds (see Ref. [15] and Section 3). Hence, analysis of the respective second-order correction  $\mathbf{P}_{(2)}$  is required when looking for the similarity expected. To this end, an efficient method of derivation of members of the power series for the CBO matrix is required. The approach suggested recently [15], and based on the direct solution of the commutation equation for the one-electron density matrix by means of passing to the basis of noncanonical MOs of parent AHs [13] and application of the noncommutative Rayleigh–Schrödinger perturbation theory [18, 19], appears promising in this field. It is also worth noting that the significance of second-order corrections to CBO matrices of PAHs is not limited to description of alterations in neighboring bond orders due to perturbation. This additional anticipation is based on the important role of the second-order correction  $\mathbf{P}_{(2)}$  in the formation of the stabilization energy of any perturbed system revealed recently [20, 21].

Total energies of molecules are known to be alternatively obtainable [14, 22, 23] on the basis of expressions for the one-electron density matrix (CBO matrix) and the well-known general relation between these two principal characteristics of molecules instead of summing up the eigenvalues of the Hamiltonian matrix corresponding to occupied canonical MOs. On this basis, two interdependent components of opposite signs have been revealed within any member  $E_{(k)}$  of the resulting power series for the total energy  $E$  [20]. Moreover, these components were found to be determined by corrections  $\mathbf{P}_{(k)}$  of different orders ( $k$ ). In particular, the second-order energy  $E_{(2)}$  (which is responsible for stabilization (or destabilization) of perturbed systems vs. those described by the zero-order Hamiltonian matrices [21]) consists of the  $\mathbf{P}_{(1)}$ -containing component and of the  $\mathbf{P}_{(2)}$ -containing one [20, 21], the absolute value of the former exceeding twice that of the latter. Just this result allowed the conclusion to be drawn about the role of the second-order correction  $\mathbf{P}_{(2)}$  being as important as that of the first-order one in the formation of the stabilization energy of the perturbed system. Finally, the above-mentioned

interrelation between the absolute values of the two principal components of the second-order energy formed the basis for expressing the total correction either in terms of the  $\mathbf{P}_{(1)}$ -containing component or via the  $\mathbf{P}_{(2)}$ -containing one.

Given that the above-overviewed general results are applicable to perturbed AHs, these may be expected to yield an additional insight into the content of the classical formulae for total energies in terms of self-polarizabilities of atoms and bonds [5, 6, 14] as it was the case with the Dewar formula [21]. Moreover, the similarity between PAHs originating from the same parent hydrocarbon in respect of alterations in the neighboring bond orders (if established) would also be manifested as a proportionality between respective stabilization energies. The latter relation, in turn, is likely to imply a certain interdependence between the self-polarizabilities referring to the formation of aromatic heterocycles and of composite hydrocarbons.

The principal aim of the present work consists of verifying the above-enumerated expectations. To this end, we are about to derive and analyze the expressions for second-order corrections to CBO matrices of PAHs and to the relevant total energies using the approaches discussed above. We will focus our attention to comparison of results referring to pairs of PAHs originating from the same parent hydrocarbon.

This work is organized as follows. We begin, in Section 2, with an overview of general conclusions concerning total energies and demonstrate their applicability to PAHs. In Section 3, expressions for the second-order corrections  $\mathbf{P}_{(2)}$  are analyzed and compared with the first-order corrections. Section 4 is devoted to exploration of corrections describing the PAHs of the same origin. Specific examples are studied in Section 5.

## 2. Role of Second-Order Effects in the Formation of Stabilization Energies of PAHs

Given that our system is described by a certain one-electron Hamiltonian matrix  $\mathbf{H}$  (e.g., of the Hückel type), the relevant energy is simply expressed as follows [14, 22, 23]:

$$E = \text{Trace}(\mathbf{P}\mathbf{H}), \quad (1)$$

where  $\mathbf{P}$  is the respective representation of the one-electron density matrix (the CBO matrix). Let us assume that the matrix  $\mathbf{H}$  consists of the zero-order

and first-order members, i.e.,

$$\mathbf{H} = \mathbf{H}_{(0)} + \mathbf{H}_{(1)}. \quad (2)$$

As a result, two components generally arise within any correction  $E_{(k)}$ , viz.

$$E_{(k)}^{(k,0)} = \text{Trace}[\mathbf{P}_{(k)}\mathbf{H}_{(0)}], \quad E_{(k)}^{(k-1,1)} = \text{Trace}[\mathbf{P}_{(k-1)}\mathbf{H}_{(1)}], \quad (3)$$

where  $\mathbf{P}_{(k)}$  coincide with members of the power series for the matrix  $\mathbf{P}$ ,  $k$  here and below stands for the order parameter and the superscripts of the left-hand sides of these definitions indicate the orders of corrections  $\mathbf{P}_{(k)}$  and  $\mathbf{H}_{(k)}$  contained within the respective right-hand sides. In particular, the first three members  $E_{(k)}$ ,  $k = 0, 1, 2$  of the power series for the energy  $E$  take the form

$$\begin{aligned} E_{(0)} &= E_{(0)}^{(0,0)} = \text{Trace}[\mathbf{P}_{(0)}\mathbf{H}_{(0)}], \\ E_{(1)} &= E_{(1)}^{(1,0)} + E_{(1)}^{(0,1)} \\ &= \text{Trace}[\mathbf{P}_{(1)}\mathbf{H}_{(0)}] + \text{Trace}[\mathbf{P}_{(0)}\mathbf{H}_{(1)}], \\ E_{(2)} &= E_{(2)}^{(2,0)} + E_{(2)}^{(1,1)} \\ &= \text{Trace}[\mathbf{P}_{(2)}\mathbf{H}_{(0)}] + \text{Trace}[\mathbf{P}_{(1)}\mathbf{H}_{(1)}]. \end{aligned} \quad (4)$$

It is seen that the second-order correction  $\mathbf{P}_{(2)}$  to the CBO matrix of our system  $\mathbf{P}$  contributes to the formation of the second-order energy  $E_{(2)}$  along with the first-order correction  $\mathbf{P}_{(1)}$ .

Let us turn now to alternant hydrocarbons and their perturbations within the framework of the simple Hückel model [1, 4–16, 24, 25]. The basis set  $\{\chi\}$  of any AH consisting of  $2p_z$  AOs of carbon atoms may always be divided into two subsets  $\{\chi^*\}$  and  $\{\chi^\circ\}$ , so that the intrasubset resonance parameters take zero values. This happens because the neighboring pairs of AOs characterized by nonzero resonance parameters in the Hückel model get into different subsets. Moreover, the Coulomb parameters representing AOs usually are assumed to take uniform values  $\alpha$ , and the equality  $\alpha = 0$  is accepted for convenience. As a result, the one-electron Hamiltonian matrices of AHs acquire a common form containing zero submatrices (blocks) in its diagonal positions [8, 13, 15, 24, 25], viz.

$$\mathbf{H}_{(0)} = \begin{vmatrix} \mathbf{0} & \mathbf{B} \\ \mathbf{B}^+ & \mathbf{0} \end{vmatrix}. \quad (5)$$

Again,  $\mathbf{B}$  and  $\mathbf{B}^+$  are off-diagonal blocks containing intersubset resonance parameters. Nonzero elements of these blocks represent the neighboring pairs of  $2p_z$  AOs. The mean value of the latter  $\beta$  will be used here as a (negative) energy unit by accepting

the equality  $\beta = 1$ . The superscript  $+$  in Eq. (5) designates the transposed matrix  $\mathbf{B}$ . (Note  $\mathbf{B} \neq \mathbf{B}^+$  in the general case.) The Hamiltonian matrix of Eq. (5) will serve as the zero-order matrix in our study and it is accordingly supplied with the subscript (0). The first-order matrix  $\mathbf{H}_{(1)}$  also will be divided into four submatrices (blocks) in accordance with the above-described partition of the basis set  $\{\chi\}$ . We then obtain

$$\mathbf{H}_{(1)} = \begin{vmatrix} \mathbf{A}_{(1)} & \mathbf{W}_{(1)} \\ \mathbf{W}_{(1)}^+ & \mathbf{D}_{(1)} \end{vmatrix}. \quad (6)$$

No specifying of submatrices  $\mathbf{A}_{(1)}$ ,  $\mathbf{D}_{(1)}$  and  $\mathbf{W}_{(1)}$  is undertaken in this section.

An important property of the matrix  $\mathbf{H}_{(0)}$  of Eq. (5) consists of the possibility of transforming this matrix into a block-diagonal form, using an unitary transformation matrix [13]. Inasmuch as a block-diagonal Hamiltonian matrix refers to the basis of noncanonical molecular orbitals (NCMOs) of the given system in accordance with the Brillouin theorem [26–32], the above-mentioned transformation describes passing to the basis of NCMOs of parent AHs. The same transformation may be evidently applied to the first order matrix  $\mathbf{H}_{(1)}$  of Eq. (6). As a result, the total Hamiltonian matrix of PAHs represented in the basis of NCMOs of parent AHs contains a block-diagonal zero-order term. Hamiltonian matrices of just this constitution underlie the so-called noncommutative Rayleigh–Schrödinger perturbation theory [18, 19, 31] used to obtain members of the power series both for the one-electron density matrix (DM) [31] and for total energy [20, 21]. Thus, these results may be applied straightforwardly to PAHs in the basis of NCMOs of parent AHs. To turn to the usual representation of the DM in the basis of  $2p_z$  AOs  $\{\chi\}$  (i.e., to the CBO matrix of PAHs), members  $\tilde{\mathbf{P}}_{(k)}$  of the above-mentioned power series should be retransformed into the set  $\{\chi\}$  again. Just this procedure formed the basis of derivation of the first-order correction  $\mathbf{P}_{(1)}$  to the CBO matrix of PAHs in the previous study [15], and it will be extended to the correction  $\mathbf{P}_{(2)}$  in Section 3. In this section, we will focus on application to PAHs of the results concerning the total energy  $E$  [20, 21].

The principal result under our interest is the interrelation between the two components  $E_{(k)}^{(k,0)}$  and  $E_{(k)}^{(k-1,1)}$  of Eq. (3) established for  $k \geq 2$  in Ref. [20]. For the second-order correction  $E_{(2)}$ , these relations take the form

$$E_{(2)}^{(1,1)} = -2E_{(2)}^{(2,0)}, \quad E_{(2)} = \frac{1}{2}E_{(2)}^{(1,1)}, \quad E_{(2)} = -E_{(2)}^{(2,0)} \quad (7)$$

and originally correspond to the basis of NCMOs of the parent hydrocarbon in our case. Applicability of the same relations to the initial Hamiltonian matrix of PAHs represented in the basis of  $2p_z$  AOs  $\{\chi\}$  follow immediately from the invariance of Traces against an unitary transformation of basis set. The first relation of Eq. (7) indicates the two components of the second-order energy  $E_{(2)}$  to be interdependent and to acquire opposite signs, whatever the actual structure of the system. Accordingly, the remaining relations exhibit the expressibility of the total correction  $E_{(2)}$  in terms of either  $E_{(2)}^{(1,1)}$  or  $E_{(2)}^{(2,0)}$ .

Let us now turn to a separate discussion of corrections  $E_{(0)}$ ,  $E_{(1)}$ , and  $E_{(2)}$  for PAHs. From the first expression of Eq. (4), it follows that the zero-order member  $E_{(0)}$  depends only on the term  $\mathbf{P}_{(0)}$  referring to the Hamiltonian matrix of AHs ( $\mathbf{H}_{(0)}$ ) of Eq. (5). The correction  $\mathbf{P}_{(0)}$  was originally derived in Ref. [25] and rederived recently [13] on the basis of solution of the respective commutation equation. Two alternative forms of this matrix have been obtained:

$$\mathbf{P}_{(0)} = \begin{vmatrix} \mathbf{I} & \mathbf{BQ} \\ \mathbf{QB}^+ & \mathbf{I} \end{vmatrix}, \quad \mathbf{P}_{(0)} = \begin{vmatrix} \mathbf{I} & \mathbf{SB} \\ \mathbf{B}^+\mathbf{S} & \mathbf{I} \end{vmatrix}, \quad (8)$$

where submatrices of the right-hand sides correspond to subsets  $\{\chi^*\}$  and  $\{\chi^\circ\}$  and to their interaction. Products  $\mathbf{SB}$  and  $\mathbf{BQ}$  coincide with one another, and both are unitary matrices in addition, i.e.,

$$\mathbf{SBB}^+\mathbf{S} = \mathbf{QB}^+\mathbf{BQ} = \mathbf{BQQB}^+ = \mathbf{B}^+\mathbf{SSB} = \mathbf{I}. \quad (9)$$

$\mathbf{I}$  here and below stands for the unit matrix, while matrices  $\mathbf{S}$  and  $\mathbf{Q}$  take the form

$$\mathbf{S} = (\mathbf{BB}^+)^{-1/2}, \quad \mathbf{Q} = (\mathbf{B}^+\mathbf{B})^{-1/2}. \quad (10)$$

Substituting the expressions for  $\mathbf{H}_{(0)}$  and  $\mathbf{P}_{(0)}$  of Eqs. (5) and (8) into the definition of  $E_{(0)}$  shown in Eq. (4) yields the following expression [13]:

$$E_{(0)} = 2\text{Trace}(\mathbf{BB}^+)^{1/2}. \quad (11)$$

Let us turn now to the first-order correction  $E_{(1)}$  defined by the second expression of Eq. (4). The first-order correction  $\mathbf{P}_{(1)}$  contained in Eq. (4) has been derived in Ref. [15] and represented in terms of four submatrices as follows

$$\mathbf{P}_{(1)} = \begin{vmatrix} \mathbf{X}_{(1)} & \mathbf{N}_{(1)} \\ \mathbf{N}_{(1)}^+ & \mathbf{Z}_{(1)} \end{vmatrix}. \quad (12)$$

Expressions for these submatrices will be discussed later in Section 3. For our present purpose, let us only

note that the submatrices  $\mathbf{N}_{(1)}$  proved proportional to specific skew-symmetric matrices  $\mathbf{\Delta}_{(1)}$  and  $\mathbf{\Gamma}_{(1)}$ , viz.

$$\mathbf{N}_{(1)} = -\mathbf{BQ}\mathbf{\Delta}_{(1)} = -\mathbf{\Gamma}_{(1)}\mathbf{BQ}, \quad (13)$$

where  $\mathbf{\Delta}_{(1)}^+ = -\mathbf{\Delta}_{(1)}$  and  $\mathbf{\Gamma}_{(1)}^+ = -\mathbf{\Gamma}_{(1)}$ . From Eq. (13), it follows that the  $\mathbf{P}_{(1)}$ -containing component  $E_{(1)}^{(1,0)}$  does not contribute to the first-order energy  $E_{(1)}$ , i.e.,

$$E_{(1)}^{(1,0)} = \text{Trace}(\mathbf{N}_{(1)}\mathbf{B}^+ + \mathbf{N}_{(1)}^+\mathbf{B}) = 0 \quad (14)$$

and

$$\begin{aligned} E_{(1)} &= E_{(1)}^{(0,1)} = \text{Trace}[\mathbf{P}_{(0)}\mathbf{H}_{(1)}] \\ &= \text{Trace}[\mathbf{A}_{(1)} + \mathbf{D}_{(1)} + \mathbf{BQW}_{(1)}^+ + \mathbf{QB}^+\mathbf{W}_{(1)}]. \end{aligned} \quad (15)$$

Specific results following from this expression coincide with the classical ones. To demonstrate this, let us introduce the most popular types of perturbation.

Let us start with the local alteration in the Coulomb parameter of the AO  $\chi_1$  denoted by  $\alpha$ . Instead of Eq. (6), we then obtain

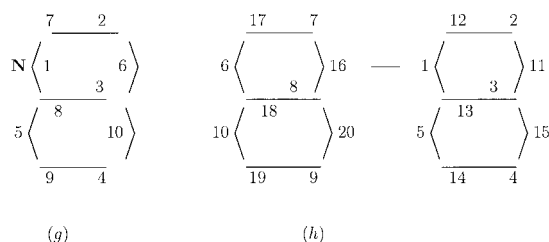
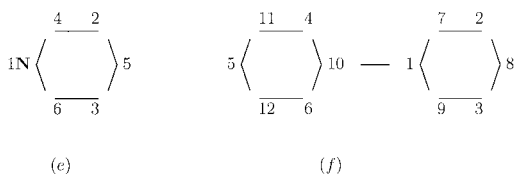
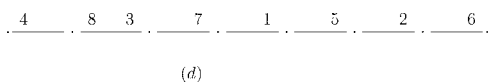
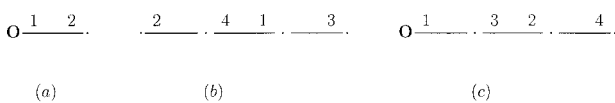
$$A_{(1)ij} = \alpha\delta_{i1}\delta_{j1}, \quad \mathbf{D}_{(1)} = \mathbf{0}, \quad \mathbf{W}_{(1)} = \mathbf{W}_{(1)}^+ = \mathbf{0}. \quad (16)$$

Substituting Eq. (16) into Eq. (15) yields  $E_{(1)loc} = \alpha$ , in accordance with the known results [1], where the subscript *loc* serves to denote the above-described perturbation.

The second example consists of formation of a new bond between two identical parent AHs R and R', so that the resulting composite hydrocarbon R-R' also belongs to AHs. Accordingly, the subsets  $\{\chi^*\}$  and  $\{\chi^\circ\}$  of the total basis set  $\{\chi\}$  will be subdivided into four subsets  $\{\chi_R^*\}$ ,  $\{\chi_{R'}^*\}$ ,  $\{\chi_R^\circ\}$ , and  $\{\chi_{R'}^\circ\}$ . The new bond is supposed to be formed between the first AOs of subsets  $\{\chi_R^*\}$  and  $\{\chi_{R'}^*\}$ , further denoted by  $\chi_1$  and  $\chi_{1'}$  for simplicity. Under the latter condition, the similarity of numberings of AOs inside the parent AHs R and R' may be easily preserved by interchanging the subsets of the second subsystem (R') relatively to those of the first one (R) as illustrated in Section 5 (see also Scheme 2). For total matrices  $\mathbf{B}_{comp}$ ,  $\mathbf{Q}_{comp}$ , and for blocks of the relevant perturbation matrix  $\mathbf{H}_{(1)comp}$ , we then obtain

$$\begin{aligned} \mathbf{B}_{comp} &= \begin{vmatrix} \mathbf{B}_R & \mathbf{0} \\ \mathbf{0} & \mathbf{B}_R^+ \end{vmatrix}, & \mathbf{Q}_{comp} &= \begin{vmatrix} \mathbf{Q}_R & \mathbf{0} \\ \mathbf{0} & \mathbf{S}_R \end{vmatrix}, \\ \mathbf{A}_{(1)} = \mathbf{D}_{(1)} &= \mathbf{0}, & \mathbf{W}_{(1)comp} &= \begin{vmatrix} \mathbf{0} & \mathbf{K}_{(1)} \\ \mathbf{0} & \mathbf{0} \end{vmatrix}, \end{aligned} \quad (17)$$

## GINEITYTE



**SCHEME 2.** Numbering of  $2p_z$  AOs of a carbonyl group (a), butadiene (b), acroleine (c), octatriene (d), pyridine (e), biphenyl (f), quinoline (g), and binaphthyl (h).

where  $\mathbf{B}_R$  and  $\mathbf{Q}_R$  represent a single parent AH and the subscript comp here and below refers to formation of a composite AH. (Note that the transposed matrix  $\mathbf{B}_R^+$  and the matrix  $\mathbf{S}_R$  arise instead of  $\mathbf{B}_R$  and  $\mathbf{Q}_R$  owing to interchange of subsets for the second parent AH  $R'$ .) Elements of the interparent block  $\mathbf{K}_{(1)}$  take zero values except for a single element  $K_{(1)11}$ , i.e.,

$$K_{(1)ij} = \gamma \delta_{i1} \delta_{j1}, \quad (18)$$

where  $\gamma$  stands for the resonance parameter of the newly formed bond. Substituting these particular expressions for matrices  $\mathbf{B}$ ,  $\mathbf{Q}$ , and  $\mathbf{W}_{(1)}$  into Eq. (15) yields a zero value for the first-order correction  $E_{(1)\text{comp}}$  in accordance with the known result for intermolecular perturbation [1].

Let us turn now to the second-order energy  $E_{(2)}$  defined by the last expression of Eq. (4). Substituting Eqs. (6) and (12) into the definition of the  $\mathbf{P}_{(1)}$ -containing component  $E_{(2)}^{(1,1)}$  yields the following formula:

$$E_{(2)}^{(1,1)} = \text{Trace}[\mathbf{X}_{(1)}\mathbf{A}_{(1)} + \mathbf{Z}_{(1)}\mathbf{D}_{(1)} + \mathbf{N}_{(1)}\mathbf{W}_{(1)}^+ + \mathbf{N}_{(1)}^+\mathbf{W}_{(1)}] \quad (19)$$

generally containing all submatrices of the first-order correction  $\mathbf{P}_{(1)}$ . For a local one-center perturbation defined by Eq. (16), we then obtain

$$E_{(2)\text{loc}}^{(1,1)} = X_{(1)11}^{\text{loc}} \alpha = \Pi_{11} \alpha^2, \quad (20)$$

where  $X_{(1)11}^{\text{loc}}$  coincides with the relevant element of the first-order correction  $\mathbf{P}_{(1)\text{loc}}$  [see Eq. (12)]. The last relation of the right-hand side of Eq. (20) follows after invoking the definition of the self-polarizability of the atom  $C_1$ , viz.

$$\Pi_{11} = \frac{\partial X_{(1)11}^{\text{loc}}}{\partial A_{(1)11}} = \frac{\partial X_{(1)11}^{\text{loc}}}{\partial \alpha}. \quad (21)$$

It is seen that the  $\mathbf{P}_{(1)}$ -containing component of the second order energy is proportional to the population acquired by the AO  $\chi_1$  after perturbation. In this connection, this increment may be interpreted as the contribution to the total second-order energy  $E_{(2)\text{loc}}$  due to lowering of the one-electron energy of electrons acquired by the AO  $\chi_1$ . Comparison of Eq. (20) with the classical expression to the total second-order energy  $E_{(2)\text{loc}}$  [6, 14], viz.

$$E_{(2)\text{loc}} = \frac{1}{2} \Pi_{11} \alpha^2 \quad (22)$$

indicates the increment  $E_{(2)\text{loc}}^{(1,1)}$  to yield the stabilizing contribution to the total correction  $E_{(2)\text{loc}}$ , which is twice as large as the final one in accordance with Eq. (7). (Note that  $\Pi_{11} > 0$  and  $E_{(2)\text{loc}}^{(1,1)} > 0$  in our negative energy units.) Inasmuch as the first-order correction  $\mathbf{P}_{(1)}$  to the CBO matrix of PAHs contains the primary effects of perturbation on charge and bond order distributions, the component  $E_{(2)\text{loc}}^{(1,1)}$  may be referred to accordingly as describing the primary stabilizing increment of perturbation upon the second order energy.

An analogous result follows in the case of formation of a new bond between AHs  $R$  and  $R'$  represented by Eqs. (17) and (18). From Eq. (19), we obtain

$$E_{(2)\text{comp}}^{(1,1)} = 2N_{(1)11'} \cdot \gamma = 2\Pi_{11',11'} \cdot \gamma^2, \quad (23)$$

where  $N_{(1)11'}$  is the element of the matrix  $\mathbf{N}_{(1)}$  referring to the new bond between AOs  $\chi_1$  and  $\chi_{1'}$  and  $\Pi_{11',11'} > 0$  is the self-polarizability of the bond  $C_1-C_{1'}$  corresponding to the composite parent hydrocarbon [6] and defined as a derivative of  $N_{(1)11'}$

with respect to  $\gamma$ . It is evident that  $E_{(2)\text{comp}}^{(1,1)}$  represents the stabilizing increment of the newly formed bond to the total second-order energy  $E_{(2)\text{comp}}$ . The latter is known to take the form [6, 14]

$$E_{(2)\text{comp}} = \Pi_{11',11'} \cdot \gamma^2. \quad (24)$$

The ratio between  $E_{(2)\text{comp}}$  and  $E_{(2)\text{comp}}^{(1,1)}$  also meets the relations of Eq. (7), i.e., the primary stabilizing increment of perturbation exceeds twice the final stabilization energy.

Let us now turn to the remaining component of the second-order energy, i.e., to  $E_{(2)}^{(2,0)}$ . Opposite signs of the two components of the correction  $E_{(2)}$  seen from the first relation of Eq. (7) ensure the destabilizing nature of the  $\mathbf{P}_{(2)}$ -containing component  $E_{(2)}^{(2,0)}$ , provided the system becomes stabilized due to perturbation. As a result, the final second-order energy [ $E_{(2)}$ ] actually follows from the difference between the stabilizing primary increment of perturbation [ $E_{(2)}^{(1,1)}$ ] and the destabilizing secondary contribution [ $E_{(2)}^{(2,0)}$ ]. In this context, the role of the  $\mathbf{P}_{(2)}$ -containing component may be concluded to consist in reducing twice the above-discussed primary increments of perturbation originating from the  $\mathbf{P}_{(1)}$ -containing component. Thus, the second-order corrections  $\mathbf{P}_{(2)}$  to CBO matrices of AHs play an important part in the formation of the final stabilization energies of these systems.

From the definition of the destabilizing component  $E_{(2)}^{(2,0)}$  of Eq. (4), it follows that the latter actually contains only those elements of the second-order matrix  $\mathbf{P}_{(2)}$  that correspond to the nonzero elements of the Hamiltonian matrix of the parent AHs [ $\mathbf{H}_{(0)}$ ], i.e., only the increments originating from the second-order alterations in the neighboring bond orders due to the given perturbation. As was mentioned already, the first-order corrections  $\mathbf{P}_{(1)}$  do not contribute to alterations in the orders of actual chemical bonds (see also Section 3). Hence, stabilization of the system vs. the parent hydrocarbon necessarily is accompanied by prevalent weakening of chemical bonds due to perturbation. Finally, the last relation of Eq. (7) indicates that the total second-order energy  $E_{(2)}$  is alternatively expressible in terms of the above-discussed alterations in the neighboring bond orders.

To discuss the  $\mathbf{P}_{(2)}$ -containing component of the second-order energy in greater detail, we are about to derive and analyze the second-order correction  $\mathbf{P}_{(2)}$  to the CBO matrix of PAHs in the next section.

### 3. Analysis of Second-Order Corrections to Charge-Bond Order Matrices of Perturbed AHs in Comparison With the First-Order Ones

As was already mentioned, the first-order correction  $\mathbf{P}_{(1)}$  to the CBO matrix of AHs [ $\mathbf{P}_{(0)}$ ] has been obtained in Ref. [15] by retransforming the relevant correction  $\tilde{\mathbf{P}}_{(1)}$  referring to the basis of NCMOs of parent AHs [13] into the basis of AOs  $\{\chi\}$ . The second-order correction  $\mathbf{P}_{(2)}$  of the same power series may be derived analogously after retransforming the correction  $\tilde{\mathbf{P}}_{(2)}$  of Ref. [31]. Inasmuch as the latter is of a more involved constitution as compared to  $\tilde{\mathbf{P}}_{(1)}$ , the same refers also to the transformed correction  $\mathbf{P}_{(2)}$ . Thus, the general expression for  $\mathbf{P}_{(2)}$  corresponding to the perturbation matrix of an arbitrary structure shown in Eq. (6) takes the form

$$\mathbf{P}_{(2)} = \begin{vmatrix} \mathbf{X}_{(2)} + \mathbf{K}_{(2)} & \mathbf{M}_{(2)} + \mathbf{N}_{(2)} \\ \mathbf{M}_{(2)}^+ + \mathbf{N}_{(2)}^+ & \mathbf{Z}_{(2)} + \mathbf{L}_{(2)} \end{vmatrix}. \quad (25)$$

Submatrices  $\mathbf{X}_{(2)}$ ,  $\mathbf{Z}_{(2)}$ , and  $\mathbf{N}_{(2)}$  are the second-order analogues of those contained within the correction  $\mathbf{P}_{(1)}$  of Eq. (12). For both  $k = 1$  and  $k = 2$ , the diagonal blocks  $\mathbf{X}_{(k)}$  and  $\mathbf{Z}_{(k)}$  take the common form

$$\begin{aligned} \mathbf{X}_{(k)} &= -\mathbf{BQ}\mathbf{G}_{(k)}^+ - \mathbf{G}_{(k)}\mathbf{QB}^+, \\ \mathbf{Z}_{(k)} &= \mathbf{G}_{(k)}^+\mathbf{BQ} + \mathbf{QB}^+\mathbf{G}_{(k)}. \end{aligned} \quad (26)$$

Accordingly, the off-diagonal submatrices  $\mathbf{N}_{(k)}$  are related to skew-Hermitian matrices  $\mathbf{\Delta}_{(k)}$  and  $\mathbf{\Gamma}_{(k)}$ , i.e.,

$$\mathbf{N}_{(k)} = -\mathbf{BQ}\mathbf{\Delta}_{(k)} = -\mathbf{\Gamma}_{(k)}\mathbf{BQ}, \quad (27)$$

where

$$\begin{aligned} \mathbf{\Delta}_{(k)} &= \mathbf{G}_{(k)}^+\mathbf{BQ} - \mathbf{QB}^+\mathbf{G}_{(k)}, \\ \mathbf{\Gamma}_{(k)} &= \mathbf{BQ}\mathbf{G}_{(k)}^+ - \mathbf{G}_{(k)}\mathbf{QB}^+ \end{aligned} \quad (28)$$

for both  $k = 1$  and  $k = 2$ .

The principal matrices  $\mathbf{G}_{(k)}$  contained within these expressions meet the following equation:

$$\mathbf{G}_{(k)}\mathbf{Q} + \mathbf{S}\mathbf{G}_{(k)} + \mathbf{S}\mathbf{V}_{(k)}\mathbf{Q} = 0, \quad (29)$$

where

$$\begin{aligned} \mathbf{V}_{(1)} &= \frac{1}{2} \{ \mathbf{A}_{(1)}\mathbf{BQ} - \mathbf{BQD}_{(1)} \\ &\quad + \mathbf{BQ}[\mathbf{W}_{(1)}^+\mathbf{BQ} - \mathbf{QB}^+\mathbf{W}_{(1)}] \}, \end{aligned} \quad (30)$$

$$\begin{aligned} \mathbf{V}_{(2)} = & \frac{1}{2} \{ [\mathbf{A}_{(1)} + \mathbf{BQD}_{(1)}\mathbf{QB}^+] \mathbf{G}_{(1)} \\ & + [\mathbf{BQW}_{(1)}^+ + \mathbf{W}_{(1)}\mathbf{QB}^+] \mathbf{G}_{(1)} \\ & - \mathbf{G}_{(1)} [\mathbf{QB}^+ \mathbf{A}_{(1)} \mathbf{BQ} + \mathbf{D}_{(1)}] \\ & + \mathbf{G}_{(1)} [\mathbf{W}_{(1)}^+ \mathbf{BQ} + \mathbf{QB}^+ \mathbf{W}_{(1)}] \}. \quad (31) \end{aligned}$$

As opposed to matrices  $\mathbf{X}_{(k)}$ ,  $\mathbf{Z}_{(k)}$ , and  $\mathbf{N}_{(k)}$ , the remaining submatrices of the second-order correction  $\mathbf{P}_{(2)}$ , i.e.,  $\mathbf{M}_{(2)}$ ,  $\mathbf{K}_{(2)}$ , and  $\mathbf{L}_{(2)}$ , have no analogues in the first-order correction  $\mathbf{P}_{(1)}$ . [These new blocks of the correction  $\mathbf{P}_{(2)}$  originate from nonzero diagonal blocks of the matrix  $\tilde{\mathbf{P}}_{(2)}$  of Ref. [31] that are absent in the first-order matrix  $\tilde{\mathbf{P}}_{(1)}$ .] The expressions for the additional submatrices of the matrix  $\mathbf{P}_{(2)}$  are as follows:

$$\begin{aligned} \mathbf{K}_{(2)} &= -\mathbf{G}_{(1)}\mathbf{G}_{(1)}^+ + \mathbf{BQG}_{(1)}^+\mathbf{G}_{(1)}\mathbf{QB}^+, \\ \mathbf{L}_{(2)} &= \mathbf{G}_{(1)}^+\mathbf{G}_{(1)} - \mathbf{QB}^+\mathbf{G}_{(1)}\mathbf{G}_{(1)}^+\mathbf{BQ} \quad (32) \end{aligned}$$

and

$$\mathbf{M}_{(2)} = -\mathbf{BQ}\mathbf{\Omega}_{(2)} = -\mathbf{\Lambda}_{(2)}\mathbf{BQ}, \quad (33)$$

where  $\mathbf{\Omega}_{(2)}$  and  $\mathbf{\Lambda}_{(2)}$  are Hermitian matrices as opposed to  $\mathbf{\Delta}_{(2)}$  and  $\mathbf{\Gamma}_{(2)}$  of Eq. (27). The expressions for matrices  $\mathbf{\Omega}_{(2)}$  and  $\mathbf{\Lambda}_{(2)}$  take the form

$$\begin{aligned} \mathbf{\Omega}_{(2)} &= \mathbf{G}_{(1)}^+\mathbf{G}_{(1)} + \mathbf{QB}^+\mathbf{G}_{(1)}\mathbf{G}_{(1)}^+\mathbf{BQ}, \\ \mathbf{\Lambda}_{(2)} &= \mathbf{G}_{(1)}\mathbf{G}_{(1)}^+ + \mathbf{BQG}_{(1)}^+\mathbf{G}_{(1)}\mathbf{QB}^+. \quad (34) \end{aligned}$$

Finally, the following interrelations between separate submatrices may be mentioned:

$$\mathbf{X}_{(k)} = -\mathbf{BQZ}_{(k)}\mathbf{QB}^+, \quad \mathbf{\Gamma}_{(k)} = \mathbf{BQ}\mathbf{\Delta}_{(k)}\mathbf{QB}^+ \quad (35)$$

and

$$\mathbf{K}_{(2)} = \mathbf{BQL}_{(2)}\mathbf{QB}^+. \quad (36)$$

Analysis of the above-outlined general expressions for the correction  $\mathbf{P}_{(2)}$  may be performed by using the procedure of Ref. [15]. To this end, let us distinguish the so-called block-diagonal perturbation matrix ( $\mathbf{H}_{(1)}^{(\alpha)}$ ) and the anti-block-diagonal one ( $\mathbf{H}_{(1)}^{(\beta)}$ ) corresponding to assumptions that  $\mathbf{W}_{(1)} = \mathbf{W}_{(1)}^+ = \mathbf{0}$  and  $\mathbf{A}_{(1)} = \mathbf{D}_{(1)} = \mathbf{0}$ , respectively, in the general form of the first-order Hamiltonian matrix  $\mathbf{H}_{(1)}$  of Eq. (6). It should be noted immediately that the perturbations represented by Eqs. (16) and (17), (18) correspond to particular cases of matrices  $\mathbf{H}_{(1)}^{(\alpha)}$  and  $\mathbf{H}_{(1)}^{(\beta)}$ .

Before turning to a discussion of corrections  $\mathbf{P}_{(2)}^{(\alpha)}$  and  $\mathbf{P}_{(2)}^{(\beta)}$  correspondingly, referring to the above-introduced perturbations  $\mathbf{H}_{(1)}^{(\alpha)}$  and  $\mathbf{H}_{(1)}^{(\beta)}$ , let us briefly overview the results of analysis of the relevant corrections  $\mathbf{P}_{(1)}^{(\alpha)}$  and  $\mathbf{P}_{(1)}^{(\beta)}$  [15]. Let us begin with the notation that the latter were found to be of opposite constitutions for perturbation matrices  $\mathbf{H}_{(1)}^{(\alpha)}$  and  $\mathbf{H}_{(1)}^{(\beta)}$ , viz.

$$\mathbf{P}_{(1)}^{(\alpha)} = \begin{vmatrix} \mathbf{X}_{(1)}^{(\alpha)} & \mathbf{0} \\ \mathbf{0} & \mathbf{Z}_{(1)}^{(\alpha)} \end{vmatrix}, \quad \mathbf{P}_{(1)}^{(\beta)} = \begin{vmatrix} \mathbf{0} & \mathbf{N}_{(1)}^{(\beta)} \\ \mathbf{N}_{(1)}^{(\beta)+} & \mathbf{0} \end{vmatrix}, \quad (37)$$

where nonzero submatrices (these are also accordingly denoted by the superscripts  $(\alpha)$  and  $(\beta)$ ) have been expressed in terms of relevant principal matrices  $\mathbf{G}_{(1)}^{(\alpha)}$  and  $\mathbf{G}_{(1)}^{(\beta)}$  as follows:

$$\mathbf{X}_{(1)}^{(\alpha)} = -2\mathbf{G}_{(1)}^{(\alpha)}\mathbf{QB}^+, \quad \mathbf{Z}_{(1)}^{(\alpha)} = 2\mathbf{G}_{(1)}^{(\alpha)+}\mathbf{BQ} \quad (38)$$

and

$$\mathbf{N}_{(1)}^{(\beta)} = -\mathbf{BQ}\mathbf{\Delta}_{(1)}^{(\beta)} = -2\mathbf{BQ}\mathbf{G}_{(1)}^{(\beta)+}\mathbf{BQ} \quad (39)$$

instead of Eqs. (26)–(28). Just this “opposite” constitution of corrections  $\mathbf{P}_{(1)}^{(\alpha)}$  and  $\mathbf{P}_{(1)}^{(\beta)}$  proved responsible for distinct primary effects of perturbations  $\mathbf{H}_{(1)}^{(\alpha)}$  and  $\mathbf{H}_{(1)}^{(\beta)}$  on populations of AOs and bond orders.

It is also essential within this context that the corrections of Eq. (37) yield no increments to the neighboring bond orders for both the local alteration in the Coulomb parameter and the formation of the interparent bond as described by Eqs. (16)–(18). In the former case, the above-drawn conclusion follows directly from the block-diagonal form of the correction  $\mathbf{P}_{(1)}^{(\alpha)}$  of Eq. (37) (note that the neighboring bond orders are positioned within off-diagonal blocks of this matrix). For the case of an interparent bonding represented by Eqs. (17) and (18), the relevant matrices  $\mathbf{\Delta}_{(1)\text{comp}}^{(\beta)}$  and  $\mathbf{N}_{(1)\text{comp}}^{(\beta)}$  take the following anti-block-diagonal form [15]

$$\begin{aligned} \mathbf{\Delta}_{(1)\text{comp}}^{(\beta)} &= \begin{vmatrix} \mathbf{0} & \mathbf{\Delta}_{(1)\text{inter}}^{(\beta)} \\ -\mathbf{\Delta}_{(1)\text{inter}}^{(\beta)+} & \mathbf{0} \end{vmatrix}, \\ \mathbf{N}_{(1)\text{comp}}^{(\beta)} &= \begin{vmatrix} \mathbf{0} & \mathbf{N}_{(1)\text{inter}}^{(\beta)} \\ \overline{\mathbf{N}}_{(1)\text{inter}}^{(\beta)} & \mathbf{0} \end{vmatrix}, \quad (40) \end{aligned}$$

where the subscripts inter are used to denote the submatrices of the interparent type and

$$\overline{\mathbf{N}}_{(1)\text{inter}}^{(\beta)} = \mathbf{B}_R^+\mathbf{S}_R\mathbf{\Delta}_{(1)\text{inter}}^{(\beta)+}. \quad (41)$$



The submatrix  $\Delta_{(1)\text{inter}}^{(\beta)}$ , in turn, meets the equation

$$\mathbf{Q}_R \Delta_{(1)\text{inter}}^{(\beta)} + \Delta_{(1)\text{inter}}^{(\beta)} \mathbf{S}_R + \mathbf{Q}_R^2 \mathbf{B}_R^+ \mathbf{K}_{(1)} \mathbf{S}_R = \mathbf{0}. \quad (42)$$

It deserves separate mention that elements of submatrices  $\mathbf{N}_{(1)\text{inter}}^{(\beta)}$  and  $\bar{\mathbf{N}}_{(1)\text{inter}}^{(\beta)}$  describe bond orders between parent AHs. The intraparent bond orders (if any) would emerge in the diagonal positions of total matrices  $\mathbf{N}_{(1)\text{comp}}^{(\beta)}$ . Zero submatrices standing there ensure zero contributions of perturbation of Eqs. (17) and (18) to neighboring bond orders inside the parent AHs. Thus, influences of perturbations on bond orders are determined by the second-order corrections  $\mathbf{P}_{(2)}^{(\alpha)}$  and  $\mathbf{P}_{(2)}^{(\beta)}$ .

As opposed to first-order corrections  $\mathbf{P}_{(1)}^{(\alpha)}$  and  $\mathbf{P}_{(1)}^{(\beta)}$  of Eq. (37), analysis of Eqs. (27)–(34) for the cases of perturbations  $\mathbf{H}_{(1)}^{(\alpha)}$  and  $\mathbf{H}_{(1)}^{(\beta)}$  yields a common anti-block-diagonal form for both corrections  $\mathbf{P}_{(2)}^{(\alpha)}$  and  $\mathbf{P}_{(2)}^{(\beta)}$ , viz.

$$\mathbf{P}_{(2)}^{(\alpha)} = \begin{vmatrix} \mathbf{0} & \mathbf{M}_{(2)}^{(\alpha)} + \mathbf{N}_{(2)}^{(\alpha)} \\ \mathbf{M}_{(2)}^{(\alpha)+} + \mathbf{N}_{(2)}^{(\alpha)+} & \mathbf{0} \end{vmatrix},$$

$$\mathbf{P}_{(2)}^{(\beta)} = \begin{vmatrix} \mathbf{0} & \mathbf{M}_{(2)}^{(\beta)} + \mathbf{N}_{(2)}^{(\beta)} \\ \mathbf{M}_{(2)}^{(\beta)+} + \mathbf{N}_{(2)}^{(\beta)+} & \mathbf{0} \end{vmatrix}. \quad (43)$$

The submatrices  $\mathbf{M}_{(2)}^{(\alpha)}$  and  $\mathbf{M}_{(2)}^{(\beta)}$  are expressible algebraically in terms of blocks of the first-order corrections of Eq. (37) as follows:

$$\mathbf{M}_{(2)}^{(\alpha)} = -2\mathbf{B}\mathbf{Q}\mathbf{G}_{(1)}^{(\alpha)+} \mathbf{G}_{(1)}^{(\alpha)} = -\frac{1}{2}(\mathbf{X}_{(1)}^{(\alpha)})^2 \mathbf{B}\mathbf{Q}$$

$$= -\frac{1}{2}\mathbf{B}\mathbf{Q}(\mathbf{Z}_{(1)}^{(\alpha)})^2 \quad (44)$$

and

$$\mathbf{M}_{(2)}^{(\beta)} = -2\mathbf{B}\mathbf{Q}\mathbf{G}_{(1)}^{(\beta)+} \mathbf{G}_{(1)}^{(\beta)} = -\frac{1}{2}\mathbf{B}\mathbf{Q}\Delta_{(1)}^{(\beta)} \Delta_{(1)}^{(\beta)+}$$

$$= -\frac{1}{2}\mathbf{N}_{(1)}^{(\beta)} \mathbf{N}_{(1)}^{(\beta)+} \mathbf{B}\mathbf{Q}. \quad (45)$$

In these expressions, passing from matrices  $\mathbf{G}_{(1)}^{(\alpha)}$  and  $\mathbf{G}_{(1)}^{(\beta)}$  to  $\mathbf{X}_{(1)}^{(\alpha)}$  and  $\Delta_{(1)}^{(\beta)}$ , respectively, is correspondingly based on Eqs. (38) and (39) and on the unitarity condition for the matrix  $\mathbf{B}\mathbf{Q}$  seen in Eq. (9). Moreover, the relations of Eqs. (13) and (35) also are invoked when obtaining the last expressions of Eqs. (44) and (45).

Furthermore, the skew-symmetric matrices  $\Delta_{(2)}^{(\alpha)}$  and  $\Delta_{(2)}^{(\beta)}$  determining the remaining blocks  $\mathbf{N}_{(2)}^{(\alpha)}$  and  $\mathbf{N}_{(2)}^{(\beta)}$  of corrections  $\mathbf{P}_{(2)}^{(\alpha)}$  and  $\mathbf{P}_{(2)}^{(\beta)}$  in accordance with Eq. (27) meet the standard matrix equation of the

common form

$$\mathbf{Q}\Delta_{(2)} + \Delta_{(2)}\mathbf{Q} + \mathbf{F}_{(2)} = \mathbf{0}. \quad (46)$$

For perturbations  $\mathbf{H}_{(1)}^{(\alpha)}$  and  $\mathbf{H}_{(1)}^{(\beta)}$ , the respective  $\Delta_{(2)}$ -free terms  $\mathbf{F}_{(2)}^{(\alpha)}$  and  $\mathbf{F}_{(2)}^{(\beta)}$  are

$$\mathbf{F}_{(2)}^{(\alpha)} = \frac{1}{2} \left\{ \mathbf{Q}^2 \mathbf{B}^+ [\mathbf{A}_{(1)} \mathbf{X}_{(1)}^{(\alpha)} - \mathbf{X}_{(1)}^{(\alpha)} \mathbf{A}_{(1)}] \mathbf{B}\mathbf{Q}^2 \right. \\ \left. - \mathbf{Q} [\mathbf{D}_{(1)} \mathbf{Z}_{(1)}^{(\alpha)} - \mathbf{Z}_{(1)}^{(\alpha)} \mathbf{D}_{(1)}] \mathbf{Q} \right\} \quad (47)$$

$$\mathbf{F}_{(2)}^{(\beta)} = \frac{1}{2} \mathbf{Q} [\Delta_{(1)}^{(\beta)} \mathbf{Q}\mathbf{B}^+ \mathbf{W}_{(1)} - \mathbf{W}_{(1)}^+ \mathbf{B}\mathbf{Q}\Delta_{(1)}^{(\beta)+}] \mathbf{Q} \\ + \frac{1}{2} \mathbf{Q}^2 \mathbf{B}^+ [\mathbf{W}_{(1)} \Delta_{(1)}^{(\beta)} \mathbf{Q}\mathbf{B}^+ - \mathbf{B}\mathbf{Q}\Delta_{(1)}^{(\beta)+} \mathbf{W}_{(1)}^+] \mathbf{B}\mathbf{Q}^2. \quad (48)$$

The solution of matrix equations like that of Eq. (46) may be represented in the form of an integral [33], i.e.,

$$\Delta_{(2)} = - \int_0^\infty \exp[-\mathbf{Q}t] \cdot \mathbf{F}_{(2)} \cdot \exp[-\mathbf{Q}t] dt. \quad (49)$$

Thus, submatrices  $\Delta_{(2)}^{(\alpha)}$  and  $\Delta_{(2)}^{(\beta)}$  and thereby  $\mathbf{N}_{(2)}^{(\alpha)}$  and  $\mathbf{N}_{(2)}^{(\beta)}$  are also expressible in terms of entire blocks of respective first-order corrections  $\mathbf{P}_{(1)}^{(\alpha)}$  and  $\mathbf{P}_{(1)}^{(\beta)}$ . [Note that the matrix  $\mathbf{F}_{(2)}^{(\beta)}$  of Eq. (48) may be represented alternatively in terms of  $\mathbf{N}_{(1)}^{(\beta)}$  using Eq. (39).] Hence, the second-order effects resulting from matrices  $\mathbf{P}_{(2)}^{(\alpha)}$  and  $\mathbf{P}_{(2)}^{(\beta)}$  may be considered consequences of first-order ones and thereby referred to as secondary effects of the given perturbation upon charge- and bond-order distribution.

For the case of the formation of an interparent bond, a more detailed information about structures of the relevant matrices  $\mathbf{M}_{(2)\text{comp}}^{(\beta)}$  and  $\mathbf{N}_{(2)\text{comp}}^{(\beta)}$  may be obtained after substituting Eqs. (17) and (40) into Eqs. (45) and (48). The resulting matrix  $\mathbf{M}_{(2)\text{comp}}^{(\beta)}$  proves to be of a block-diagonal constitution; i.e., it contains the direct sum of two matrices  $\mathbf{M}_{(2)R}^{(\beta)}$  and  $\mathbf{M}_{(2)R'}^{(\beta)}$  referring to separate subsystems  $R$  and  $R'$ . These submatrices, in turn, may be expressed as follows:

$$\mathbf{M}_{(2)R}^{(\beta)} = -\frac{1}{2} \mathbf{B}_R \mathbf{Q}_R \Delta_{(1)\text{inter}}^{(\beta)} \Delta_{(1)\text{inter}}^{(\beta)+}$$

$$= -\frac{1}{2} \bar{\mathbf{N}}_{(1)\text{inter}}^{(\beta)} \mathbf{N}_{(1)\text{inter}}^{(\beta)+} \mathbf{B}_R \mathbf{Q}_R,$$

$$\mathbf{M}_{(2)R'}^{(\beta)} = -\frac{1}{2} \mathbf{B}_R^+ \mathbf{S}_R \Delta_{(1)\text{inter}}^{(\beta)+} \Delta_{(1)\text{inter}}^{(\beta)}$$

$$= -\frac{1}{2} \bar{\mathbf{N}}_{(1)\text{inter}}^{(\beta)} \bar{\mathbf{N}}_{(1)\text{inter}}^{(\beta)+} \mathbf{B}_R^+ \mathbf{S}_R, \quad (50)$$

where  $\Delta_{(1)\text{inter}}^{(\beta)}$  is defined by Eq. (42). The last relation of Eq. (50) is obtained using Eq. (41). It is seen that the intraparent blocks  $\mathbf{M}_{(2)R}^{(\beta)}$  and  $\mathbf{M}_{(2)R'}^{(\beta)}$  are built up of interparent bond orders contained within submatrices  $\mathbf{N}_{(1)\text{inter}}^{(\beta)}$  and  $\overline{\mathbf{N}}_{(1)\text{inter}}^{(\beta)}$ . The interrelation between matrices  $\mathbf{M}_{(2)R}^{(\beta)}$  and  $\mathbf{M}_{(2)R'}^{(\beta)}$  will be considered in Section 4.

The remaining submatrix  $\Delta_{(2)\text{comp}}^{(\beta)}$  and thereby  $\mathbf{N}_{(2)\text{comp}}^{(\beta)}$  is also of a block-diagonal constitution. The blocks  $\Delta_{(2)R}^{(\beta)}$  and  $\Delta_{(2)R'}^{(\beta)}$  referring to parent AHs R and R', respectively, are determined by equations

$$\mathbf{Q}_R \Delta_{(2)R}^{(\beta)} + \Delta_{(2)R}^{(\beta)} \mathbf{Q}_R + \mathbf{F}_{(2)R}^{(\beta)} = \mathbf{0}, \quad (51)$$

$$\mathbf{S}_R \Delta_{(2)R'}^{(\beta)} + \Delta_{(2)R'}^{(\beta)} \mathbf{S}_R + \mathbf{F}_{(2)R'}^{(\beta)} = \mathbf{0} \quad (52)$$

following from Eq. (46) after employment Eqs. (17), (40), and (48). Matrices  $\mathbf{F}_{(2)R}^{(\beta)}$  and  $\mathbf{F}_{(2)R'}^{(\beta)}$  take the form

$$\mathbf{F}_{(2)R}^{(\beta)} = \frac{1}{2} \mathbf{Q}_R [\Delta_{(1)\text{inter}}^{(\beta)} \mathbf{K}_{(1)}^+ \mathbf{B}_R \mathbf{Q}_R - \mathbf{Q}_R \mathbf{B}_R^+ \mathbf{K}_{(1)} \Delta_{(1)\text{inter}}^{(\beta)+}] \mathbf{Q}_R, \quad (53)$$

$$\mathbf{F}_{(2)R'}^{(\beta)} = \frac{1}{2} \mathbf{S}_R [\mathbf{K}_{(1)}^+ \mathbf{B}_R \mathbf{Q}_R \Delta_{(1)\text{inter}}^{(\beta)} - \Delta_{(1)\text{inter}}^{(\beta)+} \mathbf{Q}_R \mathbf{B}_R^+ \mathbf{K}_{(1)}] \mathbf{S}_R. \quad (54)$$

The relevant blocks  $\mathbf{N}_{(2)R}^{(\beta)}$  and  $\mathbf{N}_{(2)R'}^{(\beta)}$  of the matrix  $\mathbf{N}_{(2)\text{comp}}^{(\beta)}$  follow from Eq. (27) after substituting the block-diagonal matrix  $\Delta_{(2)\text{comp}}^{(\beta)}$  along with respective matrices  $\mathbf{B}_{\text{comp}}$  and  $\mathbf{Q}_{\text{comp}}$  of Eq. (17). We obtain

$$\begin{aligned} \mathbf{N}_{(2)R}^{(\beta)} &= -\mathbf{B}_R \mathbf{Q}_R \Delta_{(2)R}^{(\beta)} \\ \mathbf{N}_{(2)R'}^{(\beta)} &= -\mathbf{B}_R^+ \mathbf{S}_R \Delta_{(2)R'}^{(\beta)} = -\mathbf{Q}_R \mathbf{B}_R^+ \Delta_{(2)R'}^{(\beta)}. \end{aligned} \quad (55)$$

(The last relation follows after invoking the equality  $\mathbf{S}_R \mathbf{B}_R = \mathbf{B}_R \mathbf{Q}_R$  for the subsystem R.) The role of the interparent bond orders in the formation of matrices  $\mathbf{N}_{(2)R}^{(\beta)}$  and  $\mathbf{N}_{(2)R'}^{(\beta)}$  is also evident.

Before finishing this section, let us draw some additional conclusions concerning the  $\mathbf{P}_{(2)}$ -containing component of the second-order energy [ $E_{(2)}^{(2,0)}$ ] and the correction itself [ $E_{(2)}$ ]. Using Eqs. (4), (5), (7), and (43), we obtain

$$E_{(2)} = -E_{(2)}^{(2,0)} = -\text{Trace}[\mathbf{M}_{(2)} \mathbf{B}^+ + \mathbf{M}_{(2)}^+ \mathbf{B}] \quad (56)$$

for both perturbations  $\mathbf{H}_{(1)}^{(\alpha)}$  and  $\mathbf{H}_{(1)}^{(\beta)}$ . The contribution of the matrix  $\mathbf{N}_{(2)}$  vanishes owing to the

skew-symmetric nature of matrices  $\Delta_{(2)}^{(\alpha)}$  and  $\Delta_{(2)}^{(\beta)}$ , as it was the case with the increment of the matrix  $\mathbf{N}_{(1)}$  to the first-order energy  $E_{(1)}$  [see Eq. (14)]. Hence, both  $E_{(2)}^{(2,0)}$  and  $E_{(2)}$  are expressible in terms of second-order effects on the neighboring bond orders described by matrices  $\mathbf{M}_{(2)}^{(\alpha)}$  and  $\mathbf{M}_{(2)}^{(\beta)}$ . Thus, destabilization of the system due to perturbation originates just from these matrices. Again, alterations in the neighboring bond orders determined by matrices  $\mathbf{N}_{(2)}^{(\alpha)}$  and  $\mathbf{N}_{(2)}^{(\beta)}$  (if any) are predicted to be energy-free effects. Finally, additivity of the second-order energy  $E_{(2)}$  with respect to contributions of individual chemical bonds follows from Eq. (56). Additivity of the same energy relatively to parent fragments of the composite hydrocarbon also is evident.

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#### 4. Comparison of Second-Order Effects for PAHs Originating From the Same Parent AH

We will focus in this section on comparison of second-order effects for pairs of perturbed compounds originating from a single parent AH R, as described by Eqs. (16)–(18) and exemplified by Scheme 2 in Section 5. The  $2p_z$  AOs of our systems  $\{\chi\}$  always may be enumerated in such a way that the matrix  $\mathbf{B}_R$  describing the fragment R in the composite AH R–R' coincides with that of the hydrocarbon R undergoing the one-center perturbation; i.e.,  $\mathbf{B}_R = \mathbf{B}$ . As a consequence, the equalities  $\mathbf{Q}_R = \mathbf{Q}$  and  $\mathbf{S}_R = \mathbf{S}$  also may be accepted for AHs under comparison. Coincidence between matrices  $\mathbf{A}_{(1)}$  and  $\mathbf{K}_{(1)}$  of Eqs. (16) and (18) also is evident provided that  $\alpha = \gamma$ . Alterations in the neighboring bond orders of AHs under study are described by elements of matrices  $\mathbf{M}_{(2)\text{loc}}^{(\alpha)}$  and  $\mathbf{M}_{(2)R}^{(\beta)}$  [ $\mathbf{M}_{(2)R'}^{(\beta)}$ ], as well as of  $\mathbf{N}_{(2)\text{loc}}^{(\alpha)}$  and  $\mathbf{N}_{(2)R}^{(\beta)}$  [ $\mathbf{N}_{(2)R'}^{(\beta)}$ ]. Thus, the aim of the present section consists of establishing relations between these pairs of matrices.

Inasmuch as submatrices of the second-order are expressed in terms of those of the first-order as discussed in Section 3, we begin with exploration of an interrelation between the latter. To this end, let us take the matrix equation for  $\mathbf{G}_{(1)}^{(\omega)}$  following from Eqs. (29) and (30) under an assumption that  $\mathbf{D}_{(1)} = \mathbf{W}_{(1)} = \mathbf{0}$ . After turning to the complex-conjugate counterpart of the relation, we obtain the matrix equation for  $2\mathbf{G}_{(1)}^{(\omega)+}$  of the following form

$$\mathbf{Q}[2\mathbf{G}_{(1)}^{(\omega)+}] + [2\mathbf{G}_{(1)}^{(\omega)+}] \mathbf{S} + \mathbf{Q}^2 \mathbf{B}^+ \mathbf{A}_{(1)} \mathbf{S} = \mathbf{0}. \quad (57)$$

Comparison of the above relation with Eq. (42) shows that submatrices  $2\mathbf{G}_{(1)}^{(\alpha)+}$  and  $\mathbf{\Delta}_{(1)\text{inter}}^{(\beta)}$  actually follow from the same matrix equation if the above assumptions, i.e.,  $\mathbf{B}_R = \mathbf{B}$ ,  $\mathbf{Q}_R = \mathbf{Q}$ ,  $\mathbf{S}_R = \mathbf{S}$ , and  $\mathbf{A}_{(1)} = \mathbf{K}_{(1)}$ , are taken into consideration. This result allows us to conclude that

$$\mathbf{\Delta}_{(1)\text{inter}}^{(\beta)} = 2\mathbf{G}_{(1)}^{(\alpha)+} = \mathbf{Z}_{(1)\text{loc}}^{(\alpha)} \mathbf{Q}_R \mathbf{B}_R^+ \quad (58)$$

where the last equality follows from the second expression of Eq. (38) along with unitarity of the matrix  $\mathbf{B}_R \mathbf{Q}_R$  shown in Eq. (9). After multiplying the relation of Eq. (58) by  $\mathbf{B}_R \mathbf{Q}_R$  from the left-hand side and invoking Eqs. (13) and (35), we obtain

$$\mathbf{X}_{(1)\text{loc}}^{(\alpha)} = \mathbf{N}_{(1)\text{inter}}^{(\beta)} = -\mathbf{B}_R \mathbf{Q}_R \mathbf{\Delta}_{(1)\text{inter}}^{(\beta)} \quad (59)$$

The first of the above relations indicates coincidence of submatrices of the first-order corrections  $\mathbf{P}_{(1)\text{loc}}^{(\alpha)}$  and  $\mathbf{P}_{(1)\text{comp}}^{(\beta)}$  corresponding to nonzero blocks of the relevant perturbation matrices, i.e., to  $\mathbf{A}_{(1)}$  and  $\mathbf{K}_{(1)}$ . An analogous relation may easily be obtained as well for the remaining nonzero submatrices of the same matrices, i.e., for  $\mathbf{Z}_{(1)\text{loc}}^{(\alpha)}$  and  $\overline{\mathbf{N}}_{(1)\text{inter}}^{(\beta)}$  [see Eqs. (37), (40), and (41)]. To do this, no more is required as to express  $\mathbf{\Delta}_{(1)\text{inter}}^{(\beta)+}$  as follows:

$$\mathbf{\Delta}_{(1)\text{inter}}^{(\beta)+} = \mathbf{B}_R \mathbf{Q}_R \mathbf{Z}_{(1)\text{loc}}^{(\alpha)} \quad (60)$$

on the basis of Eq. (58), and to substitute it into the definition of  $\overline{\mathbf{N}}_{(1)\text{inter}}^{(\beta)}$  of Eq. (41). Thereupon, the relations of Eq. (9) along with coincidence between products  $\mathbf{B}_R \mathbf{Q}_R$  and  $\mathbf{S}_R \mathbf{B}_R$  yields the result

$$\overline{\mathbf{N}}_{(1)\text{inter}}^{(\beta)} = \mathbf{Z}_{(1)\text{loc}}^{(\alpha)} \quad (61)$$

Therefore, the first-order corrections  $\mathbf{P}_{(1)\text{loc}}^{(\alpha)}$  and  $\mathbf{P}_{(1)\text{comp}}^{(\beta)}$  referring to the systems under comparison actually consist of the same two submatrices, provided that  $\alpha = \gamma$ . More explicitly, the submatrices  $\mathbf{X}_{(1)\text{loc}}^{(\alpha)}$  and  $\mathbf{Z}_{(1)\text{loc}}^{(\alpha)}$  describing charge and bond order redistributions inside subsets  $\{\chi_R^*\}$  and  $\{\chi_R^\circ\}$  under influence of the one-center perturbation of the Coulomb parameter of the AO  $\chi_1^*$  of the AH R coincide with submatrices  $\mathbf{N}_{(1)\text{inter}}^{(\beta)}$  and  $\overline{\mathbf{N}}_{(1)\text{inter}}^{(\beta)}$  describing the interparent bond orders of the composite system R–R' due to formation of the new bond between AOs  $\chi_1$  and  $\chi_{1'}$  belonging to subsets  $\{\chi_R^*\}$  and  $\{\chi_{R'}^\circ\}$ . The above-obtained coincidence between pairs of submatrices shown in Eqs. (59) and (61) evidently implies coincidence of their individual elements.

This fact along with the definition of polarizabilities of AOs like that of Eq. (21) and the equality  $\alpha = \gamma$  allows us to establish interdependences between specific pairs of polarizabilities for systems under comparison. In particular, the choice of elements  $X_{(1)\text{loc},11}^{(\alpha)}$  and  $N_{(1)\text{inter},1,1'}^{(\beta)}$  referring to the sites of perturbation of our systems and making a notation that any AO  $\chi_r$  may acquire the number 1, we obtain the coincidence of self-polarizabilities, i.e.,

$$\Pi_{rr} = \Pi_{rr',rr'} \quad (62)$$

for the systems under comparison. An analogous result easily follows also from the relevant classical definitions of self-polarizabilities in terms of coefficients of canonical MOs and their energies [6, 14] under an assumption of coinciding constitutions of fragments R and R' of the composite system R–R'. This result is an independent verification of relations obtained in the present study.

Let us turn now to the second-order matrices  $\mathbf{M}_{(2)\text{loc}}^{(\alpha)}$  and  $\mathbf{M}_{(2)R}^{(\beta)}$  [ $\mathbf{M}_{(2)R'}^{(\beta)}$ ], as well as to  $\mathbf{N}_{(2)\text{loc}}^{(\alpha)}$  and  $\mathbf{N}_{(2)R}^{(\beta)}$  [ $\mathbf{N}_{(2)R'}^{(\beta)}$ ]. Substituting Eq. (59) into the definition of matrices  $\mathbf{M}_{(2)\text{loc}}^{(\alpha)}$  and  $\mathbf{M}_{(2)R}^{(\beta)}$  shown in Eqs. (44) and (50) indicates that  $\mathbf{M}_{(2)\text{loc}}^{(\alpha)}$  coincides with  $\mathbf{M}_{(2)R}^{(\beta)}$ . To compare the matrix  $\mathbf{M}_{(2)R}^{(\beta)}$  to  $\mathbf{M}_{(2)R'}^{(\beta)}$ , the relations of Eqs. (9) and (35) should be additionally invoked. The result takes the form

$$\mathbf{M}_{(2)\text{loc}}^{(\alpha)} = \mathbf{M}_{(2)R}^{(\beta)} = \mathbf{M}_{(2)R'}^{(\beta)+} \quad (63)$$

where the last relation is in accordance with our enumeration of AOs inside the subsystem R' [see also the matrix  $\mathbf{B}_{\text{comp}}$  of Eq. (17)].

To compare the matrices  $\mathbf{N}_{(2)\text{loc}}^{(\alpha)}$  and  $\mathbf{N}_{(2)R}^{(\beta)}$ , the expressions for  $\mathbf{F}_{(2)}^{(\alpha)}$  of Eq. (47) corresponding to  $\mathbf{D}_{(1)} = \mathbf{0}$  and for  $\mathbf{F}_{(2)R}^{(\beta)}$  of Eq. (53) should be analyzed. Employment of the second relation of Eq. (59) allows Eq. (47) to be reformulated in terms of  $\mathbf{\Delta}_{(1)\text{inter}}^{(\beta)}$  and thereby to be compared with Eq. (53). The result consists in coincidence between matrices  $\mathbf{F}_{(2)\text{loc}}^{(\alpha)}$  and  $\mathbf{F}_{(2)R}^{(\beta)}$  and thereby between  $\mathbf{N}_{(2)\text{loc}}^{(\alpha)}$  and  $\mathbf{N}_{(2)R}^{(\beta)}$ . As opposed to matrices shown in Eq. (63), comparison of matrices  $\mathbf{N}_{(2)R}^{(\beta)}$  and  $\mathbf{N}_{(2)R'}^{(\beta)}$  is a rather cumbersome procedure. The point is that matrix equations for  $\mathbf{\Delta}_{(2)R}^{(\beta)}$  and  $\mathbf{\Delta}_{(2)R'}^{(\beta)}$  are formulated in terms of different matrices  $\mathbf{Q}_R$  and  $\mathbf{S}_R$  as seen from Eqs. (51) and (52). Thus, the first step of this procedure consists of multiplying Eq. (52) by  $\mathbf{B}_R^+$  and  $\mathbf{B}_R$  from the left- and right-hand sides, respectively, and in eliminating the matrix  $\mathbf{S}_R$  by

employment the equality  $\mathbf{S}_R \mathbf{B}_R = \mathbf{B}_R \mathbf{Q}_R$ . The result is as follows:

$$\begin{aligned} \mathbf{Q}_R \mathbf{B}_R^+ \Delta_{(2)R'}^{(\beta)} \mathbf{B}_R + \mathbf{B}_R^+ \Delta_{(2)R'}^{(\beta)} \mathbf{B}_R \mathbf{Q}_R \\ + \frac{1}{2} \mathbf{Q}_R \mathbf{B}_R^+ [\mathbf{K}_{(1)}^+ \mathbf{B}_R \mathbf{Q}_R \Delta_{(1)inter}^{(\beta)} \\ - \Delta_{(1)inter}^{(\beta)+} \mathbf{Q}_R \mathbf{B}_R^+ \mathbf{K}_{(1)}] \mathbf{B}_R \mathbf{Q}_R = 0. \end{aligned} \quad (64)$$

Thereupon, we suppose that  $\mathbf{N}_{(2)R} = \mathbf{N}_{(2)R'}^+$  and obtain the relation

$$\Delta_{(2)R}^{(\beta)} = -\mathbf{Q}_R \mathbf{B}_R^+ \Delta_{(2)R'}^{(\beta)} \mathbf{B}_R \mathbf{Q}_R \quad (65)$$

as implication. Finally, we multiply Eq. (64) by  $\mathbf{Q}_R$  from both sides and demonstrate that the resulting equation resolves itself into that shown in Eqs. (51) and (53) just under an assumption of Eq. (65). Thus, the result of the overall comparison is as follows:

$$\mathbf{N}_{(2)loc}^{(\alpha)} = \mathbf{N}_{(2)R}^{(\beta)} = \mathbf{N}_{(2)R'}^{(\beta)+} \quad (66)$$

Therefore, coinciding second-order effects are actually obtained for perturbations under comparison. In particular, alterations in the orders of chemical bonds under the influence of these perturbations take the same values, provided that  $\alpha = \gamma$ . The interrelation between the respective second-order energies, viz.

$$E_{(2)comp} = 2E_{(2)loc} \quad (67)$$

may be added here. This result easily follows from Eqs. (22), (24), and (62) and implies coincidence between stabilization energies referring to a single fragment R in both PAHs.

Before finishing the section, let us note that the above-suggested approach in general may be considered as an extension of the PMO theory in respects of both methodology and results. Indeed, the use of an alternative basis of noncanonical MOs of parent AHs along with a new version of the perturbation theory developed in Refs. [18, 19] allows the derivation of second-order corrections to CBO matrices of PAHs that is hardly possible in the framework of the original PMO theory based on the usual perturbative expansions in the basis of canonical MOs. Again, coincidence is observed between the results of both approaches concerning the first-order corrections to CBO matrices and the relevant increments to total energies (Section 2), and this fact holds no surprise.

## 5. Studies of Individual Molecules as Examples

Let us turn now to illustration of our conclusions by consideration of particular pairs of molecules originating from the same parent AH. Numbering of respective  $2p_z$  AOs that ensures the validity of Eqs. (16)–(18) is shown in the Scheme 2.

The simplest case of one-dimensional subsets of AOs may be exemplified by the carbonyl group and butadiene. For the former, we obtain

$$\{\chi_R^*\} = \{\chi_1\}, \quad \{\chi_R^\circ\} = \{\chi_2\}, \quad (68)$$

whereas the four subsets of the latter take the form

$$\begin{aligned} \{\chi_R^*\} = \{\chi_1\}, \quad \{\chi_{R'}^*\} = \{\chi_2\}, \\ \{\chi_R^\circ\} = \{\chi_3\}, \quad \{\chi_{R'}^\circ\} = \{\chi_4\}, \end{aligned} \quad (69)$$

and  $\chi_{1'}$  coincides with  $\chi_4$ . Instead of matrices  $\mathbf{B}$ ,  $\mathbf{Q}$ ,  $\mathbf{BQ}$ ,  $\mathbf{X}_{(1)loc}^{(\alpha)}$  and  $\mathbf{Z}_{(1)loc}^{(\alpha)}$ , one-dimensional quantities follow, viz.

$$B = Q = BQ = 1, \quad X_{(1)loc}^{(\alpha)} = \frac{1}{2}\alpha, \quad Z_{(1)loc}^{(\alpha)} = -\frac{1}{2}\alpha. \quad (70)$$

In accordance with relations of Eqs. (59) and (61), the last two quantities of Eq. (70) represent first-order contributions not only to populations of AOs of the carbonyl group, but also to the interparent bond orders of butadiene. Thus, the contribution to the population of the AO of the oxygen atom of the former ( $1/2\alpha$ ) coincides with that to the bond order between AOs of the newly joined atoms  $C_1$  and  $C_4$  of the latter ( $1/2\gamma$ ), under assumption that  $\alpha = \gamma$ , and both are described by the one-dimensional quantity  $X_{(1)loc}^{(\alpha)}$ . Similarly, the increment to the population of the AO  $\chi_2$  of carbonyl coincides with the relevant interparent bond order between terminal AOs  $\chi_2$  and  $\chi_3$  of butadiene. As far as the remaining bond orders are concerned, these are determined by the term  $M_{(2)loc}^{(\alpha)} (M_{(2)R}^{(\beta)})$  following from Eq. (44) and coinciding with  $-1/8\alpha^2 (-1/8\gamma^2)$ . [The increment originating from  $N_{(2)loc}^{(\alpha)} (N_{(2)R}^{(\beta)})$  takes a zero value owing to the vanishing  $\Delta_{(2)}$ -free term  $F_{(2)}^{(\alpha)}$  in Eq. (47).] Thus, the bond order of the only bond of carbonyl and those of the two intraparent bonds of butadiene ( $C_1$ – $C_3$  and  $C_2$ – $C_4$ ) are predicted to be reduced by the same value provided that  $\alpha = \gamma$ . Coincidence of the above results concerning both intra- and interparent bond orders of butadiene to those of Ref. [34] should be

also mentioned as an independent verification of the former (this coincidence follows after turning to the equality  $\alpha = \gamma = 1$  used in Ref. [34]).

Let us turn now to the acroleine and octatriene molecules that serve as examples of two-dimensional subsets of AOs. Instead of Eqs. (68) and (69), we then obtain

$$\{\chi_R^*\} = \{\chi_1, \chi_2\}, \quad \{\chi_R^\circ\} = \{\chi_3, \chi_4\}, \quad (71)$$

and

$$\begin{aligned} \{\chi_R^*\} &= \{\chi_1, \chi_2\}, & \{\chi_{R'}^*\} &= \{\chi_3, \chi_4\}, \\ \{\chi_R^\circ\} &= \{\chi_5, \chi_6\}, & \{\chi_{R'}^\circ\} &= \{\chi_7, \chi_8\} \end{aligned} \quad (72)$$

and  $\chi_{1'}$  coincides with  $\chi_7$ . We may easily write down the relevant initial matrices, viz.

$$\mathbf{B} = \begin{vmatrix} 1 & 0 \\ 1 & 1 \end{vmatrix}, \quad \mathbf{B}^+ = \begin{vmatrix} 1 & 1 \\ 0 & 1 \end{vmatrix}, \quad \mathbf{B}^+\mathbf{B} = \begin{vmatrix} 2 & 1 \\ 1 & 1 \end{vmatrix}, \quad (73)$$

and note that the corresponding matrix  $\mathbf{Q}$  may be found by diagonalizing the last one (i.e.,  $\mathbf{B}^+\mathbf{B}$ ) in accordance with Eq. (10) [the same also refers to the matrix  $\exp[-\mathbf{Q}t]$  used when solving equations like that of Eq. (46), as shown in Eq. (49)]. Derivation of matrices  $\mathbf{X}_{(1)loc}^{(\alpha)}$  and  $\mathbf{Z}_{(1)loc}^{(\alpha)}$  may be carried out as described in Ref. [15]. The result is as follows:

$$\begin{aligned} \mathbf{X}_{(1)loc}^{(\alpha)} &= \alpha \begin{vmatrix} 0.629 & -0.136 \\ -0.136 & 0.043 \end{vmatrix}, \\ \mathbf{Z}_{(1)loc}^{(\alpha)} &= -\alpha \begin{vmatrix} 0.402 & -0.316 \\ -0.316 & 0.268 \end{vmatrix}. \end{aligned} \quad (74)$$

These matrices evidently represent both the charge- and bond-order redistributions inside subsets  $\{\chi_R^*\}$  and  $\{\chi_R^\circ\}$  of acroleine and the interparent bond orders of octatriene, as was the case in the examples discussed above. Moreover, elements of these matrices determine various types of polarizabilities [15] for butadiene. It is therefore, no surprise that the signs of diagonal elements are in line with the rule of alternating polarity for AHs [5, 6, 9–12, 15, 16].

The respective matrix  $\mathbf{M}_{(2)loc}^{(\alpha)}[\mathbf{M}_{(2)R}^{(\beta)}]$  may be easily obtained using Eqs. (44) and (74), while  $\mathbf{N}_{(2)loc}^{(\alpha)}[\mathbf{N}_{(2)R}^{(\beta)}]$  follows from Eqs. (27), (46), (47), and (49). We obtain

$$\begin{aligned} \mathbf{M}_{(2)loc}^{(\alpha)} &= \alpha^2 \begin{vmatrix} -0.165 & 0.134 \\ 0.036 & -0.030 \end{vmatrix}, \\ \mathbf{N}_{(2)loc}^{(\alpha)} &= \alpha^2 \begin{vmatrix} -0.013 & -0.027 \\ 0.027 & -0.013 \end{vmatrix}. \end{aligned} \quad (75)$$

It is seen that the most important effect following from the matrix  $\mathbf{M}_{(2)loc}^{(\alpha)}[\mathbf{M}_{(2)R}^{(\beta)}]$  consists in lowering by  $0.165\alpha^2$  of orders of bonds attached to the site of perturbation. This refers to the bond  $O_1-C_3$  in acroleine and to bonds  $C_1-C_5$  and  $C_3-C_7$  in octatriene. The remaining alterations determined by the same matrix prove considerably weaker and acquire both positive and negative signs. For example, the growing order of the  $C_2-C_3$  bond and the decreasing order of the  $C_2-C_4$  bond of acroleine may be mentioned (the relevant changes coincide with 0.036 and  $-0.030$ , respectively).

As opposed to the matrix  $\mathbf{M}_{(2)loc}^{(\alpha)}[\mathbf{M}_{(2)R}^{(\beta)}]$ , the matrix  $\mathbf{N}_{(2)loc}^{(\alpha)}[\mathbf{N}_{(2)R}^{(\beta)}]$  of Eq. (75) yields alterations in orders of all bonds of alternating nature. For example, changes referring to the  $O_1-C_3$ ,  $C_3-C_2$ , and  $C_2-C_4$  bonds in acroleine correspondingly equal to  $-0.013$ ,  $+0.026$ , and  $-0.013$ . It is also worth noting that the total absolute value of negative alterations coincides with the only positive alteration in accordance with the energy-free character of the relevant effect (Section 3).

The pyridine and biphenyl molecules represent the case of three-dimensional subsets of AOs. Moreover, these systems seem to offer the most illustrative example in various respects, including representability of the principal matrices in terms of whole numbers. Let us begin with matrices  $\mathbf{X}_{(1)loc}^{(\alpha)}$  and  $\mathbf{Z}_{(1)loc}^{(\alpha)}$  derived in Ref. [15]. These take the form

$$\begin{aligned} \mathbf{X}_{(1)loc}^{(\alpha)} &= \frac{\alpha}{108} \begin{vmatrix} 43 & -5 & -5 \\ -5 & 1 & 1 \\ -5 & 1 & 1 \end{vmatrix}, \\ \mathbf{Z}_{(1)loc}^{(\alpha)} &= -\frac{\alpha}{108} \begin{vmatrix} 17 & -13 & 17 \\ -13 & 11 & -13 \\ 17 & -13 & 17 \end{vmatrix}. \end{aligned} \quad (76)$$

As was discussed already, the matrices  $\mathbf{X}_{(1)loc}^{(\alpha)}$  and  $\mathbf{Z}_{(1)loc}^{(\alpha)}$  represent both charge- and bond-order redistributions inside subsets  $\{\chi_R^*\}$  and  $\{\chi_R^\circ\}$  of pyridine and the interparent bond orders of biphenyl referring to pairs of subsets  $\{\chi_R^*\}$ ,  $\{\chi_{R'}^\circ\}$  and  $\{\chi_{R'}^*\}$ ,  $\{\chi_R^\circ\}$ , respectively. This fact implies coincidence between excessive populations of AOs of pyridine and the respective interparent bond orders in biphenyl. In particular, the population acquired by the nitrogen atom of the heterocycle coincides with the bond order between the newly joined atoms  $C_1$  and  $C_{10}$  of biphenyl and both are described by the element  $X_{(1)11}^{(\alpha)}$ . Accordingly, the populations acquired by the *meta*-position carbon atoms ( $C_2$  and  $C_3$ ) with respect

to the nitrogen atom coincide with bond orders between meta-positioned pairs of carbon atoms in biphenyl, i.e., between C<sub>2</sub> and C<sub>11</sub> and between C<sub>3</sub> and C<sub>12</sub>. The latter are represented by the remaining positive diagonal elements of the matrix  $\mathbf{X}_{(1)}^{(\alpha)}$ . The same interpretation refers to elements of the matrix  $\mathbf{Z}_{(1)}^{(\alpha)}$ : negative diagonal elements represent both populations lost by *ortho*- and *para*-position carbon atoms of pyridine and the bond orders between respective pairs of AOs in biphenyl.

On the basis of the above conclusions, an illustrative interpretation may be suggested for the results of the present study in general, i.e., both types of perturbation considered may be assumed to give rise to the same pattern of population redistribution. The excessive populations are employed in formation of interparent bond orders and thereby no actual charges on atoms are observed in the composite AHs. By contrast, the same additional populations are not employed and an actual alternation of occupation numbers of AOs arises in the heterocycles. Coincidence of second-order effects for these systems is also compatible with this assumption.

Let us now consider the structures of second-order matrices of pyridine and biphenyl. Elements of the matrix  $\mathbf{M}_{(2)loc}^{(\alpha)}$  ( $\mathbf{M}_{(2)R}^{(\beta)}$ ) are as follows:

$$\begin{aligned} \mathbf{M}_{(2)loc,14}^{(\alpha)} &= \mathbf{M}_{(2)loc,16}^{(\alpha)} = -\frac{397}{7776}\alpha^2 = -0.0511\alpha^2, \\ \mathbf{M}_{(2)loc,24}^{(\alpha)} &= \mathbf{M}_{(2)loc,36}^{(\alpha)} = \frac{47}{7776}\alpha^2 = 0.0060\alpha^2, \\ \mathbf{M}_{(2)loc,25}^{(\alpha)} &= \mathbf{M}_{(2)loc,35}^{(\alpha)} = -\frac{37}{7776}\alpha^2 = -0.0048\alpha^2, \end{aligned} \quad (77)$$

where the subscripts refer to numbers of AOs of pyridine. It is seen that elements  $\mathbf{M}_{(2)loc,14}^{(\alpha)}$  and  $\mathbf{M}_{(2)loc,16}^{(\alpha)}$  attached to the site of perturbation (C<sub>1</sub>) are approximately 10 times as large as the remaining ones. The negative signs of these elements is also noteworthy. Therefore, a significant weakening of bonds C<sub>1</sub>–C<sub>4</sub> and C<sub>1</sub>–C<sub>6</sub> in pyridine results from the matrix  $\mathbf{M}_{(2)loc}^{(\alpha)}$ . This effect is directly related to the predominant concentration of population at the nitrogen atom. [The relevant element  $X_{(1)loc,11}^{(\alpha)}$  also is more than 10 times as large as the remaining diagonal elements as Eq. (76) indicates.] In the case of biphenyl, weakening of four bonds follows, viz. of C<sub>1</sub>–C<sub>7</sub>, C<sub>1</sub>–C<sub>9</sub>, C<sub>4</sub>–C<sub>10</sub>, and C<sub>10</sub>–C<sub>6</sub>, and this effect is accordingly related to formation of a new bond between atoms C<sub>1</sub> and C<sub>10</sub>. As far as the remaining elements of Eq. (77) are concerned, these indicate a certain strengthening of

bonds C<sub>2</sub>–C<sub>4</sub> and C<sub>3</sub>–C<sub>6</sub> and weakening of bonds C<sub>2</sub>–C<sub>5</sub> and C<sub>3</sub>–C<sub>5</sub>. These alterations resemble those following from an increment of *para*-quinoidal structures of Scheme 1. Hence, the matrix  $\mathbf{M}_{(2)loc}^{(\alpha)}$  [ $\mathbf{M}_{(2)R}^{(\beta)}$ ] yields an essentially local effect consisting of predominant weakening of bonds attached to the site of perturbation. It is no surprise that this effect is accompanied by destabilization of the system [see Eq. (56)].

Using the same numbers of AOs of pyridine, we obtain elements of the matrix  $\mathbf{N}_{(2)loc}^{(\alpha)}$  [ $\mathbf{N}_{(2)R}^{(\beta)}$ ] too, viz.

$$\begin{aligned} \mathbf{N}_{(2)loc,14}^{(\alpha)} &= \mathbf{N}_{(2)loc,16}^{(\alpha)} = \mathbf{N}_{(2)loc,25}^{(\alpha)} \\ &= \mathbf{N}_{(2)loc,35}^{(\alpha)} = -\frac{5}{1944}\alpha^2 = -0.0026\alpha^2, \\ \mathbf{N}_{(2)loc,24}^{(\alpha)} &= \mathbf{N}_{(2)loc,36}^{(\alpha)} = \frac{10}{1944}\alpha^2 = 0.0051\alpha^2. \end{aligned} \quad (78)$$

It is seen that alterations in the neighboring bond orders resulting from the matrix  $\mathbf{N}_{(2)loc}^{(\alpha)}$  [ $\mathbf{N}_{(2)R}^{(\beta)}$ ] are of comparable absolute values for all bonds. Furthermore, the increase in the orders of bonds C<sub>2</sub>–C<sub>4</sub> and C<sub>3</sub>–C<sub>6</sub> of pyridine is twice as large as the decrease in the remaining bond orders. This conclusion perfectly illustrates the energy-free nature of the relevant contribution. Coincidence of the above-enumerated trends to those following from the *para*-quinoidal structure is also evident.

The last example concerns the quinoline and binaphthyl molecules representing the more involved systems. Discussion of this example would closely resemble the previous ones. In this connection, let us confine ourselves to consideration of second-order matrices  $\mathbf{M}_{(2)loc}^{(\alpha)}$  [ $\mathbf{M}_{(2)R}^{(\beta)}$ ] and  $\mathbf{N}_{(2)loc}^{(\alpha)}$  [ $\mathbf{N}_{(2)R}^{(\beta)}$ ]. Elements of the former are as follows:

$$\begin{aligned} \mathbf{M}_{(2)loc,17}^{(\alpha)} &= -0.0723\alpha^2, & \mathbf{M}_{(2)loc,18}^{(\alpha)} &= -0.0401\alpha^2, \\ \mathbf{M}_{(2)loc,27}^{(\alpha)} &= 0.0115\alpha^2, & \mathbf{M}_{(2)loc,26}^{(\alpha)} &= -0.0092\alpha^2, \\ \mathbf{M}_{(2)loc,36}^{(\alpha)} &= -0.0045\alpha^2, & \mathbf{M}_{(2)loc,38}^{(\alpha)} &= 0.0035\alpha^2, \\ \mathbf{M}_{(2)loc,3,10}^{(\alpha)} &= 0.0016\alpha^2, & \mathbf{M}_{(2)loc,4,10}^{(\alpha)} &= -0.0017\alpha^2, \\ \mathbf{M}_{(2)loc,49}^{(\alpha)} &= 0.0022\alpha^2, & \mathbf{M}_{(2)loc,59}^{(\alpha)} &= -0.0050\alpha^2, \\ \mathbf{M}_{(2)loc,58}^{(\alpha)} &= 0.0080\alpha^2 \end{aligned} \quad (79)$$

where the subscripts refer to numbers of AOs of quinoline. It is seen that the principal aspect of the relevant effect consists in lowering of orders of bonds N<sub>1</sub>–C<sub>7</sub> and N<sub>1</sub>–C<sub>8</sub>, i.e., of those attached to the site

of perturbation. Moreover, the mean absolute value of the relevant alterations (equal to 0.056) is close to the respective value for pyridine and biphenyl seen in Eq. (77). Thus, the essentially local nature of the effect is supported for more involved systems too. So far as the remaining alterations are concerned, the *para*-quinoidal structure reveals itself in the ring undergoing the perturbation and a particular Kekule structure corresponding to strengthening of the bonds C<sub>3</sub>–C<sub>10</sub>, C<sub>4</sub>–C<sub>9</sub>, and C<sub>5</sub>–C<sub>8</sub> manifests itself in the another ring of quinoline. An analogous conclusion follows also in the case of binaphthyl. The respective elements of the matrix  $\mathbf{N}_{(2)loc}^{(\alpha)}(\mathbf{N}_{(2)R}^{(\beta)})$  are as follows:

$$\begin{aligned} \mathbf{N}_{(2)loc,17}^{(\alpha)} &= -0.0026\alpha^2, & \mathbf{N}_{(2)loc,18}^{(\alpha)} &= -0.0103\alpha^2, \\ \mathbf{N}_{(2)loc,27}^{(\alpha)} &= 0.0093\alpha^2, & \mathbf{N}_{(2)loc,26}^{(\alpha)} &= -0.0049\alpha^2, \\ \mathbf{N}_{(2)loc,36}^{(\alpha)} &= -0.0005\alpha^2, & \mathbf{N}_{(2)loc,38}^{(\alpha)} &= 0.0026\alpha^2, \\ \mathbf{N}_{(2)loc,3,10}^{(\alpha)} &= -0.0018\alpha^2, & \mathbf{N}_{(2)loc,4,10}^{(\alpha)} &= 0.0019\alpha^2, \\ \mathbf{N}_{(2)loc,49}^{(\alpha)} &= -0.0012\alpha^2, & \mathbf{N}_{(2)loc,59}^{(\alpha)} &= -0.0015\alpha^2, \\ \mathbf{N}_{(2)loc,58}^{(\alpha)} &= 0.0090\alpha^2. & & (80) \end{aligned}$$

Two *para*-quinoidal structures may be revealed after analysis of these elements, the first one resulting into strengthening of bonds C<sub>2</sub>–C<sub>7</sub> and C<sub>3</sub>–C<sub>8</sub> and the second one manifesting itself as growing orders of bonds C<sub>5</sub>–C<sub>8</sub> and C<sub>4</sub>–C<sub>10</sub>. A significant lowering of the order of the C<sub>1</sub>–C<sub>8</sub> bond, in turn, is in line with strengthening of the two adjacent bonds, viz. of C<sub>3</sub>–C<sub>8</sub> and C<sub>5</sub>–C<sub>8</sub>. It should also be added here that the total value of positive alterations coincides with the total absolute value of negative changes in accordance with the energy-free nature of the effect.

## Conclusions

The second-order corrections to CBO matrices of PAHs determine the following aspects of electronic structures of these compounds: (i) Alterations in bond orders of chemically bound pairs of atoms vs. their initial values in parent AHs of both destabilizing and energy-free nature; (ii) The two-fold reduction of the stabilization energy vs. the primary stabilizing increment of perturbation; (iii) Additivity of the final stabilization energy of PAHs with respect to increments of individual chemical bonds; (iv) Concentration of the stabilizing component of

the total energy alteration on the site of perturbation accompanied by destabilization of the remaining part of the molecule.

The principal peculiarities of the second-order corrections to CBO matrices of PAHs are as follows: (i) These corrections are expressible in terms of respective first-order corrections and may be considered as describing the secondary consequences of perturbation, (ii) The second-order corrections are energetically coupled with the first-order ones, viz. the more extended effects originate from the latter, the more noticeable consequences of the former may be expected with respect to energy increments; and (iii) The second-order corrections exhibit a large extent of similarity for heteroaromatic compounds and for composite hydrocarbons.

The last of the above-mentioned peculiarities of second-order corrections determines resemblance between electronic structures of PAHs originating from the same parent AHs that embraces (i) similar alterations in the orders of chemical bonds, (ii) mutually proportional stabilization energies, and (iii) coinciding values of self-polarizabilities for the atom under perturbation and for the newly emerging bond.

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