A Simple Topological Factor Determining the Allowance of Pericyclic Reactions

V. GINEITYTE

Institute of Theoretical Physics and Astronomy, Vilnius University, Gostauto 12, LT-01108 Vilnius, Lithuania

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ABSTRACT: The study is aimed at revealing the possible manifestation of the overlap topology of AOs at early stages of pericyclic reactions. To this end, formation of an evenmembered cycle of carbon atoms is considered as a unified model, wherein relatively strong (C═C) bonds alternate with weak ones. A direct perturbative method is applied to derive algebraic expressions for energy and bond order corrections due to cyclization. To represent the overlap topology of $2p_z$ AOs over the cycle, a new concept of the roundabout interaction is introduced. The relevant definition contains a product of resonance parameters (or overlap integrals) between orbitals of all neighboring pairs of C═C bonds and a certain N-dependent parity factor, where N coincides with the total number of these bonds. The principal result of the study consists in demonstration of proportionality of both energy and bond order corrections to the roundabout interaction of the given cycle and thereby of a direct dependence between these corrections and the overlap topology of AOs. Moreover, the sign of the roundabout interaction is shown to determine the allowance of the given way of the process, viz. cycles described by positive (negative) roundabout interactions refer to allowed (forbidden) ways. Thus, an analog of the famous Woodward-Hoffmann rule is obtained, wherein the overlap topology of AOs stands instead of symmetry of molecular orbitals. Along with stabilization of the cycle vs. the initial open chain, the allowed processes also are necessarily characterized by growing uniformity of all bond orders over the cycle, while the forbidden ones are accompanied by both destabilization and an increasing distinction between strong and weak bonds. The results obtained also yield a new definition of the concerted nature of pericyclic processes. The general conclusions of the study are illustrated by consideration of specific examples including the electrocyclic closure of polyene chains. © 2008 Wiley Periodicals, Inc. Int J Quantum Chem 108: 1141–1154, 2008

Key words: pericyclic reactions; overlap topology; direct and indirect interorbital interactions; selection rule; electrocyclic closure of polyenes

Correspondence to: V. Gineityte; e-mail: gineityte@itpa.lt

1. Introduction

Molecular topology is known to play an important role in the formation of various observed characteristics of chemical compounds [1, 2]. This fact determines applicability and fruitfulness of popular concepts of molecular graphs and of their adjacency matrices in theoretical chemistry [3–5]. Given that these matrices may be additionally related to respective Hamiltonian matrices, the approach allows an investigation of the dependence between topological properties and electronic structures. Studies of this type are especially popular in the case of conjugated hydrocarbons [4–7], where the relevant Hückel model Hamiltonian matrices are proportional to adjacency matrices of molecular graphs describing the C-skeletons [4, 5]. It deserves mentioning here, however, that the resulting interdependences between electronic structures and adjacency matrices usually are cumbersome and difficult to analyze. The square-root-like dependence between the charge-bond order matrix and the respective adjacency matrix [5, 8] serves as an excellent illustration of the above assertion.

Reorganization of bonding is expected to take place in molecular systems during chemical reactions. This implies that some molecular topologies break down and new ones are formed while the reaction proceeds. At early stages of these formation processes, a perturbative treatment of the newly emerging molecular topologies is likely to be feasible. Relations of a direct (linear) nature may be then expected to be derivable between topological characteristics of the reacting system and those describing the relevant electronic structure, e.g. the total energy, electron density distribution, etc. Simple interdependences of the above-anticipated form (if established) contribute to our understanding of the reaction mechanism, in general, and of the role of topological factors in choice of a certain way of the process, in particular.

The present study addresses the pericyclic organic reactions [9–11]. The principal feature of these popular processes consists in the formation of even-membered cycles of continuously bounded atoms when approaching the respective transition state. So far as the initial and the final compounds are concerned, these are representable as open chain(s) involving mostly one or two gaps. Thus, a certain cyclization process followed by recyclization underlies any pericyclic reaction. In this connection, allowance of a particular way of the given pericyclic process is likely to be directly determined by topological properties of the cycle under formation including the total number of participating atoms and the signs of overlap integrals between the neighboring pairs of AOs (the so-called overlap topology). Applicability of the concept of the Hückel and Möbius aromaticity [12–14], as well as of the topological analysis of the electron localization function (a measure of the local Pauli repulsion) [15–19] to the relevant transition states serves as an indirect support for the above-formulated hypothesis. The present study is aimed at its direct verification.

To this end, we are about to apply the perturbative method of obtaining the one-electron density matrix (DM) of the system (**P**) directly [20,21] on the basis of solution of the relevant commutation equation to an early stage of the cyclization process. The respective total energy (E), in turn, follows from the well-known interdependence $E = \mathrm{Trace}(\mathbf{PH})$, where **H** is the Hamiltonian matrix [22]. Solution of the eigenvalue equation for the latter and thereby passing into the basis of delocalized molecular orbitals (MOs) is not required here. We also intend to abandon the popular belief that the molecular graph and/or its adjacency matrix is the only algebraic representation of molecular topology. Moreover, we avoid introducing any topological characteristic a priori. Instead, we will analyze the actual expressions for members of the power series for both the DM and total energy referring to early stages of pericyclic reactions to reveal there some specific terms representing the overlap topology of AOs over the cycle under formation.

Members of the power series for the DM **P** were shown to be expressible [20, 21] in terms of specific matrices $\mathbf{G}_{(k)}$, describing the direct (through-space) and indirect (through-bond) interactions of basis orbitals (k here and below stands for the order parameter). These interactions, in turn, are proportional to certain products of resonance parameters and/or of overlap integrals. It may be expected on this basis that elements of the resulting DMs and thereby the related total energies contain a dependence upon the relevant overlap topology of AOs of the cycle. Our specific aim consists just in derivation of a compact form of the above-anticipated dependence.

We start with an overview of expressions for one-electron DMs and total energies in Section 2. Thereupon, we describe a certain unified model of pericyclic reactions that reflects the formation of a cycle and the subsequent recyclization. The principal features of direct and indirect interorbital interactions representing this model also are discussed in Section 3. Section 4 deals with overlap-topology-dependent contributions to elements of the DM and to total energies of our unified model. The final Section 5 contains an illustration of the general results by consideration of specific reactions, as well as a comparison of the present approach to related approaches and methods.

2. Overview of Expressions for the One-Electron DMs and Total Energies

As it was mentioned earlier, elements of the one-electron DM have been expressed in Refs. 20 and 21 in terms of those of certain principal matrices $\mathbf{G}_{(k)}$ describing the direct and indirect interactions of basis orbitals. In this connection, let us start with definitions of the elements $G_{(k)ij}$. Let us assume that our basis set $\{\varphi\}$ consists of I initially occupied basis orbitals and of J initially vacant ones. These basis functions will be correspondingly abbreviated as IOBOs and IVBOs and supplemented with subscripts (+) and (−), viz. $\varphi_{(+)i}, \quad i = 1, 2 \ldots I$ and $\varphi_{(-)j}, \quad j = 1, 2 .. J$. Then the first order element $G_{(1)ij}$ may be expressed as follows

$$G_{(1)ij} = -\frac{\langle \varphi_{(+)i} \mid \widehat{H} \mid \varphi_{(-)j} \rangle}{\varepsilon_{(+)i} - \varepsilon_{(-)j}} \tag{1}$$

and describes the direct (through-space) interaction between orbitals $\varphi_{(+)i}$ and $\varphi_{(-)j}$. The numerator of the right-hand side of Eq.(1) contains the Hückel type Hamiltonian matrix element (resonance parameter) between basis orbitals indicated within the bra- and ket-vectors, and the denominator involves the relevant difference in one-electron energies.

Similarly, the second order element $G_{(2)ij}$ describes the indirect interaction between the same orbitals by means of a single mediator. This element takes the form

$$\begin{aligned} G_{(2)ij} = {} & \frac{1}{\varepsilon_{(+)i} - \varepsilon_{(-)j}} \\ & \times \left\{ \sum_{m}^{\text{IOBOs}} \frac{V_{im} R_{mj}}{\varepsilon_{(+)m} - \varepsilon_{(-)j}} - \sum_{n}^{\text{IVBOs}} \frac{R_{in} Q_{nj}}{\varepsilon_{(+)i} - \varepsilon_{(-)n}} \right\}, \end{aligned} \tag{2}$$

where the meanings of designations coincide with those of Eq.(1), and

$$\begin{aligned} V_{im} &= \langle \varphi_{(+)i} \mid \widehat{H} \mid \varphi_{(+)m} \rangle, \\ R_{mj} &= \langle \varphi_{(+)m} \mid \widehat{H} \mid \varphi_{(-)j} \rangle, \\ Q_{nj} &= \langle \varphi_{(-)n} \mid \widehat{H} \mid \varphi_{(-)j} \rangle. \end{aligned} \tag{3}$$

It is seen that both IOBOs and IVBOs play the role of mediators in the indirect interaction between orbitals $\varphi_{(+)i}$ and $\varphi_{(-)j}$. To be an efficient mediator, however, the orbital under consideration ($\varphi_{(+)m}$ or $\varphi_{(-)n}$) should overlap with both $\varphi_{(+)i}$ and $\varphi_{(-)j}$. Hence, orbitals situated in between the indirectly interacting orbitals meet this condition best of all.

The element $G_{(3)ij}$ describes the indirect interaction of the same orbitals $\varphi_{(+)i}$ and $\varphi_{(-)j}$ by means of two mediators. The relevant expression is as follows [21]:

$$\begin{aligned} G_{(3)ij} = {} & \frac{-1}{\varepsilon_{(+)i} - \varepsilon_{(-)j}} \\ & \times \left\{ \sum_{n}^{\text{IOBOs}} \sum_{m}^{\text{IOBOs}} \frac{V_{in} V_{nm} R_{mj}}{(\varepsilon_{(+)n} - \varepsilon_{(-)j})(\varepsilon_{(+)m} - \varepsilon_{(-)j})} \right. \\ & - \sum_{n}^{\text{IOBOs}} \sum_{r}^{\text{IVBOs}} \left[\frac{V_{in} R_{nr} Q_{rj}}{(\varepsilon_{(+)n} - \varepsilon_{(-)j})(\varepsilon_{(+)n} - \varepsilon_{(-)r})} \right. \\ & + \frac{V_{in} R_{nr} Q_{rj}}{(\varepsilon_{(+)i} - \varepsilon_{(-)r})(\varepsilon_{(+)n} - \varepsilon_{(-)r})} \\ & + \frac{R_{ir} R^{+}_{rn} R_{nj}}{(\varepsilon_{(+)n} - \varepsilon_{(-)r})(\varepsilon_{(+)n} - \varepsilon_{(-)j})} \\ & \left. + \frac{R_{ir} R^{+}_{rn} R_{nj}}{(\varepsilon_{(+)i} - \varepsilon_{(-)r})(\varepsilon_{(+)n} - \varepsilon_{(-)r})} \right] \\ & \left. + \sum_{r}^{\text{IVBOs}} \sum_{p}^{\text{IVBOs}} \frac{R_{ir} Q_{rp} Q_{pj}}{(\varepsilon_{(+)i} - \varepsilon_{(-)p})(\varepsilon_{(+)i} - \varepsilon_{(-)r})} \right\}. \end{aligned} \tag{4}$$

Pairs of mutually overlapping orbitals situated in between the orbitals $\varphi_{(+)i}$ and $\varphi_{(-)j}$ are the most efficient mediators of this indirect interaction.

The above-exhibited expressions for elements $G_{(k)ij}$ may be considered in a more formalized manner [23] as follows: Any product of resonance parameters of Eqs. (2) and (4) represents a pathway from the IOBO $\varphi_{(+)i}$ to the IVBO $\varphi_{(-)j}$ via a bridge consisting of mediating orbitals. For example, the product $V_{im} R_{mj}$ of Eq. (2) describes a pathway between orbitals $\varphi_{(+)i}$ and $\varphi_{(-)j}$ via a single IOBO $\varphi_{(+)m}$, while $V_{in} V_{nm} R_{mj}$ of Eq. (4) represents an analogous pathway via two IOBOs $\varphi_{(+)n}$ and $\varphi_{(+)m}$. Accordingly, the expression for a certain element $G_{(k)ij}$ contains increments of all possible pathways from $\varphi_{(+)i}$ and $\varphi_{(-)j}$ via $k-1$ mediators. In particular, four types of fractions of Eq. (4)

correspond to bridges of four possible constitution, namely $(\varphi_{(+)n}, \varphi_{(+)m})$, $(\varphi_{(+)n}, \varphi_{(-)r})$, $(\varphi_{(-)r}, \varphi_{(+)n})$, and $(\varphi_{(-)r}, \varphi_{(-)p})$. On the whole, the higher is the order parameter k of the element $G_{(k)ij}$, the larger is the total number of different fractions and/or bridges. It should be emphasized here in addition that the pathway under consideration actually contributes to the total element $G_{(k)ij}$ only if all resonance parameters contained within the relevant product take nonzero values. Consequently, revealing of the principal contributing pathways is required for evaluation of a certain element $G_{(k)ij}$. Another remark to be made here consists in the fact that the series of interorbital interactions $G_{(1)ij}, G_{(2)ij} \dots G_{(k)ij} \dots$ converges if resonance parameters of numerators of fractions take sufficiently small values vs. the energy gaps between IOBOs and IVBOs. This implies the respective condition to be imposed on the basis set $\{\varphi\}$ (Section 3).

Let us turn now to the representation of the one-electron DM in the basis $\{\varphi\}$. Let this matrix to be denoted by $\widetilde{\mathbf{P}}$ [The symbol ~ serves here to distinguish the above-specified representation of the DM from that referring to the basis of AOs (Section 4)]. As it was mentioned earlier, the matrix $\widetilde{\mathbf{P}}$ has been derived in Refs. 20 and 21 in the form of power series. Accordingly, the expressions for elements $\widetilde{P}_{ij}$ contain sums of corrections $\widetilde{P}^{(k)}_{ij}$ of various orders (k).

Given that the subscripts i and j correspond to an IOBO ($\varphi_{(+)i}$) and to an IVBO ($\varphi_{(-)j}$), the respective corrections $\widetilde{P}^{(k)}_{(+)i,(-)j}$ $(k = 1, 2, 3 \dots)$ take the form

$$\widetilde{P}^{(k)}_{(+)i,(-)j} = -2G_{(k)ij}, \tag{5}$$

where $G_{(k)ij}$ are elements of the principal matrices $G_{(k)}$ defined by Eqs. (1)–(4) and determining various types of direct and indirect interactions between orbitals $\varphi_{(+)i}$ and $\varphi_{(-)j}$. The zero order term $\widetilde{P}^{(0)}_{(+)i,(-)j}$ of Eq.(5) takes a zero value. If both subscripts i and j refer to IOBOs, the following expressions for the relevant corrections have been obtained

$$\widetilde{P}^{(0)}_{(+)i,(+)j} = 2\delta_{ij}; \quad \widetilde{P}^{(1)}_{(+)i,(+)j} = 0;$$

$$\widetilde{P}^{(2)}_{(+)i,(+)j} = -2 \sum_{r}^{\text{IVBOs}} G_{(1)ir} G^{+}_{(1)rj};$$

$$\widetilde{P}^{(3)}_{(+)i,(+)j} = -2 \sum_{r}^{\text{IVBOs}} \left(G_{(1)ir} G^{+}_{(2)rj} + G_{(2)ir} G^{+}_{(1)rj} \right), \tag{6}$$

where the superscripts of the left-hand sides (0), (1), etc. indicate the orders of respective corrections. The superscripts + of the right-hand sides denote elements of the Hermitian-conjugate matrices $G^{+}_{(k)}$.

Finally, for both i and j corresponding to IVBOs, the relevant corrections are

$$\widetilde{P}^{(0)}_{(-)i,(-)j} = \widetilde{P}^{(1)}_{(-)i,(-)j} = 0; \quad \widetilde{P}^{(2)}_{(-)i,(-)j} = 2 \sum_{m}^{\text{IOBOs}} G^{+}_{(1)im} G_{(1)mj};$$

$$\widetilde{P}^{(3)}_{(-)i,(-)j} = 2 \sum_{m}^{\text{IOBOs}} \left(G^{+}_{(1)im} G_{(2)mj} + G^{+}_{(2)im} G_{(1)mj} \right). \tag{7}$$

Given that j coincides with i in Eqs. (6) and (7), populations of BOs $\varphi_{(+)i}$ and $\varphi_{(-)i}$ will be obtained. It deserves mentioning here that the right-hand sides of Eqs. (6) and (7) also may be interpreted as indirect interactions between respective pairs of basis orbitals, i.e. between $\varphi_{(+)i}$ and $\varphi_{(+)j}$, and between $\varphi_{(-)i}$ and $\varphi_{(-)j}$. In this connection, it is convenient to define the relevant indirect interactions $\Gamma^{(k)}_{(+)i,(+)j}$ and $\Gamma^{(k)}_{(-)i,(-)j}$ on the basis of the following relations

$$\widetilde{P}^{(k)}_{(+)i,(+)j} = -2\Gamma^{(k)}_{(+)i,(+)j}, \quad \widetilde{P}^{(k)}_{(-)i,(-)j} = -2\Gamma^{(k)}_{(-)i,(-)j} \tag{8}$$

similar to that of Eq. (5). The expressions for $\Gamma^{(k)}_{(+)i,(+)j}$ and $\Gamma^{(k)}_{(-)i,(-)j}$ easily follow from Eqs. (6) and (7), respectively. The numbers of mediators of these new interactions coincide with $k-1$ as it was the case with $G_{(k)ij}$. For diagonal elements $\widetilde{P}^{(k)}_{(+)i,(+)i}$ and $\widetilde{P}^{(k)}_{(-)i,(-)i}$, the resulting factors $\Gamma^{(k)}_{(+)i,(+)i}$ and $\Gamma^{(k)}_{(-)i,(-)i}$ represent the indirect k-th order self-interactions of BOs $\varphi_{(+)i}$ and $\varphi_{(-)i}$, respectively. Thus, alterations in the populations of basis orbitals $\varphi_{(+)i}$ and $\varphi_{(-)i}$ against their initial values 2 and 0, respectively, are determined by the relevant self-interations.

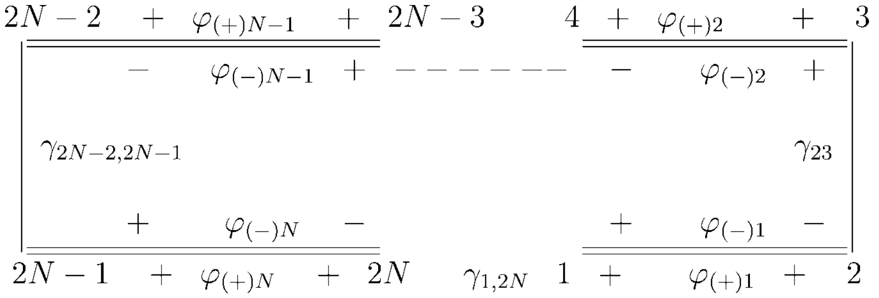
The total energy of the same system (E) is known to be related to the respective DM ($\widetilde{\mathbf{P}}$) as follows [24]:

$$E = \text{Trace}(\widetilde{\mathbf{P}}\widetilde{\mathbf{H}}), \tag{9}$$

where $\widetilde{\mathbf{H}}$ is the relevant Hamiltonian matrix in the basis $\{\varphi\}$. The latter was assumed to consist [20–22] of the sum of the zero and first order members, i.e.

$$\widetilde{\mathbf{H}} = \widetilde{\mathbf{H}}_{(0)} + \widetilde{\mathbf{H}}_{(1)}, \tag{10}$$

where $\widetilde{\mathbf{H}}_{(0)}$ coincides with a diagonal matrix containing one-electron energies of IOBOs ($\varepsilon_{(+)i}$) and of IVBOs ($\varepsilon_{(-)j}$) and $\widetilde{\mathbf{H}}_{(1)}$ involves resonance parameters defined by Eq. (3). Substituting Eq. (10) and the power series for the DM $\widetilde{\mathbf{P}}$ [20,21] into Eq. (9) yields an analogous series for the energy E [22]. The sum



SCHEME 1. The unified model of pericyclic reactions. The bonding and antibonding bond orbitals of individual initially double (C=C) bonds are denoted by $\varphi_{(+)i}$ and $\varphi_{(-)i}$, respectively, where $i = 1, 2, \ldots N$. The signs of coefficients at particular $2p_z$ AOs of these bond orbitals are indicated above and/or below the respective C=C bond. Resonance parameters of weak (initially single and initially zero) bonds are designated by γ_{23}, $\gamma_{2N-2,2N-1}$, and $\gamma_{1,2N}$, where the subscripts represent the relevant numbers of AOs.

of the zero and first order corrections ($E_{(0)} + E_{(1)}$) of this series coincides with the total energy of isolated double-occupied basis orbitals, whereas the remaining corrections $E_{(k)} (k = 2, 3, ..)$ are expressible as sums of two related components, viz.

$$E_{(k)} = E_{(k)}^{(\alpha)} + E_{(k)}^{(\beta)}, \tag{11}$$

where

$$E_{(k)}^{(\alpha)} = \mathrm{Trace}(\widetilde{\mathbf{P}}_{(k)}\widetilde{\mathbf{H}}_{(0)}), \tag{12}$$

$$E_{(k)}^{(\beta)} = \mathrm{Trace}(\widetilde{\mathbf{P}}_{(k-1)}\widetilde{\mathbf{H}}_{(1)}), \tag{13}$$

and

$$(k-1)E_{(k)}^{(\beta)} = -kE_{(k)}^{(\alpha)} \tag{14}$$

is the above-mentioned interrelation. The total correction $E_{(k)}$ may be then alternatively expressed as follows

$$E_{(k)} = \frac{1}{k}E_{(k)}^{(\beta)}, \quad E_{(k)} = -\frac{1}{k-1}E_{(k)}^{(\alpha)}. \tag{15}$$

The sum of corrections $E_{(k)}$ starting with $k = 2$ represents the stabilization (or destabilization) energy of the system due to interorbital interactions.

3. The Unified Model of Pericyclic Reactions. The Principal Properties of the Relevant Interorbital Interactions

Let us start with description of our model of pericyclic reactions. Aliphatic conjugated hydrocarbons (polyenes) are known as the most common participants of these processes [9–11]. Thus, constitution of these compounds forms the basis of our model: We will consider a formation of an even-membered cycle of carbon atoms. We will dwell on a rather early stage of this cyclization process situated in between the initial open chain and the transition state on the scale of the reaction coordinate. The principal assumption here consists in the possibility of distinguishing between strong (initially double) and weak (initially single and initially zero) bonds in the cycle.

Let our cycle of 2N carbon atoms to contain N strong (C=C) bonds and N weak (C–C) bonds alternately (Scheme 1). The atoms will be enumerated in a usual cyclic way so that C_1=C_2, C_3=C_4, etc. correspond to strong bonds. Carbon atoms will be represented by their $2p_z$ AOs $\{\chi\} = \{\chi_1, \chi_2, \ldots \chi_{2N}\}$ characterized by uniform Coulomb parameters α. The strongly overlapping pairs of AOs referring to initially double bonds will be described by uniform negative resonance parameters β. The equalities $\alpha = 0$ and $\beta = 1$ will be accepted for convenience, the latter indicating a negative energy unit to be actually chosen. The above-mentioned assumption about strong and weak bonds of our model implies resonance parameters β to be incorporated into the zero order Hamiltonian matrix $\mathbf{H}_{(0)}$. Meanwhile, resonance parameters representing the remaining pairs of AOs will be denoted by $\gamma_{23}, \gamma_{45} \ldots \gamma_{2N-2,2N-1}, \gamma_{1,2N}$ (Scheme 1) and included into the first order matrix $\mathbf{H}_{(1)}$. [The requirements of the perturbation theory underlying the expressions of Section 2 are not met in the basis $\{\chi\}$. Thus, the matrices $\mathbf{H}_{(0)}$ and $\mathbf{H}_{(1)}$ do not coincide with those of Eq. (10)]. As opposed to the parameter β, the resonance parameters γ_{mn} are assumed to take either a positive or a negative value. Positive values of these parameters will correspond to positive overlap integrals and vice versa in accordance with the negative energy unit. On the whole, a formally uniform polyene-like constitution is peculiar to our model.

Now, we are about to explore the dependence between particular elements of the one-electron DM of the model in the basis of AOs $\{\chi\}$ (i.e., of the so-called charge-bond order matrix) and the signs of N parameters $\{\gamma_{mn}\}$ representing the overlap topology over the cycle, as well as of an analogous dependence for the relevant total energy. To be able to apply the power series of Section 2, we have to turn to the basis of bonding and antibonding bond orbitals (BOs) defined below. In this alternative basis set, convergence of the power series shown in Eqs. (5)–(7) was verified in Ref. 25. It is also evident that the bonding BOs (BBOs) are initially occupied orbitals in our polyene-like model, whereas the antibonding BOs (ABOs) coincide with the initially vacant ones. This implies that the expressions of Section 2 are applicable to our model just in this basis. Thereupon, we will return to the basis of AOs again in Section 4.

BBOs and ABOs of our model will be defined as bonding and antibonding combinations of pairs of AOs of the initially double (C═C) bonds. Let the designation $\{\varphi\}$ of Section 2 to be used also to the basis of BOs, where $\varphi_{(+)i}$ and $\varphi_{(-)i}$ will stand for BBOs and for ABOs, respectively. We then obtain

$$\varphi_{(+)1}(\varphi_{(-)1}) = \frac{1}{\sqrt{2}}(\chi_1 \pm \chi_2),$$
$$\varphi_{(+)2}(\varphi_{(-)2}) = \frac{1}{\sqrt{2}}(\chi_3 \pm \chi_4), \text{etc} \quad (16)$$

where the upper and the lower signs of the right-hand sides of these expressions also correspondingly refer to BBOs and to ABOs. After passing to the basis $\{\varphi\}$, the Hamiltonian matrix of our model turns into that shown in Eq. (10), where the zero order member $\widetilde{\mathbf{H}}_{(0)}$ contains one-electron energies of BOs equal to 1 and to -1 for BBOs and ABOs, respectively.

Let us turn now to expressions of Section 2. The matrix elements $G_{(k)ij}$ of Eqs. (1)–(4) will represent now the interactions of the k-th order between the BBO $\varphi_{(+)i}$ of the Ith bond and the ABO $\varphi_{(-)j}$ of the Jth bond. Note that the definition of BOs of Eq. (16) implies the equality $R_{ii} = 0$ and thereby zero values for first order direct intrabond interactions $G_{(1)ii}$. The above-mentioned formally uniform constitution of our model is likely to imply specific features of the relevant interorbital interactions $G_{(k)ij}, \Gamma^{(k)}_{(+)i,(+)j}$, and $\Gamma^{(k)}_{(-)i,(-)j}$. Let us dwell now just on this point.

Similarity of all initially double bonds of our cycle allows the energy intervals $\varepsilon_{(+)i} - \varepsilon_{(-)j}$ of Eqs. (1), (2), and (4) to be replaced by 2. As a result, the factors $(2)^{-k}$ arise in front of any expression for an indirect interaction and products of the relevant resonance parameters actually remain inside the sums.

Let us start with a linear fragment of our cycle. The indirect interactions of the k-th order between orbitals of the C_1═C_2 and C_{2k+1}═C_{2k+2} bonds are then mediated only by orbitals of $k-1$ intervening bonds (C_3═C_4, C_5═C_6 .... C_{2k-1}═C_{2k}). In other words, the existence of the roundabout pathway between the same bonds is not taken into consideration at the present stage of our discussion. We then obtain

$$G_{(1)12} = -\frac{1}{2}R_{12}, \quad G_{(2)13} = \frac{1}{4}(V_{12}R_{23} - R_{12}Q_{23}),$$
$$G_{(3)14} = -\frac{1}{8}(V_{12}V_{23}R_{34} - 2V_{12}R_{23}Q_{34} - 2R_{12}R^{+}_{23}R_{34}$$
$$+ R_{12}Q_{23}Q_{34}), \text{etc.} \quad (17)$$

In the basis of BOs $\{\varphi\}$, any neighboring pair of initially double (C═C) bonds is characterized by four resonance parameters V_{ij}=V_{ji}, R_{ij}, R_{ji} and $Q_{ij} = Q_{ji}$ (Note that $R_{ij} \neq R_{ji}$). For example, parameters $V_{12} = V_{21}, R_{12}, R_{21}$ and $Q_{12} = Q_{21}$ refer to bonds C_1═C_2 and C_3═C_4. In the basis of AOs, however, a single nonzero parameter (γ_{23}, respectively) represents the interaction of these bonds. As a result, the former four parameters become expressible via the latter, e.g.

$$V_{12} = V_{21} = \frac{1}{2}\gamma_{23}, \quad R_{12} = \frac{1}{2}\gamma_{23}, \quad R_{21} = -\frac{1}{2}\gamma_{23},$$
$$Q_{12} = Q_{21} = -\frac{1}{2}\gamma_{23}. \quad (18)$$

After excluding the right-hand sides of the above relations, we obtain

$$V_{ij} = V_{ji} = R_{ij} = -R^{+}_{ij} = -R_{ji} = -Q_{ij} = -Q_{ji} \quad (19)$$

for any neighboring pair of C═C bonds provided that the Jth bond takes an anticlockwise position with respect to the Ith bond in the cycle of Scheme 1. Employment of Eq. (19) within Eq. (17) yields the expressions

$$G_{(1)12} = -\frac{1}{2}R_{12}, \quad G_{(2)13} = \frac{1}{2}R_{12}R_{23},$$
$$G_{(3)14} = -\frac{3}{4}R_{12}R_{23}R_{34}, \text{etc.} \quad (20)$$

Using Eq. (1) [see also Eq. (3)], the second and third relations of Eq. (20) may be reformulated in terms of products of first order interactions $G_{(1)ij}$ as follows

$$G_{(2)13} = 2G_{(1)12}G_{(1)23}, \quad G_{(3)14} = 6G_{(1)12}G_{(1)23}G_{(1)34}. \tag{21}$$

The generalized form of Eq. (21) is

$$G^{(a)}_{(K-1)1K} = a_K G_{(1)12}G_{(1)23} \dots G_{(1)K-1,K}, \tag{22}$$

where the superscript (a) of the left-hand side denotes the anticlockwise position of the 1st and Kth C=C bonds underlying Eq. (21), and a_K stands for a positive numerical coefficient. The first four members of the series of these coefficients are

$$a_2 = 1, \quad a_3 = 2, \quad a_4 = 6, \quad a_5 = 20. \tag{23}$$

The result shown in Eq. (22) will be further referred to as factorization of indirect interactions. Asmuch as Eq. (22) reflects a division of the total bridge between the 1st and the Kth C=C bonds into $K - 1$ steps, the product of the right-hand side of this relation may be conveniently referred to as the stepwise interaction between BOs $\varphi_{(+)1}$ and $\varphi_{(-)K}$. From the above discussion it also follows that the indirect interaction $G^{(a)}_{(K-1)1K}$ is determined by the product of non-neighboring resonance parameters $\gamma_{23}, \gamma_{45}, \dots$ representing the mediating fragment of the chain. Moreover, an additional factor $(-1)^{K-1}$ arises in front of the expression for $G^{(a)}_{(K-1)1K}$ in terms of parameters γ_{mn} owing to the minus sign in the right-hand side of Eq. (1). This factor gives rise to alternation of sign of the total indirect interaction $G^{(a)}_{(K-1)1K}$ [26] with increasing order parameter $k(k = K - 1)$ provided that the resonance parameters $\gamma_{23}, \gamma_{45}, \dots$ are of the same sign.

For the clockwise position of the Ith and Jth C=C bonds, the analog of Eq. (21) is as follows:

$$G^{(c)}_{(2)31} = -2G_{(1)32}G_{(1)21}, \quad G^{(c)}_{(3)41} = 6G_{(1)43}G_{(1)32}G_{(1)21}. \tag{24}$$

The relation $R_{ij} = -R_{ji}$ of Eq. (19) along with Eqs. (1) and (3) implies the equality $G_{(1)ij} = -G_{(1)ji}$. Employment of the latter within Eq. (24) yields the skew-symmetric nature of all interorbital interactions [25], viz.

$$G^{+}_{(k)ji} = G_{(k)ij} = -G_{(k)ji}, \quad k = 1, 2, 3 \dots \tag{25}$$

and the following interrelation

$$G^{(a)}_{(K-1)1K} = -G^{(c)}_{(K-1)K1}. \tag{26}$$

Let us turn now to indirect interactions between BOs of the same nature, i.e. $\Gamma^{(k)}_{(+)i,(+)j}$ and $\Gamma^{(k)}_{(-)i,(-)j}$ defined by Eqs. (6)–(8). As opposed to the above-discussed interactions $G_{(k)ij}$, both $\Gamma^{(k)}_{(+)i,(+)j}$ and $\Gamma^{(k)}_{(-)i,(-)j}$ are symmetric with respect to an interchange of BOs, viz.

$$\Gamma^{(k)}_{(+)i,(+)j} = \Gamma^{(k)}_{(+)j,(+)i}, \quad \Gamma^{(k)}_{(-)i,(-)j} = \Gamma^{(k)}_{(-)j,(-)i}. \tag{27}$$

For particular interactions between BBOs, we obtain

$$\begin{aligned} \Gamma^{(2)}_{(+)1,(+)3} &= G_{(1)12}G^{+}_{(1)23} = -G_{(1)12}G_{(1)23}, \\ \Gamma^{(3)}_{(+)1,(+)4} &= -(G_{(1)12}G_{(2)24} + G_{(2)13}G_{(1)34}) \\ &= -4G_{(1)12}G_{(1)23}G_{(1)34}, \text{etc} \end{aligned} \tag{28}$$

where the last relation follows after factorizing the second order interactions $G_{(2)24}$ and $G_{(2)13}$ in accordance with Eq. (21). For interactions between ABOs, we accordingly obtain

$$\begin{aligned} \Gamma^{(2)}_{(-)1,(-)3} &= -G^{+}_{(1)12}G_{(1)23} = G_{(1)12}G_{(1)23}, \\ \Gamma^{(3)}_{(-)1,(-)4} &= G_{(1)12}G_{(2)24} + G_{(2)13}G_{(1)34} \\ &= 4G_{(1)12}G_{(1)23}G_{(1)34}, \text{etc.} \end{aligned} \tag{29}$$

Comparison of Eqs. (21), (28), and (29) yields the following principal interrelation

$$\Gamma^{(K-1)}_{(+)1,(+)K} = -\Gamma^{(K-1)}_{(-)1,(-)K} = -b_K G^{(a)}_{(K-1)1K}, \quad k = 3, 4 \dots \tag{30}$$

where b_K stands for another positive numerical K-dependent coefficient. The first members of the series concerned are as follows

$$b_2 = 0, \quad b_3 = \frac{1}{2}, \quad b_4 = \frac{2}{3}, \quad b_5 = \frac{3}{4}. \tag{31}$$

To ensure the validity of Eq. (27), let $\Gamma^{(K-1)}_{(+)K,(+)1}$ and $\Gamma^{(K-1)}_{(-)K,(-)1}$ to be expressed as follows:

$$\Gamma^{(K-1)}_{(+)K,(+)1} = -\Gamma^{(K-1)}_{(-)K,(-)1} = b_K G^{(c)}_{(K-1)K1}, \quad k = 3, 4 \dots \tag{32}$$

[see also Eq. (26)]. Eqs. (30) and (32) indicate proportionality between various types of interorbital interactions referring to a particular pair of bonds. Moreover, invoking of Eq. (22) allows us to conclude that the interactions concerned are proportional to the same stepwise interaction shown in the right-hand side of Eq. (22).

Let us turn now to taking into consideration the cyclic structure of our model of pericyclic processes.

To this end, let us define the following N-dependent interaction

$$\Omega_{(N)} = -G_{(1)12}G_{(1)23}G_{(1)34}\dots G_{(1)N-1,N}G_{(1)N1}, \quad (33)$$

which coincides with the step-wise interaction over the whole cycle in the anticlockwise fashion. The minus sign in front of the product of the first order interactions is introduced here for convenience. Let us call $\Omega_{(N)}$ the roundabout interaction of our cycle. The AO χ_1 playes the role of both starting and terminal orbital in the definition of Eq. (33). The total roundabout interaction, however, is invariant with respect to choice of this exclusive site. Indeed, Eq. (33) may be alternatively presented as follows:

$$\Omega_{(N)} = -G_{(1)23}G_{(1)34}G_{(1)45}\dots G_{(1)N-1,N}G_{(1)N1}G_{(1)12}, \quad (34)$$

where the AO χ_2 playes the above-specified role. Finally, an alternative expression for $\Omega_{(N)}$ follows after invoking Eq. (22), viz.

$$\Omega_{(N)} = (a_N)^{-1}G_{(1)12}G_{(N-1)12} = (a_N)^{-1}G_{(1)23}G_{(N-1)23} = \dots$$
$$= (a_N)^{-1}G_{(1)1N}G_{(N-1)1N}, \quad (35)$$

where Eq. (25) is also invoked. Thus, the roundabout interaction $\Omega_{(N)}$ takes a positive value if the direct (through-space) and the indirect (through-cycle) interactions are of same signs for any pair of neighboring bonds and vice versa. It should be mentioned finally that the roundabout interaction $\Omega_{(N)}$ represents the cycle as a whole and not its separate fragments. Thus, it is a collective property of the model.

Let us dwell now on self-interactions of BOs of the Ith bond ($\Gamma_{(+)i,(+)i}$ and $\Gamma_{(-)i,(-)i}$) determining the alterations in populations of these orbitals due to interorbital interaction. Let us take the case $i = 1$ as an example. The power series for these interactions start with second order contributions of the following form

$$\Gamma^{(2)}_{(+)1,(+)1} = -\Gamma^{(2)}_{(-)1,(-)1} = (G_{(1)12})^2 + (G_{(1)1N})^2, \quad (36)$$

where Eqs. (6)–(8) are taken into consideration. The two increments of the right-hand side of Eq. (36) correspond to mediating contributions of AOs χ_2 and χ_N, respectively, to the total self-interactions concerned. Moreover, these increments refer to pathways toward the nearest-neighboring bonds and backward. It is no surprise in this connection that squares of direct interactions arise in the right-hand sides of Eq. (36). It is evident that these increments are little to do with the overlap topology of AOs over the cycle.

Analysis of corrections of higher orders to the same self-interactions shows that pathways of the "toward-backward" nature always yield contributions containing squares of direct interactions. Thus, no dependence upon signs of resonance parameters arises in these contributions. Two roundabout pathways (the clockwise one and the anticlockwise one) are important exceptions here. Contributions of the latter arise within the Nth order corrections to self-interactions and are overlap- topology-dependent.

To show this, let us turn to Eq. (30) and take $K = N + 1$ in the relation shown there. Let us also note that $N + 1$ actually coincides with 1 owing to the cyclic constitution of our model. As a result, the right-hand side of Eq. (30) becomes proportional to the roundabout interaction $\Omega_{(N)}$ [see also Eqs. (22) and (33)]. We then obtain the contributions of the anticlockwise roundabout pathway to the total Nth order self-interactions of BOs $\varphi_{(+)1}$ and $\varphi_{(-)1}$. Let the overlined notations to be used for these particular contributions. The latter then take the form

$$\overline{\Gamma}^{(N,a)}_{(+)1,(+)1} = -\overline{\Gamma}^{(N,a)}_{(-)1,(-)1} = -b_{N+1}G^{(a)}_{(N)1,N+1} \equiv$$
$$- b_{N+1}G^{(a)}_{(N)11} = a_{N+1}b_{N+1}\Omega_{(N)} = c_{N+1}\Omega_{(N)}, \quad (37)$$

where c_{N+1} stands for the product $a_{N+1}b_{N+1}$. Analogously, Eq. (32) yields the relevant contribution of the clockwise roundabout pathway to the same self-interactions of BOs, viz.

$$\overline{\Gamma}^{(N,c)}_{(+)1,(+)1} = -\overline{\Gamma}^{(N,c)}_{(-)1,(-)1} = b_{N+1}G^{(c)}_{(N)11}$$
$$= -b_{N+1}G^{(a)}_{(N)11} = c_{N+1}\Omega_{(N)}, \quad (38)$$

where passing from $G^{(c)}_{(N)11}$ to $G^{(a)}_{(N)11}$ is based on Eq. (26). It is seen that increments of Eqs. (37) and (38) coincide one with another. This result is in line with the symmetry requirement of Eq. (27) and allows us to derive total contributions of the two roundabout pathways, viz.

$$\overline{\Gamma}^{(N)}_{(+)1,(+)1} = -\overline{\Gamma}^{(N)}_{(-)1,(-)1} = 2c_{N+1}\Omega_{(N)}. \quad (39)$$

The right-hand side of the above relation contains no dependence upon the number of the bond concerned, i.e. upon i. Moreover, the same procedure of its derivation refers to any i value from 1 to N. Thus, the roundabout pathways yield uniform increments to any self-interaction $\Gamma_{(+)i,(+)i}$ and/or $\Gamma_{(-)i,(-)i}$.

Let us note finally that the roundabout interaction $\Omega_{(N)}$ is alternatively expressible in terms of resonance parameters R_{ij} using Eqs. (1) and (33). We then obtain

$$\Omega_{(N)} = (-1)^{N+1}2^{-N}R_{12}R_{23}R_{34}\ldots R_{N-1,N}R_{N1}, \qquad (40)$$

where the factor $(-1)^N$ originates from the minus sign of the right-hand side of Eq. (1). Expressibility of parameters R_{ij} via resonance parameters γ_{mn} as shown in Eq. (18), in turn, allows the relation of Eq. (40) to be reformulated as follows:

$$\Omega_{(N)} = (-1)^{N+1}2^{-2N}\gamma_{23}\gamma_{45}\gamma_{67}\ldots\gamma_{2N-2,2N-1}\gamma_{2N,1}. \qquad (41)$$

The dependence of the roundabout interaction $\Omega_{(N)}$ upon the overlap topology of AOs $\{\chi\}$ is evident from Eq. (41). The factor $(-1)^{N+1}$, in turn, depends on the total number of C=C bonds in our cycle (N). This may be referred to as the parity factor for simplicity. Thus, $\overline{\Gamma}^{(N)}_{(+)1,(+)1}$ and $\overline{\Gamma}^{(N)}_{(-)1,(-)1}$ of Eq. (39) are overlap-topology-dependent increments to self-interactions of BOs $\varphi_{(+)1}$ and $\varphi_{(-)1}$ of the Ith bond.

4. Overlap-Topology-Dependent Contributions to Bond Orders Between AOs and to the Total Energy of the Unified Model of Pericyclic Processes

In this Section, we are about to derive and analyze the overlap-topology-dependent contributions to bond orders of various bonds of our model, as well as the analogous contributions to the total energy. To this end, we have to retransform the expressions of Eqs. (5)–(7) into the AO basis $\{\chi\}$. The relevant transformation matrix may be easily constructed on the basis of Eq. (16). Moreover, we will invoke the concept of the roundabout interaction $\Omega_{(N)}$ when dealing with occupation numbers of BOs. It is also essential to note here that the relations concerning total energies and shown in Eqs. (11)–(15) are invariant against unitary transformations of the basis set including passing from AOs to BOs and/or backward. Thus, Eqs. (11)–(15) may be straightforwardly applied to power series for the charge-bond order matrix **P** and to the respective Hamiltonian matrix **H** in the basis $\{\chi\}$.

Let us start with bond orders of initially double bonds and consider the $C_1{=}C_2$ bond as an example. The respective bond order is expressible as follows

$$P_{12} = \frac{1}{2}(\widetilde{P}_{(+)1,(+)1} - \widetilde{P}_{(-)1,(-)1}), \qquad (42)$$

where the right-hand side contains populations of BOs $\varphi_{(+)1}$ and $\varphi_{(-)1}$. The latter are proportional to self-interactions $\Gamma_{(+)1,(+)1}$ and $\Gamma_{(-)1,(-)1}$, respectively [see Eq. (8)]. Substituting Eq. (8) into Eq. (42) yields a zero order term of the power series for P_{12} coinciding with 1 in accordance with the expectation (this contribution refers to an isolated C=C bond). The first order member takes a zero value in the same series, whilst the second order one follows after substituting Eq. (36) into Eqs. (8) and (42) and proves to be a negative quantity. Thus, the primary bond order of our bond (equal to 1) always becomes reduced due to interbond interaction.

Let the cyclization process to be defined as formation of a nonzero roundabout interaction $\Omega_{(N)}$ in our model. As it was discussed earlier in Section 3, the overlap-topology-dependent contribution to self-interactions of BOs and thereby to the bond order P_{12} originates from Nth order terms $\overline{\Gamma}^{(N)}_{(+)1,(+)1}$ and $\overline{\Gamma}^{(N)}_{(-)1,(-)1}$ shown in Eq. (39) and proportional to the roundabout interaction $\Omega_{(N)}$. We then obtain

$$\overline{P}^{(N)}_{12} = -2\overline{\Gamma}^{(N)}_{(+)1,(+)1} = -4c_{N+1}\Omega_{(N)}. \qquad (43)$$

It is seen that the local alteration in the order of the $C_1{=}C_2$ bond is determined by the collective property of the cycle $\Omega_{(N)}$. Moreover, the sign of this overlap-topology-dependent alteration depends on that of the roundabout interaction $\Omega_{(N)}$. Consequently, this bond order becomes reduced during the cyclization process more substantially if the relevant roundabout interation $\Omega_{(N)}$ takes a positive value and vice versa. It is also evident that the increment of Eq. (43) refers to any initially double (C=C) bond, i.e.

$$\overline{P}^{(N)}_{12} = \overline{P}^{(N)}_{34} = \overline{P}^{(N)}_{56} = \ldots \overline{P}^{(N)}_{2N-3,2N-2} = \overline{P}^{(N)}_{2N-1,2N}. \qquad (44)$$

Thus, overlap-topology-determined alterations in the orders of all initially double bonds are uniform in our model.

Let us turn now to alterations in the orders of the remaining (C—C) bonds. Let us consider the bond order $P_{1,2N}$ between AOs χ_1 and χ_{2N} as an example. Instead of Eq. (42), we then obtain [26]

$$P_{1,2N} = \frac{1}{2}(\widetilde{P}_{(+)1,(+)N} - \widetilde{P}_{(-)1,(-)N} + \widetilde{P}_{(+)N,(-)1} - \widetilde{P}_{(+)1,(-)N}). \qquad (45)$$

Using Eqs. (5), (8), (25), and (30), this expression may be simplified as follows

$$P_{1,2N} = \widetilde{P}_{(+)1,(+)N} - \widetilde{P}_{(+)1,(-)N}. \qquad (46)$$

The increments of the right-hand side of Eq. (46) may be derived using Eqs. (5) and (6). It is evident that the power series for $P_{1,2N}$ starts with the first order contribution originating from the increment $\widetilde{P}^{(1)}_{(+)1,(-)N}$, viz.

$$P^{(1)}_{1,2N} = -\widetilde{P}^{(1)}_{(+)1,(-)N} = 2G_{(1)1N} = \frac{1}{2}\gamma_{1,2N}. \tag{47}$$

[The last equality is based on Eqs. (1), (3), and (18)]. It is seen that the first order contribution to the bond order under our interest is determined exclusively by the direct (through-space) interaction between BOs of the 1st and of the Nth bond, i.e. between $\varphi_{(+)1}$ and $\varphi_{(-)N}$. Accordingly, the sign of this contribution depends on that of the respective resonance parameter $\gamma_{1,2N}$. This implies that both positive and negative values may arise here.

The dependence of the bond order $P_{1,2N}$ upon the overall constitution of the cycle and thereby upon the overlap topology of AOs $\{\chi\}$ manifests itself within the $(N-1)$th order correction $P^{(N-1)}_{1,2N}$. To reveal this dependence, the increment of the roundabout pathway from the AO χ_1 to χ_{2N} to the above-mentioned correction should be considered. This increment follows from Eqs. (5), (8), and (30) and takes the form

$$\overline{P}^{(N-1)}_{1,2N} = 2\big(G_{(N-1)1N} - \Gamma^{(N-1)}_{(+)1,(+)N}\big) = 2(1+b_N)G^{(a)}_{(N-1)1N}, \tag{48}$$

where $G^{(a)}_{(N-1)1N}$ is the indirect anticlockwise interaction between BOs $\varphi_{(+)1}$ and $\varphi_{(-)N}$ via the cycle. Alternation of sign of this interaction when the number N grows was established in Section 3 in the case of coinciding signs of resonance parameters γ_{mn}. Thus, both positive and negative signs of $\overline{P}^{(N-1)}_{1,2N}$ are possible.

The expression for the total bond order $P_{1,2N}$ may be then presented as follows

$$\begin{aligned} P_{1,2N} &= P^{(1)}_{1,2N} + \cdots + \overline{P}^{(N-1)}_{1,2N} + \cdots \\ &= 2G_{(1)1N} + \cdots + 2(1+b_N)G^{(a)}_{(N-1)1N} + \cdots \end{aligned} \tag{49}$$

where dots stand for other overlap-topology-independent increments originating from pathways of the toward-backward type (the latter may be exemplified by $(G_{(1)12})^2\, G_{(1)1N}$, $(G_{(1)12})^2 (G_{(1)23})^2 G_{(1)1N}$, etc.). From Eq. (49) it is seen that the bond order $P_{1,2N}$ takes a more significant absolute value if the direct and the indirect (through-cycle) interactions of BOs $\varphi_{(+)1}$ and $\varphi_{(-)N}$ are of the same sign. Let us take now the square of the bond order $P_{1,2N}$, viz.

$$(P_{1,2N})^2 = 4(G_{(1)1N})^2 + \cdots + 8(1+b_N)G_{(1)1N}G^{(a)}_{(N-1)1N} + \cdots \tag{50}$$

The dependence of $(P_{1,2N})^2$ upon the overlap topology of AOs is described by the product $G_{(1)1N}G^{(a)}_{(N-1)1N}$. The latter is proportional to the roundabout interaction $\Omega_{(N)}$ as Eq. (35) indicates. Thus, the overlap-topology-determined contribution to the square of the bond order $P_{1,2N}$ is as follows

$$\overline{(P_{1,2N})^2} = 8(1+b_N)a_N\Omega_{(N)}. \tag{51}$$

The same result may be evidently derived for any C—C bond of our model. Hence, overlap-topology-dependent alterations in squares of bond orders of all weak bonds of the cycle are uniform in spite of dissimilar resonance parameters γ_{mn}.

Comparison of Eqs. (43) and (51), in turn, shows that the overlap-topology-dependent alterations in the orders of strong and weak bonds are expressible in terms of the same topological factor $\Omega_{(N)}$. Moreover, the right-hand sides of these relations always are of opposite signs. Hence, the above-mentioned two types of alterations necessarily are of opposite directions. In particular, the overlap-topology-determined reduction of orders of strong bonds is accompanied by growth of absolute values of those of weak bonds if the cycle under formation is characterized by a positive roundabout interaction $\Omega_{(N)}$. Meanwhile, the above-mentioned interdependent alterations acquire opposite signs for cycles described by a negative factor $\Omega_{(N)}$.

Let us turn now to the power series for total energies. As it was mentioned earlier, members $\mathbf{H}_{(0)}$ and $\mathbf{H}_{(1)}$ of the total Hamiltonian matrix $\mathbf{H}$ contain resonance parameters referring to strong and to weak bonds, respectively, in the basis of AOs $\{\chi\}$. Moreover, parameters of the former type coincide with 1. As a result, the zero- and first-order terms of the power series for the total energy E are as follows

$$\begin{aligned} E_{(0)} &= \mathrm{Trace}(\mathbf{H}_{(0)}\mathbf{P}_{(0)}) = 2N, \\ E_{(1)} &= \mathrm{Trace}(\mathbf{H}_{(1)}\mathbf{P}_{(0)} + \mathbf{P}_{(1)}\mathbf{H}_{(0)}) = 0, \end{aligned} \tag{52}$$

where $2N$ represents the total energy of N isolated C═C bonds. The subsequent corrections $E_{(k)}$ starting with $k = 2$ are determined by Eqs. (11)–(15), where the designation ~ may be omitted in the right-hand sides of Eqs. (12) and (13) owing to invariance of Traces against unitary transformations of the basis set.

As much as the zero order Hamiltonian matrix $\mathbf{H}_{(0)}$ contains elements equal to 1 in the positions referring to the initially double (C═C) bonds, the overlap-topology-dependent Nth order corrections like that of Eq. (43) give birth to an Nth order energy correction $\overline{E}_{(N)}^{(\alpha)}$ defined by Eq. (12), viz.

$$\overline{E}_{(N)}^{(\alpha)} = \mathrm{Trace}(\mathbf{H}_{(0)}\mathbf{P}_{(N)}) = -8Nc_{N+1}\Omega_{(N)}. \tag{53}$$

This correction is made up of N uniform increments of individual C═C bonds, each of them coinciding with $2\overline{P}_{12}^{(N)}$ of Eq. (43). Hence, it represents the total energetic effect of all overlap-topology-dependent alterations in the orders of initially double bonds. It is also seen that this component of the total Nth order energy is negative in the case of a positive factor $\Omega_{(N)}$. Thus, the component $\overline{E}_{(N)}^{(\alpha)}$ describes the destabilizing effect of the overlap-topology-dependent reduction of orders of C═C bonds in this case. For cycles representable by negative $\Omega_{(N)}$ values, $\overline{E}_{(N)}^{(\alpha)}$ acquires a positive sign.

Furthermore, the $(N-1)$th order correction $\overline{P}_{1,2N}^{(N-1)}$ of Eq. (48) gives birth to the Nth order energy increment $\overline{E}_{(N)}^{(\beta)}$ defined by Eq. (13). As seen from Eq. (22), the indirect interaction $G_{(N-1)1N}^{(a)}$ contains first order interactions $G_{(1)ij}$ over the cycle except for $G_{(1)1N}$. Again, the element of the matrix $\mathbf{H}_{(1)}$, the term $\overline{P}_{1,2N}^{(N-1)}$ is multiplied by when building up the product $\mathbf{P}_{(N-1)}\mathbf{H}_{(1)}$, coincides with $\gamma_{1,2N}$, the latter being equal to $4G_{(1)1N}$ (see Eqs. (1), (3), and (18)). Thus, the element $G_{(1)1N}$ missing in the indirect interaction $G_{(N-1)1N}^{(a)}$ actually originates from the matrix $\mathbf{H}_{(1)}$. As a result, the Trace$(\mathbf{H}_{(1)}\mathbf{P}_{(N-1)})$ also contains N uniform members each of them referring to an individual C─C bond and being expressible in terms of the roundabout interaction. We then obtain

$$\begin{aligned}\overline{E}_{(N)}^{(\beta)} &= 2N\overline{P}_{1,2N}^{(N-1)} \cdot \gamma_{1,2N} = 16N(1+b_N)G_{(1)1N}G_{(N-1)1N}^{(a)} \\ &= 16Na_N(1+b_N)\Omega_{(N)},\end{aligned} \tag{54}$$

where the last equality follows after employment of Eq. (35). It is seen that $\overline{E}_{(N)}^{(\beta)} > 0$ for positive roundabout interactions $\Omega_{(N)}$. Given that this is the case, the correction $\overline{E}_{(N)}^{(\beta)}$ represents the stabilizing effect originating from the overlap-topology-dependent growth in the orders of initially single and initially zero bonds. For cycles described by negative roundabout interactions, the correction $\overline{E}_{(N)}^{(\beta)}$ becomes of the destabilizing nature.

Let us turn now to Eqs. (11), (14), and (15). The relation of Eq. (14) may be shown to be met by overlap-topology-dependent increments $\overline{E}_{(N)}^{(\alpha)}$ and $\overline{E}_{(N)}^{(\beta)}$ up to $N = 4$ inclusive using the coefficients a_N and b_N of Eqs. (23) and (31). This implies that energetic increments of overlap-topology-determined alterations in the orders of strong and of weak bonds are interdependent, viz. the more destabilized the cycle becomes owing to weakening of initially double (C═C) bonds, the higher is the stabilizing increment of increasing bond orders of the remaining bonds, and vice versa. An analogous relation is also met by partial energetic increments of individual bonds. Hence, a local interdependence may be concluded between an energetic effect of the overlap-topology-dependent alteration in the order of a certain C═C bond and that of the neighboring C─C bond.

The final stabilization (or destabilization) energy of the cycle ($\overline{E}_{(N)}$), in turn, is determined by the balance between the two increments of opposite signs $\overline{E}_{(N)}^{(\alpha)}$ and $\overline{E}_{(N)}^{(\beta)}$ in accordance with Eq. (11). As much as the absolute value of $\overline{E}_{(N)}^{(\beta)}$ always exceeds that of $\overline{E}_{(N)}^{(\alpha)}$ as Eq. (14) indicates, the sign of the total overlap-topology-dependent energy increment $\overline{E}_{(N)}$ is actually determined by that of $\overline{E}_{(N)}^{(\beta)}$. Hence, the whole system becomes additionally stabilized if $\overline{E}_{(N)}^{(\beta)}$ takes a positive value (in our negative energy units). This condition, in turn, proves to be met for cycles described by a positive roundabout interaction. Otherwise, destabilization of the system follows.

Therefore, two types of pericyclic processes reveal themselves on the basis of the above results. The first one embraces reactions representable by formation of a cycle described by a positive roundabout interaction $\Omega_{(N)}$. These processes are characterized by an additional stabilization of the whole system, as well as by two energetically coupled subprocesses, viz. by growth of absolute values of bond orders of all initially single bonds and by a significant lowering of bond orders referring to initially double bonds. The second type of reactions embraces those described by cycles of a negative roundabout interaction. These processes are accordingly characterized by destabilization of the whole system, as well as by opposite alterations in the bond orders vs. those specified above. It is evident that these two classes of reactions correspond to the allowed and to the forbidden ones. Thus, the allowance of a pericyclic reaction is determined by the sign of the roundabout interaction $\Omega_{(N)}$.

5. Illustration of the Results by Consideration of Specific Reactions. Discussion and Conclusions

Let us consider some specific pericyclic reactions for illustration. Let us start with the thermal electrocyclic closure of polyenes ($C_{2N}H_{2N+2}$) that serves as an example of monomolecular pericyclic processes [9–11]. The resonance parameters between pairs of AOs of the initially single bonds inside the polyene molecule may be assumed to take uniform positive values (in our negative energy units). Let this parameter to be denoted by γ_0. Using the designations of Section 2 we then obtain

$$\gamma_{23} = \gamma_{45} = \cdots = \gamma_{2N-2,2N-1} = \gamma_0 \qquad (55)$$

(see also Scheme 1). The new resonance parameter that is formed between the terminal AOs χ_1 and χ_{2N} during the closure process will be designated by $\gamma_{1,2N}$ as before. The sign of this parameter was shown to be positive for disrotatory processes and negative for conrotatory ones [26]. Indeed, lobes of the $2p_z$ AOs χ_1 and χ_{2N} of the same sign (e.g., the negative ones) overlap one with another most significantly during a disrotatory reaction. Thus, a positive overlap integral is formed in this case. By contrast, a conrotatory way of reaction gives rise to a primary overlap of lobes of AOs χ_1 and χ_{2N} of different signs and thereby to a negative value of the same overlap integral. In our negative energy units, the same conclusions refer also to resonance parameters $\gamma_{1,2N}$. We then obtain

$$\gamma_{1,2N}^{(\mathrm{dis})} > 0, \quad \gamma_{1,2N}^{(\mathrm{con})} < 0, \qquad (56)$$

where the supersripts (dis) and (con) correspondingly designate the disrotatory way and the conrotatory one.

The roundabout interactions $\Omega_{(2)}, \Omega_{(3)}$, and $\Omega_{(4)}$ peculiar to butadiene, hexatriene, and octatriene, respectively, result from Eq. (41). These are as follows

$$\Omega_{(2)} = -2^{-4}\gamma_0\gamma_{1,2N}, \quad \Omega_{(3)} = 2^{-6}(\gamma_0)^2\gamma_{1,2N},$$
$$\Omega_{(4)} = -2^{-8}(\gamma_0)^3\gamma_{1,2N}. \qquad (57)$$

It is seen that positive roundabout interactions are obtained for negative parameters $\gamma_{1,2N}$ in the cases $N = 2$ and $N = 4$ and for a positive parameter $\gamma_{1,2N}$ for $N = 3$. Thus, choice of the conrotatory way of closure is predicted for butadiene and octatriene molecules. Again, the disrotatory way is expected to be chosen in the case of hexatriene. These results coincide with predictions of other approaches and experimental facts [9]. Simplicity of the concept of the roundabout interaction is evident.

Other types of pericyclic reactions may be studied analogously. As for instance, the popular Diels-Alder cycloaddition reaction between butadiene and ethene [9–11] may be modeled by formation of a six-membered cycle of carbon atoms corresponding to $N = 3$. Let the resonance parameter between AOs χ_2 and χ_3 of the butadiene molecule to be denoted by γ_0 ($\gamma_0 > 0$), while those of the intermolecular type will be designated by γ'_{inter} and $\gamma''_{\mathrm{inter}}$. We then obtain

$$\Omega_{(3)} = 2^{-6}\gamma_0\gamma'_{\mathrm{inter}}\gamma''_{\mathrm{inter}}. \qquad (58)$$

It is seen that a positive roundabout interaction is obtained if both γ'_{inter} and $\gamma''_{\mathrm{inter}}$ are of the same sign. Thus, the reaction is predicted to be allowed in the supra–supra fashion in accordance with experimental facts [9].

Let us turn now to comparison of the present approach to related ones. Let us start with the notation that the majority of theoretical approaches to interpretation of pericyclic reactions in general are directly or indirectly based on consideration of the relevant delocalized (canonical) molecular orbitals (MOs) and their transformations during the process. This refers both to the pioneering studies of symmetry properties of the highest-occupied MO (HOMO) of the acyclic member of the reactant-product pair [27–29] and to more sophisticated approaches, such as the MO and/or state correlation diagrams on going from reactant through transition state to product [30], the frontier MO (FMO) theory [31], etc. Certainly, the MOs contain an implicit dependence upon the overlap topology of AOs. This dependence, however, is cumbersome and difficult to analyze even for separate MOs to say nothing about the total energy. On the basis of the present experience, we may conclude this dependence to be of an indirect nature, wherein the MOs play the role of intermediate terms. Besides, numerous approaches have been suggested lately for revealing just the role of topological factors in determining various aspects of pericyclic processes, including the nature of bonding in the relevant transition states (pericyclic or pseudopericyclic) [16–19], the regioselectivity of some specific reactions [32], the so-called torquoselectivity [33], etc. The present results on the allowance of particular reaction routes naturally join in these studies. Finally, application of the pair population analysis to electron reorganization in the course of pericyclic reaction [34] deserves a separate mentioning here, as a different pattern of reorganization of bonding is established in this contribution for an allowed reaction and for a forbidden one in accordance with the results of the present study.

Let us dwell now on the relation of the present approach to the concept of the Hückel and Möbius aromaticity of the transition state. The overall predictions of our approach coincide with those of Refs. 12 and 13. To show this, let us consider first the cycles described by all resonance parameters γ_{mn} of positive signs. The sign of the relevant roundabout interaction $\Omega_{(N)}$ is then determined by the parity factor $(-1)^{N+1}$ as Eq. (41) indicates. As a result, we then obtain negative topological factors $\Omega_{(N)}$ for even N values and positive ones for odd N values. Accordingly, the cycle is predicted to be stabilized in the latter case referring to $N = 3, 5, 7$, etc. The relevant cycles then contain 6, 10, and 14 electrons, respectively, described by the series $4n + 2$. Thus, the result actually coincides with the well-known Hückel rule [35, 36]. Given that a single parameter, say γ_{23}, takes a negative sign among resonance parameters γ_{mn}, Eq. (41) yields a positive roundabout interaction for even N values. This result is nothing more than the rule of the Möbius aromaticity [37]. It should be emphasized here, however, that the approaches under comparison are based on distinct (and even opposite) models. Thus, the concept of the Hückel and Möbius aromaticity refers to cycles consisting of uniform bonds in respect of absolute values of resonance parameters and thereby it is applied to the supposed transition states of pericyclic reactions. By contrast, the approach of the present study is based on the possibility of distinguishing strong and weak bonds alternately in the given cycle (Section 3). Consequently, the results obtained refer to initial stages of the process starting with the very early stage. Moreover, resonance parameters γ_{mn} of the weak bonds are allowed to take different absolute values in our case. Thus, we have to do here with an extension of the concept of the Hückel and Möbius aromaticity to the case of weakly interacting initially double (C=C) bonds.

Let us consider finally the relation of the present approach to that of Ref. 26. The latter refers to very early stages of the electrocyclic closure processes when the new resonance parameter $\gamma_{1,2N}$ may be considered as a first order quantity versus γ_0. As a result, the relevant energy correction was shown to takes the form

$$E_{(1)} = 2P^0_{1,2N}\gamma_{1,2N}, \tag{59}$$

where $P^0_{1,2N}$ is the bond order between the terminal AOs χ_1 and χ_{2N} in the initial (open) polyene chain. As a result, the sign of the energy correction $E_{(1)}$ and thereby the stabilization or destabilization of the chain proved to be predictable on the basis of sign of $P^0_{1,2N}$ in the initial (open) chain. Again, from first relations of Eqs. (15) and (54) it is seen that the overlap-topology-dependent energy increments $\overline{E}_{(N)}$ of the present model are expressible as follows

$$\overline{E}_{(N)} = 2\overline{P}^{(N-1)}_{1,2N}\gamma_{1,2N}, \tag{60}$$

where $\overline{P}^{(N-1)}_{1,2N}$ is defined by Eq. (48). The indirect interaction $G^{(a)}_{(N-1)1N}$ present in Eq. (48), in turn, is shown in Eq. (22). It is seen that Eq. (22) contains neither the direct interaction between BOs of terminal bonds nor the parameter $\gamma_{1,2N}$. Thus, $\overline{P}^{(N-1)}_{1,2N}$ coincides with the bond order between AOs χ_1 and χ_{2N} in an open chain. This implies that the dependence of the energy alteration upon the initial bond order between terminal AOs is extended to the case of comparable values of parameters γ_0 and $\gamma_{1,2N}$ and thereby to later stages of the process in the present study.

Conclusions that may be drawn on the basis of our results are as follows:

1. The concept of the roundabout interaction introduced in the present study allows us to describe the overlap topology of AOs over the cycle that is formed during the early stage of a certain pericyclic process. Thus, the new concept may be regarded as an alternative to the well-known adjacency matrix of the molecular graph [3–5]. In another respect, the roundabout interaction supplements the concepts of direct (through-space) and indirect (through-bond) interactions [38–41] with an appropriate description of interactions in cycles. Moreover, the concept of the roundabout interaction is applicable to both the usual cyclic arrays of $2p_z$ AOs and Möbius arrays and serves as a universal collective characteristic of the given cycle.
2. The roundabout interaction of the cycle under formation directly determines specific overlap-topology-dependent contributions both to individual elements of the charge-bond order matrix and to the total energy. These particular contributions may be studied independently from the remaining increments to the same characteristics. Passing to the basis of delocalized (canonical) MOs of the cycle is not required when applying the present approach.
3. The overlap-topology-dependent reorganization of bonding during a certain pericyclic

process necessarily embraces the whole cycle under formation in a uniform manner. Moreover, the relevant contribution to the total energy of the system consists of a sum of similar increments of individual bonds. Thus, the concerted nature of pericyclic reactions now acquires a quantum-chemical definition.

4. Contributions to the total energy originating from the overlap-topology-dependent alterations in the orders of initially double (C=C) bonds and in those of the remaining bonds are interrelated. The same also refers to local contributions of an individual C=C bond and of its neighbors. Thus, the above-specified two aspects of the overall reorganization of bonding are energetically coupled subprocesses of the whole cyclization process.
5. The nature of the given pericyclic process depends on the sign of the roundabout interaction of the cycle under formation, viz. the reaction is allowed if $\Omega_{(N)} > 0$ and forbidden otherwise. Along with stabilization of the cycle vs. the respective open chain, the allowed processes are characterized by growing absolute values of bond orders of all initially single and initially zero bonds, as well as by a simultaneous reduction of bond orders of all initially double (C=C) bonds. Reorganization of bonding referring to a forbidden process take opposite directions vs. those desribed above, and the whole system becomes destabilized in addition.
6. The overlap topology of AOs starts to manifest itself at the very early stage of a pericyclic reaction and continues to play the decisive role until reaching the transition state. In particular, choice between the usual cyclic array of $2p_z$ AOs and a Möbius array is predicted to be made just at early stages and preserved within a wide range of the reaction coordinate.

References

1. King, R. B., Ed. Chemical Applications of Topology and Graph Theory; Elsevier: Amsterdam, 1983.
2. Herges, R. Chem Rev 2006, 106, 4820.
3. Trinajstic, N. Chemical Graph Theory, 1st ed., Parts I and II; CRC Press: Boca Raton, 1983.
4. Cvetkovic, D. M.; Doob, M.; Sachs, H. Spectra of Graphs. Theory and Application; VEB Deutscher Verlag der Wissenschaften: Berlin, 1980.
5. Trinajstic, N. In Semiempirical Methods of Electronic Structure Calculations, Part A: Techniques Plenum Press: Segal, G. A., Ed.; New York and London, 1977.
6. Andre, J. M.; Champagne, B.; Perpete, E. A.; Guillaume, M. Int J Quantum Chem 2001, 84, 607.
7. Guillaume, M.; Champagne, B.; Perpete, E. A.; Andre, J. M. Theor Chem Acc 2001, 105, 431.
8. Hall, G. G. Proc R Soc (London) 1955, A229, 251.
9. Carroll, F. A. Perspectives on Structure and Mechanism in Organic Chemistry; Brooks/Cole: Pacific Grove, CA, 1998.
10. March, J. Advanced Organic Chemistry, Reactions, Mechanisms and Structure; Wiley Interscience: New York, 1985.
11. Edenborough, M. Organic Reaction Mechanisms. A Step by Step Approach; Taylor and Francies: London, 1999.
12. Dewar, M. J. S. Tetrahedron Suppl 1966, 8, 75.
13. Dewar, M. J. S.; Kirschner, S; Kollmar, H. W. J Am Chem Soc 1974, 96, 5240.
14. Rzepa, H. S. J Chem Educ 2007, 84, 1535.
15. Chamorro, E.; Santos, J. C.; Gomez, B.; Contreras, R.; Fuentealba, P. J Phys Chem 2002, 106A, 11533.
16. Chamorro, E. J Chem Phys 2003, 118, 8687.
17. Chamorro, E. E.; Notario, R. J Phys Chem 2004, 108A, 4099.
18. Cardenas, C.; Chamorro, E.; Notario, R. J Phys Chem 2005, 109A, 4352.
19. Chamorro, E.; Notario, R.; Santos, J. C.; Perez, P. Chem Phys Lett 2007, 443, 136.
20. Gineityte, V. J Mol Struct (Theochem) 1995, 343, 183.
21. Gineityte, V. J Mol Struct (Theochem) 2002, 588, 99.
22. Gineityte, V. J Mol Struct (Theochem) 2002, 585, 15.
23. Gineityte, V. J Mol Struct (Theochem) 2005, 726, 205.
24. McWeeny, R. Methods in Molecular Quantum Mechanics, 2nd ed.; Academic Press: London, 1992.
25. Gineityte, V. J Mol Struct (Theochem) 1999, 487, 231.
26. Gineityte, V. J Mol Struct (Theochem) 2005, 714, 157.
27. Woodward, R. B.; Hoffmann, R. J Am Chem Soc 1965, 87, 395.
28. Woodward, R. B.; Hoffmann, R. The Conservation of Orbital Symmetry; Verlag Chemie/ Academic Press: Weinheim, 1971.
29. Hoffmann, R.; Woodward, R. B. Acc Chem Res 1968, 1, 17.
30. Longuet-Higgins, H. C.; Abrahamson, E. W. J Am Chem Soc 1965, 87, 2045.
31. Fukui, K. Acc Chem Res 1971, 4, 57.
32. Ponec, R. J Chem Inf Comput Sci 1997, 37, 745.
33. Ponec, R.; Yuzhakov, G.; Pecka, J. J Math Chem 1996, 20, 301.
34. Ponec, R. Int J Quantum Chem 1997, 62, 171.
35. Hückel, E. Z Phys 1932, 76, 628.
36. Dewar, M. J. S.; Dougherty, R. C. The PMO Theory of Organic Chemistry; Plenum: New York, 1975.
37. Heilbronner, E. Tetrahedron Lett 1964, 29, 1923.
38. Hoffmann, R.; Imamura, A.; Hehre, W. J. J Am Chem Soc 1968, 90, 1499.
39. Heilbronner, E.; Schmelzer, A. Helvetica Chem Acta 1975, 58, 936.
40. Hoffmann, R.; Heilbronner, E.; Gleiter, R. J Am Chem Soc 1970, 92, 706.
41. Hoffmann, R. Acc Chem Res 1971, 4, 1.