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Perturbative Analogue for the Concept of Conjugated Circuits in Benzenoid Hydrocarbons

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Abstract

The study contains an application to individual Kekulé valence structures of benzenoid hydrocarbons of the general form of power series for total energies of molecules obtained previously by means of the so-called non-commutative Rayleigh-Schrödinger perturbation theory, as well as an additional derivation of expressions for energy corrections of the fifth order. The structures concerned are modeled as sets of weakly-interacting initially-double (C=C) bonds, bonding and anti-bonding orbitals of which play the role of basis functions. Accordingly, the averaged resonance parameter of initially-single (C-C) bonds is chosen to underly the energy expansion. The main aim of the study consists in revealing an anticipated interrelation between the above-specified perturbative approach to relative stabilities of separate Kekulé valence structures and the well-known models based on the concept of conjugated circuits (CC). It is shown that the principal properties of the power series for total energies resemble those of the CC models. This especially refers to additivity of contributions of individual circuits to the relevant total energy and to their extinction when the size of the circuit grows. On this basis, the approach suggested is concluded to offer a perturbative analogue for the concept of conjugated circuits in benzenoid hydrocarbons and thereby a new justification of the CC model(s). An additional discriminative potential of the approach applied vs. the CC model(s) also is concluded by demonstrating distinct total energies for Kekulé valence structures of the same composition in terms of conjugated circuits. The simplest hydrocarbons are considered in a detail as examples, viz. naphthalene, anthracene and phenanthrene.

1 Introduction

The concept of conjugated circuits has been introduced more than thirty years ago [1-3] and since then it is under an extensive development [4-13]. Nowadays this concept

plays an important role in the branch of theoretical chemistry concerning polycyclic benzenoid and non-benzenoid hydrocarbons [14]. Numerous fields of successful applications of conjugated-circuits-based (CC) model(s) may be mentioned, e.g. establishing of relative "weights" of individual Kekulé valence structures in the formation of the overall stability of a certain hydrocarbon, classification of polycyclic benzenoids, characterization of the so-called local aromaticity in extended compounds, etc. The most outstanding achievement, however, consists in evaluations of the molecular resonance energies. Additivity of this crucial energetic characteristic with respect to transferable increments of individual conjugated circuits R_n and/or Q_n $(n = 1, 2, 3...)$ and a considerable extinction of absolute values of these increments when the size of the circuit (n) grows are the most essential features of the models under discussion in the context of the present study. [Note that R_n and/or Q_n stand for circuits containing $4n + 2$ and $4n$ electrons, respectively, so that R_1 coincides with a single Kekulé valence structure of benzene, R_2 embraces five C=C and five C-C bonds alternately, etc.]. The above-described success of the CC model, in turn, stimulated studies of its quantum-chemical foundation [15-20]. The focus of attention here was the derivation of the model concerned from the Valence Bond (VB) theory, in particular from its Pauling-Wheland version. Some limitations of the standard CC model also have been reported [13, 21, 22]. Difficulties with discriminating between distinct structures containing the same sets of conjugated circuits [21] is among the most self-evident of these limitations.

Recently, a new perturbative approach [23] has been suggested to evaluate relative stabilities of pi-electron systems of conjugated hydrocarbons that has been considered as an alternative to the standard perturbational molecular orbital (PMO) theory [24]. The systems under interest have been modelled by sets of weakly interacting initially-double (C=C) bonds in this approach. Accordingly, the total energy of such a system $(\mathcal{E})$ has been expressed in the form of power series, i.e. as a sum of steadily diminishing increments $\mathcal{E}_{(k)}$ of various orders (k) with respect to an averaged resonance parameter (γ) representing the weak (initially-single) C-C bonds. Analysis of this series for some model systems [23, 25, 26] showed that the higher is the order parameter (k), the more extended fragment of the whole system is embraced by the given increment $\mathcal{E}_{(k)}$. Finally, a certain set of self-returning pathways via k basis orbitals specified below were shown to correspond to each energy correction $\mathcal{E}_{(k)}$. To a certain extent, these principal properties of the perturbative expansion for the total energy resemble those of the CC model. This especially refers to the above-discussed additivity and extinction of separate contributions to the molecular stability. It also deserves adding here that individual Kekulé

valence structures of polycyclic hydrocarbons (the concept of conjugated circuits is actually applied to) evidently may be regarded as systems consisting of weakly-interacting C=C bonds. All these circumstances give us a hint that the two approaches under discussion are somehow interrelated. Such a relation (if revealed) is likely to provide us with a perturbative analogue of conjugated circuits and thereby with a new account for the above-described success of this simple intuition-based concept. A resulting feasibility of distinguishing between structures containing uniform sets of conjugated circuits also cannot be excluded. The present study pursues just these aims.

It deserves an immediate emphasizing, however, that because of essential methodological distinctions between the two approaches outlined below, there are no grounds for expecting either a straightforward parallelism or a simple one-to-one correspondence between individual terms of the power series $\mathcal{E}_{(k)}$, on the one hand, and increments of particular conjugated circuits R_n and/or Q_n, on the other hand. Quite the reverse, a non-trivial nature of the relation under our search may be foreseen. Indeed, the series for total energies of Ref.[23] is formulated in the basis of bonding and anti-bonding orbitals of C=C bonds only that are further referred to as bond orbitals (BOs) as usual. As a result, two and zero basis orbitals are correspondingly ascribed to each C=C and to each C-C bond in the perturbative approach so that no one-to-one correspondence may be generally expected between pathways via basis orbitals and those via chemical bonds. Furthermore, numerous pathways of a non-cyclic (toward-backward) nature have been established to underly the increments $\mathcal{E}_{(k)}$ [25,26] along with the cyclic (roundabout) ones. Therefore, exhaustive studies seem to be actually required to formulate a perturbative analogue for the concept of conjugated circuits in general. As an initial stage of such a work, we will confine ourselves to benzenoid hydrocarbons and thereby to conjugated circuits of the 4n+2 series (R_n) in this study [Note that circuits of the 4n series (Q_n) are absent in benzenoids as proven in [6]].

The paper starts with an overview of the principal expressions of the perturbative approach and interpretation of separate members of the power series for total energies ($\mathcal{E}_{(k)}$) in terms of self-returning pathways via the above-defined BOs. Thereupon, we turn to analysis of increments $\mathcal{E}_{(k)}$ for individual conjugated circuits (R_n) in Section 3. The last Sections (4 and 5) are devoted to specific benzenoid hydrocarbons. The Appendix contains a derivation of algebraic expressions applied.

2 The principal expressions of the perturbative approach. Interpretation of energy increments in terms of self-returning pathways

The approach of Ref.[23] was based on application to the case of conjugated hydrocarbons of the general form of power series for total energies ($\mathcal{E}$) derived previously [27] by means of the so-called non-commutative Rayleigh-Schrödinger perturbation theory (NCRSPT) [28-30] (see also the Appendix). As already mentioned, conjugated hydrocarbons were defined as systems of weakly-interacting initially-double (C=C) bonds. Thus, individual Kekulé valence structures of benzenoids are embraced by this definition. Again, both benzenoid hydrocarbons and their separate Kekulé valence structures are known to belong to even alternant systems. The above-enumerated points will be taken into consideration when constructing the relevant Hückel type Hamiltonian matrix ($\mathbf{H}$).

Let us consider a certain Kekulé valence structure of a benzenoid hydrocarbon that is initially represented by an $2N-$dimensional basis set of $2p_z$ AOs of carbon atoms $\{\chi\}$, where N stands for the total number of C=C bonds. These AOs will be assumed to be characterized by uniform Coulomb parameters (α) as usual and the equality $\alpha = 0$ will be accepted. As it is the case in the standard Hückel model, resonance parameters between AOs of chemically bound pairs of atoms only will be assumed to take non-zero values. Further, let the basis set $\{\chi\}$ to be divided into two N-dimensional subsets $\{\chi^*\}$ and $\{\chi^\circ\}$ so that pairs of orbitals belonging to any chemical bond (C=C or C-C) find themselves in the different subsets. This implies all non-zero resonance parameters representing chemical bonds to take place in the off-diagonal (inter-subset) blocks of the Hamiltonian matrix ($\mathbf{H}$). Accordingly, zero sub-matrices stand in the two diagonal (intra-subset) positions of the matrix $\mathbf{H}$ as it is peculiar to alternant systems in general [31,32]. Finally, let us enumerate the basis functions in such a way that orbitals belonging to the same C=C bond acquire the coupled numbers i and $N + i$. As a result, resonance parameters of these strong bonds take the diagonal positions in the inter-subset blocks of the Hamiltonian matrix $\mathbf{H}$. Uniform values of these parameters (β) also is among natural assumptions here. Let our (negative) energy unit to coincide with β in addition. The usual equality $\beta = 1$ then immediately follows. Similarly, the averaged resonance parameter of weak (C-C) bonds will be denoted by γ and supposed to be a first order term vs. the above-specified energy unit.

In summary, Hamiltonian matrices of our Kekulé valence structures of benzenoids ($\mathbf{H}$) take a common form that may be represented as a sum of zero ($\mathbf{H}_{(0)}$) and first order

matrices ($\mathbf{H}_{(1)}$) including parameters of C=C and C-C bonds, respectively, viz.

$$\mathbf{H} = \mathbf{H}_{(0)} + \mathbf{H}_{(1)} = \left| \begin{array}{cc} \mathbf{0} & \mathbf{I} \\ \mathbf{I} & \mathbf{0} \end{array} \right| + \left| \begin{array}{cc} \mathbf{0} & \gamma\mathbf{B} \\ \gamma\mathbf{B}^{+} & \mathbf{0} \end{array} \right|, \tag{1}$$

where $\mathbf{I}$ here and below stands for the unit matrix and the superscript + designates the Hermitian-conjugate (transposed) matrix. It deserves adding here that unit off-diagonal elements of the sub-matrix $\mathbf{B}$ ($B_{ij} = 1, i \neq j$) correspond to C-C bonds, otherwise these take zero values. Meanwhile, the diagonal elements of the same sub-matrix (B_{ii}) vanish because entire resonance parameters of C=C bonds are included into the zero order matrix $\mathbf{H}_{(0)}$.

Let us turn now to the above-discussed basis of bond orbitals (BOs) $\{\varphi\}$ consisting of bonding and anti-bonding orbitals of C=C bonds further abbreviated as BBOs and ABOs, respectively. These orbitals will be correspondingly defined as normalized sums and differences of pairs of AOs involved in these bonds (i.e. χ_i^* and χ_{N+i}°). Passing from the basis of AOs $\{\chi\}$ to that of BOs $\{\varphi\}$ may be then represented by the following simple unitary transformation matrix

$$\mathbf{U} = \frac{1}{\sqrt{2}} \left| \begin{array}{cc} \mathbf{I} & \mathbf{I} \\ \mathbf{I} & -\mathbf{I} \end{array} \right|. \tag{2}$$

Application of this transformation to the Hamiltonian matrix $\mathbf{H}$ of Eq.(1) yields a new matrix $\mathbf{H}'$ of the following form

$$\mathbf{H}' = \mathbf{H}'_{(0)} + \mathbf{H}'_{(1)} = \left| \begin{array}{cc} \mathbf{I} & \mathbf{0} \\ \mathbf{0} & -\mathbf{I} \end{array} \right| + \left| \begin{array}{cc} \mathbf{S} & \mathbf{R} \\ \mathbf{R}^{+} & \mathbf{Q} \end{array} \right|, \tag{3}$$

where

$$\mathbf{S} = -\mathbf{Q} = \frac{\gamma}{2}(\mathbf{B} + \mathbf{B}^{+}), \qquad \mathbf{R} = \frac{\gamma}{2}(\mathbf{B}^{+} - \mathbf{B}), \tag{4}$$

and

$$S_{ii} = Q_{ii} = R_{ii} = 0 \tag{5}$$

for any i. Besides, equalities

$$\mathbf{S}^{+} = \mathbf{S}, \qquad \mathbf{Q}^{+} = \mathbf{Q}, \qquad \mathbf{R}^{+} = -\mathbf{R} \tag{6}$$

easily follow from Eq.(4) and indicate symmetric (Hermitian) and skew-symmetric (skew-Hermitian) natures of matrices $\mathbf{S}(\mathbf{Q})$ and $\mathbf{R}$, respectively.

Comparison of Eq.(3) to Eqs.(A1) and (A10) shows the transformed Hamiltonian matrix $\mathbf{H}'$ to be embraced by that of homogeneous systems defined in the Appendix. This allows the relevant formulas for separate members of power series for total energies

$\mathcal{E}_{(k)}$ $(k = 0, 1, 2, ...)$ to be straightforwardly applied to the present case of Kekulé valence structures of benzenoids. Individual members of the series are then expressible as follows:

i) The zero and first order members take system- structure- independent forms, viz.

$$\mathcal{E}_{(0)} = 2N, \qquad \mathcal{E}_{(1)} = 0; \tag{7}$$

ii) The second and third order energy corrections contain simple products of the principal matrices of the NCRSPT [27,28] of the first $(\mathbf{G}_{(1)})$ and of the second order $(\mathbf{G}_{(2)})$, viz.

$$\mathcal{E}_{(2)} = 4Trace(\mathbf{G}_{(1)}\mathbf{G}^{+}_{(1)}), \qquad \mathcal{E}_{(3)} = 4Trace(\mathbf{G}_{(2)}\mathbf{G}^{+}_{(1)}), \tag{8}$$

where

$$\mathbf{G}_{(1)} = -\frac{1}{2}\mathbf{R}, \quad \mathbf{G}_{(2)} = \frac{1}{4}(\mathbf{SR} - \mathbf{RQ}) = \frac{1}{4}(\mathbf{SR} + \mathbf{RS}), \tag{9}$$

the last relation being based on coincidence between $\mathbf{Q}$ and $-\mathbf{S}$ for alternant systems seen from Eq.(4);

iii) The fourth and fifth order members of the same series ($\mathcal{E}_{(4)}$ and $\mathcal{E}_{(5)}$) may be conveniently represented via certain supplementary third order matrices $\widetilde{\mathbf{G}}_{(3)}$ and $\overline{\mathbf{G}}_{(3)}$, respectively, as follows

$$\mathcal{E}_{(4)} = 4Trace(\widetilde{\mathbf{G}}_{(3)}\mathbf{G}^{+}_{(1)}), \qquad \mathcal{E}_{(5)} = 4Trace(\overline{\mathbf{G}}_{(3)}\mathbf{G}^{+}_{(2)}), \tag{10}$$

where

$$\widetilde{\mathbf{G}}_{(3)} = \mathbf{G}_{(3)} + \mathbf{G}_{(1)}\mathbf{G}^{+}_{(1)}\mathbf{G}_{(1)}, \quad \overline{\mathbf{G}}_{(3)} = \mathbf{G}_{(3)} - \mathbf{G}_{(1)}\mathbf{G}^{+}_{(1)}\mathbf{G}_{(1)} \tag{11}$$

and $\mathbf{G}_{(3)}$ is the principal third order matrix of the NCRSPT [27]. In our case, this matrix takes the form

$$\mathbf{G}_{(3)} = -\frac{1}{8}[(\mathbf{S})^2\mathbf{R} + 2\mathbf{SRS} + \mathbf{R}(\mathbf{S})^2] - \frac{1}{4}(\mathbf{R})^3. \tag{12}$$

Alternative expressions for matrices $\widetilde{\mathbf{G}}_{(3)}$ and $\overline{\mathbf{G}}_{(3)}$ also is possible, viz.

$$\begin{aligned} \widetilde{\mathbf{G}}_{(3)} &= -\frac{1}{2}(\mathbf{SG}_{(2)} + \mathbf{G}_{(2)}\mathbf{S}) - \mathbf{G}_{(1)}\mathbf{G}^{+}_{(1)}\mathbf{G}_{(1)}, \\ \overline{\mathbf{G}}_{(3)} &= -\frac{1}{2}(\mathbf{SG}_{(2)} + \mathbf{G}_{(2)}\mathbf{S}) - 3\mathbf{G}_{(1)}\mathbf{G}^{+}_{(1)}\mathbf{G}_{(1)}. \end{aligned} \tag{13}$$

Derivation of the principal formulas of Eqs.(7)-(13) is discussed in the Appendix in a detail. It also deserves adding here that energy corrections $\mathcal{E}_{(k)}$ of Eqs.(8) and (10) are alternatively representable as sums of increments of individual C=C bonds $\varepsilon_{(k)I}, I = 1, 2...N$, viz.

$$\mathcal{E}_{(k)} = \sum_{I} \varepsilon_{(k)I}, \tag{14}$$

where

$$\varepsilon_{(2)I} = 4\sum_{(-)l}(G_{(1)il})^2, \quad \varepsilon_{(3)I} = 4\sum_{(-)l} G_{(2)il}G^{+}_{(1)li}, \quad etc. \tag{15}$$

Notations $G_{(k)il}$ stand here for particular elements of matrices $\mathbf{G}_{(k)}$, the subscripts i and l referring to a BBO and to an ABO, respectively. These subscripts may be conveniently ascribed to the relevant C=C bonds. Let BBOs and ABOs to be additionally denoted by subscripts (+) and (-), respectively. The element $G_{(k)il}$ then connects the BBO of the Ith bond $\varphi_{(+)i}$ and ABOs of other (Lth) bonds $\varphi_{(-)l}$.

Let us turn now to interpretation of the above-exhibited formulas. Let us start with matrix elements $G_{(k)il}$ following from Eqs.(9) and (12). The first order element ($G_{(1)il}$) is proportional to the relevant resonance parameter (R_{il}) and inversely proportional to the inter-subset energy gap (2) as the first relation of Eq.(9) shows. Consequently, this element represents the direct (through-space) interaction between the BBO $\varphi_{(+)i}$ and the ABO $\varphi_{(-)l}$. It is also evident that non-zero elements $G_{(1)il}$ correspond to pairs of first-neighboring C=C bonds only (C=C bonds connected by a C-C bond are regarded here as first-neighboring). Besides, equalities $R_{ii} = 0$ (see Eq.(5)) ensure zero values of direct intrabond interactions $G_{(1)ii}$. Further, the second order elements $G_{(2)il}$ are accordingly interpretable as indirect (through-bond) interactions of the same BOs. Indeed, from Eq.(9) we obtain

$$G_{(2)il} = \frac{1}{4}\left[\sum_{(+)j} S_{ij}R_{jl} - \sum_{(-)m} R_{im}Q_{ml}\right], \tag{16}$$

where sums over $(+)j$ and over $(-)m$ correspondingly embrace all BBOs and all ABOs of the given system. It is seen that both BBOs ($\varphi_{(+)j}$) and ABOs ($\varphi_{(-)m}$) of other bonds play the role of mediators of the second order interaction between orbitals $\varphi_{(+)i}$ and $\varphi_{(-)l}$. Moreover, the orbitals $\varphi_{(+)j}$ and $\varphi_{(-)m}$ should overlap directly both with $\varphi_{(+)i}$ and with $\varphi_{(-)l}$ to be efficient mediators. That is why non-zero indirect interactions correspond to pairs of second-neighboring C=C bonds possessing a common first neighbor. Analogously, the third order elements $G_{(3)il}$ may be shown to represent the indirect interactions of the same BOs $\varphi_{(+)i}$ and $\varphi_{(-)l}$ by means of two mediators. Generally, the total number of mediators of any element of kth order ($G_{(k)il}$) coincides with $k-1$. It also deserves adding here that matrices $\mathbf{G}_{(k)}$ may be easily shown to be skew-Hermitian (skew-symmetric) ones for alternant systems [33] as it was the case with the matrix $\mathbf{R}$ (see Eq.(6)). This implies zero values of diagonal elements $G_{(k)ii}$ and thereby vanishing intrabond interactions of any order to be peculiar to these systems.

Let us turn now to energy corrections of Eqs.(8) and (10). The following rule results

immediately from these expressions: The correction $\mathcal{E}_{(k)}$ takes a non-zero value, if there is at least a single pair of orbitals $\varphi_{(+)i}$ and $\varphi_{(-)l}$ that interact both directly and indirectly by means of $k-1$ mediators [Note that the fifth order correction $\mathcal{E}_{(5)}$ is alternatively expressible in terms of first and fourth order matrices as shown in the Appendix (see Eq.(A13)]. In other words, pairs of orbitals $\varphi_{(+)i}$ and $\varphi_{(-)l}$ characterized by non-zero matrix elements $G_{(1)il}$ and $G_{(k-1)il}$ are able to contribute to the kth order energy $\mathcal{E}_{(k)}$. It is also evident that the pair of basis functions concerned contributes to stabilization (destabilization) of the system, if the above-mentioned interactions are of the same (opposite) signs (see also Ref.[34]). This statement will be further referred to as the first rule.

Let us now invoke the expressions for $G_{(k)il}$ (and/or $\widetilde{G}_{(k)il}$ and $\overline{G}_{(k)il}$) via elements of matrices **S** and **R** resulting from Eqs.(9) and (12). Let individual elements of the latter (resonance parameters) to be explicitly expressed as follows

$$S_{ij} =< \varphi_{(+)i} \mid \widehat{H} \mid \varphi_{(+)j} >, \qquad R_{il} =< \varphi_{(+)i} \mid \widehat{H} \mid \varphi_{(-)l} >, \tag{17}$$

where the basis orbitals concerned are shown inside the bra- and ket-vectors. An element $G_{(k)il}$ then takes a non-zero value, if there is at least a single non-zero product of resonance parameters, i.e.

$$< \varphi_{(+)i} \mid \widehat{H} \mid \varphi_1 >< \varphi_1 \mid \widehat{H} \mid \varphi_2 > ... < \varphi_{k-2} \mid \widehat{H} \mid \varphi_{k-1} >< \varphi_{k-1} \mid \widehat{H} \mid \varphi_{(-)l} > \neq 0, \tag{18}$$

where the notations $\varphi_1, \varphi_2, ...\varphi_{k-1}$ stand for mediating orbitals. Given that the condition of Eq.(18) is met, we will say that in the given system there is a pathway of the (k-1)th order between BOs $\varphi_{(+)i}$ and $\varphi_{(-)l}$. It also deserves emphasizing that steps inside the same C=C bond are not allowed in this pathway owing to equalities $S_{ii} = R_{ii} = 0$ of Eq.(5).

Let us turn now to contribution of the Ith C=C bond ($\varepsilon_{(k)I}$) to the energy $\mathcal{E}_{(k)}$. As is seen from Eq.(15), this contribution is determined by products of pathways of the first and of the (k-1)th orders embracing the BBO of the given (i.e. Ith) bond ($\varphi_{(+)i}$) and ABOs of the remaining bonds ($\varphi_{(-)l}$). Analogously, pathways of the second and (k-2)th orders may be used in interpretation of $\varepsilon_{(k)I}$ by invoking the relations like those of Eqs.(A15) and (A16). Hence, we may define a self-returning pathway of the kth order both starting and terminating at the BBO $\varphi_{(+)i}$ and embracing the ABO $\varphi_{(-)l}$. This pathway is able to replace products of two linear pathways. On this basis, the second rule may be formulated: The contribution of the Ith bond ($\varepsilon_{(k)I}$) to the kth order energy ($\mathcal{E}_{(k)}$) takes a non-zero value if there is at least a single bond (say, the Lth one), the

ABO of which participates in a self-returning pathway of the kth order both starting and terminating at the BBO $\varphi_{(+)i}$.

In the case of Kekulé valence structures of benzenoids, we have to do with cycles consisting of C=C and C-C bonds alternately (conjugated circuits). Thus, some additional definitions concerning self-returning pathways for just this specific case seem to be expedient. In particular, the so-called roundabout pathway [25] may be defined as a pathway which embraces the whole cycle in a clockwise or anticlockwise fashion so that any C=C bond is visited only once. Otherwise, we will have to do with a pathway of "toward-backward" nature, which embraces a certain linear fragment of the cycle and seems to be an analogue of a conjugated path [14,35].

Using the above rules and definitions, we can make some general observations regarding members of the power series for total energies of separate Kekulé valence structures of benzenoids. Let us note first that the conjugated circuits R_n ($n = 1, 2, 3...$) present in these systems contain odd numbers of C=C bonds $(3, 5, ..)$. This implies that roundabout pathways over these circuits also are of odd orders and thereby these are able to participate in the formation of energy corrections of odd orders only, viz. $\mathcal{E}_{(3)}$, $\mathcal{E}_{(5)}$, etc. Hence, just these corrections may be foreseen to reflect the presence of conjugated circuits R_n most directly. On the other hand, self-returning pathways of the "toward-backward" nature also are possible in benzenoids and these necessarily are of even orders. Thus, non-zero values of energy increments of even orders also is among expectations.

Let us now dwell on individual corrections $\mathcal{E}_{(k)}$. It is evident that any C-C bond ensures self-returning pathways of the second order referring to BBOs of the adjacent C=C bonds whatever the whole structure of the given system. Hence, a non-zero transferable increment to the overall second order energy ($\mathcal{E}_{(2)}$) originates from any C-C bond. Accordingly, the total value of the second order energy becomes proportional to the number of these bonds (Note that both separate increments and the final correction $\mathcal{E}_{(2)}$ are positive quantities as Eq.(15) indicates). Consequently, different Kekulé valence structures of the same hydrocarbon may be predicted to be characterized by coinciding values of second order energies. Meanwhile, pairs of C=C bonds, the orbitals of which interact both directly and indirectly by means of a single mediator are required to ensure a non-vanishing value of the third order energy $\mathcal{E}_{(3)}$. An alternative form of the same condition consists in the presence of at least a single self-returning pathway of the third order in the given system. It is evident that roundabout pathways over any conjugated circuit R_1 meet this condition. Thus, both presence of these principal circuits and their total number seem to play the decisive role in the formation of the third order energy. This anticipation may be sup-

ported by the non-zero third order energy of a single Kekulé structure of benzene [23]. By contrast, no cycles are required to ensure a non-zero value of the fourth order energy $\mathcal{E}_{(4)}$. In particular, a two-fold realization of a pathway of the second order embracing a certain C-C bond yields a non-zero fourth order energy increment. Furthermore, pathways of the fourth order of the "toward-backward" nature contribute to $\mathcal{E}_{(4)}$, wherein both first- and second-neighboring C=C bonds relatively to the Ith one are involved. In this respect, a certain analogy reveals itself between formations of second and fourth order energies. On the other hand, essential differences between these energies also deserve attention. In particular, the mutual arrangement of the embraced C=C bonds playes an important role in the case of the fourth order energy in contrast to the second order one. It is no surprise in this connection that the fourth order energy corrections $\mathcal{E}_{(4)}$ were shown to take distinct values for isomers of dienes containing the same numbers of both C=C and C-C bonds but different types of branching [23]. Since the second neighborhood of the given (say Ith) C=C bond generally changes due to cyclization (e.g. when passing from a linear hexadiene-like fragment to a circuit R_1), a certain dependence of relative values of the energy corrections $\mathcal{E}_{(4)}$ upon the numbers of individual conjugated circuits (R_n) of the given system also may be foreseen. The fifth order energy ($\mathcal{E}_{(5)}$), again, resembles the third order one ($\mathcal{E}_{(3)}$) in respect of participation of roundabout pathways over conjugated circuits. It is evident that the circuits R_2 containing five C=C bonds play now the role of the principal contributors. Nevertheless, the former circuits R_1 also are able to provide self-returning pathways of the fifth order and thereby to contribute to the fifth order energy. For example, combination of the roundabout pathway over the circuit R_1 and of an additional pathway of the second order like that underlying the second order energy (as discussed above) makes up a self-returning pathway of the fifth order. Consequently, the energy correction $\mathcal{E}_{(5)}$ seems to reflect the presence of both circuits R_1 and R_2.

3 Energy increments for isolated conjugated circuits

Simple linear chains consisting of C=C and C-C bonds alternately may be considered as parent systems of conjugated circuits. Thus, let us start with an application of the above-described perturbative approach just to these chains. Let the total number of C=C bonds of such a chain to be denoted by N as previously. The number of C-C bonds then accordingly equals to N-1. In accordance with the numbering of $2p_z$ AOs of carbon atoms $\{\chi\}$ underlying the matrix $\mathbf{H}$ of Eq.(1), atoms (AOs) of our chain will be enu-

merated in the following order: C_1=C_{N+1}-C_2=C_{N+2}-...-C_N=C_{2N}, where numbers 1,2...N and N+1, N+2...2N refer to subsets $\{\chi^*\}$ and $\{\chi^\circ\}$, respectively. As with Hamiltonian matrices of homogeneous chains in general, the matrices $\mathbf{B}$ of Eq.(1) are representable in our case in a common form embracing any N value. Let this unified matrix to be denoted by $\mathbf{B}(N)$ and note that it contains non-zero elements (equal to 1) just under the principal diagonal (i.e. in the positions (2,N+1), (3,N+2), etc.) and zero elements elsewhere, viz.

$$\mathbf{B}(N) = \begin{vmatrix} 0 & 0 & 0 & 0 & ... \\ 1 & 0 & 0 & 0 & ... \\ 0 & 1 & 0 & 0 & ... \\ 0 & 0 & 1 & 0 & ... \\ .. & .. & .. & .. & ... \end{vmatrix} \tag{19}$$

The above-exhibited common form of the matrix $\mathbf{B}(N)$, in turn, ensures a possibility of an analogous unified representation of both the related first order matrices $\mathbf{S}(N), \mathbf{R}(N)$ and $\mathbf{G}_{(1)}(N)$ and of those of higher orders. Indeed, substituting Eq. (19) into Eqs.(4), (9) and (11)-(13) yields the following expressions

$$\mathbf{G}_{(1)}(N) = -\frac{\gamma}{4}\begin{vmatrix} 0 & 1 & 0 & 0 & ... \\ -1 & 0 & 1 & 0 & ... \\ 0 & -1 & 0 & 1 & ... \\ 0 & 0 & -1 & 0 & ... \\ .. & .. & .. & .. & ... \end{vmatrix}, \quad \mathbf{G}_{(2)}(N) = \frac{\gamma^2}{8}\begin{vmatrix} 0 & 0 & 1 & 0 & 0 & .. \\ 0 & 0 & 0 & 1 & 0 & .. \\ -1 & 0 & 0 & 0 & 1 & .. \\ 0 & -1 & 0 & 0 & 0 & .. \\ .. & .. & .. & .. & .. & .. \end{vmatrix},$$

$$\widetilde{\mathbf{G}}_{(3)}(N) = -\frac{\gamma^3}{64}\begin{vmatrix} 0 & 0 & 0 & 5 & 0 & 0 & 0 & .. \\ 0 & 0 & 1 & 0 & 5 & 0 & 0 & .. \\ 0 & -1 & 0 & 1 & 0 & 5 & 0 & .. \\ -5 & 0 & -1 & 0 & 1 & 0 & 5 & .. \\ 0 & -5 & 0 & -1 & 0 & 1 & 0 & .. \\ .. & .. & .. & .. & .. & .. & .. & .. \end{vmatrix},$$

$$\overline{\mathbf{G}}_{(3)}(N) = \frac{\gamma^3}{64}\begin{vmatrix} 0 & 4 & 0 & -7 & 0 & 0 & 0 & .. \\ -4 & 0 & 5 & 0 & -7 & 0 & 0 & .. \\ 0 & -5 & 0 & 5 & 0 & -7 & 0 & .. \\ 7 & 0 & -5 & 0 & 5 & 0 & -7 & .. \\ 0 & 7 & 0 & -5 & 0 & 5 & 0 & .. \\ .. & .. & .. & .. & .. & .. & .. & .. \end{vmatrix}. \tag{20}$$

Finally, use of the above formulas along with Eqs.(8) and (10) results into general expressions for energy corrections $\mathcal{E}_{(k)}(N)$, viz.

$$\mathcal{E}_{(2)}(N) = \frac{\gamma^2}{2}(N-1), \quad \mathcal{E}_{(3)}(N) = 0, \quad \mathcal{E}_{(4)}(N) = \frac{\gamma^4}{32}(N-3), \quad \mathcal{E}_{(5)}(N) = 0. \tag{21}$$

[An important remark deserves to be made here: The common formulas of Eq.(20) for third order matrices $\widetilde{\mathbf{G}}_{(3)}(N)$ and $\overline{\mathbf{G}}_{(3)}(N)$ are valid for sufficiently long diene chains only

in contrast to expressions for $\mathbf{G}_{(1)}(N)$ and $\mathbf{G}_{(2)}(N)$. This fact, however, exerts no influence upon energy corrections shown in Eq.(21). For example, matrices $\widetilde{\mathbf{G}}_{(3)}(2), \widetilde{\mathbf{G}}_{(3)}(3), \widetilde{\mathbf{G}}_{(3)}(4)$ and $\widetilde{\mathbf{G}}_{(3)}(5)$ representing individual starting members of the diene series and exhibited below do not follow directly from general formulas of Eq.(20), viz.

$$\widetilde{\mathbf{G}}_{(3)}(2) = -\frac{\gamma^3}{64}\begin{vmatrix} 0 & -1 \\ 1 & 0 \end{vmatrix}, \quad \widetilde{\mathbf{G}}_{(3)}(3) = \mathbf{0}, \quad \widetilde{\mathbf{G}}_{(3)}(4) = -\frac{\gamma^3}{64}\begin{vmatrix} 0 & 0 & 0 & 5 \\ 0 & 0 & 1 & 0 \\ 0 & -1 & 0 & 0 \\ -5 & 0 & 0 & 0 \end{vmatrix},$$

$$\widetilde{\mathbf{G}}_{(3)}(5) = -\frac{\gamma^3}{64}\begin{vmatrix} 0 & 0 & 0 & 5 & 0 \\ 0 & 0 & 1 & 0 & 5 \\ 0 & -1 & 0 & 1 & 0 \\ -5 & 0 & -1 & 0 & 0 \\ 0 & -5 & 0 & 0 & 0 \end{vmatrix}, etc. \tag{22}$$

This result causes little surprise if we bear in mind that areas of irregular constitution correspond to terminal C=C bonds and to their nearest neighborhoods within matrices $\widetilde{\mathbf{G}}_{(3)}(N)$ of Eq.(20) and these bonds are not sufficiently separated one from another for small N values in addition. Nevertheless, substituting Eq.(22) into Eq.(10) yields fourth order energy corrections $\mathcal{E}_{(4)}(2), \mathcal{E}_{(4)}(3)$, $\mathcal{E}_{(4)}(4)$ and $\mathcal{E}_{(4)}(5)$ coinciding with those following from Eq.(21). The same refers also to the relevant fifth order corrections.]

Let us return again to Eq.(21). It is seen that the second order energy of our chains $\mathcal{E}_{(2)}(N)$ is a positive quantity proportional to the total number of C-C bonds (N-1), as expected in Section 2. The observation of the same Section about non-zero direct inter-orbital interactions corresponding to any C-C bond is now illustrated by the matrix $\mathbf{G}_{(1)}(N)$ of Eq.(20). Furthermore, vanishing energy increments of third and fifth orders ($\mathcal{E}_{(3)}(N)$ and $\mathcal{E}_{(5)}(N)$) also cause no surprise because of absence of self-returning pathways of odd orders in the linear chains. (Pathways of the toward-backward nature always are of even order as discussed in Section 2). An alternative accounting for zero values of both $\mathcal{E}_{(3)}(N)$ and $\mathcal{E}_{(5)}(N)$ follows from the first rule of Section 2. Indeed, pairs of matrices determining these energy corrections (viz. $\mathbf{G}_{(1)}(N)$ and $\mathbf{G}_{(2)}(N)$, as well as $\mathbf{G}_{(2)}(N)$ and $\overline{\mathbf{G}}_{(3)}(N)$ of Eq.(20)) contain non-zero elements in different positions so that products of the relevant direct and indirect inter-orbital interactions vanish. For example, non-zero elements correspond to pairs of second-neighboring C=C bonds in the matrix $\mathbf{G}_{(2)}(N)$ and to those of first-neighboring bonds within $\mathbf{G}_{(1)}(N)$. This implies that conditions $G_{(1)il} \neq 0$ and $G_{(2)il} \neq 0$ are not met simultaneously in the linear chains.

As discussed already in Section 2, no cycles are required for a non-zero value of the fourth order energy to arise. The correction $\mathcal{E}_{(4)}(N)$ of Eq.(21) is an excellent illustration of the above statement. Moreover, comparison of constitutions of matrices $\widetilde{\mathbf{G}}_{(3)}(N)$ and

$\mathbf{G}_{(1)}(N)$ is sufficient for interpretation of proportionality between $\mathcal{E}_{(4)}(N)$ and N-3. Indeed, non-zero elements correspond to all C-C bonds except for C_2-C_{N+1} and C_N-C_{2N-1} in the matrix $\widetilde{\mathbf{G}}_{(3)}(N)$, the total number of these bonds coinciding with N-3. Moreover, the same elements take non-zero values in the matrix $\mathbf{G}_{(1)}(N)$ too. Thus, a monotonous (linear) dependence of the correction $\mathcal{E}_{(4)}(N)$ upon the chain length (N) may be concluded. As opposed to the second order energy, however, the fourth order one changes its sign when the number of C=C bonds (N) grows. Indeed, the correction $\mathcal{E}_{(4)}(N)$ takes a negative value ($-\gamma^4/32$) for butadiene (N=2), vanishes for hexadiene (N=3) and becomes a positive quantity for higher N values (N=4,5...). This implies that long diene chains are stabilized relatively more as compared to the short ones. Finally, increments of individual C=C bonds to the total fourth order energy $\mathcal{E}_{(4)}(N)$ deserve some attention (see Eqs.(14) and (15)). These increments take distinct values for the 1st, 2nd and all the internal C=C bonds of a sufficiently long chain (these are 0, $\gamma^4/64$ and $\gamma^4/32$, respectively) and thereby demonstrate the role of the second neighborhoods of C=C bonds in the formation of fourth order energies. The above-specified dissimilarity of increments of individual C=C bonds, in turn, may be traced back to different numbers of self-returning pathways of the fourth order referring to the relevant BBOs (Pathways of the toward-backward nature are meant here). It is evident that the total number of these pathways grows when passing from a terminal C=C bond to an internal one and this ensures an increase of the relevant increment.

Let us now turn to a cyclic system containing an additional C-C bond between the terminal sites 1 and 2N of the former chain and representing a conjugated circuit of any size. This system will be denoted by R. As compared to the matrix $\mathbf{B}(N)$ of Eq.(19), the new matrix $\mathbf{B}(R,N)$ acquires an additional non-zero element at the upper right corner corresponding to the above-mentioned terminal positions. Accordingly, the new first order matrix $\mathbf{G}_{(1)}(R,N)$ contains non-zero elements in the upper right corner and in the lower left one, viz.

$$\mathbf{G}_{(1)}(R,N) = -\frac{\gamma}{4}\left|\begin{array}{ccccccccc} 0 & 1 & 0 & 0 & 0 & 0 & ... & 0 & -1 \\ -1 & 0 & 1 & 0 & 0 & 0 & ... & 0 & 0 \\ 0 & -1 & 0 & 1 & 0 & 0 & ... & 0 & 0 \\ 0 & 0 & -1 & 0 & 1 & 0 & ... & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 1 & ... & 0 & 0 \\ . & . & . & . & . & . & ... & . & . \\ 0 & 0 & 0 & 0 & 0 & 0 & ... & 0 & 1 \\ 1 & 0 & 0 & 0 & 0 & 0 & ... & -1 & 0 \end{array}\right| . \tag{23}$$

The new corner elements of the matrix $\mathbf{G}_{(1)}(R,N)$ give birth to additional non-zero elements in the relevant neighborhoods when building up matrices of higher orders

$\mathbf{G}_{(2)}(R,N)$, $\widetilde{\mathbf{G}}_{(3)}(R,N)$ and $\overline{\mathbf{G}}_{(3)}(R,N)$ as it was the case with matrices of Eq.(20). As a result, the overall dependence of common forms of these matrices upon the size of the circuit (N) becomes more cumbersome. The same may be expected to refer also to the relevant energy corrections. Inasmuch as we actually need the energy corrections for N=3,5 and 7 corresponding to the principal conjugated circuits of benzenoid hydrocarbons R_1, R_2 and R_3, respectively, we will dwell on each of these particular cases separately.

Let us start with the three-membered circuit R_1 coinciding with a single Kekulé valence structure of benzene. Matrices $\mathbf{G}_{(2)}(R_1)$, $\widetilde{\mathbf{G}}_{(3)}(R_1)$ and $\overline{\mathbf{G}}_{(3)}(R_1)$ prove to be proportional to the relevant parent matrix $\mathbf{G}_{(1)}(R,3)$ of Eq.(23), i.e.

$$\mathbf{G}_{(2)}(R_1) = \frac{\gamma}{2}\mathbf{G}_{(1)}(R_1), \quad \widetilde{\mathbf{G}}_{(3)}(R_1) = \frac{\gamma^2}{16}\mathbf{G}_{(1)}(R_1), \quad \overline{\mathbf{G}}_{(3)}(R_1) = -\frac{5\gamma^2}{16}\mathbf{G}_{(1)}(R_1), \tag{24}$$

where

$$\mathbf{G}_{(1)}(R_1) \equiv \mathbf{G}_{(1)}(R,3) = -\frac{\gamma}{4}\begin{vmatrix} 0 & 1 & -1 \\ -1 & 0 & 1 \\ 1 & -1 & 0 \end{vmatrix}. \tag{25}$$

It is seen that all inter-orbital interactions take non-zero values in this circuit. Moreover, interactions of different orders (k) are mutually proportional in this case. This result causes little surprise because of the highly regular structure of the circuit R_1, viz. all C=C bonds are adjacent here, all pairs of C=C bonds possess a common neighbor, etc. Proportionalities shown in Eq.(24), in turn, ensure non-zero values of all consequent energy corrections, as well as uniform contributions to these corrections originating from each C=C bond. Indeed, substituting Eqs.(24) and (25) into Eqs.(8) and (10) yield the following results

$$\mathcal{E}_{(2)}(R_1) = \frac{3\gamma^2}{2}, \quad \mathcal{E}_{(3)}(R_1) = \frac{3\gamma^3}{4}, \quad \mathcal{E}_{(4)}(R_1) = \frac{6\gamma^4}{64}, \quad \mathcal{E}_{(5)}(R_1) = -\frac{30\gamma^5}{128} \tag{26}$$

and

$$\varepsilon_{I(2)}(R_1) = \frac{\gamma^2}{2}, \quad \varepsilon_{I(3)}(R_1) = \frac{\gamma^3}{4}, \quad \varepsilon_{I(4)}(R_1) = \frac{2\gamma^4}{64}, \quad \varepsilon_{I(5)}(R_1) = -\frac{10\gamma^5}{128}, \tag{27}$$

where $\gamma^4/64$ and $\gamma^5/128$ are chosen here and below as "supplementary energy units" when discussing fourth and fifth order energies, respectively. [Such an agreement makes comparison of different corrections more convenient]. It is seen that members of the power series for the total energy of the circuit R_1 are positive quantities to within the fourth order inclusive. Meanwhile, the fifth order term of the same series takes a negative value owing to the minus sign in the right-hand side of the last relation of Eq.(24). Comparison of increments $\mathcal{E}_{(k)}(R_1)$ to the relevant reference values for hexadiene (these are γ^2, 0, 0 and 0 for k=2,3,4 and 5 as Eq.(21) shows) indicates an additional second, third and fourth

order stabilization to take place due to cyclization of the chain that is accompanied by destabilization of the fifth order. The growing second order energy of the circuit R_1 vs. hexadiene may be easily accounted for by emergence of a new C-C bond between the terminal atoms of the latter when passing to the cycle. The newly-formed third order energy of the circuit R_1 evidently arises owing to emergence of roundabout pathways of the third order over the cycle. This result is in line with expectations of Section 2. Emergence of a positive fourth order correction $\mathcal{E}_{(4)}(R_1)$, in turn, may be traced back to the fact that each C=C bond becomes an internal one when building up the circuit R_1 and thereby starts to contribute $2\gamma^4/64$ to the relevant fourth order energy in analogy with long dienes.

Let us turn now to a more extended cycle containing five C=C bonds (N=5) and coinciding with the conjugated circuit R_2. The relevant principal matrices $\mathbf{G}_{(2)}(R_2)$, $\widetilde{\mathbf{G}}_{(3)}(R_2)$ and $\overline{\mathbf{G}}_{(3)}(R_2)$ take the form

$$\begin{aligned}
\mathbf{G}_{(2)}(R_2) &= \frac{\gamma^2}{8}\begin{vmatrix} 0 & 0 & 1 & -1 & 0 \\ 0 & 0 & 0 & 1 & -1 \\ -1 & 0 & 0 & 0 & 1 \\ 1 & -1 & 0 & 0 & 0 \\ 0 & 1 & -1 & 0 & 0 \end{vmatrix}, \\
\widetilde{\mathbf{G}}_{(3)}(R_2) &= -\frac{\gamma^3}{64}\begin{vmatrix} 0 & 1 & -5 & 5 & -1 \\ -1 & 0 & 1 & -5 & 5 \\ 5 & -1 & 0 & 1 & -5 \\ -5 & 5 & -1 & 0 & 1 \\ 1 & -5 & 5 & -1 & 0 \end{vmatrix}, \\
\overline{\mathbf{G}}_{(3)}(R_2) &= \frac{\gamma^3}{64}\begin{vmatrix} 0 & 5 & 7 & -7 & -5 \\ -5 & 0 & 5 & 7 & -7 \\ -7 & -5 & 0 & 5 & 7 \\ 7 & -7 & -5 & 0 & 5 \\ 5 & 7 & -7 & -5 & 0 \end{vmatrix}
\end{aligned} \tag{28}$$

and prove to be no longer proportional to the first order matrix $\mathbf{G}_{(1)}(R_2)$ following from Eq.(23). The consequent energy corrections are then as follows

$$\mathcal{E}_{(2)}(R_2) = \frac{5\gamma^2}{2}, \quad \mathcal{E}_{(3)}(R_2) = 0, \quad \mathcal{E}_{(4)}(R_2) = \frac{10\gamma^4}{64}, \quad \mathcal{E}_{(5)}(R_2) = \frac{70\gamma^5}{128}. \tag{29}$$

For the linear chain of five C=C bonds, we accordingly obtain

$$\mathcal{E}_{(2)}(5) = 2\gamma^2, \quad \mathcal{E}_{(3)}(5) = 0, \quad \mathcal{E}_{(4)}(5) = \frac{4\gamma^4}{64}, \quad \mathcal{E}_{(5)}(5) = 0 \tag{30}$$

as Eq.(21) indicates. It is seen that the second order energy is increased by $\gamma^2/2$ due to cyclization and this result may be easily traced back to emergence of a new C-C bond as previously. Further, the vanishing third order energy of the circuit R_2 ($\mathcal{E}_{(3)}(R_2)$) originates

from the fact that conditions $G_{(1)il} \neq 0$ and $G_{(2)il} \neq 0$ are not met simultaneously by elements of matrices $\mathbf{G}_{(1)}(R_2)$ and $\mathbf{G}_{(2)}(R_2)$ of Eq.(28). In other words, the reason consists in absence of roundabout pathways of the third order in the circuit R_2 in contrast to R_1. Meanwhile, the fourth order energy $\mathcal{E}_{(4)}(R_2)$ takes a non-zero positive value and is increased by $6\gamma^4/64$ vs. $\mathcal{E}_{(4)}(5)$ of Eq.(30) as it was the case with formation of the circuit R_1. [Besides, each C=C bond of the circuit R_2 contributes $2\gamma^4/64$ to the fourth order energy $\mathcal{E}_{(4)}(R_2)$ in analogy to the former circuit R_1]. Finally, a large positive fifth order energy $\mathcal{E}_{(5)}(R_2)$ deserves attention, each C=C bond contributing $14\gamma^5/128$. This result also is in line with an anticipation based on the presence of roundabout pathways of the fifth order in the circuit R_2.

Cyclic systems consisting of more C=C bonds also may be studied similarly. For example, a cycle of seven C=C bonds corresponding to a conjugated circuit R_3 is characterized by the following energy corrections

$$\mathcal{E}_{(2)}(R_3) = \frac{7\gamma^2}{2}, \quad \mathcal{E}_{(3)}(R_3) = 0, \quad \mathcal{E}_{(4)}(R_3) = \frac{14\gamma^4}{64}, \quad \mathcal{E}_{(5)}(R_3) = 0. \tag{31}$$

It is seen that both third and fifth order energies vanish in this case in accordance with the expectation. Meanwhile, corrections $\mathcal{E}_{(2)}(R_3)$ and $\mathcal{E}_{(4)}(R_3)$ take positive values as previously and consist of transferable increments of individual bonds, e.g. each C=C bond contributes $2\gamma^4/64$ to the fourth order energy $\mathcal{E}_{(4)}(R_3)$.

Let us summarize finally the results concerning the conjugated circuits of the 4n+2 series (R_n) containing an odd number of both C=C and C-C bonds. Let this number to be denoted by N as previously and note that N=3,5,7,... correspond to n=1,2,3... The energy corrections of these circuits of even orders may be then concluded to grow monotonically with increasing N values. In particular, the second and fourth order energies are correspondingly proportional to $N\gamma^2/2$ and $N\gamma^4/32$. Moreover, any N-membered conjugated circuit proves to be characterized by a positive energy correction of the Nth order ($\mathcal{E}_{(N)}$) related to roundabout pathways over the circuit. For example, the most important conjugated circuits of benzenoids R_1 and R_2 are represented by considerable positive third and fifth order energies, respectively.

4 Consideration of the two principal Kekulé valence structures of naphthalene

Let us now dwell on the simplest polycyclic benzenoid hydrocarbon, viz. on naphthalene. Let us start with the Fries structure (I) containing two conjugated circuits R_1 (Fig. 1).

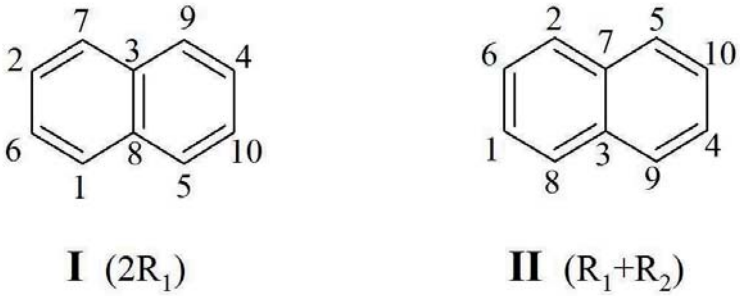

Figure 1: The two Kekulé valence structures of naphthalene (I and II) along with their compositions in terms of conjugated circuits R_1 and R_2. Numberings of $2p_z$ AOs of carbon atoms also are shown, where AOs under numbers 1,2...5 and 6,7...10 belong to subsets $\{\chi^*\}$ and $\{\chi^\circ\}$, respectively.

The relevant principal matrices of inter-orbital interactions are

$$
\begin{aligned}
\mathbf{G}_{(1)}(I) &= -\frac{\gamma}{4}\begin{vmatrix} 0 & 1 & -1 & 0 & 0 \\ -1 & 0 & 1 & 0 & 0 \\ 1 & -1 & 0 & -1 & 1 \\ 0 & 0 & 1 & 0 & -1 \\ 0 & 0 & -1 & 1 & 0 \end{vmatrix}, \\
\mathbf{G}_{(2)}(I) &= -\frac{\gamma^2}{8}\begin{vmatrix} 0 & 1 & -1 & 1 & 0 \\ -1 & 0 & 1 & 0 & -1 \\ 1 & -1 & 0 & -1 & 1 \\ -1 & 0 & 1 & 0 & -1 \\ 0 & 1 & -1 & 1 & 0 \end{vmatrix}, \\
\widetilde{\mathbf{G}}_{(3)}(I) &= -\frac{\gamma^3}{64}\begin{vmatrix} 0 & 1 & -1 & 2 & 0 \\ -1 & 0 & 1 & 0 & -2 \\ 1 & -1 & 0 & -1 & 1 \\ -2 & 0 & 1 & 0 & -1 \\ 0 & 2 & -1 & 1 & 0 \end{vmatrix}, \\
\overline{\mathbf{G}}_{(3)}(I) &= \frac{\gamma^3}{64}\begin{vmatrix} 0 & 5 & -9 & 2 & 0 \\ -5 & 0 & 9 & 0 & -2 \\ 9 & -9 & 0 & -9 & 9 \\ -2 & 0 & 9 & 0 & -5 \\ 0 & 2 & -9 & 5 & 0 \end{vmatrix}. \qquad (32)
\end{aligned}
$$

Substituting these matrices into Eqs.(8) and (10) yields the following results

$$
\begin{aligned}
\mathcal{E}_{(2)}(I) &= 2\mathcal{E}_{(2)}(R_1) = 3\gamma^2, \quad \mathcal{E}_{(3)}(I) = 2\mathcal{E}_{(3)}(R_1) = \frac{6\gamma^3}{4}, \\
\mathcal{E}_{(4)}(I) &= 2\mathcal{E}_{(4)}(R_1) = \frac{12\gamma^4}{64}, \quad \mathcal{E}_{(5)}(I) = -\frac{100\gamma^5}{128}. \qquad (33)
\end{aligned}
$$

To comment these formulas, let us start with matrices $\mathbf{G}_{(1)}(I), \mathbf{G}_{(2)}(I)$ and $\widetilde{\mathbf{G}}_{(3)}(I)$. It is evident that "connected" $3 \times 3-$dimensional blocks (taking the diagonal positions in these matrices) may be ascribed to individual conjugated circuits R_1 of the structure I. These sub-matrices may be called the intra-circuit blocks. Comparison of these blocks to matrices $\mathbf{G}_{(1)}(R_1), \mathbf{G}_{(2)}(R_1)$ and $\widetilde{\mathbf{G}}_{(3)}(R_1)$ representing an isolated circuit R_1 (see Eqs.(24) and (25)) indicates their coincidence for particular order parameters. [Overturn of signs of matrix elements of the second intra-circuit blocks is entirely due to the chosen numbering of AOs in naphthalene (Fig.1)]. In the case of first order matrices $\mathbf{G}_{(1)}(I)$ and $\mathbf{G}_{(1)}(R_1)$, the above-concluded transferability of intra-circuit blocks may be straightforwardly accounted for by the presence of two circuits R_1 in the structure I. Meanwhile, an analogous transferability of the second order sub-matrices may be traced back to the fact that pairs of C=C bonds of the left circuit R_1 possess no common first neighbors among C=C bonds of the right one and vice versa. So far as the third order matrix $\widetilde{\mathbf{G}}_{(3)}(I)$ is concerned, the overall situation is even less simple. Indeed, orbitals of C_4=C_9 and C_5=C_{10} bonds participate as mediators in the third order interactions represented by matrix elements $\widetilde{G}_{(3)13}(I)$ and $\widetilde{G}_{(3)23}(I)$. Nevertheless, the relevant contributions cancel out one another in the final formulae for these elements and consequent constitutions of intra-circuit blocks of the matrix $\widetilde{\mathbf{G}}_{(3)}(I)$ resemble those of the matrix $\widetilde{\mathbf{G}}_{(3)}(R_1)$. Finally, the remaining $2 \times 2-$dimensional corner blocks of matrices $\mathbf{G}_{(1)}(I), \mathbf{G}_{(2)}(I)$ and $\widetilde{\mathbf{G}}_{(3)}(I)$ contain inter-circuit elements. It is seen that all elements of this type take zero values in the first order matrix $\mathbf{G}_{(1)}(I)$. This implies that orbitals belonging to different circuits do not interact directly in the Fries structure of naphthalene I.

The above-concluded transferability of intra-circuit blocks of matrices $\mathbf{G}_{(1)}(I)$, $\mathbf{G}_{(2)}(I)$ and $\widetilde{\mathbf{G}}_{(3)}(I)$ along with zero direct inter-circuit interactions ensure additivity of energy corrections up to the fourth order ($k = 4$) with respect to contributions of individual conjugated circuits R_1, and the latter coincide with the relevant energy increments of isolated circuits R_1 in addition. Contributions of individual C=C bonds to energy corrections $\mathcal{E}_{(2)}(I), \mathcal{E}_{(3)}(I)$ and $\mathcal{E}_{(4)}(I)$ also exhibit an analogous additivity. For example, contributions of C_1=C_6, C_3=C_8 and C_5=C_{10} bonds to the fourth order energy $\mathcal{E}_{(4)}(I)$ equal to $2\gamma^4/64, 4\gamma^4/64$ and $2\gamma^4/64$, respectively, in accordance with the result of a simple superposition of increments of individual circuits R_1.

As opposed to the above-discussed first three members of the power series under our interest, the fifth order energy $\mathcal{E}_{(5)}(I)$ is no longer additive with respect to increments of individual circuits. Indeed, the absolute value of this negative correction (i.e. $100\gamma^5/128$) exceeds the relevant two-fold value for an isolated circuit R_1 ($60\gamma^5/128$) considerably.

This result causes little surprise if we bear in mind that the fifth order energy $\mathcal{E}_{(5)}(I)$ contains both intra- and inter-circuit increments of negative signs as multiplying of matrices $\overline{\mathbf{G}}_{(3)}(I)$ and $\mathbf{G}^{+}_{(2)}(I)$ shows. Moreover, an intra-circuit increment now coincides with $-46\gamma^5/128$ and proves to be of an increased absolute value as compared to the fifth order energy of an isolated circuit R_1 ($-30\gamma^5/128$). Thus, the fifth order intra-circuit increments are no longer transferable in addition. This fact may be entirely traced back to the changing nature of the intra-circuit blocks of the matrix $\overline{\mathbf{G}}_{(3)}(I)$ vs. $\overline{\mathbf{G}}_{(3)}(R_1)$. Indeed, elements of such a block take increased absolute values in the positions (1,3) and (2,3) as compared to the relevant elements of the matrix $\overline{\mathbf{G}}_{(3)}(R_1)$. An analogous growth in absolute values is reflected also in the contributions of individual C=C bonds to the total fifth order energy $\mathcal{E}_{(5)}(I)$. In particular, the bonds C_1=C_6, C_3=C_8 and C_5=C_{10} correspondingly contribute $-16\gamma^5/128$, $-36\gamma^5/128$ and $-16\gamma^5/128$ instead of $-10\gamma^5/128$ referring to any C=C bond of the isolated circuit R_1. In summary, a certain fifth order "inter-circuit repulsion" may be concluded to take place in the Fries structure of naphthalene (I) that gives rise to its destabilization vs. superposition of two isolated circuits R_1.

Let us now consider the anti-Fries structure of naphthalene (II) containing two conjugated circuits of different size, i.e. both R_1 and R_2 (Fig. 1). The analogues of Eqs.(32) and (33) are then as follows

$$\begin{aligned}
\mathbf{G}_{(1)}(II) &= -\frac{\gamma}{4}\begin{vmatrix} 0 & 1 & -1 & 0 & 0 \\ -1 & 0 & 1 & 0 & 1 \\ 1 & -1 & 0 & -1 & 0 \\ 0 & 0 & 1 & 0 & -1 \\ 0 & -1 & 0 & 1 & 0 \end{vmatrix}, \\
\mathbf{G}_{(2)}(II) &= -\frac{\gamma^2}{8}\begin{vmatrix} 0 & 1 & -1 & 1 & -1 \\ -1 & 0 & 1 & -1 & 0 \\ 1 & -1 & 0 & 0 & 1 \\ -1 & 1 & 0 & 0 & 0 \\ 1 & 0 & -1 & 0 & 0 \end{vmatrix}, \\
\widetilde{\mathbf{G}}_{(3)}(II) &= -\frac{\gamma^3}{64}\begin{vmatrix} 0 & 2 & -2 & 6 & -6 \\ -2 & 0 & 4 & -5 & -1 \\ 2 & -4 & 0 & 1 & 5 \\ -6 & 5 & -1 & 0 & -2 \\ 6 & 1 & -5 & 2 & 0 \end{vmatrix}, \\
\overline{\mathbf{G}}_{(3)}(II) &= \frac{\gamma^3}{64}\begin{vmatrix} 0 & 6 & -6 & -6 & 6 \\ -6 & 0 & 4 & 7 & 7 \\ 6 & -4 & 0 & -7 & -7 \\ 6 & -7 & 7 & 0 & -2 \\ -6 & -7 & 7 & 2 & 0 \end{vmatrix}
\end{aligned} \tag{34}$$

and

$$\begin{aligned}\mathcal{E}_{(2)}(II) &= 3\gamma^2, \quad \mathcal{E}_{(3)}(II) = \mathcal{E}_{(3)}(R_1) = \frac{3\gamma^3}{4}, \\ \mathcal{E}_{(4)}(II) &= \mathcal{E}_{(4)}(R_1) + \mathcal{E}_{(4)}(R_2) = \frac{16\gamma^4}{64}, \quad \mathcal{E}_{(5)}(II) = \frac{20\gamma^5}{128}, \end{aligned} \tag{35}$$

respectively. To interpret these results, let us consider the anti-Fries structure II as consisting of a circuit R_1 and the butadiene-like fragment C_5=C_{10}-C_4=C_9. Accordingly, $3\times3-$and $2\times2-$dimensional blocks taking diagonal positions within matrices of Eq.(34) represent these substructures, whereas the remaining off-diagonal sub-matrices contain the inter-subsystem interactions. It is seen that the first order matrix $\mathbf{G}_{(1)}(II)$ now contains a single intra-circuit block coinciding with $\mathbf{G}_{(1)}(R_1)$ (This specific block takes the first diagonal position). Meanwhile, the remaining parts of matrices $\mathbf{G}_{(1)}(I)$ and $\mathbf{G}_{(1)}(II)$ are of distinct constitutions. Nevertheless, the total numbers of non-zero elements are uniform in these matrices because of the same numbers of C-C bonds present in the structures I and II. Thus, coincidence of second order energies $\mathcal{E}_{(2)}(I)$ and $\mathcal{E}_{(2)}(II)$ seen from Eqs.(32) and (35) causes little surprise.

The second order matrix $\mathbf{G}_{(2)}(II)$ also contains an intra-circuit block coinciding with the matrix $\mathbf{G}_{(2)}(R_1)$. This implies that presence of the diene-like fragment C_5=C_{10}-C_4=C_9 exerts no influence upon indirect interactions via a single mediator between BOs of the principal circuit R_1. Such a result may be accounted for by emergence of no new common neighbors for pairs of BOs belonging to the circuit R_1 due to addition of the above-mentioned four-atomic fragment. Furthermore, non-zero elements take different positions within matrices $\mathbf{G}_{(1)}(II)$ and $\mathbf{G}_{(2)}(II)$ except for those referring to the circuit R_1. As a result, the third order energy $\mathcal{E}_{(3)}(II)$ coincides with that of a single isolated circuit R_1 ($\mathcal{E}_{(3)}(R_1)$) in accordance with the expectation.

Let us turn now to the fourth order energy $\mathcal{E}_{(4)}(II)$ of the anti-Fries structure of naphthalene (II). As is seen from comparison of Eqs.(26), (29) and (35), the correction $\mathcal{E}_{(4)}(II)$ coincides with the sum of fourth order energies of isolated circuits R_1 and R_2 (equal to $6\gamma^4/64$ and $10\gamma^4/64$, respectively). Meanwhile, the actual increments of individual C=C bonds to the total correction $\mathcal{E}_{(4)}(II)$ differ from those following from superposition of separate circuits R_1 and R_2 in this case (although a certain similarity of both energy distributions may be noticed). For example, the actual increments of bonds C_1=C_6, C_2=C_7 and C_5=C_{10} correspondingly equal to $4\gamma^4/64$, $5\gamma^4/64$ and $\gamma^4/64$ instead of $4\gamma^4/64$, $4\gamma^4/64$ and $2\gamma^4/64$ resulting from the simple superposition of both circuits. This seeming inconsistency indicates that the origin of additivity of $\mathcal{E}_{(4)}(II)$ is much less straightforward as

compared to that of $\mathcal{E}_{(4)}(I)$. The fact that the whole circuit R_2 (containing five C=C bonds) cannot be embraced by the fourth order correction $\mathcal{E}_{(4)}(II)$ (in contrast to R_1) also contributes to strengthening of the above anticipation about an involved origin of this additivity.

A more detailed analysis of separate increments to $\mathcal{E}_{(4)}(II)$ shows that some self-returning pathways yield negative contributions to this correction in contrast to fourth order energies of isolated circuits R_1 and R_2 (Let us note, for example, that products both $\widetilde{G}_{(3)25}G_{(1)25}$ and $\widetilde{G}_{(3)34}G_{(1)34}$ are of negative signs for the structure II). Consequently, the inter-subsystem component of the fourth order energy $\mathcal{E}_{(4)}(II)$ is a negative quantity. This fact causes little surprise because branched fragments are present in the structure II (e.g. C_8=C_3-C_7(=C_2)−C_5=C_{10}) that were shown previously to be characterized by negative fourth order energies [23]. Furthermore, the above-mentioned inter-subsystem increment and a positive contribution originating from the butadiene-like fragment C_5=C_{10}-C_4=C_9 cancel out one another in the final expression for $\mathcal{E}_{(4)}(II)$ so that the latter may be formally traced back to intra-circuit blocks of matrices $\mathbf{G}_{(1)}(II)$ and $\widetilde{\mathbf{G}}_{(3)}(II)$ referring to the circuit R_1. In this connection, the circuit R_2 participates in the formation of $\mathcal{E}_{(4)}(II)$ indirectly via increased absolute values of elements of the above-specified decisive block of the matrix $\widetilde{\mathbf{G}}_{(3)}(II)$. This especially refers to elements $\widetilde{G}_{(3)23}(II)$ and $\widetilde{G}_{(3)32}(II)$, the increased absolute values of which are unambiguously related to emergence of new roundabout pathways between orbitals of C=C bonds concerned (i.e. of C_2=C_7 and C_3=C_8) via BBOs and ABOs of the butadiene-like fragment (viz. via BOs of bonds C_4=C_9 and C_5=C_{10}). It is evident that the above-specified extra pathways become possible just owing to the presence of the circuit R_2. That is why the above-observed additivity of the fourth order energy $\mathcal{E}_{(4)}(II)$ with respect to increments of isolated circuits R_1 and R_2 is not entirely unexpected.

Finally, the fifth order energy of the structure II (i.e. $\mathcal{E}_{(5)}(II)$) remains to be discussed. Let us recall in this connection that the isolated circuits R_1 and R_2 are characterized by fifth order energies of opposite signs, namely by $-30\gamma^5/128$ and $70\gamma^5/128$, respectively (Section 3). Thus, a positive correction $\mathcal{E}_{(5)}(II)$ equal to $40\gamma^5/128$ may be expected in the case of additivity of the fifth order energy with respect to increments of individual circuits. The actual value of $\mathcal{E}_{(5)}(II)$ ($20\gamma^5/128$), however, does not amount the above-anticipated quantity. This fact indicates a certain "inter-circuit repulsion" to take place in the structure II too. Again, comparison of absolute values of these inter-circuit interactions for structures I and II indicates the latter to coincide with only a half of the former. Thus, we may conclude the overall scheme of formation of $\mathcal{E}_{(5)}(II)$ to be rather close to

an additive one, wherein negative and positive contributions correspond to circuits R_1 and R_2, respectively. Consideration of increments of individual C=C bonds to the energy $\mathcal{E}_{(5)}(II)$ also supports the above conclusion. For example, the actual increments of bonds C_1=C_6, C_2=C_7 and C_5=C_{10} correspondingly equal to 0, $-3\gamma^5/128$ and $13\gamma^5/128$, whereas the simple superposition of circuits R_1 and R_2 yields $4\gamma^5/128$, $4\gamma^5/128$ and $14\gamma^5/128$, respectively (in the isolated circuits R_1 and R_2, individual C=C bonds contribute $-10\gamma^5/128$ and $14\gamma^5/128$). It is seen, therefore, that increments of both circuits almost cancel one another for bonds C_1=C_6 and C_2=C_7 and, consequently, their actual contributions are relatively small. By contrast, the increment of the remaining C_5=C_{10} bond is close to that of an isolated circuit R_2.

5 Discussion of Kekulé valence structures of more extended benzenoids

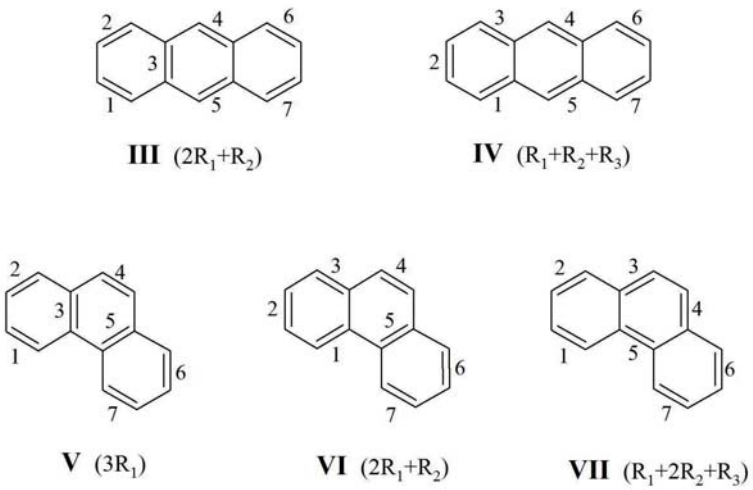

Figure 2: Kekulé valence structures of anthracene (III, IV) and phenanthrene (V-VII) along with their compositions in terms of conjugated circuits. Numbers of C=C bonds also are shown that coincide with those of AOs of the first subset $\{\chi^*\}$.

Let us dwell first on the Kekulé valence structures of anthracene (III, IV) and phenanthrene (V-VII) shown in Fig. 2.

It deserves an immediate mentioning that the overall scheme of formation of the

relevant second and third order energies closely resembles that of naphthalene (Section 4). In particular, non-zero elements of first order matrices (i.e. of $\mathbf{G}_{(1)}(III)$, $\mathbf{G}_{(1)}(IV)$, $\ldots \mathbf{G}_{(1)}(VII)$) refer to C-C bonds as previously and, consequently, the second order energies of all structures concerned equal to $9\gamma^2/2$ in accordance with nine C-C bonds present there. Furthermore, $3 \times 3-$dimensional blocks coinciding with $\mathbf{G}_{(1)}(R_1)$ and $\mathbf{G}_{(2)}(R_1)$ of Eqs.(24) and (25) correspond to any circuit R_1 in the total first and second order matrices of structures III-VII. Consequently, the relevant third order energies are proportional to numbers of circuits R_1 contained in these structures, i.e.

$$\mathcal{E}_{(3)}(V) = \frac{9\gamma^3}{4}, \quad \mathcal{E}_{(3)}(III) = \mathcal{E}_{(3)}(VI) = \frac{6\gamma^3}{4}, \quad \mathcal{E}_{(3)}(IV) = \mathcal{E}_{(3)}(VII) = \frac{3\gamma^3}{4}. \tag{36}$$

Meanwhile, the fourth order energies of the same structures are as follows

$$\begin{aligned} \mathcal{E}_{(4)}(V) &= \frac{18\gamma^4}{64}, \quad \mathcal{E}_{(4)}(III) = \mathcal{E}_{(4)}(VI) = \frac{22\gamma^4}{64}, \quad \mathcal{E}_{(4)}(IV) = \frac{26\gamma^4}{64}, \\ \mathcal{E}_{(4)}(VII) &= \frac{30\gamma^4}{64} \end{aligned} \tag{37}$$

and correlate with the relevant numbers of circuits R_2 and R_3. An analogous correlation is observed for the fifth order corrections too, viz.

$$\begin{aligned} \mathcal{E}_{(5)}(V) &= -\frac{170\gamma^5}{128}, \quad \mathcal{E}_{(5)}(III) = -\frac{50\gamma^5}{128}, \quad \mathcal{E}_{(5)}(VI) = -\frac{30\gamma^5}{128}, \\ \mathcal{E}_{(5)}(IV) &= \frac{20\gamma^5}{128}, \quad \mathcal{E}_{(5)}(VII) = \frac{70\gamma^5}{128}. \end{aligned} \tag{38}$$

Thus, an interdependence is beyond any doubt between energy corrections and numbers of conjugated circuits R_n in this case as well. Let us turn now to a more detailed discussion of these results.

Let us start with the structure V characterized by three uniform circuits R_1 and by the largest third order energy as Eq.(36) indicates. The overall scheme of formation of the relevant fourth order energy $\mathcal{E}_{(4)}(V)$ resembles that of the Fries structure of naphthalene (I). In particular, three connected $3 \times 3-$dimensional intra-circuit blocks are present in the matrix $\widetilde{\mathbf{G}}_{(3)}(V)$, each of them coinciding with $\widetilde{\mathbf{G}}_{(3)}(R_1)$ and contributing $6\gamma^4/64$ to the total fourth order energy $\mathcal{E}_{(4)}(V)$. As a result, the latter equals to the threefold fourth order energy of a single Kekulé structure of benzene as Eq. (37) shows. Structures III and VI, in turn, are characterized by coinciding fourth order energies in accordance with their uniform composition in terms of conjugated circuits ($2R_1$+R_2). Moreover, the value of these energies ($22\gamma^4/64$) equals to the sum of increments of isolated circuits $2R_1$ and R_2 as it was the case with the anti-Fries structure of naphthalene (II). A detailed analysis of the overall schemes of formation of corrections $\mathcal{E}_{(4)}(III)$ and $\mathcal{E}_{(4)}(VI)$ also supports

their similarity to $\mathcal{E}_{(4)}(II)$. In particular, matrices $\widetilde{\mathbf{G}}_{(3)}(III)$ and $\widetilde{\mathbf{G}}_{(3)}(VI)$ both contain a single intra-circuit block coinciding with $\widetilde{\mathbf{G}}_{(3)}(R_1)$ and contributing $6\gamma^4/64$ to the total fourth order energy. These blocks correspond to cycles (1,2,3) and (5,6,7) of the structures III and VI, respectively. Furthermore, the same third order matrices (i.e. $\widetilde{\mathbf{G}}_{(3)}(III)$ and $\widetilde{\mathbf{G}}_{(3)}(VI)$) contain "perturbed" intra-circuit blocks like the first sub-matrix of the matrix $\widetilde{\mathbf{G}}_{(3)}(II)$ of Eq.(34). These blocks embrace the cycles (3,4,5) and (1,2,3) of structures III and VI, respectively, and contribute $16\gamma^4/64$ to the total fourth order energy as it was the case with the anti-Fries structure of naphthalene II. Since the remaining increments cancel out one another when building up both $\mathcal{E}_{(4)}(III)$ and $\mathcal{E}_{(4)}(VI)$ in a close resemblance with $\mathcal{E}_{(4)}(II)$, the above-concluded additivity of fourth order energies with respect to increments of isolated circuits is obtained. As with $\mathcal{E}_{(4)}(II)$, this additivity also is not accompanied by a complete coincidence of increments of individual C=C bonds with those following from a simple superposition of contributions of isolated circuits. For example, the second, third, fourth and sixth C=C bonds of the structure III actually contribute $2\gamma^4/64$, $6\gamma^4/64$, $5\gamma^4/64$ and $\gamma^4/64$, respectively, whereas the superposition of individual circuits correspondingly yields $2\gamma^4/64, 6\gamma^4/64$, $4\gamma^4/64$ and $2\gamma^4/64$. Similar distinctions are observed in the structure VI too.

The fourth order energies of the remaining structures IV and VII do not amount the relevant sums of increments of isolated conjugated circuits (although proportionality to numbers of these circuits is still preserved and thereby the last structure VII proves to be characterized by the largest $\mathcal{E}_{(4)}$ value). Nevertheless, formation of the energy corrections $\mathcal{E}_{(4)}(IV)$ and $\mathcal{E}_{(4)}(VII)$ may be easily rationalized on the basis of previous experience. Let us dwell first on the structure IV and note that contributions of the right butadiene-like fragment (containing the 6th and 7th C=C bonds) and of its interaction with the central ring cancel out one another as it was the case with the anti-Fries structure of naphthalene (II). Accordingly, the left ring (1,2,3) contributes $16\gamma^4/64$ to the total fourth order energy $\mathcal{E}_{(4)}(IV)$. The remaining increment ($10\gamma^4/64$) to the same energy may be traced back to the 4th and 5th C=C bonds characterized by largely increased absolute values of elements $\widetilde{G}_{(3)45}(IV)$ and $\widetilde{G}_{(3)54}(IV)$ because of the presence of roundabout pathways between BOs of these bonds via orbitals of the 6th and 7th C=C bond. So far as the last Kekulé structure of phenanthrene VII is concerned, the most part of the significant fourth order stabilization may be ascribed to the central ring (3,4,5) embraced by both circuits R_2. Indeed, the third order matrix $\widetilde{\mathbf{G}}_{(3)}(VII)$ contains a "perturbed" intra-circuit block of

the following constitution

$$\widetilde{\mathbf{G}}_{(3)}(VII) = -\frac{\gamma^3}{64}\begin{vmatrix} .. & .. & .. & .. & .. \\ .. & 0 & 3 & -5 & .. \\ .. & -3 & 0 & 5 & .. \\ .. & 5 & -5 & 0 & .. \\ .. & .. & .. & .. & .. \end{vmatrix}, \tag{39}$$

which refers to the cycle (3,4,5) and yields $26\gamma^4/64$ after multiplying it by $\mathbf{G}^{+}_{(1)}(R_1)$. Furthermore, an additional contribution to the total $\mathcal{E}_{(4)}(VII)$ (equal to $4\gamma^4/64$) arises owing to differences between increments of terminal butadiene-like fragments and those of their interaction with the central ring (3,4,5).

Let us turn now to interpretation of the fifth order energies and start with the structure V as previously. As already mentioned, this structure resembles the Fries structure of naphthalene (I) in respect of formation of third and fourth order energies. This analogy embraces the relevant fifth order energies too. Indeed, the absolute value of the actual correction $\mathcal{E}_{(5)}(V)$ exceeds that of the three-fold fifth order energy of an isolated circuit R_1 ($90\gamma^5/128$) considerably due to an additional intra- and inter-circuit destabilization. Besides, increments of terminal rings ((1,2,3) and (5,6,7)) coincide with the relevant values for the Fries structure of naphthalene I and equal to $-46\gamma^5/128$. Meanwhile, the central ring (3,4,5) is destabilized more significantly in the structure V (the relevant increment equals to $-62\gamma^5/128$). Finally, the two-fold inter-ring contribution ($-16\gamma^5/128$) should be added to complete the overall scheme of formation of $\mathcal{E}_{(5)}(V)$.

The fifth order energies of structures III and VI are considerably higher as compared to $\mathcal{E}_{(5)}(V)$ discussed above. This alteration resembles passing from the Fries structure of naphthalene (I) to the anti-Fries one (II). The most important point here, however, consists in distinct absolute values of $\mathcal{E}_{(5)}(III)$ and $\mathcal{E}_{(5)}(VI)$ in spite of both uniform compositions of structures concerned in terms of conjugated circuits ($2R_1$+R_2) and coinciding fourth order corrections $\mathcal{E}_{(4)}(III)$ and $\mathcal{E}_{(4)}(VI)$. Moreover, the Kekulé valence structure of phenanthrene VI is predicted to be more stable as compared to that of anthracene (III). This result shows that the perturbative approach of the present study allows us to discriminate between structures containing the same sets of conjugated circuits. This important advantage of the new approach may be unambiguously traced back to the lack of additivity of the fifth order energies with respect to increments of conjugated circuits. As a result of such an non-additive nature, the fifth order energies become sensitive to particular mutual arrangements of the conjugated circuits along with their numbers. To discuss the latter aspect in a more detail, let us consider the structures III and VI as consisting of an anti-Fries structure of naphthalene (II) (coinciding with the circuit R_2 and

referred to below as the parent structure) and of an additional circuit R_1. (For structures III and VI, the parent structure embraces the C=C bonds under numbers 3,4,5,6,7 and 1,2,3,4,5, respectively). The Kekulé valence structures under comparison (i.e. III and VI) are then characterized by distinct positions of the new circuit R_1 with respect to the parent structure. Indeed, the new circuit is attached to the circuit R_1 of the parent structure and to its diene-like fragment when building up the structures III and VI, respectively. It is evident that these cases correspondingly resemble the formation of the Fries structure of naphthalene (I) and of the relevant anti-Fries structure (II). As a result, just the first case (III) may be expected to be characterized by a more significant intra- and inter-subsystem destabilization. This anticipation is entirely supported by relative values of both total fifth order energies and of the relevant intra- and inter-ring contributions. For example, the increments of the "newly-added" circuit R_1 (i.e. of the ring (1,2,3) of III and of the ring (5,6,7) of VI) coincide with $-46\gamma^5/128$ in both cases. Meanwhile, the parent anti-Fries structure of naphthalene is additionally destabilized in the case of anthracene (III) vs. phenanthrene (VI) (the respective increments to the total fifth order energy correspondingly equal to $4\gamma^5/128$ and $20\gamma^5/128$, the latter coinciding with $\mathcal{E}_{(5)}(II)$ of Eq.(35)). Finally, the same trend is supported by the relevant inter-subsystem contributions coinciding with $-8\gamma^5/128$ and $-4\gamma^5/128$ for structures III and VI, respectively. Thus, different stabilities of Kekulé valence structures III and VI may be entirely traced back to dissimilar mutual arrangements of conjugated circuits contained. Besides, the structures III and VI may be also used to illustrate the rule of Section 3 concerning positive and negative signs of contributions of circuits R_2 and R_1, respectively, to the total fifth order energy. To this end, increments of individual C=C bonds should be invoked as previously. Consideration of these characteristics for structures under our interest shows that positive increments correspond to C=C bonds participating in the circuits R_2 only, e.g. to the 6th and 7th bond of the structure III and to the 4th bond of the structure VI. Meanwhile, bonds belonging to the "additional" circuit R_1 are characterized by negative increments of largest absolute values in both structures concerned. This especially refers to bonds 1,2 and 3 of III and to the 6th and 7th bonds of VI.

Finally, the positive fifth order energies of the remaining structures IV and VII deserve attention. Coincidence of the correction $\mathcal{E}_{(5)}(IV)$ to $\mathcal{E}_{(5)}(II)$ should be mentioned in the first place. This result causes no surprise if we bear in mind the following two points: First, the structure of anthracene (IV) differs from the anti-Fries structure of naphthalene (II) in the presence of an additional circuit R_3 and, second, this new extended circuit is characterized by a zero fifth order energy (see Eq.(31) of Section 3). Thus, the circuits

R_1 and R_2 only may be expected to determine the correction $\mathcal{E}_{(5)}(IV)$ and the equality $\mathcal{E}_{(5)}(IV) = \mathcal{E}_{(5)}(II)$ accordingly follows. On the basis of the same arguments we may then expect the last correction $\mathcal{E}_{(5)}(VII)$ to consist of increments of a single circuit R_1 and of two circuits R_2. The algebraic sum of the relevant values for isolated circuits then yields $110\gamma^5/128$. The actual value of $\mathcal{E}_{(5)}(VII)$ ($70\gamma^5/128$), however, does not amount to the above-anticipated one. This implies a certain inter-circuit interaction to take place in the structure VII as it was the case with naphthalene.

VIII **IX**

Figure 3: Two Kekulé valence structures of benzanthracene (VIII and IX) containing the same sets of conjugated circuits ($3R_1$+R_2).

Before finishing this Section, let us consider briefly another example of structures containing uniform sets of conjugated circuits, namely two Kekulé valence structures of benzanthracene VIII and IX (Fig. 3), the composition of both coinciding with $3R_1$+R_2 (discussion of these structures may be found also in Ref.[21]). These structures are represented by uniform energy increments up to the fourth order and by distinct fifth order corrections in accordance with the expectation, viz.

$$\begin{aligned} \mathcal{E}_{(2)}(VIII) &= \mathcal{E}_{(2)}(IX) = 6\gamma^2, \quad \mathcal{E}_{(3)}(VIII) = \mathcal{E}_{(3)}(IX) = \frac{9\gamma^3}{4}, \quad \mathcal{E}_{(4)}(VIII) = \\ \mathcal{E}_{(4)}(IX) &= \frac{28\gamma^4}{64}, \quad \mathcal{E}_{(5)}(VIII) = -\frac{100\gamma^5}{128}, \quad \mathcal{E}_{(5)}(IX) = -\frac{120\gamma^5}{128}. \end{aligned} \tag{40}$$

It is also seen that both third and fourth order energies of structures VIII and IX consist of sums of transferable increments of individual circuits as it was the case with former examples I-III, V and VI. On the other hand, the relevant fifth order energies indicate the structure VIII to be more stable as compared to IX. This result may be easily rationalized by considering the structures concerned as consisting of the parent structure of anthracene III and of an "additional" circuit R_1 (taking a somewhat lower position in Fig.3). The latter is then attached to circuits R_2 and R_1 of the parent structure III, when building up the structures VIII and IX, respectively, and, consequently, just the second system

(IX) is destabilized more significantly owing to the stronger inter-circuit repulsion, as it was the case with the structure III vs. VI.

Therefore, our previous conclusion concerning a possibility of discriminating between Kekulé valence structures containing the same numbers of conjugated circuits proves to be supported by another example.

6 Conclusions

The results of the present study demonstrate an unambiguous parallelism between terms of power series for total energies of individual Kekulé valence structures of benzenoid hydrocarbons ($\mathcal{E}_{(k)}$) on the one hand, and increments of particular conjugated circuits R_n (n=1,2...) in the CC model(s), on the other hand. The most important aspects of this parallelism are as follows:

i) The higher is the order parameter k of the given energy correction $\mathcal{E}_{(k)}$, the more extended conjugated circuits participate in its formation. For example, the third order energy $\mathcal{E}_{(3)}$ reflects the presence of the principal (three-membered) circuits R_1 only, whereas corrections of higher orders ($k = 4, 5...$) exhibit a dependence upon numbers of the remaining circuits R_2, R_3, etc. This implies steadily diminishing increments to correspond to conjugated circuits R_n in the power series for total energies when the size of the circuit (n) grows.

ii) A large extent of additivity with respect to transferable increments of individual conjugated circuits (R_n) proves to be peculiar to separate members of power series $\mathcal{E}_{(k)}$ and thereby to total energies of Kekulé valence structures of benzenoid hydrocarbons. Thus, the third order energies $\mathcal{E}_{(3)}$ of these structures are expressible as sums of uniform increments of the principal circuits R_1 coinciding with the third order energy of an analogous isolated circuit. As a result, the total corrections $\mathcal{E}_{(3)}$ are proportional to the actual numbers of these circuits present in the given structure. Moreover, additivity of the fourth order energies with respect to increments of individual circuits R_1 and R_2 is established for Kekulé valence structures containing no conjugated circuits of a larger size (i.e. R_3, R_4, etc.).

The above two points allow us to conclude the power series for total energies of pi-electron systems to provide us with a perturbative analogue for the concept of conjugated circuits in benzenoid hydrocarbons and thereby to contribute to revealing of quantum-chemical foundations and/or to justification of the conjugated- circuits- based model(s). Again a new cognitive potential of the perturbative approach vs. simple conjugated-

circuits- based model(s) also is demonstrated. Moreover, the approach suggested offers us an extension of the above-mentioned model(s) in some respects:

i) The approach proves to embrace perturbative analogues not only of conjugated-circuits- but also of conjugated- paths- based model(s). Indeed, contributions of both linear (non-cyclic) and cyclic conjugated fragments are shown to be taken into consideration on the unified basis in the approach applied. In particular, energy corrections of the fourth order $\mathcal{E}_{(4)}$ contain information about numbers of linear and/or branched hexadiene-like fragments present in the given Kekulé valence structure along with those of conjugated circuits. Non-zero values of fourth order energies for non-cyclic diene systems [23] serve to illustrate the above statement.

ii) The approach of the present study enables us not only to establish the very fact of additivity of a certain energy correction with respect to increments of separate conjugated fragments but also to interpret this property in terms of intra- and inter-circuit interactions. Consequently, it appears that some seemingly similar additivity relations are of rather different origins. This especially refers to the above-mentioned additivity of fourth order energies with respect to increments of individual conjugated circuits R_1 and R_2 : For systems containing the circuits R_1 only (such as the Fries structure of naphthalene I), the additivity concerned is shown to originate from coincidence of the decisive third order intra-circuit interactions with those of an isolated circuit R_1 (i.e. their transferability) along with vanishing first order (direct) inter-circuit interactions. By contrast, the same third order intra-circuit interactions are shown to be influenced by the presence of more extended circuits R_2 in the case of structures containing both types of circuits (e.g. the anti-Fries structure of naphthalene II). Nevertheless, such a lack of transferability of intra-circuit interactions goes together with additivity of fourth order energy corrections in this case.

iii) The perturbative expansion for total energies is shown to contain non-additive terms with respect to increments of individual conjugated circuits along with the above-enumerated additive increments. A non-additive nature is especially peculiar to energy corrections of the fifth order, wherein both intra- and inter-circuit increments may be distinguished, the former being no longer transferable in addition. As a result, these corrections become sensitive to particular mutual arrangements of conjugated circuits along with the total numbers of the latter. This implies an additional discriminative potential of the approach suggested vs. that of the CC model(s) in the case of Kekulé valence structures of benzenoid hydrocarbons containing the same sets of conjugated circuits.

Appendix

A The power series for total energies of molecules

Let us dwell here on the power series for total energies of molecules and/or molecular systems ($\mathcal{E}$) following from application of the non-commutative Rayleigh-Schrödinger perturbation theory (NCRSPT) [27-30] and underlying the relations of Section 2. Members of this series ($\mathcal{E}_{(k)}$) up to the fourth order ($k = 4$) have been derived in Refs. [23, 27]. An extension of the same derivation to terms of the fifth order ($k = 5$) will be discussed below.

Let us start with the most general initial Hamiltonian matrix ($\mathbf{H}$), the NCRSPT is applicable to. To this end, let us consider a molecule or molecular system consisting of a certain number of fragments. Individual chemical bonds both of saturated and of conjugated molecules, phenyl rings along with substituents and separate molecules contained in molecular systems are able to play this role. Let us note immediately that no specifying is required here either of the nature of fragments themselves or of their numbers(s). Further, let us introduce a set of basis functions ($\{\Psi\}$) localized on separate fragments of our system(s). These functions will be referred to below as fragmental orbitals. The only important assumption concerning these orbitals consists in their divisibility into initially-occupied (bonding) and initially-vacant (anti-bonding) ones separated by a substantial energy gap. The total basis set $\{\Psi\}$ then accordingly consists of two subsets so that the inter-subset interactions (resonance parameters) may be considered as first order terms vs. the above-specified gap. The Hückel type one-electron Hamiltonian matrix of our system(s) ($\mathbf{H}$) may be then expressed as a sum of first- and second order matrices as follows

$$\mathbf{H} = \mathbf{H}_{(0)} + \mathbf{H}_{(1)} = \left| \begin{array}{cc} \mathbf{E}_{(+)} & \mathbf{0} \\ \mathbf{0} & -\mathbf{E}_{(-)} \end{array} \right| + \left| \begin{array}{cc} \mathbf{S} & \mathbf{R} \\ \mathbf{R}^{+} & \mathbf{Q} \end{array} \right|, \tag{A1}$$

Sub-matrices $\mathbf{E}_{(+)} + \mathbf{S}$ and $-\mathbf{E}_{(-)} + \mathbf{Q}$ of the matrix $\mathbf{H}$ contain intra-subset interactions (resonance parameters) along with one-electron energies of fragmental orbitals, whilst the off-diagonal block $\mathbf{R}$ involves inter-subset interactions. The minus sign in front of $\mathbf{E}_{(-)}$ is introduced for convenience. The superscript + designates the Hermitian- conjugate matrix as previously. Besides, zero order intra-subset interactions are generally allowed in Eq.(A1) and these are included into sub-matrices $\mathbf{E}_{(+)}$ and $\mathbf{E}_{(-)}$.

Application of the NCRSPT to the Hamiltonian matrix of Eq.(A1) allowed us to derive members of the power series ($\mathcal{E}_{(k)}$) of the relevant total energy ($\mathcal{E}$). For $k = 0, 1, 2, 3$ and

4, the following formulas have been obtained [27]

$$\mathcal{E}_{(0)} = 2Trace\mathbf{E}_{(+)}, \quad \mathcal{E}_{(1)} = 2Trace\mathbf{S}, \tag{A2}$$

$$\mathcal{E}_{(2)} = -2Trace(\mathbf{G}_{(1)}\mathbf{R}^{+}), \tag{A3}$$

$$\mathcal{E}_{(3)} = -2Trace(\mathbf{G}_{(2)}\mathbf{R}^{+}), \tag{A4}$$

$$\mathcal{E}_{(4)} = -2Trace[(\mathbf{G}_{(3)} + \mathbf{G}_{(1)}\mathbf{G}^{+}_{(1)}\mathbf{G}_{(1)})\mathbf{R}^{+}], \tag{A5}$$

where $\mathbf{G}_{(k)}, k = 1, 2, 3...$ are the so-called principal matrices of the NCRSPT conditioned by matrix equations of the following common form

$$\mathbf{E}_{(+)}\mathbf{G}_{(k)} + \mathbf{G}_{(k)}\mathbf{E}_{(-)} + \mathbf{W}_{(k)} = \mathbf{0}, \tag{A6}$$

the last $\mathbf{G}_{(k)}-$free terms of which are expressible via matrices of lower orders, viz.

$$\begin{aligned} &\mathbf{W}_{(1)} = \mathbf{R}, \quad \mathbf{W}_{(2)} = \mathbf{S}\mathbf{G}_{(1)} - \mathbf{G}_{(1)}\mathbf{Q}, \\ &\mathbf{W}_{(3)} = \mathbf{S}\mathbf{G}_{(2)} - \mathbf{G}_{(2)}\mathbf{Q} - (\mathbf{R}\mathbf{G}^{+}_{(1)}\mathbf{G}_{(1)} + \mathbf{G}_{(1)}\mathbf{G}^{+}_{(1)}\mathbf{R}). \end{aligned} \tag{A7}$$

No essential difficulties arise in the way of extending the derivation of Ref.[27] to terms of higher orders (although the overall procedure is somewhat more cumbersome). For example, the fifth order member of the series of Eqs.(A2)-(A5) takes the form

$$\mathcal{E}_{(5)} = -2Trace[(\mathbf{G}_{(4)} + \mathbf{G}_{(2)}\mathbf{G}^{+}_{(1)}\mathbf{G}_{(1)} + \mathbf{G}_{(1)}\mathbf{G}^{+}_{(2)}\mathbf{G}_{(1)} + \mathbf{G}_{(1)}\mathbf{G}^{+}_{(1)}\mathbf{G}_{(2)})\mathbf{R}^{+}], \tag{A8}$$

where $\mathbf{G}_{(4)}$ also meets an equation of Eq.(A6) containing a new matrix $\mathbf{W}_{(4)}$, viz.

$$\mathbf{W}_{(4)} = \mathbf{S}\mathbf{G}_{(3)} - \mathbf{G}_{(3)}\mathbf{Q} - [\mathbf{R}(\mathbf{G}^{+}_{(1)}\mathbf{G}_{(2)} + \mathbf{G}^{+}_{(2)}\mathbf{G}_{(1)}) + (\mathbf{G}_{(1)}\mathbf{G}^{+}_{(2)} + \mathbf{G}_{(2)}\mathbf{G}^{+}_{(1)})\mathbf{R}]. \tag{A9}$$

Let us now dwell on the particular case of systems consisting of N uniform weakly-interacting chemical bonds. These systems will be referred to as homogeneous ones. The relevant fragmental orbitals (coinciding with bond orbitals (BOs) of Section 2 in this case) will be additionally assumed to be characterized by vanishing zero order intra-subset resonance parameters and by uniform one-electron energies inside subsets of bonding BOs (BBOs) and of anti-bonding ones (ABOs). Let the energy reference point to be chosen in the middle of the energy gap between BBOs and ABOs, whilst the energy unit will coincide with the one-electron energy of BBOs. These assumptions are representable by the following relation

$$\mathbf{E}_{(+)} = \mathbf{E}_{(-)} = \mathbf{I}, \tag{A10}$$

where $\mathbf{I}$ stands for the unit matrix. The principal equations of Eq.(A6) may be then solved algebraically for any k. As a result, the matrices $\mathbf{G}_{(k)}$ being sought become proportional

to $\mathbf{W}_{(k)}$ of Eqs.(A7) and (A9). This implies separate members of the series of matrices $\mathbf{G}_{(k)}, k = 1, 2, 3...$ to be actually connected by some recurrence relations, e.g.

$$\mathbf{G}_{(2)} = -\frac{1}{2}(\mathbf{S}\mathbf{G}_{(1)} - \mathbf{G}_{(1)}\mathbf{Q}), \tag{A11}$$

$$\mathbf{G}_{(3)} = -\frac{1}{2}(\mathbf{S}\mathbf{G}_{(2)} - \mathbf{G}_{(2)}\mathbf{Q}) - 2\mathbf{G}_{(1)}\mathbf{G}^{+}_{(1)}\mathbf{G}_{(1)}, \quad etc. \tag{A12}$$

where the matrix $\mathbf{R}$ is additionally replaced by $-2\mathbf{G}_{(1)}$ on the basis of Eq.(A6) for $k = 1$ when deriving Eq.(A12). Similarly, the matrix $\mathbf{R}$ may be eliminated from Eqs.(A3)-(A5) and (A8) so that the energy corrections $\mathcal{E}_{(k)}$ become expressed in terms of products of matrices $\mathbf{G}_{(k-1)}$ and $\mathbf{G}_{(1)}$ only. Accordingly, from Eq.(A8) we obtain

$$\mathcal{E}_{(5)} = 4Trace[(\mathbf{G}_{(4)} + 3\mathbf{G}_{(2)}\mathbf{G}^{+}_{(1)}\mathbf{G}_{(1)})\mathbf{G}^{+}_{(1)}], \tag{A13}$$

where $\mathbf{G}_{(4)}$ now follows from Eq.(A9) and takes the form

$$\mathbf{G}_{(4)} = -\frac{1}{2}(\mathbf{S}\mathbf{G}_{(3)} - \mathbf{G}_{(3)}\mathbf{Q}) - (\mathbf{G}_{(2)}\mathbf{G}^{+}_{(1)}\mathbf{G}_{(1)} + 2\mathbf{G}_{(1)}\mathbf{G}^{+}_{(2)}\mathbf{G}_{(1)} + \mathbf{G}_{(1)}\mathbf{G}^{+}_{(1)}\mathbf{G}_{(2)}). \tag{A14}$$

Formulas of Eqs.(A13) and (A14), however, prove to be rather cumbersome in practical applications. In this connection, we will invoke now the previous experience in dealing with the fourth order energy $\mathcal{E}_{(4)}$ [23]. Indeed, this correction was shown to be alternatively expressible in terms of matrices $\mathbf{G}_{(1)}$ and $\mathbf{G}_{(2)}$ only by employing the following interrelation

$$Trace(\mathbf{G}_{(3)}\mathbf{G}^{+}_{(1)}) = Trace(\mathbf{G}_{(2)}\mathbf{G}^{+}_{(2)}) - 2Trace(\mathbf{G}_{(1)}\mathbf{G}^{+}_{(1)}\mathbf{G}_{(1)}\mathbf{G}^{+}_{(1)}) \tag{A15}$$

that may be easily proven [23] on the basis of Eqs.(A11) and (A12). Thus, our aim now consists in derivation of the fifth order analogue of the above relation. To this end, let us take the $Trace(\mathbf{G}_{(4)}\mathbf{G}^{+}_{(1)})$ and substitute the right-hand side of Eq.(A14) for $\mathbf{G}_{(4)}$. Thereupon, we invoke the cyclic transposition of matrices inside the $Trace$ signs of the resulting expression along with Eq.(A11). We then obtain

$$Trace(\mathbf{G}_{(4)}\mathbf{G}^{+}_{(1)}) = Trace(\mathbf{G}_{(3)}\mathbf{G}^{+}_{(2)}) - 4Trace(\mathbf{G}_{(2)}\mathbf{G}^{+}_{(1)}\mathbf{G}_{(1)}\mathbf{G}^{+}_{(1)}). \tag{A16}$$

Use of this relation within Eq.(A13) allows the fifth order energy $\mathcal{E}_{(5)}$ to be alternatively expressed via the principal matrices up to $\mathbf{G}_{(3)}$ only.

Let us now summarize the origin of the principal formulas of Section 2.

i) Equation (7) follows from Eq.(A2) after invoking Eq.(A10) and Eq.(5) of Section 2.

ii) Expressions for $\mathcal{E}_{(2)}$ and $\mathcal{E}_{(3)}$ of Eq.(8) result from Eq.(A3) and (A4) after substituting $-2\mathbf{G}_{(1)}$ for $\mathbf{R}$.

iii) The first relation of Eq.(9) follows from solution of the matrix equation of Eq.(A6) for $k = 1$ after invoking Eq.(A10), whilst the second one results from Eq.(A11) after replacing $\mathbf{G}_{(1)}$ by $(-1/2)\mathbf{R}$ and invoking the equality $\mathbf{Q} = -\mathbf{S}$ shown in Eq.(4).

iv) Formulas for $\mathcal{E}_{(4)}$ and $\mathcal{E}_{(5)}$ of Eq.(10) along with the definition of the subsidiary matrices $\widetilde{\mathbf{G}}_{(3)}$ and $\overline{\mathbf{G}}_{(3)}$ of Eq.(11) result from Eqs.(A5) and (A13) after substituting $-2\mathbf{G}_{(1)}$ for $\mathbf{R}$. A subsequent employment of Eq.(A16) also is required for the fifth order correction $\mathcal{E}_{(5)}$.

v) The expression for $\mathbf{G}_{(3)}$ of Eq.(12) results from Eq.(A12) after substituting Eq.(9).

vi) Alternative formulas for subsidiary matrices of Eq.(13) result from Eq.(11) after invoking Eq.(A12).

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