A Common Selection Rule for Organic Reactions in Terms of Signs of Direct and Indirect Interorbital Interactions

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The semilocalized approach to chemical reactivity suggested recently is overviewed with respect to both theory and applications. The principal attention is paid to formulation of a common selection rule for organic reactions and to demonstration of its validity to various heterolytic (i. e. nucleophilic and electrophilic) and pericyclic processes. The total energy of the whole reacting system (E) is represented in this approach in the form of power series with respect to all interfragmental interactions (fragments coincide with individual chemical bonds, phenyl rings, etc.). For any reaction, a certain decisive k-th-order energy correction $E_{(k)}$ may be revealed, the sign of which depends on the actual way of the process. The allowed and forbidden reactions are then defined as those described by negative (stabilizing) and positive (destabilizing) corrections $E_{(k)}$, respectively. The condition which ensures the negative sign of $E_{(k)}$ resolves itself into a universal requirement of coinciding signs of the principal direct and indirect interactions of basis orbitals localized on separate fragments (e. g. bond orbitals). This result forms the basis for the above-mentioned selection rule. Allowed (forbidden) ways of heterolytic reactions are exemplified by the back (frontal) attack of a nucleophile upon a substituted alkane in the S_N2 process, the *meta* (*ortho*, *para*) attacks of electrophile upon the pyridine molecule, the addition of electrophile to the C_β (C_α) atom of a donor-containing derivative of ethene ($D-C_\alpha H = C_\beta H_2$), the *trans* (*cis*)-$\beta$-elimination processes of substituted alkanes, etc. Application of the same rule to pericyclic reactions is demonstrated to yield predictions coinciding with those of other approaches including the famous Woodward-Hoffmann rule.

Key words: One-Electron Density Matrix; Perturbation Theory; Fragmental Orbitals; Direct and Indirect Interactions; Semilocalized Approach.

1. Introduction

Classification of certain structures and/or processes usually is based on revealing and emphasizing specific peculiarities pertinent to each class. In some cases, however, this popular approach of natural sciences yields overestimation of differences between closely related objects. To restore the balance, general theories are subsequently developed that result in unified interpretations of these seemingly different objects using the same set of principal terms.

In the field of organic chemistry, distinction between heterolytic (i. e. nucleophilic and electrophilic) and pericyclic reactions [1 – 3] may be mentioned as an outstanding example of classification. Indeed, the pericyclic processes usually are characterized by absence of a local reaction centre [1], as well as by the neutral (or almost neutral) nature of participating compounds in respect of their electron-donating or -accepting abil-ities [3], whereas the heterolytic processes are described by opposite to that said above. In this context, search for a unified interpretation of both types of reactions is a natural course of things. Attempts of just this type are overviewed in the present paper.

The above-mentioned distinctive features of heterolytic and pericyclic reactions determine somewhat different traditions of their theoretical treatment. Thus, relative reactivities referring to alternative routes of heterolytic processes usually are assumed to vary continuously. These are most commonly correlated either to total populations of atomic orbitals (AOs) and/or of atoms [4, 5] or to their partial values referring to the so-called frontier molecular orbitals (MOs) [6 – 17] (cf. the charge- and orbital-controlled processes [4, 7, 12, 13]). Meanwhile, pericyclic reactions are traditionally considered as being governed by a certain selection rule [1], i. e., these processes are expected to be either allowed or forbidden. This view-

point may be traced back to the pioneering contributions [18–20]. Accordingly, the simplest version of the selection rule for pericyclic processes is commonly referred to as the Woodward-Hoffmann rule [1]. The overall symmetry and nodal properties of the highest occupied MO (HOMO) and/or of the lowest unoccupied one (LUMO) underly this rule.

Recently, the so-called semilocalized approach to investigate the chemical reactivity has been proposed [21, 22], wherein the principal characteristics under study (viz. the partial populations transferred between initially-occupied basis orbitals and the initially-vacant ones) have been expressed and interpreted in terms of local direct and indirect interorbital interactions instead of coefficients and/or nodal properties of the usual delocalized MOs. This alternative approach has been applied to various types of organic reactions, including the S_N2 process between a substituted alkane and nucleophile [23], the Ad_E2 reaction of substituted ethenes [22], the concerted bimolecular elimination processes [24], the electrocyclic closure of polyenes [25, 26]. A subsequent comparative analysis of these separate studies showed that the concept of the selection rule is equally applicable to both heterolytic and pericyclic organic reactions. Moreover, the approach yields a common selection rule for these processes in terms of signs of direct and indirect interorbital interactions. The present overview addresses mainly this principal achievement.

We start with discussing fundamentals of the semilocalized approach in Section 2. Analysis of the relevant expressions allows us to define the allowed and the forbidden processes deductively and thereby to formulate a general selection rule for organic reactions. The remaining part of the paper is devoted to demonstration of the actual validity of the above-mentioned rule. Studies of heterolytic processes are overviewed in Section 3. Results of such an a posteriori analysis are subsequently compared to predictions of our general selection rule of Section 2. On this basis, validity of the rule to heterolytic reactions is concluded.

Finally, we turn to pericyclic processes in Section 4 that are traditionally divided into allowed and forbidden ones. Application of our general selection rule to these processes is followed by comparison of the relevant predictions with those of the other approaches including the famous Woodward-Hoffmann rule [1], as well as to experimental facts. As a result, adequacy of the common selection rule to pericyclic reactions is also demonstrated.

2. Theory

The semilocalized approach to chemical reactivity is based on the general expression for the one-electron density matrix (DM) derived in [27] along with the direct relation between the DM and the relevant total energy. A perturbative solution of the so-called commutation equation underlies the above-mentioned derivation. Thus, we start with discussing just this way of obtaining the DM (Subsection 2.1). Thereupon, we introduce certain additional approximations that allow to interpret both elements of the DM and total energy in terms of direct and indirect interorbital interactions (Subsection 2.2). Finally, we turn to the very chemical reactivity (Subsection 2.3).

2.1. The Direct Way of Obtaining the One-Electron Density Matrix and Total Energy

The one-electron DM of a certain system and its total energy are usually derived in quantum chemistry using eigenfunctions (MOs) and eigenvalues (one-electron energies) of the relevant Hamiltonian or Fockian matrix (see e.g. [28]). This implies passing to the basis of delocalized MOs is an initial step of the whole procedure. To avoid this step and thereby to ensure the feasibility of a local interpretation of electronic structures and/or chemical reactivity, the DM has been obtained in [27] directly without solving the eigenvalue equation for the Hamiltonian matrix. To this end, fundamental principles of quantum mechanics have been employed.

Let our system be represented by a certain one-electron Hamiltonian matrix $\mathbf{H}$, e.g. of the Hückel type. The relevant total energy E is then expressible as [29, 30]

$$E = \mathrm{Spur}(\mathbf{PH}), \qquad (1)$$

where $\mathbf{P}$ is the corresponding representation matrix of the DM. The latter, in turn, is determined by three matrix equations [30], viz.

$$[\mathbf{H},\mathbf{P}]_- = \mathbf{0}, \quad \mathbf{P}^2 = 2\mathbf{P}, \quad \mathrm{Spur}\,\mathbf{P} = 2N, \qquad (2)$$

where $2N$ coincides with the even total number of electrons and the notation $[\ldots,\ldots]_-$ indicates a commutator of matrices. The first relation (the commutation condition) is the main physical requirement determining the matrix $\mathbf{P}$ and resulting from the Dirac equation for the time-independent Hamiltonian. The remaining

relations are additional system-structure-independent restrictions following from the idempotence requirement ($\mathbf{\Pi}^2 = \mathbf{\Pi}$) for the projector $\mathbf{\Pi} = \frac{1}{2}\mathbf{P}$ and the charge conservation condition, respectively.

We will dwell here on the perturbative solution of the system of matrix equations (2) (non-perturbative solutions also are possible, see e. g. [31]). In this connection, the matrix $\mathbf{H}$ will be assumed to contain a zero-order member $\mathbf{H}_{(0)}$ and a first-order term $\mathbf{H}_{(1)}$ as follows:

$$\mathbf{H} = \mathbf{H}_{(0)} + \mathbf{H}_{(1)}. \tag{3}$$

Let a certain set of orthonormalized orbitals $\{\varphi\}$ to underlie the Hamiltonian matrix $\mathbf{H}$. No need arises for specifying the nature of these orbitals at the present stage of our discussion, except for two additional conditions. First, the total basis set $\{\varphi\}$ is assumed to consist of two subsets, $\{\varphi_{(+)}\}$ and $\{\varphi_{(-)}\}$, containing initially-occupied and initially-vacant orbitals, respectively, and, second, the interactions between orbitals of different subsets are supposed to be weak as compared to those inside the subsets.

It is evident that each matrix of (3) may be represented in terms of four submatrices (blocks), referring to subsets $\{\varphi_{(+)}\}$ and $\{\varphi_{(-)}\}$, and to their interaction. Moreover, the zero-order member $\mathbf{H}_{(0)}$ contains zero intersubset blocks and changes to a block-diagonal matrix under the above-mentioned condition, viz.

$$\mathbf{H}_{(0)} = \left| \begin{array}{cc} \mathbf{E}_{(+)} & \mathbf{0} \\ \mathbf{0} & \mathbf{E}_{(-)} \end{array} \right|, \quad \mathbf{H}_{(1)} = \left| \begin{array}{cc} \mathbf{S} & \mathbf{R} \\ \mathbf{R}^+ & \mathbf{Q} \end{array} \right|. \tag{4}$$

The superscript $+$ here and below indicates the Hermitian-conjugate matrix. As with the nature of orbitals $\{\varphi\}$, no need arises for specifying either the internal constitutions of submatrices $\mathbf{E}_{(+)}, \mathbf{E}_{(-)}, \mathbf{S}, \mathbf{R}$ and $\mathbf{Q}$ or their dimensions. (These submatrices play the role of multi-dimensional parameters. In this respect, an analogy may be traced between the matrix $\mathbf{H}$ and the Hamiltonian matrix of a certain two-level system characterized by weak interorbital interaction [32]).

The above-described non-specific nature of the whole problem is preserved also when solving the matrix equations (2). To this end, the matrix $\mathbf{P}$ has been formally expressed as a sum of corrections $\mathbf{P}_{(k)}$ of various orders k. Each of these corrections, in turn, is represented in terms of four blocks being sought. As a result of such a solution, each member $\mathbf{P}_{(k)}$ is expressed in terms of entire blocks of the Hamiltonian matrix

($\mathbf{E}_{(+)}, \mathbf{E}_{(-)}, \mathbf{S}, \mathbf{R}$ and $\mathbf{Q}$) whatever the internal constitutions of the latter are. The correction $\mathbf{P}_{(k)}$ takes the form [27, 33, 34]

$$\mathbf{P}_{(k)} = \left| \begin{array}{cc} \mathbf{P}_{(k)+} & -2\mathbf{G}_{(k)} \\ -2\mathbf{G}_{(k)}^+ & \mathbf{P}_{(k)-} \end{array} \right|, \tag{5}$$

where the off-diagonal blocks $\mathbf{G}_{(k)}$ meet the matrix equations

$$\mathbf{E}_{(+)}\mathbf{G}_{(k)} - \mathbf{G}_{(k)}\mathbf{E}_{(-)} + \mathbf{W}_{(k)} = \mathbf{0}, \tag{6}$$

where the matrices $\mathbf{W}_{(k)}$ coincide with certain combinations of matrices of lower orders, e. g.

$$\mathbf{W}_{(1)} = \mathbf{R}, \qquad \mathbf{W}_{(2)} = \mathbf{S}\mathbf{G}_{(1)} - \mathbf{G}_{(1)}\mathbf{Q}. \tag{7}$$

Zero- and first-order members of the remaining blocks of (5) take the simple form

$$\mathbf{P}_{(0)+} = 2\mathbf{I}, \quad \mathbf{P}_{(0)-} = \mathbf{0}, \quad \mathbf{P}_{(1)+} = \mathbf{P}_{(1)-} = \mathbf{0} \tag{8}$$

in accordance with initial occupation numbers of basis orbitals ($\mathbf{I}$ here and below stands for the unit matrix). For higher values of the order parameter k, the submatrices $\mathbf{P}_{(k)+}$ and $\mathbf{P}_{(k)-}$ contain sums of products of pairs of matrices $\mathbf{G}_{(k-1)}, \mathbf{G}_{(k-2)}$, etc. as exemplified below:

$$\begin{array}{cc} \mathbf{P}_{(2)+} = -2\mathbf{G}_{(1)}\mathbf{G}_{(1)}^+, & \mathbf{P}_{(2)-} = 2\mathbf{G}_{(1)}^+\mathbf{G}_{(1)}, \\ \mathbf{P}_{(3)+} = -2(\mathbf{G}_{(1)}\mathbf{G}_{(2)}^+ + \mathbf{G}_{(2)}\mathbf{G}_{(1)}^+), & \text{etc.} \end{array} \tag{9}$$

It is evident that the final occupation numbers of basis orbitals are determined by the diagonal elements $P_{(k)+,ii}$ and $P_{(k)-,jj}$ of submatrices $\mathbf{P}_{(k)+}$ and $\mathbf{P}_{(k)-}$. Matrices $\mathbf{G}_{(k)}$, in turn, take off-diagonal positions in the correction $\mathbf{P}_{(k)}$ of (5). Hence, an element $G_{(k)ij}$ represents a certain coupling between an initially-occupied orbital ($\varphi_{(+)i}$) and an initially-vacant one ($\varphi_{(-)j}$). The expressions like those of (9) then allow us to define partial populations $q_{(+)i,(-)j}$ transferred between orbitals $\varphi_{(+)i}$ and $\varphi_{(-)j}$, as well as k-th-order increments of the relevant power series [34]. We then obtain

$$\begin{aligned} P_{(k)+,ii} &= -\sum_{(-)l} q^{(k)}_{(+)i,(-)l}, \\ P_{(k)-,jj} &= \sum_{(+)m} q^{(k)}_{(-)j,(+)m}, \end{aligned} \tag{10}$$

where $q^{(k)}_{(+)r,(-)s}$ coincides with $q^{(k)}_{(-)s,(+)r}$ for any r and s. Increments $q^{(k)}_{(+)i,(-)j}$, in turn, are expressible as follows:

$$q^{(2)}_{(+)i,(-)j} = 2(G_{(1)ij})^2, \tag{11}$$

$$q^{(3)}_{(+)i,(-)j} = 4G_{(1)ij}G_{(2)ij}, \tag{12}$$

$$q^{(4)}_{(+)i,(-)j} = 4G_{(1)ij}G_{(3)ij} + 2(G_{(2)ij})^2 \\ + 2G_{(1)ij}(G_{(1)}G^+_{(1)}G_{(1)})_{ij}, \tag{13}$$

$$q^{(5)}_{(+)i,(-)j} = 4G_{(1)ij}G_{(4)ij} \\ + 2G_{(1)ij}(G_{(1)}G^+_{(2)}G_{(1)})_{ij} \\ + 4G_{(2)ij}G_{(3)ij} \\ + 4G_{(2)ij}(G_{(1)}G^+_{(1)}G_{(1)})_{ij}. \tag{14}$$

(Note that members $q^{(k)}_{(+)i,(-)j}$ up to $k = 5$ were used when studying chemical reactions [24]). It is also evident that the partial populations $q_{(+)i,(-)j}$ take the form

$$q_{(+)i,(-)j} = \sum_{k=2}^{\infty} q^{(k)}_{(+)i,(-)j} \tag{15}$$

and describe the final charge redistribution in our system.

Let us return now to the total energy E defined by (1). Use of (3) along with the power series for the DM **P** yields an analogous series for the energy E. The k-th-order member of this series ($E_{(k)}$), in turn, consists of two components, $E^{(\alpha)}_{(k)}$ and $E^{(\beta)}_{(k)}$, viz.

$$E^{(\alpha)}_{(k)} = \mathrm{Spur}(\mathbf{P}_{(k)}\mathbf{H}_{(0)}), \\ E^{(\beta)}_{(k)} = \mathrm{Spur}(\mathbf{P}_{(k-1)}\mathbf{H}_{(1)}). \tag{16}$$

Moreover, these components proved to be interrelated as follows [34]:

$$(k-1)E^{(\beta)}_{(k)} = -kE^{(\alpha)}_{(k)} \tag{17}$$

for any $k = 2, 3, 4, \dots$ [members $E_{(0)}$ and $E_{(1)}$ are exhibited below in (19)]. Derivation of (17) is based on application of (5) and (6). The principal relation (17) implies that the total correction $E_{(k)}$ is alternatively representable as

$$E_{(k)} = -\frac{1}{k-1}E^{(\alpha)}_{(k)}, \quad E_{(k)} = \frac{1}{k}E^{(\beta)}_{(k)}. \tag{18}$$

Moreover, compact formulae have been derived [34] for separate corrections $E_{(k)}$, e. g.

$$E_{(0)} = 2\mathrm{Spur}\mathbf{E}_{(+)}, \quad E_{(1)} = 2\mathrm{Spur}\,\mathbf{S}, \\ E_{(2)} = -2\mathrm{Spur}(\mathbf{G}_{(1)}\mathbf{R}^+), \\ E_{(3)} = -2\mathrm{Spur}(\mathbf{G}_{(2)}\mathbf{R}^+), \quad \text{etc.} \tag{19}$$

These expressions offered a generalization [35] of the well-known Dewar formula [36–38] for total energies to the case of zero-order interactions inside subspaces of initially-occupied and initially-vacant basis orbitals. This fact demonstrates non-trivial consequences of the allowance for a non-diagonal zero-order Hamiltonian in (4). Other applications of the above-outlined general formalism may be found in [39, 40].

2.2. The Case of First-Order Interorbital Interactions. Choice of Basis Orbitals

Solution of matrix equations (6) is the main origin of difficulties in practical applications of the above outlined theory. The integral form of the solution has been analyzed in [41, 42]. It is essential to note in our context that this formal solution offers no local relations between elements of the principal matrices $\mathbf{G}_{(k)}$ and those of the Hamiltonian matrix and thereby between elements of the DM and the interorbital interactions. To achieve the latter end, submatrices $\mathbf{E}_{(+)}$ and $\mathbf{E}_{(-)}$ are assumed to take diagonal forms [27], i. e.

$$E_{(+)im} = \varepsilon_{(+)i}\delta_{im}, \quad E_{(-)jl} = \varepsilon_{(-)j}\delta_{jl}, \tag{20}$$

where $\varepsilon_{(+)i}$ and $\varepsilon_{(-)j}$ represent one-electron energies of the orbitals $\varphi_{(+)i}$ and $\varphi_{(-)j}$. This assumption evidently implies a first-order magnitude of all interorbital interactions.

Two important implications follow immediately after accepting condition (20): First, the component $E^{(\alpha)}_{(k)}$ of the energy correction $E_{(k)}$ shown in (16) depends only on corrections to populations of basis functions, i. e. on $P_{(k)+,ii}$ and $P_{(k)-,jj}$ defined by (10)–(15). As a result, this component becomes interpretable as the charge transfer energy. Moreover, expressibility of the total correction $E_{(k)}$ via $E^{(\alpha)}_{(k)}$ as shown in the first relation of (18) yields the principal formula [34]

$$E_{(k)} = \frac{1}{k-1} \sum_{(+)i} \sum_{(-)j} q^{(k)}_{(+)i,(-)j}(\varepsilon_{(+)i} - \varepsilon_{(-)j}), \tag{21}$$

for $k = 2, 3, 4, \dots$. It is seen that the energy correction $E_{(k)}$ depends on k-th-order increments to partial populations transferred between orbitals of opposite initial occupation and on the relevant energy intervals. Meanwhile, the sum $E_{(0)} + E_{(1)}$ coincides with the total energy of isolated initially-occupied basis functions.

The second consequence of (20) consists in the possibility of an algebraic solution of (6). As a result, ex-

pressions for separate elements $G_{(k)ij}$ have been obtained [27] along with their illustrative interpretation.

Let us introduce the following notations for Hamiltonian matrix elements:

$$
\begin{aligned}
S_{im} &= \langle \varphi_{(+)i} \mid \hat{H} \mid \varphi_{(+)m} \rangle, \\
R_{ij} &= \langle \varphi_{(+)i} \mid \hat{H} \mid \varphi_{(-)j} \rangle, \\
Q_{jr} &= \langle \varphi_{(-)j} \mid \hat{H} \mid \varphi_{(-)r} \rangle,
\end{aligned}
\tag{22}
$$

where the respective basis orbitals are indicated inside the bra- and ket-vectors. Then the first-order element $G_{(1)ij}$ takes the form [27]

$$
G_{(1)ij} = -\frac{R_{ij}}{\varepsilon_{(+)i} - \varepsilon_{(-)j}}
\tag{23}
$$

and describes the direct interaction between orbitals $\varphi_{(+)i}$ and $\varphi_{(-)j}$. Using the same system of designations, the second-order element $G_{(2)ij}$ may be expressed as [27]

$$
G_{(2)ij} = \frac{1}{\varepsilon_{(+)i} - \varepsilon_{(-)j}} \left\{ \sum_{(+)m} \frac{S_{im} R_{mj}}{\varepsilon_{(+)m} - \varepsilon_{(-)j}} - \sum_{(-)r} \frac{R_{ir} Q_{rj}}{\varepsilon_{(+)i} - \varepsilon_{(-)r}} \right\}.
\tag{24}
$$

This element represents the indirect interaction between the same orbitals ($\varphi_{(+)i}$ and $\varphi_{(-)j}$) by means of a single mediator. Both an initially-occupied orbital ($\varphi_{(+)m}$) and an initially-vacant one ($\varphi_{(-)r}$) are able to play this role. To be an efficient mediator, however, the orbital concerned should interact directly with both $\varphi_{(+)i}$ and $\varphi_{(-)j}$. Similarly, $G_{(3)ij}$ describes the indirect interaction between orbitals $\varphi_{(+)i}$ and $\varphi_{(-)j}$ by means of two mediators, $G_{(4)ij}$ represents an analogous interaction by means of three mediators, etc. It is noteworthy that the higher is the order parameter k, the more cumbersome is the relevant expression. In this connection, expressions for $G_{(k)ij}$ of higher orders are not given here (these may be found in [22, 33]). It should be also added that the remaining increments of (13) and (14), i.e. $(G_{(1)} G_{(1)}^+ G_{(1)})_{ij}$ and $(G_{(1)} G_{(2)}^+ G_{(1)})_{ij}$, also may be interpreted as certain indirect interactions of the same orbitals $\varphi_{(+)i}$ and $\varphi_{(-)j}$.

On the basis of (10)–(15), (23) and (24) we may then conclude that both separate increments $q_{(+)i,(-)j}^{(k)}$ of partially transferred populations $q_{(+)i,(-)j}$ and the resulting contributions to occupation numbers of basis orbitals $P_{(k)+,ii}$ and $P_{(k)-,jj}$ can be expressed in terms

of direct and indirect interorbital interactions. Conditions underlying this representation of electronic structures are easily seen from (23) and (24), viz. energy intervals between orbitals of opposite initial occupation $(\varepsilon_{(+)i} - \varepsilon_{(-)j})$ should exceed considerably the interorbital interactions of all types.

Evaluations [27, 32, 33, 43 – 46] showed that orbitals localized on separate elementary fragments of the system under study usually meet the above requirement. Let these orbitals be referred to as fragmental orbitals (FOs). The initially-occupied FOs and the initially-vacant ones will be accordingly abbreviated by IOFOs and IVFOs. Individual chemical bonds both of saturated [27, 32, 43] and conjugated molecules [44], lone electron pairs [46], as well as aromatic (e. g. phenyl) rings along with substituents [33, 45] are able to play the role of fragments. Moreover, FOs may be regarded as orthonormalized orbitals, at least in qualitative studies [47]. In the most common case of two-centre chemical bonds, the bonding bond orbitals (BBOs) and the antibonding ones (ABOs) are usually used as IOFOs and IVFOs, respectively. Large energy intervals $(\varepsilon_{(+)i} - \varepsilon_{(-)j})$ vs. the interorbital interactions R_{ij} follow in this case from significant intrabond resonance parameters as compared to the interbond ones in the basis of hybrid AOs underlying the definition of bond orbitals [48 – 54]. Elements $G_{(1)ij}$ and $G_{(k)ij}$ ($k = 2, 3, 4....$) then accordingly represent the through-space and through-bond interactions. This concept has been originally suggested in [55 – 58] for the interpretation of photoelectron spectra of specific molecules. Analogous terms were invoked later when discussing the structures of non-canonical (localized) MOs [59 – 61]. The direct and indirect interactions represented by (23) and (24) refer to any type of mediating FOs and thereby may be considered as a certain generalization of through-space and through-bond interactions, respectively.

The same requirement (namely significant intrafragmental interactions vs. the interfragmental ones) serves also as a criterion for choosing the most appropriate fragments and thereby the basis orbitals (FOs) for a certain specific system. In this context, an essential fact is that related molecules usually consist of the same fragments joined in a uniform manner (cf. alkanes containing C-C and C-H bonds). This, in turn, implies that FOs of similar structure represent these compounds. As a result, a common Hamiltonian matrix $\mathbf{H}$ of (3) and (4) usually refers to the whole class of related compounds, where individual molecules are character-

ized by specific structures and dimensions of the multidimensional parameters $\mathbf{E}_{(+)}$, $\mathbf{E}_{(-)}$, $\mathbf{S}$, $\mathbf{R}$ and $\mathbf{Q}$. Given that this is the case, the single matrix problem (2) represents the whole class. In this connection, the present theory proved to be applicable for the investigation of common peculiarities of electronic structures of related compounds. For instance, alkanes [32, 43, 48, 49], their heteroatom-containing derivatives [62], and disubstituted benzenes [33] may be mentioned.

Let us return again to expressions (23) and (24) and assume that certain fragmental orbitals play the role of the basis functions $\{\varphi\}$ in the above outlined formalism. Let us define neighbouring fragments as those described by the non-zero interorbital interactions shown in (22) and thereby by the non-zero matrix elements $G_{(1)ij}$ of (23). Accordingly, elements $G_{(2)ij}$ take non-zero values for fragments possessing a common neighbour (the so-called second neighbours), whilst $G_{(3)ij} \neq 0$ refer to third neighbours, etc. On the whole, the higher is the order parameter k, the more remote fragments are embraced by the relevant indirect interaction $G_{(k)ij}$. Meanwhile, the absolute value of the latter generally becomes lower when the parameter k increases in accordance with the usual requirements of converging perturbative expansions.

Similar trends are observed also in the case of increments $q_{(+)i,(-)j}^{(k)}$ under growing values of the parameter k. [Note that $q_{(+)i,(-)j}^{(k)}$ consists of sums of products of elements $G_{(k-1)ij}, G_{(k-2)ij}$, etc. as (11)–(14) indicate.] As a result, any partial transferred population $q_{(+)i,(-)j}$ depends predominantly on the nearest environment of orbitals $\varphi_{(+)i}$ and $\varphi_{(-)j}$ and exhibits an extinction when the distance between the two fragments concerned grows. An analogous dependence mostly on the nearest neighbourhood easily follows also for total alterations in occupation numbers of separate orbitals defined by (10). On the whole, these principal conclusions imply a semilocalized description of electronic structures to follow from the above outlined theory under assumption (20). Applications of this approach to various problems of ground states of molecules may be found in [32, 33, 43–45, 48, 49, 53, 62–64].

2.3. The Semilocalized Approach to Chemical Reactivity. Definition of Allowed and Forbidden Reactions

A formal application of the above summarized expressions to the case of two interacting molecules A and B was undertaken in [21]. Orbitals localized on fragments of both participants of the process were included into the basis set $\{\varphi\}$. The first-order Hamiltonian matrix $\mathbf{H}_{(1)}$ of (3) contained both intra- and intermolecular interactions. Electron density redistributions both inside and between molecules A and B were the principal characteristics under study. To discuss these redistributions, the following definitions have been introduced: First, two principal fragments have been revealed in molecules A and B that interact one with another directly. These fragments have been called the reaction centres and denoted by RC(A) and RC(B). Second, the fragments, the orbitals of which interact directly only with those of reaction centres of their own molecules (but not with orbitals of the opposite compound), have been referred to as the nearest-neighbouring fragments and denoted by NN(A) and NN(B). Finally, the next-nearest-neighbouring fragments have been defined and so on.

Any correction $\mathbf{P}_{(k)}$ of the total DM of two interacting molecules $\mathbf{P}$ was shown to be representable as [21]

$$\mathbf{P}_{(k)} = \mathbf{P}_{(k)}^{(A)} \oplus \mathbf{P}_{(k)}^{(B)} + \delta\mathbf{P}_{(k)}, \qquad (25)$$

where $\mathbf{P}_{(k)}^{(A)}$ and $\mathbf{P}_{(k)}^{(B)}$ are the relevant corrections for the isolated molecules A and B, respectively. The symbol $\oplus$ indicates a direct sum of matrices. The last term $\delta\mathbf{P}_{(k)}$ is an additional component that may be entirely traced back to the intermolecular interaction. Analysis of the general expression for $\delta\mathbf{P}_{(k)}$ [21] supports our previous expectation that the higher is the order parameter k, the more distant fragments are embraced by the resulting charge redistribution. In particular, the second- and third-order increments $\delta\mathbf{P}_{(2)}$ and $\delta\mathbf{P}_{(3)}$ were shown to describe charge redistributions inside and between the reaction centres RC(A) and RC(B). This result has been considered as the quantum-mechanical analogue of the supposed direct participation of the RC(A) and RC(B) fragments in a certain process. The fourth-order increments $\delta\mathbf{P}_{(4)}$, in turn, were shown to contain additive components of an indirect participation of a certain NN(A) or NN(B) fragment in the same reaction. In the case of a more remote fragment, terms of even higher orders are required to describe the relevant effects. Thus, extinction of an indirect influence has been predicted when the distance between the given fragment and the respective reaction centre grows. These results formed the basis for choice of local models of chemical processes containing orbitals of the supposed reaction centres and

those of some neighbouring fragments of particular interest. Models of this type along with the principal expressions (10)–(15), (21), (23) and (24) make the essence of the semilocalized approach to chemical reactivity. This approach has been successfully applied to investigate various aspects of organic reactions, both heterolytic and pericyclic. Several examples may be mentioned here: The origin of the enhanced reactivity of α-halocarbonyl compounds as compared to alkyl halogenides has been revealed [65]. Different relative reactivities of carbon atoms of butadiene towards electrophiles and/or nucleophiles have been related to dissimilar indirect influences of the $H_2C=CH$-substituent upon the reacting $H_2C=CH$-fragment for alternative directions of the attack of the reagent [66]. Internal changes have been revealed in the reacting allyl ions that result in the so-called deconjugation effect [67]. Finally, the role of the overlap topology of AOs at early stages of pericyclic reactions has been explored [26].

Let us turn now to the deductive definition of allowed and forbidden reactions. To this end, let us consider separate members $E_{(k)}$ of the power series for the total energy E of a certain reacting system shown in (21), where $q^{(k)}_{(+)i,(-)j}$ are defined by (11)–(14).

The principal contribution $E_{(2)}$ to the energy alteration of our system depends on squares of direct interorbital interactions as (11) and (21) indicate. Positive signs of the increments $q^{(2)}_{(+)i,(-)j}$ of (11) and negative signs of energy intervals $(\varepsilon_{(+)i} - \varepsilon_{(-)j})$ determine the stabilizing nature of the second-order energy correction $E_{(2)}$ whatever the actual signs of the direct interactions $G_{(k)ij}$ are. Meanwhile, the signs of the remaining terms of the power series for the energy E, i.e. of $E_{(3)}, E_{(4)}$, etc., can not be established a priori. As already mentioned, the direct interactions $G_{(1)ij}$ take non-zero values if the orbitals concerned, i.e. $\varphi_{(+)i}$ and $\varphi_{(-)j}$, belong to neighbouring fragments. The same evidently refers to second-order partial transferred populations $q^{(2)}_{(+)i,(-)j}$. Alternative routes of chemical reactions, however, are most commonly characterized by different spatial arrangements of non-neighbouring fragments; for example, the α- and β-attacks of electrophile upon a substituted ethene $Z\text{-}C_\alpha H=C_\beta H_2$ are described by different positions of the reagent relatively to the substituent Z. Hence, the predominant way of a certain reaction may be expected to be determined by signs of energy corrections $E_{(k)}$ of higher orders k. In this context, chemical reactions may be conveniently classified on the basis of the order parameter k, the decisive energy correction is described by. For example, reactions governed by the sign of the third-order energy $E_{(3)}$ may be referred to as third-order processes, etc. It is also evident that the higher-order increments $E_{(k)}$, $k > 2$, contribute to an additional stabilization of the whole system if the respective partial transferred populations $q^{(k)}_{(+)i,(-)j}$ have positive signs. As is seen from (12)–(14), positive partial transferred populations $q^{(3)}_{(+)i,(-)j}, q^{(4)}_{(+)i,(-)j}$, etc. follow if the interorbital interactions contained within their definitions, i.e. $G_{(1)ij}, G_{(2)ij}, G_{(3)ij}, (G_{(1)} G^+_{(1)} G_{(1)})_{ij}$, etc., are of coinciding signs for separate pairs of FOs. Thus, it is the signs of direct and indirect interorbital interactions that may be expected to determine the predominant ways of chemical reactions.

From (21) it follows also that the k-th-order energy $E_{(k)}$ consists of contributions of all pairs of FOs of opposite initial occupation (the subscripts i and j embrace all IOFOs and all IVFOs, respectively). In this context, correlations between signs of interorbital interactions referring to different pairs of FOs become essential. Three cases may be distinguished here. The first one embraces reactions described by all (or almost all) positive increments $q^{(k)}_{(+)i,(-)j}$ to the decisive k-th-order energy correction $E_{(k)}$, so that the negative sign of the latter is unambiguosly ensured. These processes will be referred to as allowed k-th-order reactions. The second case embraces processes represented by all (or almost all) negative increments $q^{(k)}_{(+)i,(-)j}$ and thereby by a positive k-th-order correction $E_{(k)}$. The term "the forbidden k-th-order reactions" will be employed in this case. An intermediate case also is possible here when the principal pairs of FOs of opposite initial occupation yield contributions of different signs to the above specified corrections. Due to the strong correlation of signs of interorbital interactions for different pairs of FOs peculiar to specific reactions (Section 3), the actual processes prove to belong to either allowed or forbidden ones.

Let an additional remark to be made before finishing this subsection. Let us assume that a certain interorbital interaction $G_{(k)ij}$ consists of two components, $G^{(a)}_{(k)ij}$ and $G^{(b)}_{(k)ij}$, i.e.

$$G_{(k)ij} = G^{(a)}_{(k)ij} + G^{(b)}_{(k)ij} \qquad (26)$$

(the components may refer, for example, to increments of different mediators). These components also may

be considered as separate interorbital interactions. Accordingly, coinciding signs of $G_{(k)ij}^{(a)}$ and $G_{(k)ij}^{(b)}$ ensure the largest absolute value of the square of the total interaction $G_{(k)ij}$, i. e. of $(G_{(k)ij})^2$, and thereby the largest negative value of the relevant energy increment. In particular, two components of the first-order interaction $G_{(1)ij}$ of the same sign yield the largest negative value of the stabilization energy $E_{(2)}$. Similarly, coinciding signs of $G_{(1)ij}^{(a)}$, $G_{(1)ij}^{(b)}$ and $G_{(2)ij}$ yield a negative third-order energy $E_{(3)}$, etc.

The deductive definitions of this section will be illustrated by particular reactions in Sections 3 and 4.

3. Comparative Analysis of Heterolytic Reactions

In this section, the heterolytic processes are classified on the basis of the order parameter k, by which the decisive energy correction is described.

3.1. The Third-Order Processes

Let us start with the S_N2 process between a substituted alkane Z-$C_\alpha H_2$-$C_\beta H_2$-... and nucleophile Nu [23], where Z stands for a heteroatom (nucleofuge). A back attack of the reagent and not a frontal one is commonly assumed to give rise to a subsequent substitution process [2–4, 7, 38, 68]. Thus, comparison of these two alternatives with respect to allowance of the relevant reaction is of particular interest.

Three principal basis orbitals were shown to be sufficient when studying the S_N2 process, viz. the electron-donating orbital of nucleophile ($\varphi_{(+)d}$), the electron-accepting (antibonding) orbital of the C_α-Z bond ($\varphi_{(-)a}$) and a single mediating IOFO denoted previously [23] by $\varphi_{(+)2}$ and belonging either to C_α-C_β or to C_α-H bonds. Regard for the latter orbital allowed us to distinguish between the two possible ways of the reaction even if the interactions (resonance parameters) between orbitals $\varphi_{(+)d}$ and $\varphi_{(-)a}$ are of coinciding absolute values for both types of the attack. (Similar values of these parameters are expected on the basis of the relevant estimations.) Confinement to the single orbital $\varphi_{(+)2}$ instead of three BBOs of the C_α-C_β (C_α-H) bonds is based on their uniform contributions to transferred populations $q_{(+)d,(-)a}^{(3)}$. Increments of respective ABOs were shown to take zero values. That is why these orbitals are not included into the local model of the reaction.

The second-order energy $E_{(2)}$ of the whole reacting system was shown to be determined by two

partial transferred populations in this case, namely by $q_{(+)d,(-)a}^{(2)}$ and $q_{(+)2,(-)a}^{(2)}$. Owing to an additional assumption about coinciding absolute values of direct intermolecular interactions $G_{(1)da}$ for the frontal and the back attacks of nucleophile, no differences in stabilization energies $E_{(2)}$ arise for the two possible routes of the reaction. Distinction between these alternatives is then based on consideration of the respective third-order increments $q_{(+)d,(-)a}^{(3)}$ and $q_{(+)2,(-)a}^{(3)}$. Analysis of the relevant results of the study [23] shows that the principal interorbital interactions determining these increments are of the following signs:

$$G_{(1)da}^{(b)} < 0, \quad G_{(1)da}^{(f)} > 0, \quad G_{(2)da} < 0,$$
$$G_{(1)2a} > 0, \quad G_{(2)2a}^{(b)} > 0, \quad G_{(2)2a}^{(f)} < 0, \tag{27}$$

where $G_{(2)da}$ and $G_{(2)2a}$ were mediated by orbitals $\varphi_{(+)2}$ and $\varphi_{(+)d}$, respectively, and the superscripts (b) and (f) correspondingly refer to the back and frontal positions of the nucleophile. The interactions $G_{(2)da}$ and $G_{(1)2a}$ of (27) do not depend on the direction of the attack. It is seen that the back attack is represented by first- and second-order interorbital interactions of the same sign and thereby by positive third-order partial transferred populations $q_{(+)d,(-)a}^{(3)}$ and $q_{(+)2,(-)a}^{(3)}$. Meanwhile, the frontal attack of the reagent is described by analogous interactions of opposite signs and, consequently, by negative partial transferred populations. These results evidently are in line with our definitions of allowed and forbidden third-order reactions. Thus, the back attack of nucleophile may be concluded to be followed by an allowed substitution process. Again, a forbidden reaction refers to the frontal attack.

The bimolecular electrophilic substitution (S_E2) reaction of pyridine [69] serves as another example of third-order processes. Exclusively the *meta*-substituted pyridines are known to result from these reactions [38, 70, 71]. The usual (canonical) MOs of benzene play the role of FOs in this case [69] along with a single IVFO of electrophile ($\varphi_{(-)E}$). As a result, direct intramolecular interactions emerge even in an isolated pyridine, but these do not depend on the position of the electrophile. The direct intermolecular interactions, in turn, are not influenced by the intramolecular perturbation due to introduction of the nitrogen atom. Consequently, the second-order populations acquired by the electrophile prove

to be of coinciding values for various directions of the attack.

The relevant third-order populations are primarily determined by the partial increment $q^{(3)}_{(+)2,(-)E}$, where $\varphi_{(+)2}$ is the HOMO of benzene of the appropriate symmetry (viz. symmetric relatively to the plane embracing the first and the fourth carbon atoms, the former corresponding to the site of substitution). The above-mentioned increment, in turn, contains two components ascribed to mediating effects of the HOMO $\varphi_{(+)2}$ itself (the so-called self-mediating effect) and of the LUMO of benzene of the same symmetry ($\varphi_{(-)5}$). Moreover, the sign of the first component does not depend on the direction of the attack. Hence, it is the increment related to the LUMO $\varphi_{(-)5}$ that plays the decisive role in distinguishing the electron-donating abilities of various positions of pyridine towards an approaching electrophile. The signs of the direct and indirect interactions contained within the definition of the above specified decisive third-order member may be easily established using the results of contribution [69]. In particular, the direct interorbital interactions $G_{(1)2E}$ are conditioned by the structure of the orbital $\varphi_{(+)2}$ and acquire the following signs for *ortho* (*o*), *meta* (*m*) and *para* (*p*) attacks, respectively:

$$G^{(o)}_{(1)2E} < 0, \quad G^{(m)}_{(1)2E} > 0, \quad G^{(p)}_{(1)2E} > 0. \quad (28)$$

The indirect interactions $G_{(2)2E}$ between orbitals $\varphi_{(+)2}$ and $\varphi_{(-)E}$ by means of the LUMO $\varphi_{(-)5}$ are determined by the structure of the latter. We then obtain

$$G^{(o)}_{(2)2E} > 0, \quad G^{(m)}_{(2)2E} > 0, \quad G^{(p)}_{(2)2E} < 0. \quad (29)$$

Comparison of (28) and (29) indicates that the concerned interorbital interactions are of coinciding signs just for the *meta* attack. It is not surprising in this context that the decisive increment to the third-order population acquired by the *meta*-attacking electrophile is a positive quantity. In the case of remaining (*ortho* or *para*) positions of the reagent, the relevant interorbital interactions acquire opposite signs and yield positive third-order contributions $E_{(3)}$.

To make our comparison more complete, let us consider also the intramolecular charge transfer inside the pyridine ring due to the influence of the electrophile. The second-order partial transferred population $q^{(2)}_{(+)2,(-)5}$ does not depend on the relative position of the electrophile. The electrophile-mediated component of the relevant third-order increment is determined by the product of the direct interaction $G_{(1)25}$

and of the indirect interaction $G_{(2)25}$, the former having a negative sign for all directions of the attack. The signs of the second-order element $G_{(2)25}$ are as follows:

$$G^{(o)}_{(2)25} > 0, \quad G^{(m)}_{(2)25} < 0, \quad G^{(p)}_{(2)25} > 0. \quad (30)$$

It is seen that both $G^{(m)}_{(1)25}$ and $G^{(m)}_{(2)25}$ are negative quantities for the *meta* attack. Hence, it is the *meta*-directed substitution that meets our definition of allowed third-order processes. Meanwhile, the *ortho* and *para* attacks of an electrophile upon pyridine are expected to be followed by forbidden reactions.

3.2. The Fourth-Order Reactions

Let us turn now to the Ad_E2 processes of substituted ethenes $H_2C_\beta=C_\alpha HZ$ and start with the case of an electron-donating substituent $Z=D$. In accordance with the well-known Markovnikov rule [1–4, 68], the C_β atom is of considerably greater relative reactivity as compared to the C_α atom in this case. Thus, let us turn to comparison of these two alternatives with respect to allowance of the respective reactions. To this end, let us invoke the local model of the reaction used [22]. This model contains four principal orbitals, viz. the electron-donating orbital of the substituent D ($\varphi_{(+)d}$), the electron-accepting orbital of electrophile ($\varphi_{(-)E}$), as well as two bond orbitals (BOs) of the ethene fragment denoted by $\varphi_{(+)e}$ and $\varphi_{(-)e}$.

As with the above discussed S_N2 process, coinciding values of intermolecular resonance parameters are assumed for both directions of the attack. As a result, the second-order partial transferred populations do not contribute to differences in the stabilization energies of the whole reacting system referring to the α- and β-attacks. The third-order increments to the same differences also vanish in the case of the Ad_E2 reaction in contrast to the S_N2 process. The reason for this consists in the absence of direct interaction between orbitals $\varphi_{(+)d}$ and $\varphi_{(-)E}$ in the present model. Just this fact determined the decisive role of the fourth-order partial transferred populations $q^{(4)}_{(+)i,(-)j}$ in the formation of different reactivities of the C_α and C_β atoms. Thus, let us turn to the definition of these populations shown in (13).

Let us start with the notation that increments of the last term of the right-hand side of (13) do not contribute to differences under our interest [22]. For directly interacting pairs of FOs namely for $\varphi_{(+)d}$, $\varphi_{(-)e}$

and $\varphi_{(+)e}$, $\varphi_{(-)E}$, the principal contributions to fourth-order partial populations originate from the first term of the same definition. The signs of the direct interorbital interactions contained there are

$$G_{(1)de} > 0, \quad G_{(1)eE} < 0 \tag{31}$$

and do not depend on the direction of the attack. Meanwhile, the signs of the respective indirect interactions are electrophile-position-dependent, viz.

$$
\begin{aligned}
G_{(3)de}^{(\alpha)} < 0, \quad & G_{(3)de}^{(\beta)} > 0, \\
G_{(3)eE}^{(\alpha)} > 0, \quad & G_{(3)eE}^{(\beta)} < 0,
\end{aligned}
\tag{32}
$$

where the superscripts (α) and (β) refer to the α- and β-attacks, respectively. The interactions $G_{(3)de}$ and $G_{(3)eE}$ are mediated here by pairs of the orbitals $\varphi_{(+)e}$, $\varphi_{(-)a}$ and $\varphi_{(+)d}$, $\varphi_{(-)e}$, respectively. Comparison of (31) and (32) indicates that the β-attack is represented by first- and third-order interactions of the same sign and thereby by positive increments $q_{(+)d,(-)e}^{(4,\beta)}$ and $q_{(+)e,(-)E}^{(4,\beta)}$. Negative signs of the increments $q_{(+)d,(-)e}^{(4,\alpha)}$ and $q_{(+)e,(-)E}^{(4,\alpha)}$ easily follow for the α-attack.

The remaining two pairs of basis orbitals (interacting only indirectly) also deserve to be considered, viz. $\varphi_{(+)d}$, $\varphi_{(-)E}$ and $\varphi_{(+)e}$, $\varphi_{(-)e}$. The relevant fourth-order partial transferred populations are determined by the second terms of (13) and thereby no doubts arise about their positive signs. So far as their absolute values are concerned, these prove to be considerably greater for the β-attack as compared to the α-position of the electrophile. The main reason for that consists in coinciding signs of the two components of indirect interactions $G_{(2)dE}$ and $G_{(2)ee}$ for the β-attack and opposite signs of the same components for the α-attack. The components describe here the contributions of the mediating IOFO and IVFO to the above specified interactions. This result supplements the above conclusion about the β-attack being characterized by the principal interorbital interactions of the same sign. Therefore, just the β-attack meets the definition of the allowed fourth-order process. Meanwhile, the α-attack of an electrophile upon the molecule $H_2C_\beta{=}C_\alpha HD$ is predicted to be accompanied by a forbidden reaction.

Let us turn now to substituted ethenes containing an electron-accepting substituent A (Z = A). The C_α atoms are known to be more reactive as compared to the C_β atoms in this case [1 – 3]. The relevant model

contains an electron-accepting orbital $\varphi_{(-)a}$ instead of the electron-donating basis function $\varphi_{(+)d}$ of the previous one. Two pairs of directly interacting orbitals of opposite initial occupation reveal themselves here, namely $\varphi_{(+)e}$, $\varphi_{(-)E}$ and $\varphi_{(+)e}$, $\varphi_{(-)a}$. The direct interactions inside these pairs take negative signs whatever the direction of the attack is, viz.

$$G_{(1)ea} < 0, \quad G_{(1)eE} < 0. \tag{33}$$

The relevant third-order interactions, in turn, are of the following signs:

$$
\begin{aligned}
G_{(3)ea}^{(\alpha)} < 0, \quad & G_{(3)ea}^{(\beta)} > 0, \\
G_{(3)eE}^{(\alpha)} < 0, \quad & G_{(3)eE}^{(\beta)} > 0.
\end{aligned}
\tag{34}
$$

It is seen that coinciding signs of first- and third-order interactions follow for the α-attack. This position of the electrophile was also characterized by a larger absolute value of the second-order interaction $G_{(2)ee}$ owing to coinciding signs of the two components of this matrix element referring to mediating effects of orbitals $\varphi_{(-)a}$ and $\varphi_{(-)E}$. Hence, it is the α-attack of the electrophile that results in an allowed reaction in the case of the acceptor-containing ethene.

Let an essential notation to be made before finishing this subsection. The above analysis of addition processes of substituted ethenes was based on the results of the study [22]. The latter, in turn, were shown to be easily extendable to the case of an electrophilic attack upon any substituted conjugated hydrocarbon, including substituted benzenes. An analogous extension then refers also to the above drawn conclusion about allowed and forbidden ways of reactions. In particular, the formation of *ortho-* and *para-*disubstituted benzenes as a result of an electrophilic substitution process of donor-containing mono-derivatives may be concluded to result from an allowed fourth-order reaction. Meanwhile, the relevant *meta* attack will correspond to a forbidden process. Coincidence of the initial steps of both $Ad_E 2$ and $S_N 2$ processes with the addition of the reagent to the π-electron system of the reactant [1 – 3] is also taken into consideration here.

3.3. An Example of Fifth-Order Processes

The above anticipated example concerns the stereoselective concerted bimolecular β-elimination reactions of substituted alkanes $Z\text{-}C_\alpha H_2\text{-}C_\beta H_2\text{-}C_\gamma H_2{-}$ [24]. As opposed to $S_N 2$ processes, it is the

H-C$_\beta$ bond that is assumed to be under attack of an external base in this case. As a result, the E2 reaction embraces more bonds of the reactant as compared to the S$_N$2 process. Consequently, a considerably more extended model is used in the relevant study that contains the electron-donating orbital of the external base ($\varphi_{(+)d}$), two orbitals of the H-C$_\beta$ bond ($\varphi_{(+)1}$, $\varphi_{(-)2}$), two BOs of the C$_\beta$-C$_\alpha$ bond ($\varphi_{(+)3}$, $\varphi_{(-)4}$), and the electron-accepting orbital of the Z-C$_\alpha$ bond ($\varphi_{(-)a}$). Accordingly, distinction between *trans*- and *cis*-elimination processes is based on different signs of fifth-order partial transferred populations defined by (14). In particular, the signs of the increments

$$q^{(5,1)}_{(+)1,(-)a} = 4G_{(1)1a}G_{(4)1a},$$

$$q^{(5,2)}_{(+)1,(-)a} = 4G_{(2)1a}G_{(3)1a}, \tag{35}$$

$$q^{(5)}_{(+)d,(-)a} = 4G_{(2)da}G_{(3)da}$$

are shown to play the decisive role in the formation of the well-known predominance of the *trans* β-elimination over the relevant *cis*-process [1 – 3, 72]. To compare these alternatives, the terms of (35) are evaluated under assumptions of *cis*- and *trans*-arrangements of the Z-C$_\alpha$ and C$_\beta$-H bonds in the substituted alkanes. The resulting signs of interorbital interactions contained within (35) are

$$G^{(trans)}_{(1)1a} < 0, \quad G^{(trans)}_{(2)1a} < 0, \quad G^{(trans)}_{(3)1a} < 0,$$

$$G^{(trans)}_{(4)1a} < 0, \quad G^{(trans)}_{(2)da} > 0, \quad G^{(trans)}_{(3)da} > 0 \tag{36}$$

for the *trans*-arranged bonds, and

$$G^{(cis)}_{(1)1a} > 0, \quad G^{(cis)}_{(2)1a} < 0, \quad G^{(cis)}_{(3)1a} > 0,$$

$$G^{(cis)}_{(4)1a} < 0, \quad G^{(cis)}_{(2)da} < 0, \quad G^{(cis)}_{(3)da} > 0 \tag{37}$$

for the *cis*-arranged ones. It is seen that pairs of interorbital interactions of the same sign make up the fifth-order increments of (35) for the *trans*-arranged bonds and thereby positive signs of these increments are ensured. Meanwhile, pairs of interactions of opposite signs arise in (35) referring to *cis*-arranged bonds and negative fifth-order increments follow.

Therefore, the *trans*-β-elimination may be considered as an allowed fifth-order process, whereas the respective *cis*-elimination becomes a forbidden one.

On the whole, the results of this section demonstrate the validity of our selection rule to heterolytic reactions.
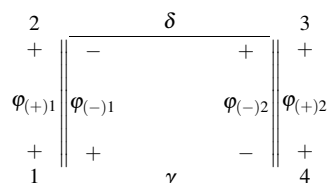
4. Studies of Pericyclic Reactions

As it was mentioned already in Section 1, pericyclic reactions are usually interpreted in terms of delocalized (canonical) MOs. This refers not only to the relevant pioneering contributions [18 – 20], but also to more sophisticated approaches suggested later [73 – 76]. Applicability of the semilocalized approach to the same processes has been verified recently [25, 26]. In this section, we are about to apply the common selection rule of Section 2 to the thermal electrocyclic closure of polyenes and to some cycloaddition processes of aliphatic hydrocarbons. These reactions serve as typical examples of mono- and bimolecular pericyclic processes [1]. An additional remark deserves to be made here: As opposed to heterolytic processes, no essential charge redistribution is expected to take place during the pericyclic reactions owing to the neutral (or almost neutral) nature of participating compounds in respect of their electron-donating (or -accepting) abilities [1 – 3]. The partial transferred populations studied below then describe a virtual population exchange between interacting fragments.
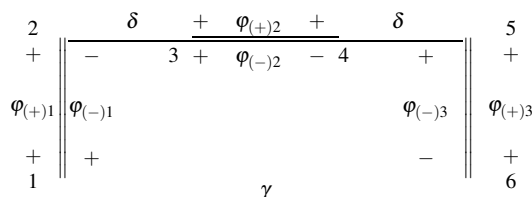
4.1. The Model of the Thermal Electrocyclic Closure. The Simplest Case of Butadiene

Let us start with the thermal electrocyclic closure of polyenes. Our initial system coincides with an open polyene chain (C$_{2N}$H$_{2N+2}$) containing N C=C bonds. As in the related studies [25, 26, 44] BOs of initially-double (C=C) bonds will play the role of FOs, whilst the interactions between BOs of the neighbouring pairs of these bonds will be considered as a perturbation. The chain will be assumed to be placed on the xy-plane so that the carbon atoms are characterized by their 2p$_z$ AOs $\{\chi\}$. The numbers $1, 2, \ldots, 2N$ are ascribed to both AOs and atoms of the chain, where 1 and $2N$ refer to the terminal positions. The AOs $\chi_1, \chi_2, \ldots, \chi_{2N}$ are supposed to be characterized by uniform Coulomb parameters α. Similarly, the initially-double (C=C) bonds will be represented by uniform resonance parameters β. Let the equalities $\alpha = 0$ and $\beta = 1$ to be accepted for convenience, the latter implying a choice of a negative energy unit. The resonance parameters between pairs of AOs referring to initially-single (C-C) bonds will be denoted by δ, where $0 < \delta < 1$ in our energy units.
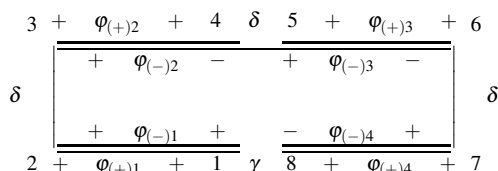
The closure process of our chain will be modelled by emergence of an additional resonance parameter γ

```
    2              δ                3
    +  ║  −              +    ║   +
φ(+)1 ║ φ(−)1        φ(−)2 ║ φ(+)2
    +  ║    +            −    ║   +
    1              γ                4
```
Scheme 1. Model of the electrocyclic closure of butadiene.

```
    2        δ      +  φ(+)2  +      δ        5
    +  ║  −      3 +  φ(−)2  − 4      +   ║   +
φ(+)1 ║ φ(−)1                    φ(−)3 ║ φ(+)3
    +  ║    +                       −    ║   +
    1                γ                     6
```
Scheme 2. Model of the electrocyclic closure of hexatriene.

```
    3  +  φ(+)2  +   4  δ  5  +  φ(+)3  +  6
         +  φ(−)2  −        +  φ(−)3  −
  δ                                          δ
         +  φ(−)1  +        −  φ(−)4  +
    2  +  φ(+)1  +   1  γ  8  +  φ(+)4  +  7
```
Scheme 3. Model of the electrocyclic closure of octatriene.

between the terminal AOs χ_1 and χ_{2N}. As discussed previuosly [25, 26], the lobes of the AOs of the same sign (e. g. the negative lower lobes) overlap one with another most significantly during a disrotatory reaction. Consequently, a disrotatory process is accompanied by formation of a positive overlap integral between AOs χ_1 and χ_{2N} and thereby of a positive parameter γ in our negative energy units. Again, a conrotatory way of reaction gives rise to the primary overlap of lobes of AOs χ_1 and χ_{2N} of opposite signs and thereby to a negative value of the same parameter. We may then conclude that

$$\gamma_{\text{dis}} > 0, \quad \gamma_{\text{con}} < 0. \tag{38}$$

Let us assume in addition that parameters δ and γ are of comparable absolute values so that these may be treated on the unified basis in our perturbation theory.

Let the BBOs and the ABOs of the initially-double (C=C) bonds be defined correspondingly as normalized sums and differences of the relevant pairs of $2p_z$ AOs. The positive coefficients of ABOs refer to odd-numbered AOs, whilst the negative ones are attached to even-numbered basis functions. For example, the bond orbitals of the first and of the last C=C bond take the form

$$\varphi_{(+)1}(\varphi_{(−)1}) = \frac{1}{\sqrt{2}}(\chi_1 \pm \chi_2),$$

$$\varphi_{(+)N}(\varphi_{(−)N}) = \frac{1}{\sqrt{2}}(\chi_{2N−1} \pm \chi_{2N}), \tag{39}$$

where the upper and lower signs of the right-hand sides correspond to BBOs and ABOs, respectively. For specific polyenes, the structures of BOs are shown in Schemes 1 – 3. The signs of BBOs ($\varphi_{(+)i}$) and of ABOs ($\varphi_{(−)j}$) are indicated near the initially-double (C=C) bonds, whilst resonance parameters (δ, γ, etc.) are attached to initially-single (C-C) bonds. It is evident that non-zero direct interactions $G_{(1)ij}$ correspond to pairs of BBOs and ABOs of the neighbouring C=C bonds including the pair of the terminal bonds. (Note that intrabond interactions $G_{(1)ii}$ take zero values owing to the equality $R_{ii} = 0$ for our BOs.) More precisely, a pair of interrelated direct interactions, viz. $G_{(1)ij}$ and $G_{(1)ji} = −G_{(1)ij}$ [44], refers to any initially-single (C-C) bond of our chain. The newly formed bond between the terminal AOs χ_1 and χ_{2N} is no exception here.

For the "internal" C-C bonds, the respective direct interactions $G_{(1)ij}$ of (23) are proportional to the resonance parameter δ, e. g.

$$G_{(1)12}^{(\delta)} = −G_{(1)21}^{(\delta)} = −\frac{1}{4}\delta, \tag{40}$$

where the superscript (δ) is used here and below to distinguish the δ-dependent interactions from the γ-dependent ones. The latter correspond to newly formed bonds between terminal AOs and are expressible as

$$G_{(1)1N}^{(\gamma)} = −G_{(1)N1}^{(\gamma)} = \frac{1}{4}\gamma, \tag{41}$$

where the subscript $1N$ represents the pair of BOs $\varphi_{(+)1}$ and $\varphi_{(−)N}$. It is seen that the right-hand sides of (40) and (41) do not depend on the total number of the C=C bonds (N).

Let us turn now to the consideration of partial transferred populations $q_{(+)i,(−)j}^{(k)}$. The above enumerated direct interorbital interactions give birth to the respective second-order increments $q_{(+)i,(−)j}^{(2)}$ and $q_{(+)j,(−)i}^{(2)}$ that coincide one with another, e. g.

$$q_{(+)1,(−)2}^{(2,\delta)} = q_{(+)2,(−)1}^{(2,\delta)} = \frac{1}{8}\delta^2 \tag{42}$$

and

$$q_{(+)1,(−)N}^{(2,\gamma)} = q_{(+)N,(−)1}^{(2,\gamma)} = \frac{1}{8}\gamma^2. \tag{43}$$

Consequently, the extents of the virtual population exchange do not depend on the signs of the parameter γ and thereby on the chosen way of closure of the chain within the second-order approximation.

To reveal the above anticipated dependence, indirect interactions between BOs and the respective partial transferred populations of higher orders k should be considered. To this end, the total number of C=C bonds, N, should be specified. Indirect interactions in hexatriene ($N = 3$) and octatriene ($N = 4$) are considered in the next subsections. Before finishing this subsection, let us dwell on the electrocyclic closure of butadiene ($N = 2$). Indeed, this simplest polyene makes an exception, where direct interactions between BOs of the C=C bonds determine the predominant way of reaction.

It is evident that two principal direct interactions are peculiar to this simple system, viz. the δ-dependent interaction $G_{(1)12}^{(\delta)}$ corresponding to the C2-C3 bond and the γ-dependent interaction $G_{(1)12}^{(\gamma)}$ referring to the newly formed bond C1-C4 (Scheme 1). As a result, the total direct interaction $G_{(1)12}$ between the BBO $\varphi_{(+)1}$ and the ABO $\varphi_{(-)2}$ (as well as $G_{(1)21}$ between BOs $\varphi_{(+)2}$ and $\varphi_{(-)1}$) consists of two components defined by (40) and (41), i. e.

$$G_{(1)12} = -G_{(1)21} = G_{(1)12}^{(\delta)} + G_{(1)12}^{(\gamma)} = \frac{1}{4}(\gamma - \delta). \quad (44)$$

This expression serves as an example of (26) for $k = 1$. Consequently, mixed increments proportional to the products $G_{(1)12}^{(\delta)}G_{(1)12}^{(\gamma)}$ and/or $G_{(1)21}^{(\delta)}G_{(1)21}^{(\gamma)}$ emerge in the final expressions for the total second-order transferred populations $q_{(+)1,(-)2}^{(2)}$ and $q_{(+)2,(-)1}^{(2)}$ along with δ^2- and γ^2-dependent terms of (42) and (43). We then obtain

$$\begin{aligned} q_{(+)1,(-)2}^{(2)} &= q_{(+)2,(-)1}^{(2)} \\ &= 2(G_{(1)12}^{(\delta)})^2 + 2(G_{(1)12}^{(\gamma)})^2 + 4G_{(1)12}^{(\delta)}G_{(1)12}^{(\gamma)} \\ &= \frac{1}{8}[\delta^2 + \gamma^2 - 2\delta\gamma]. \end{aligned} \quad (45)$$

It is seen that the signs of the two principal direct interactions, viz. of $G_{(1)12}^{(\delta)}$ and $G_{(1)12}^{(\gamma)}$, determine the relative value of the population $q_{(+)1,(-)2}^{(2)}$ and thereby of the relevant second-order energy. Inasmuch as $G_{(1)12}^{(\delta)}$ is a negative quantity as (40) indicates (note that $\delta > 0$),

a negative sign of the interaction $G_{(1)12}^{(\gamma)}$ also is required to ensure a large absolute value of $q_{(+)1,(-)2}^{(2)}$. This condition is met for a negative resonance parameter γ as (41) shows and thereby for a conrotatory way of closure.

Hence, it is the conrotatory reaction that is predicted to be allowed for butadiene on the basis of our selection rule. The disrotatory reaction is accordingly expected to be forbidden. The above analysis also shows that the overall closure process of butadiene is governed by second-order terms of power series. Thus, it may be referred to as a second-order process.

4.2. The Closure Process of Hexatriene

Let us turn now to the hexatriene molecule ($N = 3$). Let us dwell first on the pair of terminal bonds C1=C2 and C5=C6 (Scheme 2). Orbitals of these bonds, e. g. $\varphi_{(+)1}$ and $\varphi_{(-)3}$, interact both directly by means of the element $G_{(1)13}^{(\gamma)}$ following from (41) for $N = 3$ and indirectly through orbitals of the remaining C3=C4 bond. The interaction of the former type gives birth to the second-order partial transferred population $q_{(+)1,(-)3}^{(2)}$ defined by (43). The indirect interactions $G_{(2)13}^{(\delta)}$ and $G_{(2)31}^{(\delta)}$ follow from (24) and take the form

$$G_{(2)13}^{(\delta)} = -G_{(2)31}^{(\delta)} = \frac{1}{8}\delta^2 > 0. \quad (46)$$

It is seen that $G_{(2)13}^{(\delta)}$ of (46) always is a positive quantity. Hence, a positive sign of the direct interaction $G_{(1)13}$ also is required to ensure positive signs of the third-order partial transferred populations $q_{(+)1,(-)3}^{(3)}$ and $q_{(+)3,(-)1}^{(3)}$ following from (12). This condition proves to be met for positive γ values as (41) indicates. An analogous result may be also easily obtained for interactions of the remaining pairs of bonds of hexatriene. For example, the BOs $\varphi_{(+)1}$ and $\varphi_{(-)2}$ of bonds C1=C2 and C3=C4 interact directly by means of the negative element $G_{(1)12}$ following from (40). Meanwhile, the newly formed resonance parameter γ between AOs χ_1 and χ_6 of hexatriene offers a new pathway for the relevant indirect interactions. The respective second-order elements are

$$G_{(2)12} = -G_{(2)21} = -\frac{1}{8}\delta\gamma. \quad (47)$$

Comparison of (40) and (47) indicates that coinciding signs of both elements, i. e. of $G_{(1)12}$ and $G_{(2)12}$, and thereby a positive sign of the third-order partial transferred population $q^{(3)}_{(+)1,(-)2}$ are ensured for positive parameters γ. It is also evident that the case of bonds C3=C4 and C5=C6 completely resembles the above considered one. It should be also mentioned that the third-order terms of intrabond nature (e. g. $q^{(3)}_{(+)1,(-)1}$) vanish owing to the equality $G_{(1)ii} = 0$. After invoking (38) we may then conclude that the disrotatory way of closure is predicted to be allowed for hexatriene on the basis of our selection rule, whereas the conrotatory way is expected to be forbidden. Moreover, the closure process is governed by third-order terms in this case.

4.3. The Electrocyclic Closure of Octatriene

Let us consider finally the octatriene molecule ($N = 4$) (Scheme 3). In case of the terminal bonds C1=C2 and C7=C8, (41) and (43) may be directly applied to obtain the second-order partial transferred populations $q^{(2)}_{(+)1,(-)4}$ and $q^{(2)}_{(+)4,(-)1}$. Furthermore, the indirect interactions $G_{(2)14}$ and $G_{(2)41}$ vanish for octatriene because of absence of mediators between the orbitals concerned. This implies zero values for the respective third-order partial transferred populations $q^{(3)}_{(+)1,(-)4}$ and $q^{(3)}_{(+)4,(-)1}$ and thereby the relevance of the fourth-order corrections $q^{(4)}_{(+)1,(-)4}$ and $q^{(4)}_{(+)4,(-)1}$. The latter are defined by (13), where the $(G_{(2)14})^2$-containing increment vanishes for reasons mentioned above. The resulting expression for $q^{(4)}_{(+)1,(-)4}$ is

$$q^{(4)}_{(+)1,(-)4} = 4G_{(1)14}[G_{(3)14} + \frac{1}{2}(G_{(1)}G^+_{(1)}G_{(1)})_{14}], \quad (48)$$

where $G_{(1)14}$ is shown in (41). The third-order interactions contained within the square brackets of (48) may be derived as described previously [25]. These are

$$G^{(\delta)}_{(3)14} = -\frac{3}{32}\delta^3 < 0,$$
$$(G_{(1)}G^+_{(1)}G_{(1)})_{14} = -\frac{1}{64}\delta^3 < 0 \quad (49)$$

and make up a negative quantity. Substituting (41) and (49) into (48) yields the following result:

$$q^{(4)}_{(+)1,(-)4} = -\frac{13}{128}\delta^3\gamma. \quad (50)$$

It is seen that coinciding signs of both $G_{(1)14}$ and of the total third-order interaction contained within the square brackets of (48) and thereby a positive sign of $q^{(4)}_{(+)1,(-)4}$ are ensured if the newly formed resonance parameter γ is a negative quantity.

Let us turn now to the remaining pairs of bonds of octatriene. The cases of neighbouring bonds closely resemble that of the terminal bonds as it was demonstrated for the hexatriene molecule. By contrast, the next-neighbouring pairs (such as C1=C2 and C5=C6) are of some additional interest. The point is that second-order indirect interaction is peculiar to these pairs (e. g. $G_{(2)13}$ for the above-mentioned bonds). This interaction is mediated by orbitals of both intermediate bonds, i. e. of C3=C4 and C7=C8. The total element $G_{(2)13}$ defined by (24) then consists of two contributions, viz.

$$G_{(2)13} = \frac{1}{8}(\delta^2 - \delta\gamma). \quad (51)$$

The increments $\frac{1}{8}\delta^2$ and $-\frac{1}{8}\delta\gamma$ correspond here to the mediating effects of orbitals of the C3=C4 and C7=C8 bonds, respectively [see (46) for comparison]. The element $G_{(2)13}$ of (51), in turn, gives birth to a fourth-order partial transferred population defined as
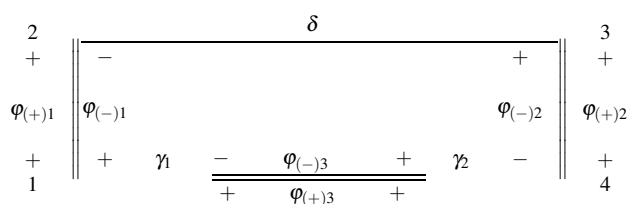
$$q^{(4)}_{(+)1,(-)3} = 2(G_{(2)13})^2. \quad (52)$$

It is seen that the above specified partial transferred population takes a larger absolute value if the two components of the second-order interaction are of the same sign. The latter condition, in turn, is ensured for a negative value of the parameter γ.

On the whole, the electrocyclic closure of octatriene is predicted to be allowed, if the newly emerged parameter γ is negative. After invoking (38) we may conclude that the allowed process coincides with the conrotatory one.

4.4. Summarizing Discussion of the Electrocyclic Closure of Polyenes. Consideration of the Diels-Alder Reaction

Let us start with the fact that a conrotatory closure of the chain is predicted by our selection rule for even N values, whereas a disrotatory process follows for odd N values. Inasmuch as $4n$ and $(4n + 2)$ electrons, respectively, correspond to these cases, the above established result coincides with that of the Woodward-Hoffmann rule [18 – 20]. Coincidence of this conclusion to those of more sophisticated approaches to the

$$
\begin{array}{c}
\begin{array}{ccc}
2 & & 3 \\
+ & \delta & + \\
\varphi_{(+)1} \quad \left|\left| \begin{array}{c} - \qquad\qquad\qquad\qquad\qquad + \\ \varphi_{(-)1} \qquad\qquad\qquad\qquad \varphi_{(-)2} \end{array} \right|\right| \quad \varphi_{(+)2} \\
\begin{array}{c} + \\ 1 \end{array} \quad \left|\left| \begin{array}{ccccc} + & \gamma_1 & - & \varphi_{(-)3} & + & \gamma_2 & - \\ & & + & \varphi_{(+)3} & + \end{array} \right|\right| \quad \begin{array}{c} + \\ 4 \end{array}
\end{array}
\end{array}
$$

Scheme 4. Model of the Diels-Alder reaction between butadiene and ethene.

same reaction [26, 73 – 76], as well as to experimental results [1 – 4] also may be mentioned. Thus, adequacy of our selection rule for the thermal electrocyclic closure of polyenes is beyond any doubt.

The above obtained results provide us also with an interpretation of the observed alternation of the allowed way of closure between the conrotatory and the disrotatory one if the number N grows. The main point here is that an N-independent direct interaction is multiplied by an N-dependent indirect interaction when making up the decisive partial transferred population, and the signs of the latter interactions alternate with growing N values in addition. In particular, the N-independent direct interaction $G_{(1)1N}^{(\gamma)}$ of (41) is multiplied by the negative first-order element $G_{(1)12}^{(\delta)}$ of (40), by the positive second-order interaction $G_{(2)13}^{(\delta)}$ of (46), and by the negative total third-order term within the square brackets of (48) for the cases $N = 2$, 3 and 4, respectively. The sign of the direct interaction is then chosen so as to 'neutralize' the alternation of signs of indirect interactions and thereby to ensure the positive sign of the product. As a result, the above specified alternation of the allowed way of closure follows. It is seen, therefore, that the choice of the allowed way of the closure process is actually determined by the signs of indirect (through-bond) interactions of BOs of terminal bonds. An analogous dependence was obtained previously [25] by consideration of the very early stage of the closure process characterized by the relation $\gamma \ll \delta$.

The above performed study of the closure processes allows us also to conclude that the size of the cycle under formation plays the decisive role in the predictions of allowed and forbidden processes. That is why analysis of cycloaddition reactions of aliphatic conjugated hydrocarbons closely resembles that of respective closure processes. To demonstrate this, let us consider the most popular Diels-Alder reaction between butadiene and ethene [1] (Scheme 4). Let the BOs of butadiene be denoted as in the above study. The intramolecu-

lar resonance parameter between AOs χ_2 and χ_3 will retain the designation δ, where $0 < \delta < 1$. The BBO and the ABO of the only C=C bond of the approaching ethene will be designated by $\varphi_{(+)3}$ and $\varphi_{(-)3}$, respectively. The signs of ABOs $\varphi_{(-)1}$, $\varphi_{(-)2}$, and $\varphi_{(-)3}$ will be chosen as shown in Scheme 4. The intermolecular resonance parameters will be denoted by γ_1 and γ_2.

Comparison of the cycles of Schemes 2 and 4 indicates them to differ one from another only in the designations of the resonance parameters between $2p_z$ AOs. The principal direct and indirect interorbital interactions representing the Diels-Alder reaction take then the form

$$
\begin{aligned}
G_{(1)13} &= \frac{1}{4}\gamma_1, \quad G_{(2)13} = \frac{1}{8}\delta\gamma_2, \\
G_{(1)12} &= -\frac{1}{4}\delta, \quad G_{(2)12} = -\frac{1}{8}\gamma_1\gamma_2.
\end{aligned}
\tag{53}
$$

These interactions yield positive third-order partial transferred populations if the signs of the newly formed resonance parameters γ_1 and γ_2 are uniform, i. e. both of them are either positive quantities or negative ones. Consequently, the Diels-Alder reaction is predicted to be allowed in either the supra-supra or antara-antara fashion. This result coincides with the relevant predictions of other approaches, including the generalized Woodward-Hoffmann rule [77], as well as with experimental facts [1]. Thus, the applicability of our selection rule to bimolecular cycloaddition processes is also supported.

5. Concluding Remarks

1. The principal contribution of the overviewed studies to the theory of chemical reactivity consists in the development of a unified quantum-chemical description of both heterolytic and pericyclic processes resolving itself into a common selection rule. The fact that direct and indirect interorbital interactions play the role of the principal terms in this rule indicates a rather universal nature of this concept.

2. The direct and indirect interorbital interactions underlying the suggested selection rule embrace fragments of the whole reacting system instead of those of an isolated reactant. This implies that both intra- and intermolecular interactions play equally important roles in the choice of the predominant ways of organic reactions.

3. Non-zero values of the resonance parameters are sufficient for direct and indirect interorbital interactions to arise. Thus, the validity of the suggested common selection rule for organic reactions indicates the choice of the predominant way of a chemical process to be made at its very early stage. It is also noteworthy that weak intermolecular interactions vs. the intramolecular ones are not required in the approach applied in contrast to the standard perturbative approaches [4 – 17]. Hence, an invariance of the chosen way within an extended range of the reaction coordinate may be expected.

4. The signs of direct and indirect interorbital interactions underlying our selection rule are determined by those of interorbital resonance parameters and/or of the related overlap integrals. Thus, the choice of the predominant way of any organic reaction may be concluded to be conditioned by the overlap topology of a certain set of principal orbitals (as it was shown to be the case with pericyclic precesses [26], in particular).

5. Delocalized (canonical) MOs neither of the isolated reactant nor of the whole reacting system are invoked in the approach applied. Moreover, the present approach may be considered as a part of the non-canonical theory of MOs [27, 32, 43, 44]. Hence, the success in formulating the common selection rule for organic reactions indicates the efficiency and fruitfulness of the non-canonical MO method, in general, and of the localized way of representing electronic structures and their alterations during chemical reactions, in particular.

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