QUASI-CLASSICAL ALTERNATIVES IN QUANTUM CHEMISTRY

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Abstract

The article contains an overview of authors achievements in developement of alternative quantum-chemical approaches oriented towards revival of the classical tradition of qualitative chemical thinking instead of obtaining numerical results. The above-mentioned tradition is concluded to be based mainly on principles (rules) of additivity, transferability and locality of molecular properties. Accordingly, model Hamiltonian matrices are used in the approaches under developement (called quasi-classical alternatives), wherein algebraic parameters play the role of matrix elements and these are assumed to be transferable for similar atoms and/or atomic orbitals in addition. Further, passing to delocalized descriptions of electronic structures (as usual) is expected to be the main origin of difficulties seeking to formulate quasi-classical alternatives. In the framework of the canonical method of molecular orbitals (MOs), delocalization is shown to be partially avoidable by invoking a recently-suggested approach to secular (eigenvalue) equations for model Hamiltonian matrices, wherein the usual initial imposing of the zero-determinant condition is replaced by a certain reformulation of the problem itself. The most efficient way of achieving the same end, however, is shown to consist in passing to non-canonical one-electron problems. The latter may be exemplified by the block-diagonalization problem for the relevant Hamiltonian matrix following from the Brillouin theorem and yielding non-canonical (localized) MOs and by the commutation equation for the respective one-electron density matrix (charge- bond order matrix). In this connection, most of attention is paid in the article to perturbative solutions of the above-mentioned non-canonical problems and to their implications, including common quantum-chemical descriptions of entire classes of chemical compounds.

1 Introduction. Quantum-mechanical and classical perspectives on molecular structure and reactivity

Chemistry experienced a period of a great invasion of quantum mechanics during the last several decades. Consequently, numerical solutions of various approximate versions of the Schrödinger equation (such as the Hartree-Fock (HF) equation (see e.g. [1-3])) started to play a central role in the theoretical chemistry instead of traditional qualitative reasoning based on simple models of interatomic interactions. The term 'computational chemistry' is currently used to refer to this new branch of chemical science [4-6].

Significant achievements of computations are beyond any doubt, especially so far as quantitative aspects of molecular structures and properties are concerned. Moreover, characteristics of both isolated molecules and chemical reactions often are predictable nowadays as accurately as it is required and thereby computations are able to precede or even to replace expensive experiments. Unfortunately, these achievements go with essential losses. Indeed, the most fundamental and fruitful classical generalities seem to be left outside the contemporary theoretical chemistry, e.g. series and/or classes of related compounds, functional groups (fragments), derivatives, reaction center, various common effects including the inductive one, etc. The same refers also to the main principles (rules) of the qualitative chemical thinking, namely additivity, transferability and locality of molecular properties, as well as to intuitition-based relations, e.g. between local structures and local properties. This implies in summary that the classical tradition of thinking about common trends in chemical behaviour becomes broken off and we actually have to content ourselves with studies of particular cases only. The aim of contributions overviewed in this article consists in both revival of the above-discussed classical tradition of qualitative thinking and its realization in terms of quantum chemistry. These attempts are jointly called quasi-classical alternatives.

To reveal the reasons why the above-mentioned gap between the contemporary quantum chemistry and the classical generalities arises, let us start with perspectives on molecular structures, in general, and on their similarities, in particular, underlying the quantum mechanics and the classical chemistry.

Molecules are considered as consisting of electrons and of nuclei in quantum mechanics [2,3,7]. Accordingly, numbers of these particles are the principal parameters both of the Schrödinger equation and of its approximate versions. Hence, specifying of these numbers is imperative to obtain a solution, the latter thereby always referring to an individual molecule. Although some similarity between two or several compounds may be revealed 'a posteriori' (i.e. after comparison of the final results), no immanent relation may be established between the relevant principal equations even if the chemical structures of compounds concerned are very similar (e.g. methane and ethane). Another important feature of these solutions (we mean here of wave functions) consists in their generally delocalized nature [1-3,8]. In other words, these functions usually embrace the entire system under study and depend on its whole constitution in a rather intricate manner (except for special cases when additional conditions of localization are imposed [8]).

By contrast, chemical constitutions of molecules (see e.g. [9]) are defined in terms of atoms involved in the given compound and the way these are bound together (chemical bonds). Moreover, exact meanings of both atoms in molecules and bonds are not essential in practice. Accordingly, compounds consisting of uniform groups of atoms (elementary fragments) connected one with another in a same manner are *a priori* considered to be similar whatever the actual number of these groups. As a result, a certain set of similar molecules arises that is usually referred to as a class of related compounds and regarded as a single object characterized by specific properties (e.g. alkanes, acids [10,11], etc.). In other words, the definition of the principal classical generality (i.e. of a class of molecules) is based on common peculiarities of local constitutions, whereas the overall structure of a particular molecule (the global structure) may vary in a wide range. For example, the local structure of alkanes involves both four-valency of carbon atoms and tetrahedral arrangement of respective quartets of bonds, whilst the global structure embraces the total number of atoms, the presence of cycles, branchings, etc. Accordingly, the relation 'structure/properties' is expected to reveal itself in two ways: i) as a relation between local structures and local properties and ii) as that between the global constitution and global properties. The first of these aspects usually concerns common properties of the whole class under study and is alternatively referred to as the principle (rule) of locality. Given that certain details of structures and properties are ignored in addition, the transferability rule for local characteristics follows [This rule is usually applied to characteristics of atoms, bonds and functional groups of related compounds [9]]. It also deserves adding here that the principles of locality and transferability provide a basis for definition of the reaction center (Section 9). Meanwhile, the relation between global structures and global properties refers to individual representatives of the class and gives birth to the well-known principle (rule) of additivity for properties ascribed to the whole molecule [8].

The above comparative discussion demonstrates dramatic differences between the two alternative perspectives on molecules and thereby their low compatibility [12]. This fact evidently is among the main reasons of the above-asserted gap between the computational and the classical branches of chemistry. On the other hand, the same discussion gives us some hints concerning the principal ways of developement of quasi-classical approaches: First, the principle of locality should be realized as extensively as possible in the approach concerned and preserved until obtaining the final description of the whole system (if possible). Second, the transferability rule should be invoked to unify quantum-mechanical problems for similar molecules. Employment of models proves to be especially helpful in achieving the latter end as discussed in Section 2 in a detail. So far as realization of the locality principle is concerned, the overall state of things is somewhat more complicated.

To clarify this point, let us turn again to the well-known canonical HF equation [1-3] for molecules based on the concept of one-electron orbitals (molecular orbitals (MOs)). These orbitals (MOs) are known to be additionally expressed in the form of linear combinations of atomic orbitals (AOs). The latter approach (usually called the LCAO approximation [1-3]) evidently is of classical origin and may be regarded as an important step towards realization of the locality principle. Indeed, elements of the representation matrix of the self-consistent Fockian are attached to separate atoms and/or their pairs in the basis of AOs. Besides, employment of hybrid AOs

(HAOs) as basis functions [13,14] instead of usual AOs is even more appropriate as the largest off-diagonal Fockian elements then correspond to chemical bonds. These important achievements, however, become lost almost entirely after passing to the basis of the standard (canonical) MOs (CMOs), because just these MOs usually are delocalized over the whole system under study and depend on its overall structure [1,2,8] as it is the case with wave functions in general. Moreover, identical chemical bonds and their groups are not, as a rule, accompanied by equivalent CMOs [8]. Finally, the link between CMO sets of related compounds is even more complicated.

Two options seem to be possible in this situation. The first (conservative) option consists in invoking additional approaches and/or modifications to preserve the locality principle in the framework of the canonical method of MOs. Some achievements of this type are discussed in Sections 3, 4 and 13. The second (radical) option lies in turning to alternative one-electron problems with respect to the canonical one, namely to the Brillouin theorem (block-diagonalization problem) and the commutation equation for the one-electron density matrix. The relevant achievements (the so-called PNCMO theory) are discussed in Sections 5-12.

2 The quasi-classical nature of the Hückel model

The very offspring of quantum chemistry was associated with developements of simple models of electronic structures of polyatomic molecules that are generally much closer to the classical chemistry as compared to the contemporary numerical methods. The so-called 'curly arrow chemistry' based on the well-known octet rule [15], the simplest version of the valence bond (VB) method usually referred to as the resonance theory [16] and the Hückel theory of molecular orbitals (HMO theory) [17,18] may be mentioned here as the most outstanding examples. In this Section, we will dwell on the Hückel model, both the standard HMO theory and studies overviewed in this article are based on.

First of all, we should come to an agreement about the meaning of the term 'the Hückel model'. Let us start with a notation that the original HMO theory [19,20] was based on solution of secular (eigenvalue) equations for respective model Hamiltonian matrices. As it turned out recently (see Sections 5 and 6), however, applications of the Hückel type Hamiltonian matrices are not restricted to solutions of these most popular equations. Moreover, just the employments of these matrices beyond the limits of the canonical MO method offers us new quasi-classical alternatives. This implies the term 'the Hückel model' to mean much more than the standard HMO theory.

Another important point here concerns the qualitative content of the Hückel model. To discuss this aspect in a more detail, let us start with recalling that the original version of the HMO theory [19,20] was intended to be among the first semiempirical methods of calculation of electronic structures of polyatomic molecules. The principal elements of the relevant model Hamiltonian matrices (i.e. parameters α and β) were accordingly determined on the basis of the best coincidence of results of calculation for a few reference compounds with the relevant experimental data. It is no surprise, therefore, that understanding of the HMO theory as an extremely approximate method of calculation of electronic structures is a

widespread viewpoint up to now. This popular attitude is additionally supported by an obvious fact that the Hückel type Hamiltonian matrix may be considered as a rough approximation to the respective matrix of the self-consistent Fockian. The qualitative content of the Hückel model, however, has little to do either with the numerical values of its parameters or with computations. The main point here is that the structure of the model Hamiltonian matrix reflects the spatial and/or chemical constitution of the respective molecule including both local and global aspects. Indeed, certain basis orbitals (AOs or HAOs) are assumed to correspond to diagonal elements (α) of the Hückel type Hamiltonian matrices (**H**), whilst the off-diagonal elements (β) represent the interactions between these orbitals. The latter, in turn, are usually supposed to be proportional to overlap integrals [21] being directly dependent on both the respective internuclear distance and the spatial arrangement of basis orbitals. As a result, the above-mentioned interrelation arises between the structure of the matrix **H** and that of the given molecule. For conjugated and/or aromatic hydrocarbons, this relation is known to acquire an extremely simple form, namely, the relevant model Hamiltonian matrix **H** is proportional to the adjacency matrix of the graph describing the structure of the C-skeleton of the given molecule [22]. In the case of saturated hydrocarbons, an analogous relation also may be established (Sections 3 and 4). Thus, we will concentrate ourselves on the above-described qualitative aspects when using the term 'the Hückel model' and/or the 'Hückel type model Hamiltonian matrix' throughout this paper.

Furthermore, just the above-described relations between the Hückel type Hamiltonian matrices and chemical structures of molecules serve as the principal argument for the quasi-classical nature of the Hückel model [In Ref.[12] the model has been considered as taking an intermediate place in between quantum mechanics and the classical chemistry on the same basis]. Other arguments for this important conclusion follow from essential common features between the model under discussion and the chemical perspective on molecular structures:

First, neither the basis orbitals (AOs or HAOs) nor the one-electron Hamiltonian operator underlying the Hückel type Hamiltonian matrix **H** are defined explicitly in the model as it is the case with the classical atoms in molecules and chemical bonds. Second, the role of the number of electrons in the formation of electronic structures is extremely reduced in the Hückel model (Molecular orbitals are sought here without regard to the number of electrons). Finally, the way the similarity of related molecules is desribed in the model resembles that of the classical chemistry. The last point deserves a separate discussion.

Thus, uniform α and β parameters are usually accepted *a priori* for conjugated and/or aromatic hydrocarbons [17,21] in accordance with the classical transferability rule. This implies that less important details of structures of individual systems are ignored for the benefit of generality. Consequently, common model Hamiltonian matrices are constructable for some simple series of related compounds (e.g. for polyenes, polyacenes, etc.) and thereby common solutions of the relevant secular equations are obtainable that contain the numbers of similar fragments as the principal parameters (see Ref.[18] for an overview of these solutions). The series of molecules concerned then becomes described as a single object in the Hückel model as it is the case with the classical chemistry. Hydrocarbons and their heteroatom-containing derivatives is another example of similar molecules. The respective

Hückel Hamiltonian matrices usually differ one from another only in the value of a single parameter, viz. of the Coulomb parameter (α_X) referring to the site of substitution [21,23]. As a result, the two similar problems may be regarded as a single problem, wherein the parameter α_X plays the role of perturbation [23]. This way of investigation is evidently in line with the classical concept of the derivative.

Therefore, the quasi-classical nature of the Hückel model (in the above-described qualitative sense) is beyond any doubt. That is why just this model has been chosen to underly the attempts to construct the analogues for the classical rules and generalities overviewed below. It is evident that no numerical values of the Hamiltonian matrix elements are required to achieve this end. Instead, algebraic methods are employed when dealing with the relevant principal equations. Consequently, we actually return to the 'world of deduction and modeling'[24].

3 An alternative way of dealing with eigenvalue equations for Hamiltonian matrices

As already mentioned, the present Section is devoted to quasi-classical alternatives in the framework of the canonical theory of MOs. In this connection, we will dwell on secular (eigenvalue) equations for Hückel type model Hamiltonian matrices (**H**) that yield the so-called one-electron properties of molecules, viz. CMOs and respective one-electron energies (coinciding with eigenfunctions and eigenvalues of the matrix **H**, respectively). Moreover, eigenvalues referring to occupied CMOs are additionally related to ionisation potentials of molecules measured experimentally by the photoelectron spectroscopy [25] (cf. the Koopmans theorem [2,26]). Accordingly, squares of the MO LCAO coefficients represent the extents of participation of separate AOs in the ionisation of molecule from the respective energy level.

Let us start with a notation that the principal rules of the qualitative chemical thinking (Section 1) are usually applied to the so-called 'collective' properties of molecules [23], e.g. heats of formation and/or atomisation, dipole moments, polarizabilities, etc. (the term 'collective' is of quantum chemical origin here and indicates the property concerned to be determined by all electrons and/or by all occupied one-electron states of the system). Nevertheless, there are reasons to expect that the classical principle of locality manifests itself in the one-electron characteristics too. Indeed, existance of common peculiarities both of one-electron energy spectra and of CMOs of related molecules follows from numerous theoretical and experimental facts exemplified below and these peculiarities may be traced back to similar local structures of compounds concerned. The most outstanding theoretical fact worth mentioning is that CMOs of extended compounds are expressible as linear combinations of those of elementary fragments provided that the interfragmental interactions are weak and thereby the perturbation theory is applicable (cf. the so-called PMO theory [23]). This implies the local constitutions of CMOs of related molecules to depend upon those of respective elementary fragments. [A question arises here immediately whether these achievements may be generalized to the case of comparable intra- and interfragmental interactions]. So far as experimental arguments for common features of one-electron spectra of similar molecules are concerned, the photoelectron spectra (PES) of alkanes [27-30] are especially illustrative. Thus, two

groups of ionization potentials (two energy bands) reveal themselves in these spectra at 17-26 and 10-16 eV, respectively. The first of these bands (the so-called high-energy band (HEB)) is of particular interest in our context. Indeed, the HEB of an alkane C_NH_{2N+2} or C_NH_{2N} always consists of N peaks, the level distribution pattern of which closely resembles the spectrum of the respective simple chain G_0 (Fig. 1). Given that the band concerned is traced back to ionization of electrons mostly from $2s$ AOs of carbon atoms (this is the simplest and commonly accepted interpretation [27-30]), the above-mentioned level distribution pattern seems to be due to similar local environments of these AOs over the chain, i.e. to the uniform local constitution of alkanes. Among facts under present interest, common spectral properties of alternant hydrocarbons [22,31] also may be mentioned that may be found in almost all quantum chemistry textbooks [A question here concerns the presence of common elementary fragments (see below)].

It is evident that revealing of the influence of local structure upon one-electron characteristics and thereby developement of the desired quasi-classical alternative becomes feasible if we avoid an immediate passing to the basis of delocalized MOs (CMOs). In this connection, an alternative way of dealing with secular equations for Hamiltonian matrices ($\mathbf{H}$) of related chemical compounds has been suggested in Ref.[32], the essence of which consists in an inverted order of the principal operations vs. the standard one when solving the problem. Indeed, the first step of the standard solution procedure coincides with imposing the zero-determinant requirement and search for eigenvalues, whereas the second one lies in obtaining the eigenfunctions. By contrast, we start with reformulating the secular problem itself in order to reveal the structures of eigenfunctions, whilst the eigenvalues follow from the second step. The initial reformulating of the problem resolves itself into eliminating most of variables (MO LCAO coefficients) by preserving only one of them for each elementary fragment of the compound concerned. This variable-elimination (reduction) procedure yields an effective $N \times N-$ dimensional secular problem, wherein a single equation corresponds to each of N elementary fragments. Elements of the relevant reduced Hamiltonian matrix (to be diagonalized during the second step) generally depend on the energy variable ε and the notation $\widetilde{\mathbf{H}}(\varepsilon)$ is used below in this connection. It is evident that diagonal and off-diagonal elements of this new matrix represent elementary fragments and their interactions, respectively. The off-diagonal elements often prove to be additionally reducible to either 1 or 0 and thereby describe the adjacencies of fragments. Given that this is the case, the local structure of the given chain becomes represented implicitly via ε-dependent intrafragmental elements $\widetilde{H}_{ii}(\varepsilon)$, whereas the respective global structure keeps to be reflected explicitly in the overall constitution of the reduced matrix $\widetilde{\mathbf{H}}(\varepsilon)$. Moreover, any element $\widetilde{H}_{ii}(\varepsilon)$ was shown to depend mostly on the structure of the Ith elementary fragment and (to a certain extent) on its nearest environment [Elements $\widetilde{H}_{ii}(\varepsilon)$ prove to be uniform or almost uniform for the same elementary fragments in analogous environments]. Further, the above-desribed variable-elimination procedure yields expressions for eigenfunctions of the initial Hamiltonian matrix $\mathbf{H}$ (i.e. for CMOs) in the form of linear combinations of N $\varepsilon-$dependent non-orthogonal basis orbitals that are more or less localized on individual elementary fragments and depend on constitution of the latter. In some cases, these basis orbitals prove to

be additionally related to MOs of elementary fragments. Coefficients of the above-specified combinations, in turn, coincide with those of eigenvectors of the reduced matrix $\widetilde{\mathbf{H}}(\varepsilon)$ and thereby are determined by the relevant global structure. In summary, the roles of local and of global structures in the formation of both one-electron spectra and CMOs are expected to follow from the first and the second step of the new approach, respectively. Thus, a feasibility of their separation arises, at least in principle. It also deserves emphasizing that no assumptions about relatively weak interfragmental interactions are invoked here and thereby a certain generalization of the above-mentioned perturbation- theory- based approaches [23] is actually obtained.

Admitedly, acomplishing of the above-outlined alternative is not an easy problem in practice. This especially refers to the ultimate diagonalization of the $\varepsilon-$dependent reduced Hamiltonian matrix $\widetilde{\mathbf{H}}(\varepsilon)$. In this connection, three particular cases may be distinguished that are characterized by relatively simple second steps.

a) The case, when an energy-variable- independent reduced Hamiltonian matrix ($\widetilde{\mathbf{H}}$) is obtainable [33], may be mentioned in the first place. The well-known even alternant hydrocarbons (AHs) serve as an excellent example here. To demonstrate this, let us introduce the $2N-$dimensional basis of $2p_z$ AOs of carbon atoms $\{\chi\}$ and divide it into two $N-$dimensional subsets $\{\chi^*\}$ and $\{\chi^\circ\}$ as usual [22, 31, 33, 34]. The common Hückel Hamiltonian matrix of AHs may be then represented in terms of four submatrices (blocks) as follows

$$\mathbf{H} = \left| \begin{array}{cc} \mathbf{0} & \mathbf{B} \\ \mathbf{B}^+ & \mathbf{0} \end{array} \right|, \tag{3.1}$$

where the non-zero blocks $\mathbf{B}$ and $\mathbf{B}^+$ contain resonance parameters of chemical bonds (see Ref. [33] for details) and the superscript + here and below designates the Hermitian-conjugate (transposed) matrix. As originally shown in [35], the initial $2N \times 2N-$dimensional secular problem for the matrix $\mathbf{H}$ of Eq.(3.1) resolves itself into two $N \times N-$dimensional problems

$$(\mathbf{BB}^+)\mathbf{U} = \varepsilon^2\mathbf{U}, \qquad (\mathbf{B}^+\mathbf{B})\mathbf{V} = \varepsilon^2\mathbf{V}, \tag{3.2}$$

where $\mathbf{U}$ and $\mathbf{V}$ are column- matrices of MO LCAO coefficients referring to subsets subsets of AOs $\{\chi^*\}$ and $\{\chi^\circ\}$, respectively, and ε is the usual energy variable. It is easily seen that any matrix problem of Eq.(3.2) may be reformulated into a secular equation of the standard form for an $\varepsilon-$dependent effective Hamiltonian matrix, e.g.

$$\widetilde{\mathbf{H}}(\varepsilon) = \mathbf{BB}^+ + \varepsilon(1-\varepsilon)\mathbf{I}, \tag{3.3}$$

where $\mathbf{I}$ here and below stands for the unit matrix of the relevant dimension (coinciding with N in our case). Moreover, matrices $\mathbf{BB}^+$ and $\widetilde{\mathbf{H}}(\varepsilon)$ commute one with another and thereby possess a common set of eigenvectors contained within the column-matrix $\mathbf{U}$. Consequently, the $\varepsilon-$dependent matrix $\widetilde{\mathbf{H}}(\varepsilon)$ of Eq.(3.3) may be successfully replaced by the energy- variable- independent matrix $\widetilde{\mathbf{H}} = \mathbf{BB}^+$ that was shown to represent [33] adjacencies of elementary fragments of AHs specified below. Accordingly, a generalized ($\varepsilon-$dependent) representation has been obtained

for eigenfunctions of the matrix $\mathbf{H}$ of Eq.(3.1) and thereby CMOs of AHs, viz.

$$\psi(\varepsilon) = \frac{1}{\sqrt{2}} \sum_{i=1}^{(*)} \varphi_i(\varepsilon) U_i, \tag{3.4}$$

where the sum embraces AOs of the starred subset $\{\chi^*\}$, U_i stand for elements of the column- matrix $\mathbf{U}$ and $\varphi_i(\varepsilon)$ are $\varepsilon-$dependent basis orbitals of the following constitution

$$\varphi_i(\varepsilon) = \chi_i^* + \varepsilon^{-1} \sum_{k=1}^{(\circ)} \chi_k^\circ B_{ki}^+ \tag{3.5}$$

containing a sum over AOs of the remaining (unstarred) subset $\{\chi^\circ\}$ and referred to [33] as generalized basis orbitals (GBOs). After substituting specific eigenvalues ε_m, equations (3.4) and (3.5) yield the usual expressions for respective CMOs of AHs. It is also seen that each generalized basis orbital $\varphi_i(\varepsilon)$ is attached to a certain AO of the starred subset χ_i^* and contains additional contributions of nearest-neighboring unstarred AOs χ_k°. This implies the constitution of the particular basis orbital $\varphi_i(\varepsilon)$ to be determined mostly by the nearest environment of its principal AO χ_i^* and thereby by the local structure [although a certain influence of the global structure also manifests itself via the energy variable ε]. Consequently, an interrelation has been concluded between local constitutions of AHs and local shapes of their CMOs. A more detailed analysis of Eq.(3.5) showed that three types of basis orbitals $\varphi_i(\varepsilon)$ are actually peculiar to AHs in accordance with three possible valencies of carbon atoms, namely two-, three- and four-center orbitals. Moreover, the above-enumerated orbitals correspondingly coincide with generalized ($\varepsilon-$dependent) MOs of ethene, allyle and trimethylenmethane. Thus, just these rather simple systems were concluded to play the role of common elementary fragments of AHs. Existance of these common fragments, in turn, formed the basis for a conclusion that AHs may be considered as a separate class of chemical compounds.

b) The case of weak actual dependences of elements of the reduced Hamiltonian matrix upon energy variable ε may be mentioned as a second one [36,37]. Elements $\widetilde{H}_{ii}(\varepsilon)$ may be approximated by an appropriate constant (or a few constants) in this case. The above-discussed HEB region of PES of alkanes [27-30] is an excellent example here. A simple one-parameter Hückel type Hamiltonian matrix [28-30] designated by $\mathbf{H}_1$ proves to be an adequate model in this case. The mean value of resonance integrals between bonding bond orbitals (BBOs) of the nearest (geminal) bonds (β) playes the role of the only parameter of this matrix. Moreover, the matrix $\mathbf{H}_1$ is representable as follows

$$\mathbf{H}_1 = \alpha\mathbf{I} + \beta\mathbf{A}(G_H), \tag{3.6}$$

where $\mathbf{A}(G_H)$ stands for the adjacency matrix (AM) of the graph G_H (further referred to as the Hamiltonian matrix graph) and α is the relevant averaged Coulomb parameter (Note that the equality $A_{ii}(G_H) = 1$ for any i has been accepted for convenience). Graphs G_H are exhibited in Fig.1. It is seen that full subgraphs (tetrahedrons) correspond to quartets of bonds attached to the same carbon atom in these graphs. It is also noteworthy that subspectra of matrices $\mathbf{A}(G_H)$ corresponding to the HEB region reflect both the above-discussed similarity to spectra of respective simple chains G_0 and the distinctive features of HEBs of alkanes.

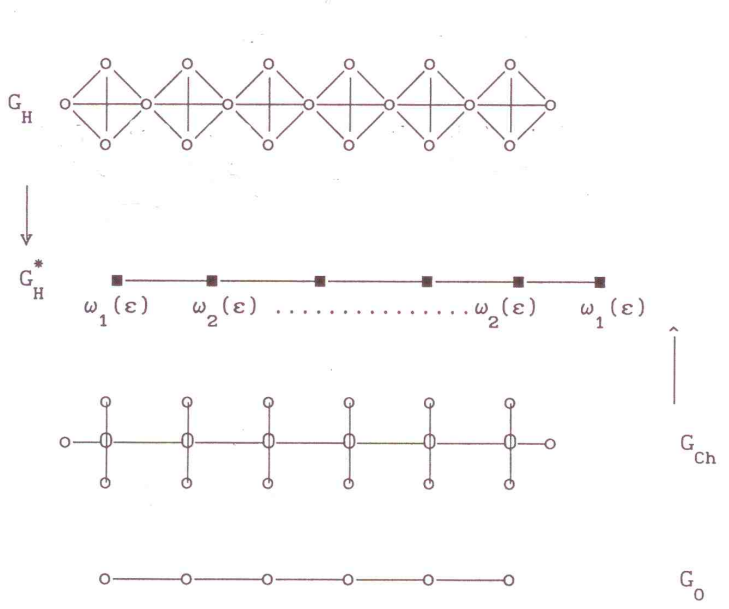

Figure 1: The Hamiltonian matrix graph of the hexane molecule (G_H), the chemical graph of the same hydrocarbon in terms of atoms (G_{Ch}), and their common reduced form ($G^*_H \equiv G^*_{Ch}$). The relevant reduction procedures are indicated by arrows. The one-dimensional chain (G_0) also is shown.

Application of the above-described alternative approach to secular problems for the AMs $\mathbf{A}(G_H)$ yields an $N-$dimensional reduced problem for any alkane C_NH_{2N+2} instead of the initial $3N+1-$dimensional problem, where $3N+1$ coincides with the respective total number of bonding orbitals and/or chemical bonds. The most general way of performing the appropriate reduction procedure [37] was based on constructing a new variable $z = (C_a+C_b+C_c+C_d)/\varepsilon$ for each full subgraph (tetrahedron) of the graph G_H containing four vertices a, b, c and d and in reformulating the initial secular problem in terms of N variables $z_k, k = 1, 2, ..N$ ($C_i, i = a, b..$, stand here for coefficients of eigenvectors of the AM $\mathbf{A}(G_H)$). As a result, an equation of the following form

$$\sum_m z_m + \omega_v(\varepsilon) z_p = \varepsilon z_p \tag{3.7}$$

has been derived for each (pth) tetrahedron, where $p = 1, 2...N$ and the sum over m embraces the variables z_m corresponding to neighboring tetrahedrons with respect to the pth one. The functions $\omega_v(\varepsilon)$ of Eq.(3.7) depend on both the energy variable (ε) and the valency of the respective (i.e. pth) vertex of the reduced graph G^*_H (Fig.1) according to the general expression

$$\omega_v(\varepsilon) = 3 + \frac{4-v}{\varepsilon}. \tag{3.8}$$

These functions evidently contain information about local structures of the initial graph G_H including both the given tetrahedron and its nearest environment. As

is seen from Eq.(3.7) and Fig.1, the reduced graph G_H^* resembles the respective simple chain G_0 except for a more involved expression for diagonal elements of the respective new AM $\mathbf{A}(G_H^*)$ coinciding with $\omega_v(\varepsilon)$ of Eq.(3.8). Hence, the extent of similarity between graphs G_H and G_0 (in respect of both structures and spectra) depends on the behaviour of functions $\omega_v(\varepsilon)$ within the $\varepsilon-$ region under interest.

The band limits of spectra of graphs G_H^* and thereby of G_H were shown to be conditioned by the equality $-2 < [\varepsilon - \omega_2(\varepsilon)] < 2$. This requirement yields two intervals $\Delta\varepsilon_1 = (-0.37; -1)$ and $\Delta\varepsilon_2 = (2; 5.37)$, the latter corresponding to the HEB. A weak dependence of functions $\omega_v(\varepsilon)$ on ε and insignificant differences between these functions for various valencies (v) have been established in the above-specified region [36,37]. This principal result indicates the local structures to be almost uniform over the chain in accordance with the above expectation. Meanwhile, the global structures of particular alkanes prove to be represented by respective simple chains G_0. Furthermore, the same result allowed all diagonal elements of the reduced AM $\mathbf{A}(G_H^*)$ to be replaced by a single constant (ϖ), which exceeds 3 as Eq.(3.8) indicates. Hence, the influence of the common local structure of alkanes has been concluded to resolve itself mostly to a shift of the whole level system by the value $\varpi - 1$ in the spectral region concerned. Just this fact explains the observed similarity between HEBs of alkanes and spectra of the simple chains G_0 [27-30]. Besides, no assumption is required here about a significant energy gap between $2s$ and $2p$ AOs in contrast to ascribing the HEB to ionization of electrons from the $2s$ AOs.

For eigenfunctions (Ψ_i) of the initial AMs $\mathbf{A}(G_H)$, expressions like those of Eqs. (3.4) and (3.5) have been obtained, where the variables $z_k, k = 1, 2, ..N$ play the role of coefficients of linear combinations. These coefficients, in turn, may be approximated by respective values for the relevant simple chain G_0. So far as generalized ($\varepsilon-$dependent) basis orbitals of alkanes are concerned, these also depend on the above-specified valency (v). As a result, four distinct orbitals $\eta_v(\varepsilon), v = 1, 2, 3, 4$ have been derived. Thus, the nearest neighborhood of the given tetrahedron also playes some role in the formation of these orbitals. Nevertheless, a more detailed analysis of these basis functions within the HEB region $\Delta\varepsilon_2$ allowed us to conclude their dependence upon the valency v to be actually insignificant. Moreover, the orbitals $\eta_v(\varepsilon)$ for any v resemble the lowest completely symetric MO of methane. Hence, the above-discussed interelation between local structures of compounds concerned and those of respective CMOs proves to be additionally supported.

c) The last example coincides with the so-called regular quasi-one- dimensional systems characterized by translational symmetry [32,38]. In other words, we turn now to chain-like molecules of cyclic global constitution. These systems are known to serve as models of polymers and solid state [39]. Accordingly, concepts and methods of the solid-state theory [39-41] are most commonly applied to study the relevant one-electron spectra. In this context, our approach proves to be a conseptual alternative to the above-mentioned popular theory. This point deserves a somewhat more detailed discussion.

Indeed, application of the solid state theory starts with taking into account the translational symmetry of the whole chain and thereby its global constitution. The usual way of doing this lies in passing to the basis of delocalized Bloch functions being an analogue of CMOs. Moreover, a $\cos(\mathbf{ka})-$ like dispersion curve usually cor-

responds to each Bloch function and/or to each translationally- symmetric subchain of the whole chain, where **k** and **a** stand for the quasi-momentum vector and the elementary cell's position vector, respectively. The second step of the solid state theory coincides with diagonalization of a block of the transformed Hamiltonian matrix corresponding to an elementary cell and thereby with taking into account the local structure. This implies the final dispersion curves to follow from the 'interaction' between the above-specified $\cos(\mathbf{ka})-$ like curves in this standard theory. By contrast, our initial step consists in the regard for local constitution of the same chain by reducing the initial system of secular equations into an effective $N \times N-$ dimensional problem as discussed above, where a single equation corresponds to each of N elementary cells and/or fragments. Meanwhile, the translational symmetry may be taken into consideration later when solving the reduced secular problem. It deserves emphasizing here that symmetry properties of the initial system may be easily preserved when performing the variable-elimination (reduction) procedure. To this end, the retained variables (MO LCAO coefficients) should be chosen to coincide with those referring to equivalent AOs. Finally, the reduced secular problem proves to be representable by a certain new effective chain, wherein extra bonds generally arise vs. the original ones, e.g. between second neighboring pairs of AOs. As a result, the final dispersion curves appear to be superpositions of $\cos(\mathbf{ka})-, \cos(2\mathbf{ka})-$, etc. elementary curves.

For illustration, let us consider just the secular problem for the above-described one-parameter Hamiltonian matrix ($\mathbf{H}_1$) of a cyclic alkane C_NH_{2N}. The first step of our analysis consists in reducing this problem into an $N-$dimensional one by means of passing to the set of similar variables $z_p, p = 1, 2, ..N$. As already mentioned, the relevant reduced chain G_H^* resembles the simple one (G_0) except for diagonal parameters $\omega_v(\varepsilon)$ defined by Eq.(3.8). (It is evident that $\omega_2(\varepsilon)$ remains in the present case). The translational symmetry of the reduced chain also may be taken into account as usual. As a result, we obtain an implicit form of the dispersion relation, viz.

$$\varepsilon = \omega_2(\varepsilon) + 2\cos[(\frac{2\pi}{N})j], \tag{3.9}$$

where $j = 1, 2...N$ and the function $\omega_2(\varepsilon)$ is defined by Eq.(3.8). Using the above-introduced vectors **k** and **a**, the above relation may be reformulated as follows

$$\varepsilon = \omega_2(\varepsilon) + 2\cos(\mathbf{ka}). \tag{3.10}$$

After substituting Eq.(3.8) and expressing ε, the usual explicit form of the dispersion relation may be easily obtained. The above-exhibited forms of Eqs.(3.9) and (3.10), however, offer us a new interpretation of dispersion curves. As already mentioned, the function $\omega_2(\varepsilon)$ contains information about the local structure of the chain. As is seen from the above formulae, the same function now playes the role of an additive component of our dispersion relation and describes the deviation of the actual dispersion curve from the standard $\cos(\mathbf{ka})-$ like shape. Thus, this deviation may be unambiguously ascribed to the effect of the local (internal) constitution of the chain. Analogous implicit forms of the level density function also have been derived. Finally, an eigenfunction (Ψ_i) of the initial AM $\mathbf{A}(G_H)$ takes the form of a Bloch sum of N energy- variable- dependent local-structure- determined basis orbitals $\eta_2(\varepsilon)$.

Efficiency of the approach under present discussion is especially evident if we turn to regular chains of more involved constitutions. In particular, the secular problem for an extended model Hamiltonian matrix of the cyclic polyethylene chain has been successfully studied [38], wherein resonance parameters between BBOs of vicinal C-C(C-H) bonds have been taken into consideration along with those of the above-described matrix $\mathbf{H}_1$. [This new model Hamiltonian matrix describes the whole spectrum of this polymer adequately]. The implicit form of the final dispersion relation for polyethylene then contains three additive components, viz.

$$\varepsilon = \delta(\varepsilon) + 2\tau(\varepsilon)\cos(\mathbf{ka}) + 2\sigma(\varepsilon)\cos(2\mathbf{ka}), \tag{3.11}$$

where

$$\begin{aligned} \delta(\varepsilon) =& -\varepsilon^2 + 4\varepsilon + 2 + 2s(1+2s), \\ \tau(\varepsilon) =& \varepsilon - s(\varepsilon - 5 + 2s), \quad \sigma(\varepsilon) = s(9 - 2\varepsilon) \end{aligned} \tag{3.12}$$

and s stands for the resonance parameter between bonding orbitals of two vicinal gauche-arranged bonds [for trans-arranged bonds, the same parameter equals to $-2s$]. The energy- variable- dependent function $\delta(\varepsilon)$ describes effective interactions inside a separate CH_2-group embedded into the chain and proves to be a generalization of the function $\omega_2(\varepsilon)$ of Eqs. (3.9) and (3.10). Meanwhile, the remaining functions ($\tau(\varepsilon)$ and $\sigma(\varepsilon)$) represent analogous interactions between pairs of first- and second-neighboring CH_2-groups, respectively. Accordingly, a superposition of $\cos(\mathbf{ka})-$ like and $\cos(2\mathbf{ka})-$ like increments arises in the dispersion relation of polyethylene. The actual shapes of dispersion curves prove to be determined by relative mean values of functions $\tau(\varepsilon)$ and $\sigma(\varepsilon)$ within the ε region under interest. On this basis, a new accounting has been suggested for emergence of an unusual minimum within the low-energy branch of the dispersion curves of polyethylene situated at a low symmetry point of the first Brillouin zone ($k \approx 0.6\pi/a$), namely this minimum has been established to appear owing to considerable values of effective interactions between the second-neighboring CH_2-groups within the respective energy interval. Similarity and differences between these results and those of the standard solid state theory are discussed in Ref. [32] in a detail.

In summary, the results of this Section support manifestation of the classical locality principle in the formation of both one-electron spectra and CMOs of molecules. Moreover, the above-described alternative approach makes it possible to study the roles of local and of global structures separately.

4 Invoking of the concept of the Line graph

The alternative approach of Section 3 is applicable to Hückel type Hamiltonian matrices of molecules, the latter being based on description of these systems in terms of orbitals and their interactions (Section 2). Meanwhile, atoms and interatomic (chemical) bonds play the role of the principal terms in the classical chemistry (Section 1). Hence, an important question is whether one-electron characteristics of molecules (including energy spectra) may be related to (local and/or global) classical chemical structures in terms of atoms and bonds, i.e. to (local and/or

global) peculiarities of the relevant chemical formulae (graphs). The present Section addresses studies in this direction.

Let us start with emphasizing that, generally, there is no one-to-one correspondence between basis orbitals (e.g. atomic orbitals (AOs)) and atoms. For example, one and four AOs (HAOs) represent any hydrogen and any carbon atom in alkanes, respectively. As a result, an alkane C_NH_{2N+2} containing $3N+2$ atoms is described by $6N+2$ basis orbitals. Although the latter number may be reduced substantially by passing to the basis of bond orbitals (BOs) [28] and confining oneself to the subset of bonding BOs (BBOs) (Section 3), the above-specified one-to-one correspondence is still not ensured (we obtain $3N+1$ bonding BO for an alkane C_NH_{2N+2}). Just this fact makes difficult any straightforward interpretation of one-electron properties and/or spectra of molecules in terms of peculiarities of the relevant chemical formulae and/or graphs. Nevertheless, the above-specified end may be achieved by invoking the concept of the so-called Line graph [42].

To demonstrate this, let us dwell again on one-electron spectra of alkanes (Section 3). These were shown to result from secular equations for AMs $\mathbf{A}(G_H)$ of the relevant Hamiltonian matrix graphs G_H referring to the basis of BBOs (Fig.1). From the one-to-one correspondence between BBOs and chemical bonds it follows immediately that the same graph represents the interactions (adjacencies) of chemical bonds. Thus, a chemical graph in terms of bonds has been formally introduced for any alkane. Let this new graph to be denoted by G^b_{ch} and note that $G_H \equiv G^b_{ch}$.

According to the standard definition [42], the vertices of the unique Line graph $L(G)$ with respect to the given graph G correspond to the edges of the latter, whereas the edges of the new graph $L(G)$ represent the adjacencies of the edges of the initial graph G (Note that the two edges are called adjacent if they possess a common vertex). Moreover, secular polynomials (SPs) of any pair of graphs G and $L(G)$ are interrelated as follows

$$P_{L(G)}(\lambda-2)=\lambda^{p-q}P[\lambda\mathbf{I}-\mathbf{A}(G)-\mathbf{D}(G)], \tag{4.1}$$

where λ stands for the SP variable. The right-hand side of Eq.(4.1) contains characteristics of the graph G, viz. the number of edges (p) and that of vertices (q), as well as the respective adjacency matrix $\mathbf{A}(G)$ and the diagonal matrix of valencies $\mathbf{D}(G)$. The notation $P[...]$ stands for the SP of the total matrix within the braces. The left-hand side of Eq.(4.1) contains the SP of the graph $L(G)$, where $\lambda-2$ plays the role of the variable.

Let us return again to the case of alkanes. It is evident that the above-discussed graph in terms of chemical bonds (G^b_{ch}) is the Line graph with respect to the usual chemical graph of an alkane in terms of atoms (G^a_{ch}), i.e. $G^b_{ch}=L(G^a_{ch})$. Hence, graphs G^b_{ch} and G^a_{ch} describe the chemical structure of an alkane in terms of bonds and atoms, respectively. This implies the same information to be involved within both G^b_{ch} and G^a_{ch}. Then, the unambiguity requirement for the relation structure-spectrum served as a basis for imposing the isospectrality condition on the AMs of the above-mentioned graphs. To this end, just the relation of Eq.(4.1) has been applied. To guarrantee a direct link between the SPs of graphs G^b_{ch} and G^a_{ch} necessary for ensuring their isospectrality, a modified AM $\mathbf{B}(G^a_{ch})$ of the graph G^a_{ch} has been defined, viz.

$$\mathbf{B}(G^a_{ch})=\mathbf{A}(G^a_{ch})+\mathbf{D}(G^a_{ch}). \tag{4.2}$$

Having in mind the choice $A_{ii}(G^b_{ch}) = 1$ (Section 3), we obtain the values of $B_{ii}(G^a_{ch})$ equal to 3 and 0 for C and H atoms, respectively. Furthermore, equalities $p-q = -1$ and $p-q = 0$ refer to non-cyclic and cyclic alkanes, correspondingly. Thus, the index $s(s = 1, 0)$ has been ascribed to the difference $q-p$. Finally, a new variable $\varepsilon = \lambda-1$ may be introduced. From Eq.(4.1) we then obtain

$$(\varepsilon + 1)^s P[\mathbf{A}(G^b_{ch})](\varepsilon) = P[\mathbf{B}(G^a_{ch})](\varepsilon), \tag{4.3}$$

i.e. a coincidence between the SPs of graphs G^b_{ch} and G^a_{ch} accurate to a constant factor. As a result, the graphs G^b_{ch} and G^a_{ch} are isospectral apart from the additional root $\varepsilon' = -1$ appearing for non-cyclic alkanes.

The so-called high-energy bands (HEBs) of alkanes have been traced back to definite subspectra of graphs $G_H \equiv G^b_{ch}$, namely to the energy region $\Delta\varepsilon_2 = (2; 5.37)$ (Section 3). The above-concluded isospectrality of graphs G^b_{ch} and G^a_{ch} then implies the same HEB to be related also to the analogous subspectra of the usual chemical graphs of alkanes in terms of atoms (G^a_{ch}). Just the latter achievement allowed an interpretation of these energy bands in terms of peculiarities of the relevant chemical formulae. This possibility is even more surprising if we have in mind that AMs of graphs G^a_{ch} are not related to Hamiltonian matrices of systems concerned. It is also evident that both principal graphs of alkanes (i.e. G^b_{ch} and G^a_{ch}) are reducible to the same graph $G^{b*}_{ch} \equiv G^{a*}_{ch} \equiv G^*_H$. For the graph $G^b_{ch} \equiv G_H$, the relevant procedure has been described in Section 3. To reduce the graph G^a_{ch} into G^{a*}_{ch}, no more is required as to eliminate the coefficients at the monovalent vertices (H atoms) (C_h) from the secular problem for the matrix $\mathbf{B}(G^a_{ch})$. As a result, an $N-$dimensional problem for the reduced matrix $\mathbf{B}(G^{a*}_{ch})$ coinciding with $\mathbf{A}(G^{b*}_{ch}) \equiv \mathbf{A}(G^*_H)$ easily follows. On this basis, a new interpretation of individual members of the expression for $\omega_v(\varepsilon)$ of Eq.(3.8) may be formulated in terms of local chemical structure, viz. the term 3 may be considered as the contribution of the carbon atom, whereas the $\varepsilon-$dependent term $((4-v)/\varepsilon)$ proportional to the number of the adjacent hydrogen atoms $(4-v)$ reflects the contribution of the latter. Accordingly, the observed similarity between HEBs of alkanes and the spectra of the simple chains G_0 (Section 3) may be accounted for by relatively weak effect of C-H bonds on spectra of respective C-skeletons. Moreover, the effect is almost uniform over the whole chain (see also Section 13).

Let us turn now to eigenfunctions of our adjacency matrices [37]. It is evident that an eigenfunction (Φ_i) of the matrix $\mathbf{B}(G^a_{Ch})$ may be ascribed to any energy level (ε_i) of the spectral region $\Delta\varepsilon_2$ along with the former function Ψ_i (Section 3) referring to AMs $\mathbf{A}(G_H) \equiv \mathbf{A}(G^b_{ch})$. As opposed to Ψ_i, however, the eigenfunction Φ_i has nothing to do with the relevant Hamiltonian matrix and thereby with canonical MOs of alkanes. Further, the above-mentioned reducibility of both graphs G^b_{ch} and G^a_{Ch} into the same graph $(G^{b*}_{ch} \equiv G^{a*}_{ch})$ yields an expression for Φ_i of the following form

$$\Phi_i = \sum_{k=1}^{N} \mu_k(\varepsilon_i) z_{ki} \ , \tag{4.4}$$

where the coefficients z_{ki} follow from eigenvectors of the reduced AMs of graphs $G^{b*}_{ch} \equiv G^{a*}_{ch}$ as previously (Section 3) and $\mu_k(\varepsilon)$ are the relevant $\varepsilon-$dependent basis functions pertinent to individual CH_r- like subgraphs of the graph G^a_{Ch}. These generalized orbitals, in turn, are expressible in terms of certain unspecified basis

functions of carbon ($\kappa_{(c)k}$) and of hydrogen atoms ($\kappa_{(h)kp}$), viz.

$$\mu_k(\varepsilon) = \kappa_{(c)k} + \frac{1}{\varepsilon}\sum_{m=1}^{r}\kappa_{(h)km}, \tag{4.5}$$

where the sum over m embraces all the hydrogen atoms attached to the kth carbon atom. The coefficient z_{ki} now represents the contribution of the kth CH_r- group to the eigenfunction Φ_i. Moreover, the same coefficient describes the increment of the kth carbon atom as substituting of Eq.(4.5) into Eq.(4.4) shows. In this connection, squares of coefficients z_{ki} have been interpreted as the extents of participation of separate carbon atoms in the ionization of molecule from the respective energy level ε_i [37]. These characteristics evidently are determined by the global structure of the chain. To derive the extent of participation of the attached hydrogen atom(s), the square $\mid z_{ki} \mid^2$ should be multiplied by an additional factor $1/\varepsilon^2$ as Eq.(4.5) indicates. Thus, participations of hydrogen atoms are related to those of the neighboring carbon atom and vice versa and this relation is independent of the global structure of the chain. It also deserves mentioning here that no need actually arises for specifying the basis functions $\kappa_{(c)k}$ and $\kappa_{(h)kp}$. This fact is in line with the chemical perspective on molecular world (Section 2).

A more detailed analysis of the relation of Eq.(4.3) has been carried out in Ref.[43]. Coincidence has been established between local terms of SPs $P[\mathbf{A}(G^b_{ch})]$ and $P[\mathbf{B}(G^a_{ch})]$ corresponding to definite subgraphs of graphs G^b_{ch} and G^a_{ch}. On this basis, non-canonical expressions have been derived for these SPs in terms of the same second-class Chebyshev polynomials $U_p(Q)$ of the variable Q proportional to the SP $q_2(\varepsilon)$ of an isolated CH_r-like subgraph. Common spectral properties of graphs G^b_{ch} and G^a_{ch} have been then related to those of $U_p(Q)$.

Therefore, invoking of the concept of the Line graph yields non-trivial relations between one-electron characteristics of molecules and peculiarities of their chemical formulae. Moreover, we actually obtain an analogue of the classical principle of locality regarding one-electron spectra.

5 Choice of the block-diagonalization problem instead of the secular equation

As discussed already, the delocalized nature of the usual canonical MOs (CMOs) is the main origin of difficulties in revealing quantum-chemical analogues for classical chemical concepts. Again, the well-known success of various additive models (schemes) in evaluating collective properties of extended compounds (e.g. dipole moments) [8,9] indicates the feasibility of a localized quantum chemical approach to electronic structures. The concept of electron pairs pertaining to separate bonds also gives us a similar hint.

In the framework of the MO method, the above-anticipated approach may be realized by invoking alternative sets of one-electron orbitals (MOs), in particular the so-called localized MOs (LMOs) [1,2,8,21]. The latter may be obtained either indirectly, i.e. by transforming the set of occupied CMOs into that of LMOs using various localization criteria [8] or directly by means of the Brillouin theorem [8, 44-47]. Passing to the basis of delocalized CMOs may be entirely avoided just in the

latter case. This fact is among the principal reasons of our choice of the Brillouin theorem as the method to be employed. Another reason consists in no need for specific localization criteria when applying this theorem.

Among particular forms of the Brillouin theorem there is a zero value requirement for an off-diagonal element of the Fockian operator referring to an occupied and a vacant MO [48]. In its matrix form, this requirement resolves itself into the zero matrix condition for the occupied-vacant off-diagonal block (submatrix) of the total Fockian matrix in the basis of non-canonical MOs (NCMOs) being sought [44-46]. As a result, the block-diagonalization problem for the Fockian matrix actually arises (see below), which becomes a real alternative to the usual diagonalization problem and/or to the secular equation. As with the latter, the Hückel model may be invoked in the new problem so that the Fockian matrix becomes replaced by the relevant Hückel type Hamiltonian matrix containing *a priori* uniform (transferable) parameters for analogous atoms and bonds in related chemical compounds.

As opposed to the usual secular (eigenvalue) equation, the block-diagonalization problem does not yield a unique set of LMOs [Note that no unique NCMOs may be defined in contrast to CMOs [48]]. To reduce the extent of this natural ambiguity, the block-diagonalization problem has been supplemented with an orthogonality requirement for NCMOs (LMOs) being sought in our studies [49-54] overviewed also in [55]. Meanwhile, orthogonality of basis orbitals is not imperative [52].

Let the system under study to be represented by a certain N-dimensional basis set $\{\Phi\}$, wherein the relevant Hückel type Hamiltonian matrix $\mathbf{H}$ and the overlap matrix of basis orbitals $\mathbf{S}$ are defined. Moreover, the system is assumed to contain an even number of electrons (say $2n$). The most general form of the overall matrix problem then resolves itself into two requirements [52], viz.

$$\mathbf{C}^{+}\mathbf{H}\mathbf{C} = \left| \begin{array}{cc} \mathbf{E}_1^{(n\times n)} & \mathbf{0}^{(n\times s)} \\ \mathbf{0}^{(s\times n)} & \mathbf{E}_2^{(s\times s)} \end{array} \right| \equiv \mathbf{E}, \quad \mathbf{C}^{+}\mathbf{S}\mathbf{C} = \mathbf{I}, \tag{5.1}$$

where $\mathbf{E}_1^{(n\times n)}$ and $\mathbf{E}_2^{(s\times s)}$ are the so-called eigenblocks of the initial Hamiltonian matrix $\mathbf{H}$ referring to subspaces of double-occupied and vacant one-electron orbitals (NCMOs), respectively [Note that $s = N - n$], $\mathbf{C}$ stands for the relevant representation matrix of NCMOs (LMOs) being sought and $\mathbf{E}$ is the block-diagonal matrix of the right-hand side of the first relation. Given that the basis orbitals $\{\Phi\}$ are orthonormalized in addition, the second relation of Eq.(5.1) takes the form of an unitarity condition for the transformation matrix $\mathbf{C}$, viz.

$$\mathbf{C}^{+}\mathbf{C} = \mathbf{I}. \tag{5.2}$$

The above-described matrix problems, in turn, may be alternatively represented as follows

$$\mathbf{H}\mathbf{C} = \mathbf{S}\mathbf{C}\mathbf{E}, \qquad \mathbf{H}\mathbf{C} = \mathbf{C}\mathbf{E}. \tag{5.3}$$

The second relation of Eq.(5.3) has been conveniently called the eigenblock equation for the matrix $\mathbf{H}$. The first relation is then a generalization of the latter to the case of a non-orthogonal basis set. [For saturated systems, the basis set orthogonality assumption has been substantiated in [56]].

Although the overall forms of equations shown in Eq.(5.3) closely resemble those of the usual secular problems for matrices, their solution is much more complicated.

Again, solutions of Eqs.(5.1)-(5.3) discussed below prove to be of a more general nature vs. those of secular equations, namely these are expressed in terms of entire submatrices (blocks) of the initial Hamiltonian matrix and embrace entire classes of molecules.

In this Section, we will dwell on the perturbative solution of the eigenblock equation. In this connection, certain additional requirements have been imposed on the initial Hamiltonian matrix **H**. [Non-perturbative solutions also are possible for some particular cases and these are discussed in Section 12]. The perturbative solution of the first matrix problem of Eq.(5.3) has been obtained and analyzed in Ref.[52]. Because of its rather cumbersome nature, however, this result acquired no further applications. Thus, let us confine ourselves to the more simple second problem.

Let the basis set $\{\Phi\}$ to consist of n double-occupied orbitals and of s vacant ones. Besides, the bonding and antibonding orbitals of separate bonds (Sections 3 and 4) may be referred to here as examples. Further, let the above-specified orbitals to be collected into two subsets $\{\Phi_1\}$ and $\{\Phi_2\}$ [Notations $\{\Phi_{(+)}\}$ and $\{\Phi_{(-)}\}$ used previously also will be preserved]. To be able to look for the matrix **C** and for the eigenblocks $\mathbf{E}_1^{(n\times n)}$ and $\mathbf{E}_2^{(s\times s)}$ in the form of power series (i.e. as sums of contributions of various orders (k)), the subsets $\{\Phi_1\}$ and $\{\Phi_2\}$ will be assumed to be separated by a substantial energy gap vs. the intersubset interactions. In this connection, let the matrix **H** to contain a sum of zero and first order matrices ($\mathbf{H}_{(0)}$ and $\mathbf{H}_{(1)}$, respectively), the former taking a block-diagonal form [51, 53-55], viz.

$$\mathbf{H} = \mathbf{H}_{(0)} + \mathbf{H}_{(1)} = \left| \begin{array}{cc} \mathbf{E}_{(+)} & \mathbf{0} \\ \mathbf{0} & -\mathbf{E}_{(-)} \end{array} \right| + \left| \begin{array}{cc} \mathbf{T} & \mathbf{R} \\ \mathbf{R}^{+} & \mathbf{Q} \end{array} \right|, \tag{5.4}$$

where the minus sign in front of $\mathbf{E}_{(-)}$ is introduced for further convenience. The blocks $\mathbf{E}_{(+)}, \mathbf{E}_{(-)}, \mathbf{T}, \mathbf{R}$ and **Q** correspond here to subsets $\{\Phi_{(+)}\}$ and $\{\Phi_{(-)}\}$ and to their interaction, and the supersript + represents the Hermitian- conjugate (transposed) counterpart of the matrix **R**. It should be emphasized here that no specifying either of internal constitutions of the above-enumerated blocks or their dimensions is required [In this connection, the superscripts $(n \times n), (n \times s), etc.$ are omitted in Eq.(5.4) and below for simplicity]. Finally, members ($\mathbf{C}_{(k)}$) of the power series for the matrix **C** also may be represented in terms of four blocks of respective dimensions, viz.

$$\mathbf{C}_{(k)} = \left| \begin{array}{cc} \mathbf{C}_{11}^{(k)} & \mathbf{C}_{12}^{(k)} \\ \mathbf{C}_{21}^{(k)} & \mathbf{C}_{22}^{(k)} \end{array} \right|, \tag{5.5}$$

where the order parameter (k) takes the upper position for convenience. It also deserves mentioning here that the above-formulated problem proves to be a matrix generalization of a two-level problem, wherein non-commutative quantities (submatrices) stand instead of usual (one-dimensional) Coulomb and resonance parameters [50]. In this connection, the perturbation theory (PT) used for its solution (see below) has been referred to as the non-commutative Rayleigh- Schrödinger PT (NCRSPT) [53,55] (see also Section 13).

Let us turn now to an overview of solution of the eigenblock equation of Eq.(5.3). Let us note first that a certain ambiguity in determining NCMOs still remains even after imposing an orthogonality condition on the latter. In this connection, let the zero order member $\mathbf{C}_{(0)}$ to coincide with the unit matrix (**I**). It is noteworthy

that choice $\mathbf{C}_{(0)} = \mathbf{I}$ complies with all requirements concerned. This implies that we may actually confine ourselves to NCMOs (LMOs) of the basis-orbital- and-tail constitution. Further, the two off-diagonal blocks ($\mathbf{C}_{12}^{(k)}$ and $\mathbf{C}_{21}^{(k)}$) of the kth order matrix $\mathbf{C}_{(k)}$ $(k = 1, 2, 3...)$ of Eq.(5.5) were shown to be expressible via the same matrix $\widetilde{\mathbf{G}}_{(k)}$, i.e.

$$\mathbf{C}_{12}^{(k)} = \widetilde{\mathbf{G}}_{(k)}, \qquad \mathbf{C}_{21}^{(k)} = -\widetilde{\mathbf{G}}_{(k)}^{+}. \tag{5.6}$$

Matrices $\widetilde{\mathbf{G}}_{(k)}, (k = 1, 2, 3...)$, in turn, proved to be conditioned by equations of the common form, viz.

$$\mathbf{E}_{(+)}\widetilde{\mathbf{G}}_{(k)} + \widetilde{\mathbf{G}}_{(k)}\mathbf{E}_{(-)} + \widetilde{\mathbf{V}}_{(k)} = \mathbf{0} \tag{5.7}$$

containing a series of matrices $\widetilde{\mathbf{V}}_{(k)}, (k = 1, 2, 3...)$ defined as follows

$$\begin{aligned} &\mathbf{V}_{(1)} = \mathbf{R}, \qquad \mathbf{V}_{(2)} = \mathbf{T}\mathbf{G}_{(1)} - \mathbf{G}_{(1)}\mathbf{Q}, \\ &\widetilde{\mathbf{V}}_{(3)} = \mathbf{T}\mathbf{G}_{(2)} - \mathbf{G}_{(2)}\mathbf{Q} - \frac{1}{2}(\mathbf{R}\mathbf{G}_{(1)}^{+}\mathbf{G}_{(1)} + \mathbf{G}_{(1)}\mathbf{G}_{(1)}^{+}\mathbf{R} + \mathbf{G}_{(\mathbf{1})}\mathbf{R}\mathbf{G}_{(\mathbf{1})}^{+}), etc. \end{aligned} \tag{5.8}$$

[The symbol ˜ serves to distinguish between the principal matrices of the present Section resulting from the block-diagonalization problem and those following from the commutation equation of Section 6. The distiction concerned, however, actually manifests itself starting from $k = 3$ only and thereby the symbol ˜ is omitted for $k = 1$ and $k = 2$ in Eq.(5.8)].

Again, the blocks $\mathbf{C}_{11}^{(k)}$ and $\mathbf{C}_{22}^{(k)}$ taking the diagonal positions within the same matrices $\mathbf{C}_{(k)}$ of Eq.(5.5) are expressible via matrices $\widetilde{\mathbf{G}}_{(k)}$ of lower orders, e.g.

$$\begin{aligned} &\mathbf{C}_{11}^{(2)} = -\frac{1}{2}\mathbf{G}_{(1)}\mathbf{G}_{(1)}^{+}, \quad \mathbf{C}_{22}^{(2)} = -\frac{1}{2}\mathbf{G}_{(1)}^{+}\mathbf{G}_{(1)}, \\ &\mathbf{C}_{11}^{(3)} = -\frac{1}{2}(\mathbf{G}_{(1)}\mathbf{G}_{(2)}^{+} + \mathbf{G}_{(2)}\mathbf{G}_{(1)}^{+}), \quad etc. \end{aligned} \tag{5.9}$$

[Note that $\mathbf{C}_{11}^{(1)} = \mathbf{C}_{22}^{(1)} = \mathbf{0}$]. Finally, similar expressions follow for members of power series for eigenblocks $\mathbf{E}_1$ and $\mathbf{E}_2$ (Section 13).

Let the occupied NCMOs $(\psi_{1,i})$ to be collected into the ket-vector $\mid \Psi_1 >$. The latter is then expressible as follows

$$\mid \Psi_1 > = \mid \Phi_1 > \mathbf{C}_{11} + \mid \Phi_2 > \mathbf{C}_{21}, \tag{5.10}$$

where $\mid \Phi_1 >$ and $\mid \Phi_2 >$ are ket-vectors correspondingly embracing the subsets of basis functions $\{\Phi_1\}$ and $\{\Phi_2\}$. Substituting the power series expansions for submatrices $\mathbf{C}_{11}$ and $\mathbf{C}_{21}$ into Eq.(5.10) then yields the following result

$$\mid \Psi_1 > = \mid \Phi_1 > (\mathbf{I} - \frac{1}{2}\mathbf{G}_{(\mathbf{1})}\mathbf{G}_{(\mathbf{1})}^{+}) - \mid \Phi_2 > (\mathbf{G}_{(1)}^{+} + \mathbf{G}_{(2)}^{+}), \tag{5.11}$$

where terms to within the second order inclusive are shown. It is seen that each occupied LMO is attached to an individual basis orbital in accordance with the equality $\mathbf{C}_{(0)} = \mathbf{I}$ and contains a certain tail extending over the remaining occupied and vacant basis functions in addition. Moreover, tails of the former type are determined by elements of the matrix $\mathbf{G}_{(\mathbf{1})}\mathbf{G}_{(\mathbf{1})}^{+}$, whilst those embracing vacant basis

orbitals coincide with elements of the sum of the principal matrices $\widetilde{\mathbf{G}}_{(\mathbf{k})}$. This implies that explicit expressions for LMOs are actually obtainable if matrix equations of Eq.(5.7) may be solved algebraically.

General solutions of matrix problems like that of Eq.(5.7) are known to take the form of an integral [57]. This integral, however, yields no explicit relations between elements of matrices $\widetilde{\mathbf{G}}_{(k)}$ and $\widetilde{\mathbf{V}}_{(k)}$ and thereby does not permit us to study the dependence of LMOs upon the structure of the given system. In this connection, some particular cases deserve distinguishing that allow the above-specified relations to be obtained.

First, let us assume the zero order submatrices $\mathbf{E}_{(+)}$ and $\mathbf{E}_{(-)}$ of our Hamiltonian matrix $\mathbf{H}$ to take diagonal forms, i.e.

$$E_{(+)ij} = \varepsilon_{(+)i}\delta_{ij}, \qquad E_{(-)lm} = \varepsilon_{(-)l}\delta_{lm}, \tag{5.12}$$

where $\varepsilon_{(+)i}$ and $\varepsilon_{(-)l}$ coincide with one-electron energies of separate basis orbitals $\varphi_{(+)i}$ and $\varphi_{(-)l}$. Relations of Eq.(5.12) imply all interorbital interactions to be first order terms vs. energy gaps between occupied and vacant basis orbitals.

Let us now define the so-called fragmentary molecules as those consisting of certain weakly-interacting elementary fragments, e.g. chemical bonds, phenyl rings, etc. In other words, intrafragmental resonance parameters will be assumed here to exceed the interfragmental ones considerably. Accordingly, let our basis functions $\{\Phi\}$ to coincide with eigenfunctions of intrafragmental blocks of the relevant Hamiltonian matrix. These orbitals will be then localized on separate elementary fragments and referred to as fragmental orbitals (FOs). It is evident that the above-defined fragmentary systems meet the requirement of Eq.(5.12). It deserves adding here that this definition embraces numerous classes of chemical compounds in the chemical sense.

Before passing to specific properties of LMOs of fragmentary molecules, let us note that matrix equations of Eq.(5.7) may be solved algebraically [53] under the assumption of Eq.(5.12). For the first and second order elements, we obtain

$$G^{(f)}_{(1)il} = -\frac{R_{il}}{\varepsilon_{(+)i} + \varepsilon_{(-)l}}, \tag{5.13}$$

$$G^{(f)}_{(2)il} = \frac{1}{\varepsilon_{(+)i} + \varepsilon_{(-)l}} \left\{ \sum_{(+)j} \frac{T_{ij}R_{jl}}{\varepsilon_{(+)j} + \varepsilon_{(-)l}} - \sum_{(-)r} \frac{R_{ir}Q_{rl}}{\varepsilon_{(+)i} + \varepsilon_{(-)r}} \right\}, \tag{5.14}$$

whilst elements of higher orders take somewhat more cumbersome forms (see e.g.[58]). Sums over $(+)j$ and $(-)r$ correspondingly embrace here all occupied and all vacant FOs of the system. The superscript (f) indicates the relevant formulae to refer just to fragmentary systems. Elements of Eqs.(5.13) and (5.14) have been interpreted as the direct (through-space) interaction between orbitals $\varphi_{(+)i}$ and $\varphi_{(-)l}$ and as the relevant indirect interaction by means of a single mediator, respectively. Both occupied ($\varphi_{(+)j}$) and vacant FOs ($\varphi_{(-)r}$) are able to play the role of mediators in the second interaction as Eq.(5.14) shows. To be an efficient mediator, however, the orbitals concerned should interact directly with both $\varphi_{(+)i}$ and $\varphi_{(-)l}$. Accordingly, elements of higher orders (i.e. $\widetilde{G}_{(3)il}, \widetilde{G}_{(4)il}, etc.$) are interpretable as indirect interactions of the same orbitals by means of a chain-like set of $k-1$ mediators.

Additivity of indirect interactions with respect to contributions of individual mediators is among the principal conclusions following from analysis of expressions for separate elements $\widetilde{G}^{(f)}_{(k)il}$ [In particular, this property is easily seen from Eq.(5.14)]. Furthermore, the well-known extinction of resonance parameters when the distance between orbitals concerned grows [21] allows us to expect an analogous behaviour of elements $\widetilde{G}^{(f)}_{(k)il}$. Just this circumstance forms the basis for locality and transferability of interorbital interactions [provided that the resonance parameters involved are transferable]. Finally, elements of matrix products $\mathbf{G_{(1)}}\mathbf{G^{+}_{(1)}}$ are interpretable as indirect interaction between occupied basis orbitals via vacant ones and also may be easily shown to be additive with respect to increments of the latter. After turning to Eq.(5.11) we may then conclude that additivity, locality and transferability are the principal distinctive features of LMOs of fragmentary molecules.

Let us introduce now some more particular cases. First, let us define the so-called simple fragmentary systems as those consisting of chemical bonds and lone electron pairs only. It is evident that FOs then coincide with bonding and antibonding bond orbitals (BOs) [Note that orbitals of lone electron pairs may be considered as a particular case of BOs [51]). Further, homogeneous fragmentary molecules may be distinguished, wherein uniform elementary fragments are assumed to be contained. Given that the latter coincide with chemical bonds in addition, the term 'simple homogeneous compounds' seems to be adequate. Let us dwell now just on the latter case.

One electron energies of all bonding BOs (BBOs) ($\varepsilon_{(+)i}$) and of all antibonding BOs (ABOs) ($\varepsilon_{(-)l}$) take uniform values for these systems and thereby may be replaced by constants $\varepsilon_{(+)}$ and $\varepsilon_{(-)}$, respectively. Further, let the energy reference point to be chosen in the middle of the energy gap between the subsets of basis orbitals, whilst the energy unit will coincide with parameters $\varepsilon_{(+)}$ and/or $\varepsilon_{(-)}$. Consequently, the equality $\mathbf{E}_{(+)} = \mathbf{E}_{(-)} = \mathbf{I}$ follows that allows entire matrices $\widetilde{\mathbf{G}}^{(f)}_{(k)}$ of the above-defined simple homogeneous systems to be expressed algebraically in terms of entire submatrices of the initial Hamiltonian matrix [49-51] as follows

$$\mathbf{G}^{(f)}_{(1)} = -\frac{1}{2}\mathbf{R}, \qquad \mathbf{G}^{(f)}_{(2)} = \frac{1}{4}(\mathbf{TR} - \mathbf{RQ}), etc. \tag{5.15}$$

For the ket-vector of occupied LMOs, we accordingly obtain

$$\mid \Psi_1 > = \mid \Phi_1 > (\mathbf{I} - \frac{1}{8}\mathbf{R}\mathbf{R}^{+}) + \frac{1}{2} \mid \Phi_2 > [\mathbf{R}^{+} + \frac{1}{2}(\mathbf{R}^{+}\mathbf{T} - \mathbf{Q}\mathbf{R}^{+})]. \tag{5.16}$$

On the whole, expressibility of electronic structure characteristics in terms of entire Hamiltonian matrix blocks seems to be among the most important distinctive features of simple homogeneous systems.

To illustrate the above-overviewed results, let us consider the class of alkanes as an example [49,50,56]. The C-C and C-H bonds may be regarded as uniform in this case because of negligible differences in the relevant Coulomb and resonance parameters. As a result, alkanes meet the definition of simple homogeneous systems. As already mentioned, bond orbitals (BBOs and ABOs) play the role of FOs in this case. Consequently, LMOs of the bonding-bond- orbital- and-tail constitution prove to be peculiar to alkanes that possess first order tails embracing ABOs of the remaining bonds. These tails are determined by elements of the matrix $\frac{1}{2}\mathbf{R}^{+}$ and thereby by

direct interactions between BBOs and ABOs. [Because of the definition of BOs as eigenfunctions of the relevant $2 \times 2-$dimensional Hamiltonian matrix blocks, the equality $R_{ii} = 0$ is valid for any i. That is why the ABO of the same bond does not contribute to the first order tail of the respective LMO]. The above-discussed extinction of resonance parameters when the distance between bonds concerned grows [21] then implies the most significant first order tails to embrace ABOs of the nearest-neighboring bonds with respect to the given one. Numbers of such neighbours, in turn, are constant for all C-C and for all C-H bonds in alkanes and equal to six and three, respectively. Thus, similar structures are expected for LMOs belonging to all C-C and to all C-H bonds provided that the relevant elements R_{ji} are transferable [such an assumption is supported by estimations [28, 59]]. Finally, LMOs referring to all C-H bonds are predicted to resemble an equivalent MO of methane. Analysis of the respective second order tails may be found in Ref.[49].

Therefore, choice of the non-canonical (i.e. block-diagonalization) problem instead of the standard eigenvalue equation allows general solutions to be obtained for extended classes of chemical compounds. These solutions, in turn, yield common expressions for the relevant LMOs. Finally, LMOs of fragmentary molecules are shown to obey the classical rules of locality, transferability and additivity (in contrast to the canonical MOs).

6 The direct way of obtaining the one-electron density matrix

One-electron density matrix (DM) is among the most fundamental quantum-mechanical characteristics of molecule describing the respective charge distribution and thereby related to numerous observed properties. Moreover, the DM is a unique characteristic [1,2] of the given system in contrast to NCMOs and/or LMOs.

The most popular way of obtaining the DM of a certain molecule consists in constructing a projector to the relevant set of occupied one-electron orbitals [1,2,48], the latter usually coinciding with the canonical MOs (CMOs) [Although NCMOs (or LMOs) also are able to play this role as discussed in the next Section]. Molecular orbitals, in turn, usually are expressed as linear combinations of certain basis functions, e.g. of AOs. Consequently, elements of the relevant representation matrix of the DM (commonly referred to as the charge- bond order (CBO) matrix) are generally determined by sums over all occupied MOs of products of respective coefficients of the above-specified linear combinations (MO LCAO coefficients), i.e. by all electrons of the given system. This implies both the CBO matrix $\mathbf{P}$ and the resulting charge distribution to belong to collective properties of molecules (Section 3). That is why applicability of classical principles of locality, additivity and transferability both to separate elements of the CBO matrix and to the overall charge distribution is among natural expectations.

It is evident that relations are required between elements of the CBO matrix, on the one hand, and those of the initial Hamiltonian matrix, on the other hand, to prove the above anticipations in practice. These relations, however, are extremely intricate and difficult to analyze when using the above-outlined indirect way of derivation of the DM, especially if delocalized CMOs play the role of one-electron

orbitals. This implies an involved nature of the overall link between charge distributions and the relevant chemical structures to say nothing about interrelations between CBO matrices and/or charge distributions of similar chemical compounds. Just these circumstances stimulated our turning to an alternative (direct) way of obtaining the same matrix by means of solution of the so-called commutation equation. It deserves an immediate emphasizing that no passing to the basis of either CMOs or NCMOs is required when applying this less known alternative approach. Instead, the following system of matrix equations should be solved [60]

$$[\mathbf{H},\mathbf{P}]_- = \mathbf{0}, \quad \mathbf{P}^2 = 2\mathbf{P}; \quad Spur\mathbf{P} = 2n, \tag{6.1}$$

where $\mathbf{H}$ stands for the initial Hamiltonian matrix and $2n$ coincides with the total number of electrons as previously, and the notation $[..,..]_-$ indicates a commutator of matrices. The first relation of Eq.(6.1) (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.

For the specific model Hamiltonian matrix defined by Eq.(5.4), the matrix problem of Eq.(6.1) may be solved perturbatively [51] analogously to the block-diagonalization problem of Section 5. To this end, any member $\mathbf{P}_{(k)}$ of the power series for the CBO matrix $\mathbf{P}$ also has been represented in terms of four blocks as shown in Eq.(5.5). Moreover, comparative analysis of matrix problems of Eqs. (5.1) and (6.1) for the case $\mathbf{S} = \mathbf{I}$ (Section 5) showed them to yield similar intermediate equations [51]. On this basis, a deep interrelation has been concluded between these problems (i.e. between the commutation equation for the DM and the Brillouin theorem) for the matrix $\mathbf{H}$ of Eq.(5.4) and thereby between the relevant solutions (i.e. the CBO matrix $\mathbf{P}$ and the LMO representation matrix $\mathbf{C}$). Indeed, the two matrices prove to be largely similar and representable in terms of the same entire blocks of the initial Hamiltonian matrix without specifying either the structures or dimensions of the latter. In particular, the off-diagonal blocks of the correction $\mathbf{P}_{(k)}$ take the form

$$\mathbf{P}_{12}^{(k)} = -2\mathbf{G}_{(k)}, \qquad \mathbf{P}_{21}^{(k)} = -2\mathbf{G}_{(k)}^{+}, \tag{6.2}$$

where $\mathbf{G}_{(k)}$ are conditioned by matrix equations like that of Eq.(5.7). Elements of these blocks represent bond orders between FOs of opposite initial occupation. It is evident that the relations of Eq.(6.2) closely resemble those shown in Eq.(5.6). Expressions for separate terms of power series for submatrices $\mathbf{P}_{11}$ and $\mathbf{P}_{22}$ determining both the occupation numbers of FOs and bond orders between FOs of the same initial occupation and taking the diagonal positions within the CBO matrix $\mathbf{P}$, in turn, are of the following form

$$\begin{aligned}
&\mathbf{P}_{11}^{(0)} = 2\mathbf{I}, \quad \mathbf{P}_{22}^{(0)} = \mathbf{P}_{11}^{(1)} = \mathbf{P}_{22}^{(1)} = \mathbf{0}, \\
&\mathbf{P}_{11}^{(2)} = -2\mathbf{G}_{(1)}\mathbf{G}_{(1)}^{+}, \quad \mathbf{P}_{22}^{(2)} = 2\mathbf{G}_{(1)}^{+}\mathbf{G}_{(1)}, \\
&\mathbf{P}_{11}^{(3)} = -2(\mathbf{G}_{(1)}\mathbf{G}_{(2)}^{+} + \mathbf{G}_{(2)}\mathbf{G}_{(1)}^{+}), \quad etc.
\end{aligned} \tag{6.3}$$

that closely resemble the respective formulae of Eq.(5.9). The actual extent of similarity between corrections $\mathbf{P}_{(k)}$ and $\mathbf{C}_{(k)}$, however, depends on that between matrices $\widetilde{\mathbf{V}}_{(k)}$ and $\mathbf{V}_{(k)}$ (see Eq.(5.7)) and thereby on the value of the order parameter k:

The starting members of the series of matrices $\widetilde{\mathbf{V}}_{(k)}$ and $\mathbf{V}_{(k)}$ are uniform, i.e. $\widetilde{\mathbf{V}}_{(1)} = \mathbf{V}_{(1)}$ and $\widetilde{\mathbf{V}}_{(2)} = \mathbf{V}_{(2)}$. This implies coincidences between respective principal matrices $\widetilde{\mathbf{G}}_{(k)}$ and $\mathbf{G}_{(k)}$ referring to $k = 1$ and $k = 2$. Equalities $\widetilde{\mathbf{G}}_{(1)} = \mathbf{G}_{(1)}$ and $\widetilde{\mathbf{G}}_{(2)} = \mathbf{G}_{(2)}$ along with the common form of matrix relations of Eqs.(5.9) and (6.3) then indicate a large extent of similarity between corrections $\mathbf{P}_{(1)}$ and $\mathbf{C}_{(1)}$, as well as between $\mathbf{P}_{(2)}$ and $\mathbf{C}_{(2)}$. Moreover, these corrections prove to be actually expressible via the same submatrices $\mathbf{G}_{(1)}$, $\mathbf{G}_{(2)}$, $\mathbf{G}_{(1)}\mathbf{G}^{+}_{(1)}$ and $\mathbf{G}^{+}_{(1)}\mathbf{G}_{(1)}$ with distinct numerical coefficients [51]. So far as corrections of the same series of higher orders ($k = 3, 4...$) are concerned, the relations between $\mathbf{P}_{(k)}$ and $\mathbf{C}_{(k)}$ become of a somewhat more involved nature [54]. Nevertheless, expressibility of corrections $\mathbf{P}_{(k)}$ and $\mathbf{C}_{(k)}$ via the same principal matrices $\mathbf{G}_{(k)}$ is still preserved. Let us consider this point in more detail.

Let us note first that distinct expressions are obtained for matrices $\widetilde{\mathbf{V}}_{(k)}$ and $\mathbf{V}_{(k)}$ of Eq.(5.7) for $k = 3, 4...$ As for instance, the third order matrix $\mathbf{V}_{(3)}$ takes the form

$$\mathbf{V}_{(3)} = \mathbf{T}\mathbf{G}_{(2)} - \mathbf{G}_{(2)}\mathbf{Q} - (\mathbf{R}\mathbf{G}^{+}_{(1)}\mathbf{G}_{(1)} + \mathbf{G}_{(1)}\mathbf{G}^{+}_{(1)}\mathbf{R}) \tag{6.4}$$

that differs from that of $\widetilde{\mathbf{V}}_{(3)}$ as comparison of Eqs.(5.8) and (6.4) shows. As a result, different matrices $\widetilde{\mathbf{G}}_{(k)}$ and $\mathbf{G}_{(k)}$ follow for $k = 3, 4...$ These matrices, however, are actually conditioned by similar matrix equations shown in Eq.(5.7). It is no surprise in this connection that certain matrix relations connecting $\widetilde{\mathbf{G}}_{(k)}$ and $\mathbf{G}_{(k)}$ may be established [54], e.g.

$$\mathbf{G}_{(3)} = \widetilde{\mathbf{G}}_{(3)} - \frac{1}{2}\mathbf{G}_{(1)}\mathbf{G}^{+}_{(1)}\mathbf{G}_{(1)}. \tag{6.5}$$

[Relations of this type follow from coincidence between expressions for the CBO matrix derived directly as described above and indirectly by constructing a projector to the set of occupied LMOs of Section 5]. It is evident that Eq.(6.5) allows us to eliminate the matrix $\widetilde{\mathbf{G}}_{(3)}$ from the expression for the correction $\mathbf{C}_{(3)}$ and thereby to represent the latter in terms of matrices $\mathbf{G}_{(1)}$, $\mathbf{G}_{(2)}$ and $\mathbf{G}_{(3)}$ and their products as it is the case with the correction $\mathbf{P}_{(3)}$.

In summary, the CBO matrix $\mathbf{P}$ and the LMO representation matrix $\mathbf{C}$ are expressible via the same submatrices and thereby depend on the constitution of the given system in the same manner. Thus, the matrix $\mathbf{P}$ also may be concluded to belong to the localized way of representing electronic structures along with LMOs. Accordingly, the rules of locality, additivity and transferability established in the previous Section may be easily extended to elements of the CBO matrix.

To demonstrate this, let us dwell on diagonal elements of the CBO matrix $\mathbf{P}$ (i.e. $P_{11,ii}$ and $P_{22,ll}$) following from expressions like that of Eq.(6.3) and representing occupation numbers (populations) of basis orbitals ($\varphi_{1,i}$ and $\varphi_{2,l}$, respectively). Notations $X_{(+)i}$ and $X_{(-)l}$ will correspondingly stand below just for these populations. Members of the respective power series will be accordingly denoted by $X^{(k)}_{(+)i}$ and $X^{(k)}_{(-)l}$. Additivity of matrix products ($\mathbf{G}_{(1)}\mathbf{G}^{+}_{(1)}, \mathbf{G}_{(1)}\mathbf{G}^{+}_{(2)}, etc.$) with respect to mediators (Section 5) implies expressibility of occupation numbers $X_{(+)i}$ and $X_{(-)l}$ in

the following forms [61]

$$X_{(+)i} = 2 - \sum_{(-)m} x_{(+)i,(-)m}, \quad X_{(-)l} = \sum_{(+)j} x_{(-)l,(+)j}. \tag{6.6}$$

Sums over $(+)j$ and over $(-)m$ embrace here the occupied and vacant basis orbitals, respectively, and $x_{(+)i,(-)m}$ stand for partial populations transferred between orbitals of opposite initial occupation that meet the charge conservation condition , i.e.

$$x_{(+)i,(-)m} = x_{(-)m,(+)i}. \tag{6.7}$$

From Eq.(6.3), expressions for members of the power series for $x_{(+)i,(-)m}$ easily follows, viz.

$$\begin{aligned} x^{(2)}_{(+)i,(-)m} =& 2(G_{(1)im})^2, \quad x^{(3)}_{(+)i,(-)m} = 4G_{(1)im}G_{(2)im} \\ x^{(4)}_{(+)i,(-)m} =& 4G_{(1)im}G_{(3)im} + 2G_{(1)im}(\mathbf{G}_{(1)}\mathbf{G}^{+}_{(1)}, \mathbf{G}_{(1)})_{im} + 2(G_{(2)im})^2, etc. \end{aligned} \tag{6.8}$$

Thus, additivity of actual occupation numbers of initially-occupied basis functions with respect to contributions of various electron-accepting orbitals proves to be supported.

Let us dwell now on particular cases defined in Section 5. For fragmentary compounds, elements $G_{(k)im}$ represent various types of interactions between occupied and vacant FOs as it was the case with $\widetilde{G}_{(3)im}$ (Section 5). Accordingly, $x^{(2)}_{(+)i,(-)m}$ of Eq.(6.8) depends on the absolute value of the direct interaction between FOs $\varphi_{1,i}$ and $\varphi_{2,m}$. As a result, extinction of the second order partial transferred population $x^{(2)}_{(+)i,(-)m}$ follows straightforwardly from the analogous properties of elements $G_{(1)im}$ when the distance between the above-specified orbitals grows. Further, the relevant third order increment $x^{(3)}_{(+)i,(-)m}$ does not vanish if the orbitals $\varphi_{1,i}$ and $\varphi_{2,m}$ interact one with another both directly and indirectly by means of a single mediator (say φ_s). This condition evidently cannot be met for remote FOs $\varphi_{1,i}$ and $\varphi_{2,m}$. An analogous conclusion may be drawn also for $k = 4$ and thereby the local nature of occupation numbers in general becomes supported. Transferability of these numbers, in turn, follows from the above-mentioned locality provided that the relevant elements of the initial Hamiltonian matrix are transferable.

In the case of simple homogeneous systems consisting of uniform bonds (Section 5), expressions for matrices $\mathbf{G}_{(k)}$ in terms of entire blocks of the initial Hamiltonian matrix (see Eq.(5.15)) allow analogous formulae to be obtained for members $(\mathbf{P}_{(k)})$ of the power series for the CBO matrix $\mathbf{P}$. As a result, the first and second order terms of the series concerned are as follows [49,50]

$$\mathbf{P}_{(1)} = \begin{vmatrix} \mathbf{0} & \mathbf{R} \\ \mathbf{R}^{+} & \mathbf{0} \end{vmatrix}, \quad \mathbf{P}_{(2)} = \frac{1}{2} \begin{vmatrix} -\mathbf{R}\mathbf{R}^{+} & \mathbf{R}\mathbf{Q} - \mathbf{T}\mathbf{R} \\ \mathbf{Q}\mathbf{R}^{+} - \mathbf{R}^{+}\mathbf{T} & \mathbf{R}^{+}\mathbf{R} \end{vmatrix}. \tag{6.9}$$

(Note that the zero order member $\mathbf{P}_{(0)}$ follows straightforwardly from Eq.(6.1) and contains matrices $2\mathbf{I}$ and $\mathbf{0}$ in its diagonal positions). It is seen that matrices $\mathbf{R}, \mathbf{R}\mathbf{R}^{+}, \mathbf{R}^{+}\mathbf{R}$ and $\mathbf{R}\mathbf{Q} - \mathbf{T}\mathbf{R}$ play the role of building blocks here as it was the case with LMOs (see Eq.(5.16)). This implies the LMOs of simple homogeneous

systems and the respective CBO matrix to be extremely similar localized representations of electronic structures.

Finally, let us dwell on the case of alkanes for illustration and recall that BBOs and ABOs of separate chemical bonds play the role of basis functions in this case. From expressibility of both the LMO representation matrix **C** and the CBO matrix **P** via the same submatrices then follows immediately that bond orders between BOs of alkanes are proportional to the respective tails of LMOs [49]. As a result, these two characteristics prove to be equivalent measures of the electron delocalization. Another straightforward conclusion here is that most significant bond orders embrace the neighboring (geminal) pairs of bonds. These bond orders are determined by the direct (through-space) interactions between BOs of these bonds of the opposite initial occupation. Accordingly, zero bond orders easily follow for BOs of the same bond.

On the whole, the direct way of obtaining the DM yields general expressions for CBO matrices of extended classes of chemical compounds as it was the case with the Brillouin theorem for LMOs (Section 5). Moreover, both the common CBO matrix of fragmentary molecules **P** and the relevant LMO representation matrix **C** largely resemble one another, especially in respect of their dependences upon particular Hamiltonian matrix blocks and their products. Additivity, transferability and locality of the CBO matrix elements then are among natural consequences of the above-mentioned similarity. Since CBO matrix elements are known to determine local charge distributions, a relation may be concluded between the latter and peculiarities of the relevant local structures.

7 Alternative expressions for occupation numbers of basis orbitals in terms of delocalization coefficients of LMOs

The fundamental concept of electron pairs pertinent to individual chemical bonds suggested by Lewis [62] may be regarded as taking an intermediate place in between the classical and modern theoretical chemistry. This concept forms the basis for popular interpretations of various structural changes in organic compounds (including chemical reactions) in terms of shifts of separate pairs of electrons (cf. the so-called 'curly arrow chemistry' [15]). It is also essential in our context that these interpretations are in line with the classical principle of locality: Only a few pairs are usually assumed to undergo essential shifts, namely those referring to the center of the given effect or process, whilst the remaining pairs are considerd as inactive.

As discussed already, the occupation number (population) of a basis function is defined in quantum chemistry as a sum of increments of all occupied one-electron states (cf. the collective nature of charge distribution). This definition evidently yields no relation between an alteration in the occupation number of a certain basis orbital and reshaping of a single pair of electrons. Again, just the above-expected relations are required to reflect the above-outlined Lewis perspective on the CBO matrix. In this connection, we will look for possibilities of getting rid of sums over all occupied one-electron orbitals (MOs) in the expressions for occupation numbers

of basis orbitals in the present Section.

The above-mentioned standard definition of an occupation number follows from the projector to the relevant set of occupied one-electron orbitals. In the present section, we will assume the localized MOs of Section 5 to play the role of orbitals underlying the projector instead of CMOs as usual. Good prospects of this alternative originate from the feasibility of extending the above-discussed one-to-one correspondence between basis orbitals and LMOs to embrace alterations in the relevant characteristics due to interaction. Before implementing this scheme, however, some additional definitions are required.

Let us start with expressions for an individual occupied LMO $\psi_{(+)i}$ and a vacant one $\psi_{(-)m}$ following from formulae like that of Eq.(5.10), viz.

$$\begin{aligned}\psi_{(+)i} &= \sum_{(+)j} \varphi_{(+)j} C_{11,ji} + \sum_{(-)l} \varphi_{(-)l} C_{21,li}, \\ \psi_{(-)m} &= \sum_{(+)j} \varphi_{(+)j} C_{12,jm} + \sum_{(-)l} \varphi_{(-)l} C_{22,lm}, \end{aligned} \tag{7.1}$$

where sums over over $(+)j$ and $(-)l$ here and below embrace the occupied and vacant basis functions, respectively. It is seen that elements of submatrices $\mathbf{C}_{21}$ and $\mathbf{C}_{12}$ reflect tails of LMOs of the intersubset type (i.e. the intersubset delocalization), whereas those of the remaining blocks ($\mathbf{C}_{11}$ and $\mathbf{C}_{22}$) represent tails of the intrasubset nature (intrasubset delocalization). Moreover, diagonal elements of submatrices $\mathbf{C}_{11}$ and $\mathbf{C}_{22}$ describe renormalization of basis orbitals $\varphi_{(+)i}$ and $\varphi_{(-)m}$, respectively, when building up the LMOs. In this connection, matrices $\mathbf{C}_{11}$ and $\mathbf{C}_{22}$ will be called the renormalization matrices for convenience.

Let us now define the so-called partial intersubset delocalization coefficients of LMOs $\psi_{(+)i}$ and $\psi_{(-)m}$ over particular basis functions, e.g. over $\varphi_{(-)l}$ and $\varphi_{(+)j}$, respectively [50,51,54]. Let these coefficients to be correspondingly denoted by $d_{(+)i,(-)l}$ and $d_{(-)m,(+)j}$. The defitions concerned are as follows

$$\begin{aligned} d_{(+)i,(-)l} &= \mid C_{21,li} \mid^2 = \mid G^{+}_{(1)li} + G^{+}_{(2)li} + \widetilde{G}^{+}_{(3)li} + \widetilde{G}^{+}_{(4)li} + ... \mid^2, \\ d_{(-)m,(+)j} &= \mid C_{12,jm} \mid^2 = \mid G_{(1)jm} + G_{(2)jm} + \widetilde{G}_{(3)jm} + \widetilde{G}_{(4)jm} + ... \mid^2 . \end{aligned} \tag{7.2}$$

It is easily seen that the partial delocalization coefficients concerned also are expressible in the form of power series, i.e. as sums over parameter k of contributions $d^{(k)}_{(+)i,(-)l}$ and $d^{(k)}_{(-)m,(+)j}$. Further, let total delocalization coefficients of the same LMOs over all vacant and over all occupied basis functions to be defined as follows

$$D_{(+)i} = \sum_{(-)l} d_{(+)i,(-)l}, \quad D_{(-)m} = \sum_{(+)j} d_{(-)m,(+)j}. \tag{7.3}$$

From Eqs.(7.2) and (7.3) it follows that $D_{(+)i}$ and $D_{(-)m}$ actually coincide with diagonal elements of the following matrices

$$\mathbf{D}_{(+)} = \mathbf{C}^{+}_{21}\mathbf{C}_{21}, \quad \mathbf{D}_{(-)} = \mathbf{C}^{+}_{12}\mathbf{C}_{12} \tag{7.4}$$

that may be referred to as the intersubset delocalization matrices. Substituting the power series for submatrices $\mathbf{C}_{21}$ and $\mathbf{C}_{12}$ (Section 5) into Eq.(7.4) yields analogous

series for matrices $\mathbf{D}_{(+)}$ and $\mathbf{D}_{(-)}$, the starting members of which are proportional to renormalization matrices of the same order, e.g.

$$\mathbf{D}_{(+)}^{(2)} = -2\mathbf{C}_{11}^{(2)}, \quad \mathbf{D}_{(+)}^{(3)} = -2\mathbf{C}_{11}^{(3)}. \tag{7.5}$$

Meanwhile, expressions for next terms of the series are of a somewhat more involved nature [54], e.g.

$$\mathbf{D}_{(+)}^{(4)} = -2\mathbf{C}_{11}^{(4)} - (\mathbf{C}_{11}^{(2)})^2. \tag{7.6}$$

Let us turn now to the definition of the one-electron DM $P(\mathbf{r} \mid \mathbf{r}')$ as a projector [1,2] to the subset of occupied LMOs $\{\Psi_1\}$, viz.

$$P(\mathbf{r} \mid \mathbf{r}') = 2\,|\Psi_1(\mathbf{r})\rangle\,\langle\Psi_1(\mathbf{r}')|\,, \tag{7.7}$$

where $\mathbf{r}$ represents the position of an electron in the real space, and $|\Psi_1(\mathbf{r})\rangle$ and $\langle\Psi_1(\mathbf{r}')|$ correspondingly stand for the ket-vector of occupied LMOs (see Eq. (5.10)) and the relevant bra-vector. After substituting expressions like that of Eq.(5.10) into Eq.(7.7), we obtain

$$P(\mathbf{r} \mid \mathbf{r}') = \sum_{I,J=1}^{2} |\Phi_I(\mathbf{r})\rangle\,\mathbf{P}_{IJ}\,\langle\Phi_J(\mathbf{r}')|\,, \tag{7.8}$$

where $\mathbf{P}_{I,J}, I = 1,2; J = 1,2$ are multidimensional elements (blocks) of the representation of the DM in terms of two subsets of basis functions $\{\Phi_1\}$ and $\{\Phi_2\}$ introduced in Section 5. The expression of Eq.(7.8) serves as a matrix generalization of the well-known bilinear form of the DM in terms of individual basis functions [1]. For blocks $\mathbf{P}_{IJ}$, we accordingly obtain

$$\mathbf{P}_{11} = 2\mathbf{C}_{11}\mathbf{C}_{11}^{+}; \quad \mathbf{P}_{22} = 2\mathbf{C}_{21}\mathbf{C}_{21}^{+}; \quad \mathbf{P}_{12} = 2\mathbf{C}_{11}\mathbf{C}_{21}^{+}. \tag{7.9}$$

Let the submatrices $\mathbf{P}_{11}$ and $\mathbf{P}_{22}$ to be alternatively denoted by $\mathbf{X}_{(+)}$ and $\mathbf{X}_{(-)}$ (in accordance with designations $X_{(+)i}$ and $X_{(-)m}$ of Section 6 standing for the relevant diagonal elements) and called the intrasubset population matrices. Substituting the power series for $\mathbf{C}_{11}$ and $\mathbf{C}_{21}$ (Section 5) into the expression of Eq.(7.9) followed by employment of interdependences like that shown in Eqs.(7.5) and (7.6) yields the following principal results

$$\mathbf{X}_{(+)} = 2(\mathbf{I} - \mathbf{D}_{(+)}), \qquad \mathbf{X}_{(-)} = 2\mathbf{D}_{(-)}. \tag{7.10}$$

Thus, intrasubset population matrices prove to be proportional to respective intersubset delocalization matrices [54]. After passing to diagonal elements within Eq.(7.10), we accordingly obtain

$$X_{(+)i} = 2(I - D_{(+)i}), \qquad X_{(-)m} = 2D_{(-)m}. \tag{7.11}$$

Hence, the actual population of the basis function $\varphi_{(+)i}$ (or $\varphi_{(-)m}$) is determined only by the shape of the respective 'own' LMO $\psi_{(+)i}(\psi_{(-)m})$. Moreover, the population of the basis function $\varphi_{(+)i}$ lost due to the interorbital interaction is proportional to the total intersubset delocalization coefficient of the above-specified exclusive LMO. In other words, the one-to-one correspondence between basis orbitals and LMOs (seen

from the equality $\mathbf{C}_{(0)} = \mathbf{I}$) is now replenished by the following rule: The more delocalized the orbital $\varphi_{(+)i}$ becomes when building up the respective LMO $\psi_{(+)i}$, the more charge it loses and vice versa. This result may be also interpreted as a kind of simultaneous separability of both charge redistribution and delocalization into increments of separate pairs of electrons. Further, expressing both sides of Eq.(7.11) in the form of power series yields analogous relations between $X^{(k)}_{(+)i}$ and $D^{(k)}_{(+)i}$, and between $X^{(k)}_{(-)m}$ and $D^{(k)}_{(-)m}$. Finally, invoking expressions like those of Eqs.(6.6) and (7.3) yields proportionalities between partial increments, i.e.

$$x^{(k)}_{(+)i,(-)l} = 2d^{(k)}_{(+)i,(-)l}, \quad x^{(k)}_{(-)m,(+)j} = 2d^{(k)}_{(-)m,(+)j}. \tag{7.12}$$

Thus, the more population is transferred between orbitals $\varphi_{(+)i}$ and $\varphi_{(-)l}$, the larger is the partial delocalization coefficient of the LMO $\psi_{(+)i}$ over the same vacant basis function and vice versa. If we recall the definition of this coefficient as square of the relevant tail of the LMO $\psi_{(+)i}$ (see Eq.(7.2)), we may also conclude a more significant tail of this LMO over the vacant orbital $\varphi_{(-)l}$ to correspond to a more efficient charge transfer between basis functions $\varphi_{(+)i}$ and $\varphi_{(-)l}$ and vice versa. Irrelevance of the intrasubset delocalization in the formation of charge redistributions also is among the conclusions. This result evidently causes no surprise. Immediate reasons why the respective terms vanish in the expressions for occupation numbers are clarified in Ref.[54]. It deserves mentioning finally that relations of Eqs.(7.10) and (7.11) indicate both populations of basis orbitals and delocalization coefficients of LMOs to be characterized by common properties. It is evident that locality, additivity and transferability (established in Sections 5 and 6) are expected to be among these properties.

On the whole, the results of this Section may be summarized as parallelism between charge (re)distribution and delocalization. Moreover, we obtain a certain quantum-chemical analogue of the Lewis perspective on charge (re)distribution and thereby of the 'curly arrow chemistry'. Two differences between this analogue and its classical version deserve mentioning: First, LMOs are not localized completely in contrast to the relevant classical model. Second, the approach suggested allows comparisons of relative extents of shifts (reshapings) of separate pairs of electrons for related compounds and/or for alternative routes of the same process. Just the second point may be regarded as an important advantage of the new approach over the classical one. For illustration, we will confine ourselves to comparisons of related compounds in this Section (alternative routes of reactions are discussed in Section 9). To this end, let us turn to studies of alkanes and their heteroatom-containing derivatives [63] (cf. the so-called inductive effect). Rules governing the additional interbond charge transfer due to introduction of a heteroatom (Z) along with the related extra delocalization of LMOs and thereby of separate pairs of electrons have been formulated there. As a result of additivity of both characteristics with respect to contributions of individual bonds, an increase was observed both in the total population of the Z-C_α bond and in the extent of delocalization of the respective single pair of electrons when the size of the hydrocarbon fragment grows (e.g. when passing from substituted methanes to ethanes). Furthermore, the changing nature of the nearest-neighboring bond when passing from 1-mono- to 1,1′-disubstituted compounds was shown to give rise to suppression of delocalization of LMOs associated

with the C_α-Z_1 bond and thereby to reductions in the relevant occupation numbers. These conclusions proved to be in aggreement with the relevant experimental trends. Finally, both electron density redistributions and reshapings of LMOs due to introduction of the heteroatom were shown to be proportional to the extents of delocalization of LMOs in the parent hydrocarbon. Accordingly, the well-known short-range nature of the inductive effect has been accounted for by a weak interbond delocalization in alkanes. This interpretation evidently is in line with the classical perspective.

Finally, the principal result of this Section may be alternatively formulated as a kind of one-orbital representation of populations lost (acquired) by individual basis orbitals. This state of things closely resembles the one-orbital representations of ionization potentials in the canonical MO method known as the Koopmans' theorem [26]. If we recall that representation of this type are not achievable for ionization potentials and for charge (re)distributions in the NCMO and the CMO methods, respectively, the present results support the complementary nature of the above-mentioned principal approaches of quantum chemistry [34].

8 Alternative definitions of total energies and their implications

Total energies of molecules also rank among the most popular quantum- chemical characteristics. Moreover, these are comparable to experimental data even more directly, i.e. to heats of formation and/or atomization. The latter, in turn, are known to be expressible as sums of transferable bond increments [8], at least for saturated molecules, e.g. alkanes and their derivatives. Thus, total energies belong to properties the classical principles are expected to be applicable to.

In the framework of the Hückel model, the standard definition of the total energy of any molecular system ($\mathcal{E}$) contains a sum of one-electron energies referring to occupied MOs multiplied by their occupation number 2. Inasmuch as one-electron energies of delocalized (canonical) MOs usually depend on the structure of the system in an intricate manner, the above-mentioned standard definition is not the most suitable one for revealing the analogues of the classical rules within total energies. Hence, alternative definitions of the same characteristic should be invoked.

In the non-canonical MO method based on the Brillouin theorem (see Eq.(5.1)), the relevant total energy may be defined as follows

$$\mathcal{E} = 2Spur\mathbf{E}_1^{(n\times n)} = 2Spur\{\mathbf{C}^+\mathbf{HC}\}_{11}, \tag{8.1}$$

where $\mathbf{E}_1^{(n\times n)}$ is the eigenblock of the Hamiltonian matrix referring to the subset of occupied LMOs and the symbol $\{...\}_{11}$ stands here for the submatrix of the matrix product $\mathbf{C}^+\mathbf{HC}$ taking the first diagonal position. Thus, the total energy $\mathcal{E}$ may be obtained without passing to the basis of CMOs as it was the case with the transformation matrix $\mathbf{C}$ (see Sections 5 and 13). In analogy with obtaining the DM on the basis of LMOs (Section 7), employment of Eq.(8.1) may be referred to as the indirect way of derivation of the total energy. Meanwhile, the direct way consists in the use of the relation between the total energy and the one-electron DM (CBO

matrix) $\mathbf{P}$ [60], viz.

$$\mathcal{E} = Spur(\mathbf{PH}). \tag{8.2}$$

Let us dwell now on the case of a nearly block- diagonal Hamiltonian matrix $\mathbf{H}$ of Eq.(5.4) containing a block-diagonal zero order contribution $\mathbf{H}_{(0)}$ and a certain first order term $\mathbf{H}_{(1)}$. Both the CBO matrix $\mathbf{P}$ and the LMO representation matrix $\mathbf{C}$ are then expressible in the form of power series (Sections 5 and 6). The same accordingly refers to total energies defined by either Eq.(8.1) or Eq.(8.2), both of these formulae evidently yielding the same result. The first five terms of the series concerned are as follows [61,64,65]

$$\begin{aligned}
&\mathcal{E}_{(0)} = 2Spur\mathbf{E}_{(+)}, \qquad \mathcal{E}_{(1)} = 2Spur\mathbf{T}, \\
&\mathcal{E}_{(2)} = -2Spur(\mathbf{G}_{(1)}\mathbf{R}^{+}), \qquad \mathcal{E}_{(3)} = -2Spur(\mathbf{G}_{(2)}\mathbf{R}^{+}), \\
&\mathcal{E}_{(4)} = -2Spur[(\mathbf{G}_{(3)} + \mathbf{G}_{(1)}\mathbf{G}^{+}_{(1)}\mathbf{G}_{(1)})\mathbf{R}^{+}], \\
&\mathcal{E}_{(5)} = -2Spur[(\mathbf{G}_{(4)} + \mathbf{G}_{(2)}\mathbf{G}^{+}_{(1)}\mathbf{G}_{(1)} + \mathbf{G}_{(1)}\mathbf{G}^{+}_{(2)}\mathbf{G}_{(1)} + \mathbf{G}_{(1)}\mathbf{G}^{+}_{(1)}\mathbf{G}_{(2)})\mathbf{R}^{+}], etc.
\end{aligned} \tag{8.3}$$

The sum of zero and first order members of Eq.(8.3) coincides with the total energy of the set of isolated occupied basis functions in accordance with the expectation, whereas that of the remaining corrections describes stabilization (or destabilization) of the given system vs. the above-specified set. In particular, the second order correction $\mathcal{E}_{(2)}$ proved to be a generalization [66] to the case of a block- diagonal zero order Hamiltonian matrix $\mathbf{H}_{(0)}$ of the well-known Dewar formula [23], the latter corresponding to a diagonal form of $\mathbf{H}_{(0)}$ and following from the standard Rayleigh-Schrödinger perturbation theory. Accordingly, the subsequent corrections of Eq.(8.3) starting with $k = 3$ may be regarded as an extension of the usual second order approximation. Finally, additivity of the total energy with respect to pairs of basis functions of opposite initial occupation ($\varphi_{(+)i}$ and $\varphi_{(-)l}$) easily follows from Eq.(8.3), although separate increments generally are non-local in their nature.

Expressibility of the initial Hamiltonian matrix in the form of a sum of zero and first order members as shown in Eq.(5.4) along with application of Eq.(8.2) allows us also to define two components within any correction $\mathcal{E}_{(k)}$, viz.

$$\mathcal{E}_{(k)} = \mathcal{E}^{(\alpha)}_{(k)} + \mathcal{E}^{(\beta)}_{(k)}, \tag{8.4}$$

where

$$\mathcal{E}^{(\alpha)}_{(k)} = Spur(\mathbf{P}_{(k)}\mathbf{H}_{(0)}), \quad \mathcal{E}^{(\beta)}_{(k)} = Spur(\mathbf{P}_{(k-1)}\mathbf{H}_{(1)}). \tag{8.5}$$

(Note that Eq.(8.1) also may be successfully used for the same purpose). Substituting the formulae for $\mathbf{P}_{(k)}$ (Section 6) along with a definite algebraic procedure based on employment of Eq.(5.7) yields the following general relation [61]

$$(k-1)\mathcal{E}^{(\beta)}_{(k)} = -k\mathcal{E}^{(\alpha)}_{(k)} \tag{8.6}$$

for any k that indicates the components $\mathcal{E}^{(\alpha)}_{(k)}$ and $\mathcal{E}^{(\beta)}_{(k)}$ to be of opposite signs. Moreover, the absolute value of $\mathcal{E}^{(\beta)}_{(k)}$ always exceeds that of $\mathcal{E}^{(\alpha)}_{(k)}$, i.e. $\mid \mathcal{E}^{(\beta)}_{(k)} \mid > \mid \mathcal{E}^{(\alpha)}_{(k)} \mid$. Consequently, it is the sign of $\mathcal{E}^{(\beta)}_{(k)}$ that determines the actual sign of the total kth

order energy $\mathcal{E}_{(k)}$. Finally, the relation of Eq.(8.6) implies the total correction $\mathcal{E}_{(k)}$ to be alternatively representable as follows

$$\mathcal{E}_{(k)} = -\frac{1}{k-1}\mathcal{E}^{(\alpha)}_{(k)}, \qquad \mathcal{E}_{(k)} = \frac{1}{k}\mathcal{E}^{(\beta)}_{(k)}. \tag{8.7}$$

Let us dwell now on the case of fragmentary molecules (Section 5), the zero order Hamiltonian matrix of which ($\mathbf{H}_{(0)}$) takes a diagonal form containing one-electron energies of FOs. Accordingly, the component $\mathcal{E}^{(\alpha)}_{(k)}$ may be easily shown to involve populations of FOs only. After an additional expressing the latter in terms of partial increments as shown in Eq.(6.6), the component $\mathcal{E}^{(\alpha)}_{(k)}$ takes the form [61]

$$\mathcal{E}^{(\alpha)}_{(k)} = -\sum_{(+)i}\sum_{(-)l} x^{(k)}_{(+)i,(-)l}(\varepsilon_{(+)i} + \varepsilon_{(-)l}), \tag{8.8}$$

and depends upon populations transferred between FOs of opposite initial occupation. In this connection, this component has been interpreted as the charge transfer energy. Meanwhile, the remaining component ($\mathcal{E}^{(\beta)}_{(k)}$) describes the effect of formation of new bond orders between FOs upon the kth order energy due to interfragmental interaction [Note that $\mathcal{E}^{(\beta)}_{(k)}$ does not contain populations of basis orbitals because one-electron energies of FOs always may be entirely included into the zero order matrix $\mathbf{H}_{(0)}$ and thereby diagonal elements of the first order member $\mathbf{H}_{(1)}$ vanish]. It is also noteworthy that bond orders determining the component $\mathcal{E}^{(\beta)}_{(k)}$ originate from members of the (k-1)th order of the power series for the DM $\mathbf{P}$. If we recall now that populations of FOs of the kth order (i.e. $X^{(k)}_{(+)i}$ and $X^{(k)}_{(-)l}$) are expressed in terms of products of the principal matrices of lower orders ($\mathbf{G}_{(k-1)}, \mathbf{G}_{(k-2)}, etc.$) that, in turn, represent intersubset bond orders being formed within previous terms of the same series (see Eq.(6.3)), the above-established interdependence between components $\mathcal{E}^{(\alpha)}_{(k)}$ and $\mathcal{E}^{(\beta)}_{(k)}$ causes no surprise. Moreover, charge redistribution of the kth order may be then considered as a consequence (or counter-effect) of formation of intersubset bond orders within terms of lower orders of the same series for the DM $\mathbf{P}$. Thus, we have to do here with a certain gradual reorganization of bonding, the energetic increments of which are interrelated and governed by Eq.(8.6). Furthermore, the above-drawn conclusions concerning absolute values of $\mathcal{E}^{(\alpha)}_{(k)}$ and $\mathcal{E}^{(\beta)}_{(k)}$ allow us to expect that stabilization of our fragmentary system vs. the set of isolated occupied FOs (if any) is entirely due to formation of new bond orders, and the subsequent charge redistribution actually reduces this stabilizing effect. Nevertheless, the absolute value of the relevant stabilization energy is proportional to that of the respective charge transfer energy $\mathcal{E}^{(\alpha)}_{(k)}$ as the first relation of Eq.(8.7) shows. Indeed, the minus signs of Eqs.(8.7) and (8.8) cancel out one another and we obtain [61]

$$\mathcal{E}_{(k)} = \frac{1}{k-1}\sum_{(+)i}\sum_{(-)l} x^{(k)}_{(+)i,(-)l}(\varepsilon_{(+)i} + \varepsilon_{(-)l}). \tag{8.9}$$

On this basis, an interpretation of the total kth order energy as the charge transfer energy also becomes acceptable (in spite of its somewhat oversimplified nature). This interpretation along with Eq.(8.9) provides us with a quantum- chemical analogue of the intuition-based relation between stabilization and charge redistribution. If

we recall finally the above-discussed proportionality between $x^{(k)}_{(+)i,(-)l}$ and $d^{(k)}_{(+)i,(-)l}$ exhibited in Eq.(7.12), we obtain that [54]

$$\mathcal{E}_{(k)} = \frac{2}{k-1} \sum_{(+)i} \sum_{(-)l} d^{(k)}_{(+)i,(-)l} (\varepsilon_{(+)i} + \varepsilon_{(-)l}). \tag{8.10}$$

As a result, the correction $\mathcal{E}_{(k)}$ is accordingly interpretable as the energy of the intersubset delocalization of initially-localized pairs of electrons. Hence, the well-known intuition- based relation between delocalization and stabilization [10,67] also acquires a quantum- chemical support.

Let us turn now to the case of simple fragmentary systems consisting of individual chemical bonds and lone electron pairs (if any) (Section 5). Each of these two-center fragments evidently is represented by two basis functions. [Note that a faked ABO may be introduced without affecting the final results [51] in the case of a lone electron pair]. Let the Ith fragment to be accordingly described by the occupied orbital (BBO) $\varphi_{(+)i}$ and its vacant counterpart (ABO) $\varphi_{(-)l}$. As a result, the component $\mathcal{E}^{(\alpha)}_{(k)}$ and thereby the total kth order energy $\mathcal{E}_{(k)}$ is representable as a sum of contributions $\mathcal{E}_{(k)I}$ of individual fragments (bonds), where

$$\mathcal{E}_{(k)I} = \frac{1}{k-1} \sum_{(-)l} x^{(k)}_{(+)i,(-)l} (\varepsilon_{(+)i} + \varepsilon_{(-)l}) = \frac{2}{k-1} \sum_{(-)l} d^{(k)}_{(+)i,(-)l} (\varepsilon_{(+)i} + \varepsilon_{(-)l}). \tag{8.11}$$

It is seen that each individual contribution to the energy correction $\mathcal{E}_{(k)}$ is still additive with respect to increments of other fragments (ABOs). Thus, a two-fold additivity of the kth order energy may be concluded. If we now confine ourselves to simple homogeneous systems and choose a negative energy unit coinciding with $\varepsilon_{(+)i}$, the equality $\varepsilon_{(+)i} = \varepsilon_{(-)i} = 1$ for any i becomes acceptable (Section 5). Employment of the latter within Eqs. (8.9) and (8.10) yields

$$\mathcal{E}_{(k)} = \frac{2}{k-1} \sum_{(+)i} \sum_{(-)l} x^{(k)}_{(+)i,(-)l} = \frac{4}{k-1} \sum_{(+)i} \sum_{(-)l} d^{(k)}_{(+)i,(-)l}. \tag{8.12}$$

After invoking Eqs. (7.3) and (7.4), the above expression takes the form

$$\mathcal{E}_{(k)} = \frac{4}{k-1} D^{(k)}_{(+)}, \tag{8.13}$$

where $D^{(k)}_{(+)}$ is defined as follows

$$D^{(k)}_{(+)} = \sum_{(+)i} D^{(k)}_{(+)i} = Spur \mathbf{D}^{(k)}_{(+)} \tag{8.14}$$

and may be referred to as the kth order complete delocalization coefficient [50] of occupied LMOs. Thus, proportionality between delocalization and stabilization takes an especially simple form in this case.

As already mentioned (Section 5), the principal matrices $\mathbf{G}_{(k)}$ are expressible via entire submatrices of the initial Hamiltonian matrix in the case of similar homogeneous compounds as shown in Eq.(5.15). The relation between first order matrices

$\mathbf{G}_{(1)}$ and $\mathbf{R}$ is especially noteworthy here. The point is that just this relation allows us to substitute $-2\mathbf{G}_{(1)}$ for $\mathbf{R}$ within any energy correction of Eq.(8.3) and thereby to express the latter in terms of matrices $\mathbf{G}_{(k)}$ only [64,65], e.g.

$$\begin{aligned}
\mathcal{E}_{(2)} =& 4Spur(\mathbf{G}_{(1)}\mathbf{G}^{+}_{(1)}), \quad \mathcal{E}_{(3)} = 4Spur(\mathbf{G}_{(2)}\mathbf{G}^{+}_{(1)}), \\
\mathcal{E}_{(4)} =& 4Spur[(\mathbf{G}_{(3)} + \mathbf{G}_{(1)}\mathbf{G}^{+}_{(1)}\mathbf{G}_{(1)})\mathbf{G}^{+}_{(1)}], \\
\mathcal{E}_{(5)} =& 4Spur[(\mathbf{G}_{(4)} + 3\mathbf{G}_{(2)}\mathbf{G}^{+}_{(1)}\mathbf{G}_{(1)})\mathbf{G}^{+}_{(1)}], etc.
\end{aligned} \tag{8.15}$$

Moreover, alternative expressions for corrections $\mathcal{E}_{(4)}$ and $\mathcal{E}_{(5)}$ have been derived that contained the principal matrices up to $\mathbf{G}_{(2)}$ and $\mathbf{G}_{(3)}$, respectively, viz.

$$\begin{aligned}
\mathcal{E}_{(4)} =& 4Spur(\mathbf{G}_{(2)}\mathbf{G}^{+}_{(2)}) - 4Spur(\mathbf{G}_{(1)}\mathbf{G}^{+}_{(1)}\mathbf{G}_{(1)}\mathbf{G}^{+}_{(1)}), \\
\mathcal{E}_{(5)} =& 4Spur[(\mathbf{G}_{(3)} - \mathbf{G}_{(1)}\mathbf{G}^{+}_{(1)}\mathbf{G}_{(1)})\mathbf{G}^{+}_{(2)}].
\end{aligned} \tag{8.16}$$

Formulae of the above-exemplified type underly the original approach of Refs. [64,65] to evaluating and rationalizing relative stabilities of simple homogeneous compounds of similar constitutions. This approach proved to be especially successfull in the case of conjugated hydrocarbons modelled as sets of weakly-interacting initially-double (C=C) bonds, including isomers of dienes, individual Kekulé valence structures of benzenoids, etc. Local nature of stabilization of these hydrocarbons vs. the relevant sets of isolated C=C bonds and thereby the dependence of the stabilization energy upon local peculiarities of constitution was among principal conclusions here [64]. Moreover, a large extent of additivity of this extra energy with respect to transferable increments of definite substructures (fragments) has been established. On the whole, these results indicate stabilization energies of conjugated hydrocarbons to be of quasi-classical nature. Finally, the analogy between the perturbative approach under discussion and models based on the concepts of conjugated circuits [68] and paths [69] deserves mentioning here.

In summary, the results overviewed in Sections 5-8 form the basis of the perturbative non-canonical theory of molecular orbitals further referred to as the PNCMO theory [55]. The subsequent Sections 9-12 are devoted to applications of this theory.

9 Analysis of heterolytic organic reactions in terms of direct and indirect participation of separate fragments

In accordance with the classical principle of locality (Section 1), a definite functional group is regarded as taking part in the given chemical process directly and it is usually referred to as the reaction center [70]. Again, the remaining parts of molecules (e.g. substituents) are supposed to participate in the same process indirectly by exerting certain electron-donating or accepting effects upon this center. Moreover, the extents of these effects are usually considered to be quite different at various stages of the reaction [10,71]. Extinction of the indirect influence when the distance between the given fragment and the reaction center grows also is among the expectations. Besides, the above-outlined concepts originated from studies of

heterolytic (i.e. electrophilic and nucleophilic) organic reactions, the latter being often accordingly referred to as the classical ones. Specific features of homolytic (pericyclic) reactions are discussed in Section 10.

Let us note immediately that the standard quantum- chemical approaches to early stages of organic reactions [11,23, 67,70, 72-74] allow no revealing of roles of separate fragments. The point is that these approaches are based on an initial passing into the basis of delocalized (canonical) MOs of isolated compounds and thereby on the concept of a non-local intermolecular interaction even if local fragments of extended compounds actually come into contact.

To formulate quantum-chemical analogues of the above-discussed classical concepts and to be able to discuss chemical reactions in terms of local structures and/or interactions, the PNCMO theory of Sections 5-8 has been applied both to the general case of two interacting fragmentary molecules A and B [54, 75, 76] and to some specific reactions [54, 58, 77-83]. This alternative methodology has been jointly called the semilocalized approach to chemical reactivity. Electron density redistributions among basis orbitals (FOs) of both participants of the given process along with the related delocalization coefficients of LMOs [54] are the principal characteristics here instead of the total intermolecular interaction energy or constitutions of canonical MOs as usual [although the total energy also may be derived either on the basis of Eq.(8.2) or by means of Eqs. (8.9) and (8.10) as discussed in Section 10].

Let us start with the general additivity property of the total DM (CBO matrix) $\mathbf{P}$ of two interacting molecules A and B [76]. Indeed, this matrix was shown to be representable as follows

$$\mathbf{P} = \mathbf{P}^{(A)} \oplus \mathbf{P}^{(B)} + \delta\mathbf{P}, \tag{9.1}$$

where the first term coincides with the direct sum of DMs of isolated molecules A and B, and the second one ($\delta\mathbf{P}$) is a correction originating from the intermolecular interaction and vanishing if this interaction turns to zero. An analogous relation may be easily proven for the LMO representation matrix $\mathbf{C}$ too. Such an additivity property of the principal matrices $\mathbf{P}$ and $\mathbf{C}$ implies that new contributions to elements of the latter arising as a result of the intermolecular contact may be studied separately and independently from the intramolecular ones. As a result, a general formula has been derived and analyzed for an alteration ($\delta X^{(A)}_{(+)i}$) in the population of a certain initially-occupied FO ($\varphi^{(A)}_{(+)i}$) of the molecule A due to its contact with the molecule B. As with the DM $\mathbf{P}$ itself (Section 6), this alteration also takes the form of the power series with respect to intermolecular resonance parameters. Separate terms of this series, in turn, are expressible as sums of partial increments ($\delta x^{(A,k))}_{(+)i,(-)l}$) referring to various initially-vacant FOs (k stands here for the order parameter as previously). Finally, the relevant alterations in delocalization coefficients of LMOs (i.e. $\delta D^{(A)}_{(+)i}$ and $\delta D^{(A)}_{(-)m}$) also take analogous forms because of interrelations

$$\delta X^{(A)}_{(+)i} = 2\delta D^{(A)}_{(+)i}, \qquad \delta X^{(A)}_{(-)m} = 2\delta D^{(A)}_{(-)m} \tag{9.2}$$

that may be easily proven on the basis of the results of Section 7.

Before turning to an overview of both general and specific results of the semilocalized approach, let us recall some definitions of Ref.[76]. Thus, the directly interacting (contacting) fragments of molecules A and B have been called the reaction

centers and denoted by RC(A) and RC(B). (The direct contact implies that the intermolecular resonance parameters take non-zero values for pairs of FOs of only these fragments). Further, the fragments of molecules A and B, the FOs of which interact directly only with those of reaction centers of their own molecules (but not with orbitals of opposite molecule) have been referred to as the nearest-neighboring fragments and denoted by NN(A) and NN(B), respectively. Analogously, the next-nearest- neighboring fragments NNN(A) and NNN(B) have been defined and so forth. Given that all direct interorbital interactions vanish in our RC (i.e. $G_{(1)il} = 0$ for all i and l belonging to the RC), the term 'a simple RC' has been used. It is evident that reaction centers containing only a single fragment (the FOs of which are defined as eigenfunctions of the respective Hamiltonian matrix block) comply with this definition. Otherwise, we have to do with an extended RC. An assumption that both RC(A) and RC(B) are simple reaction centers usually implies that only two elementary fragments of our molecules actually come into contact. This case has been referred to as that of a local intermolecular contact. Otherwise, we have to do with the case of a non-local contact.

Let us return again to the population alteration $\delta X^{(A)}_{(+)i}$. It is evident that the underlying orbital $\varphi^{(A)}_{(+)i}$ may belong to any of the above-defined fragments (i.e. RC(A), NN(A), etc.) and, consequently, distinct population alterations $\delta X^{(A)}_{(+)i}$ actually arise. Analysis of separate members of the relevant power series showed that the higher is the order parameter of the given increment (k), the more distant fragments are embraced by the relevant charge redistribution [76].

To illustrate the above-drawn general conclusion, let us start with second order terms ($k = 2$). These terms contain an intermolecular component only that depends on squares of the relevant first order elements $G_{(1)il}$ (see Eq.(6.8)) and represents the charge transfer between orbitals of directly contacting fragments RC(A) and RC(B). The actual nature of these RCs (i.e. whether they are simple or extended) plays no essential role in the formation of these terms. By contrast, non-zero third order increments arise only if at least one of reaction centers is an extended RC. Although these contributions also embrace the reaction centers only, both intra- and intermolecular components are possible here, and these describe charge redistributions inside the extended RC and between the RC(A) and RC(B), respectively.

On the whole, the above-discussed local charge redistributions demonstrate the primary role of reaction centers in chemical processes and may be regarded as quantum chemical analogues of the supposed direct participation of the RC(A) and RC(B) fragments in the given reaction.

The fourth order terms of the same series represent additive components of an indirect influence of a certain nearest-neighboring fragment NN(A) (e.g. of a substituent) upon the reactivity of the whole system. Three principal components may be mentioned here: i) The NN(A) fragment exerts an additional electron-donating or accepting effect upon the reaction center of its own molecule (RC(A)) under influence of the approaching reaction center of the opposite molecule (RC(B)), because the latter offers its orbitals as mediators for specific indirect intramolecular interaction; ii) The NN(A) fragment exerts an analogous effect upon the reaction center of the opposite molecule (RC(B)) owing to an ability of orbitals of its own reaction center (RC(A)) to mediate specific indirect intermolecular interactions; iii)

The NN(A) fragment offers its orbitals as mediators for indirect interorbital interactions that gives rise to additional electron density redistributions both inside the reaction center of its own molecule and between RC(A) and RC(B). The whole of the above-enumerated effects may be accordingly regarded as a quantum chemical analogue of an indirect participation of the NN(A) fragment in the given reaction.

In the case of a still more remote fragment (e.g. NNN(A)), terms of even higher orders are required to describe the relevant effects. Thus, extinction of an indirect influence is predicted when the distance between the given fragment and the reaction center(s) grows. Moreover, the relative importance of higher order terms may be expected to increase when passing from the early stages of reaction to later ones. Finally, the above-enumerated results may be easily reformulated in terms of reshapings of LMOs of reacting molecules due to an intermolecular contact [54]. Thus, the classical concepts (mental images) overviewed at the beginning of this section acquire a full support.

This outcome of our analysis, however, is not the only one. Indeed, the above-outlined general results form the basis for constructing abstract semi-local models for specific reactions [54, 58, 77-83]. As opposed to popular numerical studies referring to individual compounds and/or processes, these models are intended for embracing all reactions of a certain type in accordance with their chemical classification. These models usually contain orbitals of the supposed reaction centers and of some neighboring fragments of particular interest. Meanwhile, details of specific systems may be easily ignored in these models for the benefit of both simplicity and generality. As a result, the overall approach allows direct qualitative comparisons of similar processes including alternative routes of the same reaction and processes embracing reactants or reagents of related chemical constitution (e.g. a hydrocarbon and its heteroatom-containing derivative). Let us now turn to an overview of these important points and the relevant achievements.

It is evident that a single initially-occupied (vacant) orbital $\varphi_{(+)N}$ ($\varphi_{(-)E}$) may be successfully used to represent a nucleophilic (electrophilic) reagent B when comparing alternative directions of its attack upon the same reactant A [such a one-orbital model implies that the reagent B consists only of a simple reaction center RC(B)]. Furthermore, absolute values of direct intermolecular interactions often may be assumed to be uniform in the above-discussed comparisons. [The latter assumption is based on the fact that alternative routes of a certain reaction are most commonly characterized by different spatial arrangements of non-neighboring fragments. For example, the α- and β-attacks of electrophile upon a substituted ethene (Z-C_αH=$C_\beta H_2$) are described by different positions of the reagent relatively to the substituent Z [78]. This implies the absolute value of direct intermolecular interactions and thereby the second order partial transferred populations to play no important role in the formation of predominant routes of reactions]. Finally, heterolytic organic reactions may be classified on the basis of the order parameter (k) of the decisive terms of power series [83].

For illustration, let us consider the so-called extended model [77] of the bimolecular nucleophilic substitution (S_N2) process between a substituted alkane Z-$C_\alpha H_2$-$C_\beta H_2$-... and nucleophile (Nu), where Z stands for a heteroatom (nucleofuge). As opposed to the usual local models of the same process containing the orbital of the reagent ($\varphi_{(+)N}$) and the electron-accepting (antibonding) orbital of the C_α-Z bond

($\varphi_{(-)a}$) [23,70], orbitals of the C_α-C_β and/or C_α-H bonds also have been included into our model and resonance parameters between these extra orbitals and the orbital $\varphi_{(+)N}$ have been taken into account explicitly. This implies an assumption about an extended reaction center RC(A) containing four bonds (viz. the C_α-Z bond and its three geminal neighbours). As a result, non-zero third order charge redistributions both inside the above-specified reaction center and between orbitals $\varphi_{(+)N}$ and $\varphi_{(-)a}$ were shown to be peculiar to this reaction. Moreover, the partial population ($\delta x^{(3)}_{(+)N,(-)a}$) transferred between orbitals $\varphi_{(+)N}$ and $\varphi_{(-)a}$ indirectly and defined as follows

$$\delta x^{(3)}_{(+)N,(-)a} = 4G_{(1)Na}G_{(2)Na} \tag{9.3}$$

(see Eq. (6.8)) proved to be of the largest absolute value among the third order increments concerned, where $G_{(1)Na}$ stands for the direct interaction between orbitals $\varphi_{(+)N}$ and $\varphi_{(-)a}$ and $G_{(2)Na}$ coincides with the respective indirect interaction by means of orbitals of the C_α-C_β and/or C_α-H bonds. The most important aspect here, however, consists in opposite signs of the above-mentioned principal third order partial transferred populations for alternative directions of the attack, viz. positive (negative) signs of the latter correspond to the back (frontal) position of nucleophile (see also [83]). When added (subtracted) to (from) the uniform positive second order increments, these corrections ensure a larger (smaller) value of the total population acquired by the Z-C_α bond for the back (frontal) attack of nucleophile. It is natural to assume that the more population the nucleofuge acquires, the easier it leaves. Hence, a greater efficiency of the back attack unambiguosly follows from our analysis in aggreement with the well-known experimental facts [10,23,70, 74, 84, 85]. Analogous conclusions may also be easily drawn using partial delocalization coefficients of LMOs as the principal terms [54]. In particular, a more significant partial delocalization of the lone pair of electrons of nucleophile over the Z-C_α bond is predicted to refer to the predominant back attack vs. the frontal one.

Our next example serves to illustrate comparisons of relative reactivities of related chemical compounds. We mean here the S_N2 reactions of derivatives of substituted alkanes containing additional unsaturated groups at the C_α atom. These derivatives are known to be generally characterized by largely higher relative reactivities as compared to the relevant alkyl analogues [11]. Moreover, a further increase of reactivity is observed when the C=C bond is replaced by a C=O bond, e.g. in halogen-substituted ketones (Z-$C_\alpha H_2$-RC_β=O) vs. allyl halogenides (see [11] and references therein). In this connection, increments have been comparatively analyzed [79] that represent the indirect participation of orbitals of C_β=C_γ and C_β=O bonds in the decisive third order charge transfer between the above-specified basis functions $\varphi_{(+)N}$ and $\varphi_{(-)a}$. It turned out that participation of the bonding $\pi-$orbital of the C_β=C_γ bond in the indirect interaction $G_{(2)Na}$ of Eq.(9.3) contributes to lowering of the positive partial transferred population $\delta x^{(3)back}_{(+)N,(-)a}$ and thereby of the relative reaction rate, whereas that of the antibonding $\pi-$orbital gives rise to an opposite effect. For highly electron-donating (soft) nucleophiles, the second contribution was shown to predominate over the first one in addition. Just this fact served to account for the higher reactivity of allyl halogenides vs. their alkyl analogues. Finally, passing from the C_β=C_γ to the C_β=O bond proved to be accompanied by such changes in shapes and one-electron energies of bond orbitals of the $\pi-$type

that ensure a significant reduction of the absolute value of the negative increment of the bonding orbital and a simultaneous increase of the positive contribution of the antibonding orbital to the population acquired by the Z-C_α bond. This result formed the basis for a new interpretation of the largely increased reactivity of $\alpha-$halocarbonyl compounds vs. their hydrocarbon analogues.

Similarities between reactions of seemingly different nature also are among possible outcomes of application of our approach. In this respect, comparative analysis of early stages of the above-discussed S_N2 reactions, on the one hand, and of the Ad_N2 reactions of carbonyl compounds [82], on the other hand, serves as an excellent example. Indeed, electron-accepting substituents attached to the carbon atom of the carbonyl group were shown to exert a rate-accelerating effect, the overall mechanism of which closely resembles the above-overviewed mechanism of the indirect influence of the C=O group in the S_N2 reactions of α-halocarbonyl compounds. It also deserves adding here that the double C=O bond has been represented in Ref.[82] by two equivalent bent bonds, only one of them being under attack of nucleophile.

The aromatic electrophilic substitution (S_E2) reaction of pyridine is another outstanding example of third order processes. The usual (canonical) MOs of benzene played the role of basis functions in the relevant model [81] along with a single vacant orbital of electrophile ($\varphi_{(-)E}$). After taking into account the perturbation of the Coulomb parameter (α) at the site of replacing the carbon atom by a nitrogen one, non-zero direct intramolecular interactions arise in the pyridine molecule so that the latter becomes an extended RC. As a result, third order partial populations ($\delta x^{(3)}_{(+)2,(-)E}$) transferred between the HOMO of the reactant ($\varphi_{(+)2}$) and the only orbital of the reagent ($\varphi_{(-)E}$) become responsible for alterations in relative reactivities of carbon atoms when passing from benzene to pyridine. Moreover, the corrections $\delta x^{(3)}_{(+)2,(-)E}$ proved to be negative quantities for all possible directions of the attack (i.e. ortho, meta and para) in aggreement with well-known lowered reactivities of all sites of pyridine vs. that of benzene. Finally, the correction $\delta x^{(3)meta}_{(+)2,(-)E}$ was shown to take the smallest absolute value vs. the remaining ones in accordance with the highest reactivity of meta position of pyridine.

To exemplify the fourth order processes, let us consider electrophilic addition (Ad_E2) reaction of substituted ethenes (Z-C_αH=$C_\beta H_2$). In the case of an electron-donating substituent (Z=D), the relevant semilocal model [78] contains the occupied orbital of the substituent D ($\varphi_{(+)d}$), the electron-accepting (vacant) orbital of electrophile ($\varphi_{(-)E}$), as well as two bond orbitals of the ethene fragment, i.e. the BBO $\varphi_{(+)e}$ and the ABO $\varphi_{(-)e}$. Direct interactions between orbitals $\varphi_{(+)d}$ and $\varphi_{(-)E}$ have been ignored in this model because of their small values. Consequently, our reactant (A) contains a simple RC consisting of the ethene group and an NN(A) fragment coinciding with the substituent D. That is why fourth order partial transferred populations play the decisive role in the formation of distinct reactivities of the C_α and C_β atoms under influence of the substituent D. Moreover, specific fourth order contributions and the effects underlying the latter (enumerated below) are in line with the above-discussed three principal components of an indirect influence of an NN fragment: First, the substituent D exerts an additional intramolecular electron-donating effect upon the ethene fragment under influence of the approaching electrophile. This effect proves to be governed by the following fourth order

partial population

$$\delta x^{(4)}_{(+)d,(-)e} = 4G_{(1)de}G_{(3)de}, \tag{9.4}$$

where $G_{(1)de}$ stands for the direct interaction between orbitals $\varphi_{(+)d}$ and $\varphi_{(-)e}$ and $G_{(3)de}$ represents the relevant indirect interaction mediated by orbitals $\varphi_{(+)e}$ and $\varphi_{(-)E}$. Second, the substituent D exerts influence upon the intermolecular charge transfer between the ethene fragment and electrophile described by the following correction

$$\delta x^{(4)}_{(+)e,(-)E} = 4G_{(1)eE}G_{(3)eE} \tag{9.5}$$

[The orbital $\varphi_{(+)d}$ participates here as a mediator of the indirect interaction $G_{(3)eE}$]. The indirect electron-donating effect of the substituent D upon the electrophile may be mentioned as the third contribution. This effect is represented by the fourth order partial transferred population between orbitals $\varphi_{(+)d}$ and $\varphi_{(-)E}$, viz.

$$\delta x^{(4)}_{(+)d,(-)E} = 2(G_{(2)dE})^2. \tag{9.6}$$

Furthermore, positive (negative) values of increments of Eqs.(9.4) and (9.5) have been established to refer to attacks of electrophile upon the $C_\beta(C_\alpha)$ atoms. This implies that the approaching reagent contributes to an increase of electron- donating effects both from the substituent D to the ethene fragment and from the latter to the electrophile itself provided the the C_β atom is under attack. Otherwise, both effects are predicted to be suppressed. So far as the increment of Eq.(9.6) is concerned, a large (small) absolute value of the indirect interaction $G_{(2)dE}$ and thereby of the partial transferred population $\delta x^{(4)}_{(+)d,(-)E}$ itself has been found for an attack of electrophile upon the $C_\beta(C_\alpha)$ atoms. This implies the indirect electron-donating effect of the substituent D upon the reagent to be more significant just for the β-attack.

Using interrelations between partial populations transferred between FOs and the relevant delocalization coefficients (Section 7), we may reformulate the above results in terms of LMOs [54] as follows: The lone pair of electrons of the substituent D becomes delocalized more significantly both over the antibonding orbital of the ethene fragment (C=C bond) and over the FO of electrophile, if the reagent approaches the C_β atom vs. the C_α atom. Similarly, the initially-localized pair of electrons of the C=C bond proves to be delocalized more substantially over the FO of electrophile in the case of the $\beta-$attack. In summary, the above-overviewed results indicate the C_β atom to be of greater relative reactivity as compared to the C_α atom in aggreement with the well-known Markovnikov rule [10,11, 70,85].

The case of an electron-accepting substituent (Z=A) also has been considered similarly [78]. As opposed to the above-discussed donor-containing system, no indirect charge transfer is now possible between the substituent and the reagent. As a result, two fourth order increments remain, namely partial populations transferred from the initially-occupied orbital of ethene ($\varphi_{(+)e}$) to that of the substituent ($\varphi_{(-)a}$) and to the orbital of electrophile ($\varphi_{(-)E}$). The relevant analysis showed that these corrections are of positive (negative) signs for $C_\alpha(C_\beta)$ attacks. This implies the electron-accepting effects both of the substituent A and of the reagent (E) upon the C=C bond to become strengthened for the α-attack. Otherwise, the same effects are predicted to be suppressed. Analogously, the pair of electrons of the C=C

bond becomes delocalized more substantially over the FO of electrophile just for the $\alpha-$attack [54]. These results also are in line with experimental facts [10, 11, 85].

It deserves adding finally that the above-overviewed results concerning the Ad_E2 reaction of substituted ethenes allows some conclusions to be drawn the scope of applicability of which is rather wide. This primarily refers to the above-demonstrated interdependence between the extent of an electron-donating (accepting) effect of an external subsystem and the structure of the remaining part of the whole system. In other words, we actually have to do here with the variable nature of electron-donating and accepting effects. Equivalence between an electrophile and an electron-accepting substituent (A) also is noteworthy [both are represented by an initially-vacant orbital]. It is no surprise in this connection that similar results have been obtained also when studying intersubstituent interactions [86].

Furthermore, the above-concluded variable nature of electron- donating (accepting) effects concerns not only the relative extents of the latter, but also their directions, namely a substituent proves to be able to turn from donor to acceptor (or vice versa) if the constitution of the remaining system is altered substantially. To illustrate this general statement, let us refer to an analogous study of addition reactions of butadiene [58]. In the relevant model, one of the two H_2C=CH-fragments has been supposed to be under a direct attack of the reagent (either electrophile or nucleophile) and thereby to coincide with a simple reaction center RC(A) of the reactant A. Meanwhile, the remaining H_2C=CH-group has been assumed to play the role of an NN(A) fragment (substituent), the latter being now represented by both an initially-occupied (electron-donating) and an initially-vacant (accepting) orbital. It has been demonstrated that the effects of these orbitals upon the remaining fragments of the whole system (i.e. upon the RC(A) and the reagent) may be considered independently whatever the nature of the reaction. However, a strong interdependence has been established between the actual relative extents of the above-specified two components of the total effect of the H_2C=CH-group and the electron-donating (accepting) properties of the reagent. Moreover, the H_2C=CH-group was shown to manifest itself as an electron-donating (accepting) substituent under influence of an electrophilic (nucleophilic) attack.

The stereoselective bimolecular β-elimination (E2) reactions of substituted alkanes may be mentioned finally as an example of the fifth order heterolytic processes [80]. As opposed to the competing S_N2 reaction of the same substrates discussed above, it is the H-C_β bond that is assumed to be under a direct attack of an external base ($B^{\cdot\cdot}$) in this case. As a result, the above-mentioned bond and the base may be considered as simple reaction centers RC(A) and RC(B), respectively. Accordingly, the C_α-C_β and C_α-Z bonds have been correspondingly regarded as the NN(A) and the NNN(A) fragments. It is no surprise in this connection that decisive additional indirect electron-accepting effects of the C_α-Z bond upon both C_β-H bond and the external base ($B^{\cdot\cdot}$) proved to be represented by specific fifth order partial transferred populations. Moreover, positive (negative) signs of these populations for trans (cis) elimination processes formed the basis for a conclusion about the former being the predominant route of the given reaction.

In summary, alternative routes of heterolytic reactions were shown to be accompanied by decisive partial transferred populations of opposite signs.

10 Applications of the semilocalized approach to pericyclic processes. The common selection rule for organic reactions

Numerous new organic reactions have been discovered within the last several decades including the so-called pericyclic processes [10, 11, 15]. Peculiarities of these reactions and rules governing them seem to differ significantly from those of heterolytic processes discussed in Section 9. Indeed, "a concerted reorganization of bonding occurs throughout a cyclic array of continuosly bounded atoms "[11] in this case and thereby no local reaction center is likely to be present. Another (an even more important) distinctive feature of pericyclic processes consists in their high stereospecificity that has been successfully accounted for by applying just the CMO method (cf. the famous Woodward-Hoffmann rule [87-89]). The concept of the Hückel and Möbius aromaticity (cf. the Dewar-Zimmerman rule [90-93]) also has been invoked to treat the same problem (Note that this concept is traditionally applied to delocalized π-electron systems of benzenoids). The above-enumerated circumstances usually create an impression that delocalization is an immanent feature of pericyclic reactions in contrast to heterolytic ones. In this context, a question of particular interest is about applicability to pericyclic reactions of the PNCMO theory of Sections 5-8 and thereby of the semilocalized perspective to chemical processes in general. It is evident that an affirmative answer to this principal question would imply feasibility of a unified theory for both types of reactions in terms of direct and indirect interactions of localized basis functions (FOs).

The thermal electrocyclic closure of polyenes containing N C=C bonds ($C_{2N}H_{2N+2}$) is among the most well-known examples of pericyclic processes that often serves as a common model for all reactions of this type. Thus, applicability of the PNCMO theory to initial open polyene chains becomes a necessary condition here. This point has been explored in Ref.[34]. The relevant zero and first order Hamiltonian matrices contained resonance parameters between pairs of $2p_z$ AOs referring to initially-double (C=C) and initially-single (C-C) bonds, respectively. Convergence of the power series for the CBO matrix and for the total energy of π-electrons of open polyenes has been demonstrated for chains of a small and medium size even if all carbon-carbon bonds are formally represented by resonance parameters of uniform values. Thereupon, the same approach has been employed to investigate the closure process [94]. To this end, an additional resonance parameter ($\lambda_{1,2N}$) has been assumed to emerge between the $2p_z$ AOs χ_1 and χ_{2N} of the terminal carbon atoms C_1 and C_{2N}. This new parameter has been considered as a small perturbation (vs. the intrachain ones) when studying very early stages of reactions. Accordingly, alterations in total energies of polyene chains due to perturbation $\lambda_{1,2N}$ are expressible as follows

$$\Delta\mathcal{E} = \mathcal{E}_{(1)} = 2P_{1,2N}\lambda_{1,2N}, \tag{10.1}$$

where $P_{1,2N}$ stands for bond orders between the terminal AOs χ_1 and χ_{2N} in the initial (open) chains. Formulae for $P_{1,2N}$, in turn, have been derived by invoking the retransformation procedure for the DM described below (Section 11). It turned out that the signs of bond orders $P_{1,2N}$ alternate with growing N values. Moreover, positive (negative) signs of $P_{1,2N}$ have been established for odd (even) total numbers

of C=C bonds. Consequently, positive (negative) $\lambda_{1,2N}$ values are required to ensure positive energy corrections $\Delta\mathcal{E}$ of Eq.(10.1) and thereby stabilization of the whole system (Note that negative energy units were used). Positive (negative) resonance parameters $\lambda_{1,2N}$ and /or overlap integrals, in turn, were shown to correspond to disrotatory (conrotatory) ways of closure. Thus, a conrotatory closure of the chain followed for even N values (e.g. butadiene) and a disrotatory one was expected for odd N values (e.g. hexadiene). Inasmuch as $4n$ and $4n+2$ electrons, respectively, correspond to these cases, the above-established result coincides with the Woodward-Hoffmann rule [87-89]. An important point here is that no passing to delocalized (canonical) MOs was required when obtaining this result.

Another essential aspect of the above-outlined derivation is that the decisive bond orders $P_{1,2N}$ depend on definite matrix elements ($G_{(k)il}$) describing the interactions between BOs of terminal bonds of an open polyene chain either directly (e.g. in butadiene) or indirectly by means of the remaining BOs of the chain. Accordingly, alternation of signs of $P_{1,2N}$ is determined by an analogous behaviour of the above-specified interactions with growing number of intervening bonds. Inasmuch as $\lambda_{1,2N}$ refers to the direct overlap of the terminal BOs owing the closure process, the energy correction $\Delta\mathcal{E}$ of Eq.(10.1) seems to depend upon a certain roundabout interaction over the whole cycle. The latter anticipation has been proven rigorously in Ref.[95], where a somewhat different model of pericyclic processes has been suggested that was intended for representing a later stage of the whole process. Both the newly-emerging resonance parameter ($\lambda_{1,2N}$) and those referring to initially-single (C-C) bonds were assumed to take similar and small values relatively to parameters referring to the initially-double (C=C) bonds in this alternative model. Application of the power series for the DM then accordingly resulted into an analogue of the Woodward- Hoffmann rule for pericyclic reactions in terms of the so-called roundabout interaction of the newly-formed cycle ($\Omega_{(N)}$) also alternatively referred to as topological factor. This characteristic has been defined explicitly as a product of resonance parameters (or overlap integrals) between BOs of neighboring C=C bonds over the whole cycle and contained a definite N-dependent parity factor in addition. Besides, the overall pattern of the reorganization of bonding during the reaction (including alterations in orders of intrachain bonds) also was shown to be governed by the newly-formulated analogue of the Woodward- Hoffmann rule. Finally, analysis of the same reactions in terms of delocalization coefficients of LMOs has been carried out [54]. The extents of delocalization of initially-localized pairs of electrons of C=C bonds were shown here to obey an analogue of the Woodward- Hoffmann rule too.

On the whole, the above-overviewed results demonstrate adequacy of the PNCMO theory for investigation of pericyclic reactions and thereby interpretability of these reactions in terms of direct and indirect interactions of orbitals of initially-double (C=C) bonds.

In this connection, attempts have been made to construct a unified approach to both types of reactions. Let us turn now to discussion of the most outstanding achievements in this direction.

Analysis of early stages of the most popular electrophilic and nucleophilic reactions showed certain cycles of basis orbitals [96] to be formed in this case in some analogy with pericyclic processes. For example, the initially-occupied orbital of

nucleophile ($\varphi_{(+)N}$) interacts with orbitals of both C_α-Z and C_α-C_β(C_α-H) bonds, the latter also interacting one with another. This implies closure of at least three-membered cycle to underly the S_N2 processes of substituted alkanes. To represent the overlap topologies of these newly-revealed cycles [96], a topological factor has been defined like that discussed above ($\Omega_{(N)}$). Moreover, the popular concept of the usual (Hückel) cycle and of its Möbius analogue has been generalized by defining them as cycles described by positive and negative topological factors, respectively. Accordingly, the classical $4n + 2/4n$ rule representing the Hückel [19, 20] and Möbius aromaticities [97] has been extended. The predominant routes of the most well-known heterolytic reactions are then shown to be governed by the extended $4n + 2/4n$ rule, the latter being an analogue of the Dewar-Zimmerman rule for pericyclic reactions. Thus, a common description of both types of reactions has been achieved in this case by invoking the concept Hückel [19, 20] and Möbius aromaticities [97].

Another unified description of both homolytic and heterolytic processes has been suggested in Ref.[83] and called the common selection rule for organic reactions.

To discuss this rule, let us return to the power series for the total energy $\mathcal{E}$ of fragmentary molecules, the separate members of which ($\mathcal{E}_{(k)}$) are represented either via partial populations ($x^{(k)}_{(+)i,(-)l}$) transferred between basis orbitals (FOs) of opposite initial occupation as shown in Eq.(8.9) or in terms of the related partial delocalization coefficients of LMOs ($d^{(k)}_{(+)i,(-)l}$) of Eq.(8.10). Let us dwell on the first representation for convenience. As is seen from Eq.(8.9), the correction $\mathcal{E}_{(k)}$ contributes to stabilization (destabilization) of the whole system if the partial populations $x^{(k)}_{(+)i,(-)l}$ contained within the relevant definition are of positive (negative) signs [Negative energy units are assumed to be chosen here as previously so that $\varepsilon_{(+)i} + \varepsilon_{(-)l} > 0$]. For the second order member $\mathcal{E}_{(2)}$, positive signs of $x^{(2)}_{(+)i,(-)l}$ unambiguosly follow from Eq.(6.8.8) whatever the particular FOs $\varphi_{(+)i}$ and $\varphi_{(-)l}$. So far as increments of higher orders ($k = 3, 4...$) are concerned, positive (negative) signs of the relevant partial transferred populations $x^{(k)}_{(+)i,(-)l}$ are ensured if the interorbital interactions contained within the relevant definitions of Eq.(6.8) (i.e. $G_{(1)il}, G_{(2)il}, G_{(3)il}, etc$) are of coinciding (opposite) 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. In this context, correlations between signs referring to different pairs of FOs $\varphi_{(+)i}$ and $\varphi_{(-)l}$ also become essential. Three cases may be distinguished here: The first one embraces reactions described by all (or almost all) positive increments $x^{(k)}_{(+)i,(-)j}$ to the decisive k-th order energy correction $\mathcal{E}_{(k)}$ so that the positive sign and thereby the stabilizing nature of the latter is unambiguosly ensured. These processes have been referred to as allowed k-th order reactions. The second case embraces processes represented by all (or almost all) negative increments $x^{(k)}_{(+)i,(-)l}$ and thereby by a negative k-th order correction $\mathcal{E}_{(k)}$. The term "the forbidden k-th order reactions" has been 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, the actual processes prove to belong to

either allowed or forbidden ones.

This general rule has been successfully applied to numerous specific reactions including both heterolytic and pericyclic. These achievements are overviewed in Ref. [83] in a detail. In this connection, we will confine ourselves here to third order processes and discuss their heterolytic and pericyclic representatives.

For the S_N2 reaction of substituted alkanes, the third order partial population transferred between the electron-donating orbital of nucleophile ($\varphi_{(+)N}$) and the electron-accepting (antibonding) orbital of the C_α-Z bond ($\varphi_{(-)a}$) playes the decisive role in the choice of the predominant route as discussed in Section 9. The relevant definition is exhibited in Eq.(9.3) and contains the direct interaction of these orbitals ($G_{(1)Na}$) along with their indirect interaction ($G_{(2)Na}$) by means of orbitals of C_α -C_β (C_α-H) bonds. Analysis of these matrix elements for frontal and back attacks of nucleophile yields the following result

$$G^{(b)}_{(1)Na} < 0, \qquad G^{(f)}_{(1)Na} > 0, \qquad G_{(2)Na} < 0. \tag{10.2}$$

The last relation of Eq.(10.2) indicates the sign of the indirect interaction $G_{(2)Na}$ to be independent of the position of nucleophile. It is also seen that the back attack is represented by the principal first and second order interorbital interactions of coinciding signs and thereby may be considered as an allowed process. Meanwhile, the frontal attack is characterized by the same interactions of opposite signs and proves to be forbidden.

In the cace of the S_E2 reaction of pyridine, the decisive third order partial transferred population ($\delta x^{(3)}_{(+)2,(-)E}$) refers to the HOMO of the parent system (benzene) ($\varphi_{(+)2}$) and the orbital of electrophile ($\varphi_{(-)E}$) and also is accordingly determined by interactions $G_{(1)2E}$ and $G_{(2)2E}$. Moreover, the second order (indirect) interaction $G_{(2)2E}$ and thereby the correction $\delta x^{(3)}_{(+)2,(-)E}$ contain two components representing the mediating effects of the LUMO of benzene $\varphi_{(-)5}$ and of the HOMO itself (the so-called self-mediating effect). These components are denoted below by ' and " , respectively. Analysis of the relevant expressions showed that $G''_{(2)2E}$ and thereby $\delta x^{(3)''}_{(+)2,(-)E}$ are negative quantities whatever the direction of the attack. Hence, the predominant route of the given reaction proves to be determined by the increment $\delta x^{(3)'}_{(+)2,(-)E}$ containing the LUMO $\varphi_{(-)5}$ as a mediator. The signs of the relevant indirect interactions are actually conditioned by the structure of the LUMO $\varphi_{(-)5}$ itself. We then obtain

$$G'^{(o)}_{(2)2E} > 0, \qquad G'^{(m)}_{(2)2E} > 0, \qquad G'^{(p)}_{(2)2E} < 0 \tag{10.3}$$

for the ortho-, meta- and para- positions of electrophile, respectively. Meanwhile, the relevant direct interactions $G_{(1)2E}$ are of the following signs

$$G^{(o)}_{(1)2E} < 0, \qquad G^{(m)}_{(1)2E} > 0, \qquad G^{(p)}_{(1)2E} > 0 \tag{10.4}$$

that are determined by the constitution of the HOMO of benzene $\varphi_{(+)2}$. Comparison of Eqs.(10.3) and (10.4) allows us to conclude that just the predominant meta attack of electrophile is characterized by the principal interorbital interactions of coinciding signs and thereby may be considered as an allowed process.

The electrocyclic closure of hexatriene (C_6H_8) and the Diels-Alder reaction between butadiene and ethene are the most illustrative representatives of third order pericyclic processes. These systems contain three initially-double (C=C) bonds that form six-membered cycles during the closure process. Thus, a single model may be actually applied to these reactions and the relevant conclusions also closely resemble one another. Let us consider the closure process of hexatriene as an example. Let the AOs $\chi_1, \chi_2, ...\chi_6$ of this molecule to form six BOs that acquire numbers 1,2 and 3, viz. $\varphi_{(+)1}(\varphi_{(-)1})$, $\varphi_{(+)2}(\varphi_{(-)2})$ and $\varphi_{(+)3}(\varphi_{(-)3})$. Resonance parameters between pairs of AOs inside the C=C bonds will be assumed to coincide with 1, whereas those of C-C bonds will be denoted by κ, where $0 < \kappa < 1$. Accordingly, λ will stand for the newly-formed resonance parameter between the terminal AOs χ_1 and χ_6. Orbitals of the terminal bonds C_1=C_2 and C_5=C_6, viz. $\varphi_{(+)1}$ and $\varphi_{(-)3}$, interact both directly (owing to the parameter λ) and indirectly through orbitals of the intervening C_3=C_4 bond. The latter interactions (i.e $G_{(2)13}$) coincide with $\kappa^2/8$ and are positive quantities whatever the actual way of closure. Hence, a positive sign of the direct interaction $G_{(1)13}$ also is required to ensure positive third order transferred population $\delta x^{(3)}_{(+)1,(-)3}$. Inasmuch as $G_{(1)13}$ equals to $\lambda/4$, the above condition proves to be met for positive λ values, the latter corresponding to a disrotatory way of closure. Interactions of other pairs of BOs may be considered analogously. For example, matrix elements describing the interactions between BOs $\varphi_{(+)1}$ and $\varphi_{(-)2}$ are as follows

$$G_{(1)12} = -\frac{\kappa}{4}, \qquad G_{(2)12} = -\frac{\kappa\lambda}{8} \tag{10.5}$$

It is seen that $G_{(1)12}$ and $G_{(2)12}$ are of uniform (negative) signs if λ is a positive parameter as previously. Hence, the disrotatory way of closure of hexatriene meets our definition of an allowed process in accordance with expectation and experimental facts. Hence, similarity between the pericyclic and heterolytic reactions is now supported also in respect of applicability of the common selection rule in terms of signs of direct and indirect interactions.

11 The local retransformation procedure and its applications to define environment- determined intrafragmental effects

In comparative studies of related chemical compounds, we often have to do with distinct systems containing the same fragment(s). Changes in the structures of the environment of the given fragment when passing from one compound to another seems to give rise to certain intrafragmental effects. Such an anticipation follows from numerous experiment- based conclusions. As for instance, replacement of a hydrogen atom of an alkane by a heteroatom is known to cause a definite polarization of the neighboring C-C and C-H bonds (cf. the so-called induced dipoles [85, 98]). An additional polarization of the heteroatom-containing bond under influence of an electron-donating effect of an approaching nucleophile during early stages of S_N2 reactions also may be mentioned here along with a specific reorganization of the aromatic ring into a non-aromatic system under influence of an electrophilic attack

(cf. the Wheland intermediate) [11, 15, 16, 23]. Moreover, the above-enumerated effects are always observed in similar constitutional situations and thereby are likely to be conditioned mostly by the structure of the given fragment and of its nearest environment.

It deserves an immediate mentioning that fragmental orbitals (FOs) underlying the PNCMO theory of Sections 5-8 are not the optimum basis functions in respect of describing the intrafragmental effects. Quite the reverse, just the usual bases of AOs and/or hybrid AOs (HAOs) offer much more convenient representations of the same effects. These standard basis functions, however, do not meet the requirements of the PNCMO theory. To find the way out of this situation, a certain additional procedure evidently is required. Before turning to the latter, let us recall some principles of the standard (canonical) MO method.

The essence of the above-mentioned popular method consists in passing from the initial basis of AOs or HAOs $\{\chi\}$ into that of canonical MOs(CMOs) $\{\psi\}$, wherein the Hamiltonian (or Fockian) matrix of our system $\overline{\mathbf{H}}$ takes the diagonal form [1-3]. The respective representation matrix of the one-electron DM $\overline{\mathbf{P}}$ also is diagonal in the CMO basis and involves occupation numbers of these orbitals equal to either two or zero. This implies no bond orders to arise between CMOs. To obtain the usual CBO matrix of the same system $\mathbf{P'}$ containing populations of AOs(HAOs) and bond orders between the latter, we retransform the matrix $\overline{\mathbf{P}}$ into the AO basis again. The relation concerned is as follows [1]

$$\mathbf{P'}= \mathbf{T}\overline{\mathbf{P}}\mathbf{T}^{+}, \tag{11.1}$$

where the matrix $\mathbf{T}$ contains the standard MO LCAO coefficients in its columns, and the superscript + designates the transposed (or Hermitian-conjugate) matrix as previously. This relation along with the above-specified diagonal constitution of the matrix $\overline{\mathbf{P}}$ yields the usual expressions for elements of the CBO matrix $\mathbf{P'}$ in the form of sums of the MO LCAO coefficients over occupied MOs.

In our context, the most important property of Eq.(11.1) consists in its validity for any pair of basis sets, provided that the DM of the right-hand side is known or easily constructable. The latter requirement is met in the basis of FOs $\{\Phi\}$ as the results of Section 6 indicate. Thus, the retransformation procedure like that of Eq.(11.1) may be alternatively applied [99-101] to derive the usual CBO matrix of our system(s) $\mathbf{P'}$ using the relevant DM of Section 6. Instead of Eq.(11.1) we then obtain

$$\mathbf{P'}= \mathbf{U}\mathbf{P}\mathbf{U}^{+}, \tag{11.2}$$

where $\mathbf{U}$ stands for the matrix of the FO LCAO coefficients. As opposed to the above-desribed standard procedure, the DM under transformation (i.e. $\mathbf{P}$) now contains non-zero off-diagonal elements coinciding with bond orders between FOs defined by Eqs.(6.2) and (6.3). Moreover, diagonal elements of this matrix are somewhat different from either 2 or 0 as follows from Eq.(6.3). Consequently, the actual expression for the CBO matrix being sought generally contains sums of FO LCAO coefficients over all FOs, as well as over their pairs instead of occupied MOs only.

Another important difference of the above-described procedure from the standard one consists in the block-diagonal structure of the retransformation matrix $\mathbf{U}$. To

clarify this point, let us assume our system to consist of certain fragments I,II,III, etc. The total basis of FOs $\{\Phi\}$ will be then accordingly composed of subsets $\{\Phi_I\}, \{\Phi_{II}\}, \{\Phi_{III}\}, etc.$, each of basis orbitals being localized on a single fragment only. Consequently, the total matrix $\mathbf{U}$ is representable as follows

$$\mathbf{U} = \begin{vmatrix} \mathbf{U}_I & 0 & 0 & ... \\ 0 & \mathbf{U}_{II} & 0 & ... \\ 0 & 0 & U_{III} & ... \\ . & . & . & ... \end{vmatrix} \tag{11.3}$$

where $\mathbf{U}_I, \mathbf{U}_{II}, \mathbf{U}_{III}, etc.$ are non-zero submatrices of FO LCAO coefficients of separate fragments. The DMs $\mathbf{P}$ and $\mathbf{P}'$ of Eq.(11.2) also may be divided into intra and interfragmental blocks without any restriction. Substituting the matrix $\mathbf{U}$ of Eq.(11.3) into Eq.(11.2) then allows the overall retransformation procedure to be partitioned into local ones, each of them embracing a single fragment only, e.g.

$$\mathbf{P}'_I = \mathbf{U}_I \mathbf{P}_I \mathbf{U}_I^+, \qquad \mathbf{P}'_{II} = \mathbf{U}_{II} \mathbf{P}_{II} \mathbf{U}_{II}^+, \quad etc. \tag{11.4}$$

and being performable separately. Again, we should recall here that elements of the DM $\mathbf{P}$ of Section 6 contain sums of products of interorbital interactions over the whole molecule under study (see e.g. the definition of the element $G^{(f)}_{(2)il}$ of Eq.(5.14) determining the bond orders between FOs of opposite initial occupation as Eq.(6.2) shows). This implies a particular block of the matrix $\mathbf{P}$ (e.g. $\mathbf{P}_I$) to depend implicitly upon the remaining fragments of the given system. As a result, the relevant submatrix of the CBO matrix obtained (i.e. $\mathbf{P}'_I$, respectively) reflects the influence of the remaining part of the molecule upon the charge and bond order distribution inside the given fragment (I) as demonstrated below. Inasmuch as elements of the DM $\mathbf{P}$ depend mostly on the nearest environment of the FO (FOs) concerned (Section 6), the same state of things may be expected to refer to elements of the CBO matrix $\mathbf{P}'$ too. Additivity of influences of separate neighbors is another anticipation here. The decisive role of FOs of the given fragment and thereby of the structure of the latter in the formation of intrafragmental effects also may be easily predicted on the basis of Eq.(11.4). Indeed, relations shown there indicate that both populations of AOs (HAOs) and bond orders between the latter referring to a definite fragment (I) are expressible as linear combinations of elements of the respective block of the DM $\mathbf{P}(\mathbf{P}_I)$, the nature of these combinations being determined by elements of the matrix $\mathbf{U}_I$, i.e. by the structure of FOs of the given fragment. That is why it appears that the relations of Eq.(11.4) may be analyzed for each type of fragments separately without specifying either the remaining fragments of the system or the interfragmental interaction. As a result, general algebraic expressions have been derived for intrafragmental effects inside the most popular fragments as overviewed below.

The above-outlined retransformation procedure may be easily extended to embrace other characteristics of electronic structures too. For the LMO representation matrix, we accordingly obtain [102]

$$\mathbf{C}' = \mathbf{U}\mathbf{C} \tag{11.5}$$

instead of Eq.(11.2), where $\mathbf{C}'$ refers to the basis of AOs(HAOs). Employment of the block-diagonal matrix $\mathbf{U}$ of Eq.(11.3) followed by the respective partition of

matrices $\mathbf{C}$ and $\mathbf{C}'$ into intra- and interfragmental blocks yields a series of relations

$$\mathbf{C}'_I = \mathbf{U}_I \mathbf{C}_I, \qquad \mathbf{C}'_{II} = \mathbf{U}_{II} \mathbf{C}_{II}, \quad etc. \tag{11.6}$$

representing the relevant local retransformation procedures for LMOs.

To consider the total energy, let us start with the notation that general relations between α- and β-components of corrections $\mathcal{E}_{(k)}$ shown in Eqs.(8.6) and (8.7) are invariant against unitary transformations of the basis set including the above-described retransformation. The same evidently refers to definitions of components $\mathcal{E}^{(\alpha)}_{(k)}$ and $\mathcal{E}^{(\beta)}_{(k)}$ of Eq.(8.5), where matrices $\mathbf{P}_{(k)}, \mathbf{P}_{(k-1)}$, $\mathbf{H}_{(0)}$ and $\mathbf{H}_{(1)}$ should be replaced by their stroked counterparts referring to the basis of AOs (HAOs). If we confine ourselves to fragmentary molecules defined as sets of weakly-interacting elementary fragments I, II, III, etc. (Section 5), the relevant zero order Hamiltonian matrix ($\mathbf{H}'_{(0)}$) may be assumed to take a block-diagonal form like that of Eq.(11.3), where intrafragmental blocks $\mathbf{H}'_{(0)I}, \mathbf{H}'_{(0)II}, etc.$ occupy the diagonal positions. At the same time, the relevant first order member ($\mathbf{H}'_{(1)}$) contains zero submatrices in the same positions. We may conclude on this basis that the energy component $\mathcal{E}^{(\beta)}_{(k)}$ depends on bond orders formed between AOs(HAOs) of different fragments within the correction of the CBO matrix of the (k-1)th order ($\mathbf{P}'_{(k-1)}$) and thereby may be called the interfragmental part of the kth order energy [101]. Meanwhile, the remaining component $\mathcal{E}^{(\alpha)}_{(k)}$ is determined only by intrafragmental elements of the correction $\mathbf{P}'_{(k)}$ [including both occupation numbers of AOs(HAOs) and bond orders between the latter] and proves to be the intrafragmental part of the same energy correction $\mathcal{E}_{(k)}$. Consequently, the relation of Eq.(8.6) becomes interpretable as that between energetic increments of the interfragmental interaction and of the intrafragmental response to the latter. Moreover, stabilization of the whole system due to formation of interfragmental bond orders (if any) necessarily is accompanied by an overall internal destabilization of fragments [This evidently does not imply that any individual fragment is destabilized].

Let us turn now to specific fragments. Let us start with the most widespread fragment, namely the two-center chemical bond. For the sake of generality, let us consider a heteropolar bond between a certain heteroatom (Z) and a carbon atom (C). [The homopolar bond corresponds to a particular case of the heteropolar one]. Let the bond under our interest to acquire the Ith number. Fragmental orbitals (FOs) then coincide with the BBO $\varphi_{(+)i}$ and the ABO $\varphi_{(-)i}$ and are defined as simple linear combinations of respective AOs (HAOs) χ_Z and χ_C. Diagonal elements of the original DM $\mathbf{P}$ referring to BOs $\varphi_{(+)i}$ and $\varphi_{(-)i}$ then follow from Eq.(6.3) and coincide with respective occupation numbers $X_{(+)i}$ and $X_{(-)i}$, whereas the only off-diagonal element (bond order between the same BOs) is defined by Eq.(6.2) and contains elements $G_{(1)ii}, G_{(2)ii}, etc.$ After performing the above-described local retransformation procedure, the occupation numbers of AOs (HAOs) χ_Z and χ_C have been expressed as follows [101-105]

$$\begin{aligned} X_Z\ (X_C) = & 1 \pm \cos\gamma_I + \frac{1}{2}\Delta X_{(2)I} \pm p_{(2)I} \pm d_{(2)I} + \\ & \frac{1}{2}\Delta X_{(3)I} \pm p_{(3)I} \pm d_{(3)I} + ... \end{aligned} \tag{11.7}$$

where the upper signs of the right-hand side refer to X_Z, whereas the lower ones correspond to X_C. Notation γ_I is used here for the principal parameter of our bond defined as follows

$$\gamma_I = \arctan \frac{2\beta_I}{\alpha_{IZ} - \alpha_{IC}}, \tag{11.8}$$

where α_{IZ} and α_{IC} stand for Coulomb parameters of AOs (HAOs) χ_Z and χ_C, respectively, and β_I is the relevant intrabond resonance parameter. The energy reference point and the energy unit are assumed here to be chosen so that parameters α_{IZ}, α_{IC} and β_I take positive values and the equality $\alpha_{IZ} \geqslant \alpha_{IC}$ is valid (a negative energy unit is actually accepted).

The contributions $1/2\Delta X_{(k)I}, (k = 2, 3...)$ of Eq.(11.7) are related to respective members of power series for occupation numbers of BOs ($X_{(+)i}$ and $X_{(-)i}$), viz.

$$\Delta X_{(k)I} = X^{(k)}_{(+)i} + X^{(k)}_{(-)i} - 2 \tag{11.9}$$

and represent the total kth order populations lost (acquired) by the Ith bond due to its interaction with neighboring fragments. As for instance, the second order member $\Delta X_{(2)I}$ takes the form

$$\Delta X_{(2)I} = 2 \sum_{(+)j} [(G_{(1)ji})^2 - (G_{(1)ij})^2], \tag{11.10}$$

(see Eqs.(6.6)-(6.8)). It is seen that the increment $\Delta X_{(2)I}$ actually consists of difference between absolute values of the population lost by the BBO $\varphi_{(+)i}$ and of that acquired by the ABO $\varphi_{(-)i}$. The remaining increments of Eq.(11.7) are as follows

$$p_{(k)I} = -2G_{(k)ii} \sin \gamma_I, \quad d_{(k)I} = \frac{1}{2} \Delta R_{(k)I} \cos \gamma_I, \tag{11.11}$$

where the term

$$\Delta R_{(k)I} = X^{(k)}_{(+)i} - X^{(k)}_{(-)i} - 2 \tag{11.12}$$

describes the total kth order redistributed population referring to the Ith bond. The respective second order member is accordingly representable as follows

$$\Delta R_{(2)I} = -2 \sum_{(+)j} [(G_{(1)ji})^2 + (G_{(1)ij})^2]. \tag{11.13}$$

This term is determined by the sum of absolute values of the above-mentioned lost and acquired populations. It is seen that negative contributions to $\Delta R_{(2)I}$ arise owing to both the additional occupation of the ABO $\varphi_{(-)i}$ and the partial deoccupation of the BBO $\varphi_{(+)i}$ (see Eqs.(6.6)-(6.8)) to within the second order approximation. Hence, a negative sign of the second order redistributed population $\Delta R_{(2)I}$ unambiguously follows. The analogous formula for the internal bond order (B_I) between AOs (HAOs) χ_Z and χ_C, in turn, takes the form

$$B_I = \sin \gamma_I + \lambda_{(2)I} + \omega_{(2)I} + \lambda_{(3)I} + \omega_{(3)I} + ... \tag{11.14}$$

where

$$\lambda_{(k)I} = 2G_{(k)ii} \cos \gamma_I, \quad \omega_{(k)I} = \frac{1}{2} \Delta R_{(k)I} \sin \gamma_I \tag{11.15}$$

for $k = 2, 3..etc.$

Let us turn now to interpretation of these expressions. The zero order dipole-like increment $\pm\cos\gamma_I$ to populations of orbitals χ_Z and χ_C does not depend on the structure of the whole compound and has been interpreted as the primary dipole of the Ith bond. Similarly, the zero order term of Eq.(11.14), i.e. $\sin\gamma_I$, coincides with the respective primary bond order. Alterations both in occupation numbers of orbitals χ_Z and χ_C and in the internal bond order after embedding the Ith bond into our molecule are then determined by subsequent terms of Eqs.(11.7) and (11.14) starting with $k = 2$. Additive nature of these alterations with respect to contributions of the remaining fragments of the given compound follows straightforwardly from Eqs.(11.10) and (11.13) along with the relevant property of indirect interorbital interactions $G_{(k)ij}$ (Section 5). Additivity between the environment- determined corrections and the primary characteristics of our bond also deserves mentioning. Again, dependence of the same alterations mostly on the structure of the nearest environment of the given bond may be concluded on the basis of extinction of matrix elements $G_{(k)ij}$ and $G_{(k)ii}$ when the distance between the BOs concerned grows. Thus, the environment- determined intrabond effects seem to be in line with the classical rule of locality in addition. Transferability of these effects for the same neighborhoods of the Ith bond also is among expectations. It deserves emphasizing here that the above conclusions are drawn without specifying the structure of the whole compound and thereby are of a quite general scope of validity. More information concerning the nature of the intrabond effects follows from analysis of separate second order terms of Eqs. (11.7) and (11.14).

Let us start with terms originating from the interfragmental charge redistribution (charge transfer): First, uniform increments $(1/2)\Delta X_{(2)I}$ to occupation numbers of both χ_Z and χ_C may be mentioned that coincide with a half of the total population lost (acquired) by the given bond. Meanwhile, it is the dipole-like term $\pm d_{(2)I}$ that is responsible for the non-uniform actual distribution of the same lost (acquired) population among AOs (HAOs) χ_Z and χ_C. Moreover, the *a priori* negative sign of $d_{(2)I}$ follows from the above-discussed negative sign of $\Delta R_{(2)I}$. This implies the lost (acquired) population always to give rise to lowering of the primary dipole of our bond. This effect may be easily accounted for by constitution of the BBO $\varphi_{(+)i}$ and of the ABO $\varphi_{(-)i}$ and has been accordingly called depolarization. Similarly, the contribution $\omega_{(2)I}$ to the bond order B_I also is a negative quantity depending on the same total redistributed population $\Delta R_{(2)I}$. This implies reduction of the primary bond order under influence of the interfragmental charge redistribution. The above-mentioned simultaneous effects (i.e. depolarization of an initially-heteropolar bond and the related reduction of the internal bond order) reflect a trend towards a homolytic dissociation of the given bond after including it into the molecule under study. In this connection, the term 'homolytic predissociation' seems to describe these interdependent effects [101].

Let us turn now to the remaining second order terms $p_{(2)I}$ and $\lambda_{(2)I}$ originating from the newly-formed bond order between BOs of the given bond ($\varphi_{(+)i}$ and $\varphi_{(-)i}$). The sign of the matrix element $G_{(2)ii}$ contained within the relevant expressions of Eqs.(11.11) and (11.15) cannot be established *a priori* (i.e. without specifying the structure of the system). The same then refers to signs of both $p_{(2)I}$ and $\lambda_{(2)I}$. Nevertheless, an interdependence between these signs is evident, namely reduction

of the bond order (predissociation) is expected to take place for a negative element $G_{(2)ii}$ and this effect is predicted to be accompanied by emergence of a positive dipole $p_{(2)I}$. Just this fact makes the term polarization dipole used to refer to $p_{(2)I}$ [103] even more appropriate. Inasmuch as the total dipole of our bond grows in this case, we have actually to do with the 'heterolytic predissociation' of our initially-heteropolar bond [101]. Thus, two alternative ways of predissociation reveal themselves as the principal intrabond effects in the case of a heteropolar bond. Moreover, emergence of just these effects may be entirely traced back to the structure of BOs $\varphi_{(+)i}$ and $\varphi_{(-)i}$ and thereby of the given bond. In this connection, the effects themselves may be regarded as manifestation of the principle of locality in the sense that their nature is entirely determined by the relevant local structure. This state of things is largely similar to that concerning the local constitution of MOs (Section 3). Additivity of contributions representing the homo- and heterolytic ways of the overall predissociation of our bond also is among important conclusions. Owing to the opposite nature of these two alternatives, we may then expect a certain competition to take place between them in an actual compound, the outcome of which seems to depend upon the specific constitution of the latter. An example of such a competition may be found in Ref.[105], where the additional dipole of a single or double heteroatom-containing bond has been studied that arises under influence of an electron-donating effect of an external orbital (e.g. of an approaching nucleophile). It turned out that the direction of the additional dipole depends decisively on the relative electronegativity of the heteroatom Z and thereby on the initial polarity of the bond. Moreover, predominance of the polarization dipole and thereby of the heterolytic predissociation in general has been found for bonds of relatively low initial polarity but not for those of high polarity. This result served to account for the well-known experimental fact that highly electronegative heteroatoms usually are bad nucleofuges in S_N2 processes [11,15,85].

Let us return again to expressions of Eqs.(11.7)-(11.15) and consider the particular case of a homopolar bond characterized by equalities $\alpha_{I1} = \alpha_{I2}, \gamma_I = \pi/2$ and $\cos\gamma_I = 0$. The depolarization dipole $d_{(2)I}$ is then easily seen to vanish and the homolytic predissociation actually resolves itself into lowering of the bond order in accordance with the expectation. Again, a secondary polarization $p_{(2)I}$ also may arise in homopolar bonds. In particular, these terms were shown to be responsible for the induced dipoles of C-C (C-H) bonds under influence of a heteroatom-containing bond (cf. the so-called inductive effect). Emergence of such a dipole, however, is not accompanied by reduction of the internal bond order (as $\lambda_{(2)I} = 0$ for homopolar bonds) and thereby does not imply its heterolytic predissociation.

Terms of Eqs.(11.7) and (11.14) of higher orders may be analyzed similarly. As opposed to the above-discussed second order term $\Delta R_{(2)I}$, however, the sign of the relevant third order analogue ($\Delta R_{(3)I}$) cannot be established *a priori*. Nevertheless, lowering of the bond order B_I (predissociation) corresponds to negative signs of $\Delta R_{(3)I}$ as Eq.(11.15) indicates. Consequently, the third order homolytic predissociation also may be defined for heteropolar bonds in analogy with its second order counterpart discussed above. An example of systems, when the third order increments are important, may be found in Ref.[104].

Finally, application of Eqs.(11.5) and (11.6) to our heteropolar bond allowed us to express the so-called heads of LMOs $\Psi_{(+)i}$ and $\Psi_{(-)i}$ attached to our bond [102]

as linear combinations of AOs (HAOs) χ_Z and χ_C , e.g.

$$\Psi_{(+)i} = r_I\chi_Z \ + s_I\chi_C + ... \tag{11.16}$$

where dots stand for the tail of the LMO. Thereupon, we have found twofold squares of coefficients r_I and s_I, as well as their twofold product. Comparison of these expressions to those of Eqs.(11.7) and (11.14) allowed us then to establish the contribution of the own LMO of the Ith bond and thereby of the respective "own" pair of electrons to the overall homo and/or heterolytic predissociation. The relevant study [102] showed that the heterolytic predissociation, in general, and the polarization dipole, in particular, may be entirely traced back to reshaping of the "own" LMO $\Psi_{(+)i}$ and thereby to shift of the "own" pair of electrons of the Ith bond. This conclusion embraces also the formation of secondary dipoles of initially homopolar bonds (e.g. of C-C and C-H bonds in substituted alkanes). Meanwhile, the overall situation concerning the homolytic predissociation is somewhat more complicated. Thus, the parts of the depolarization dipole $d_{(2)I}$ and of the related reduction of the bond order $\omega_{(2)I}$ originating from deoccupation of the BBO $\varphi_{(+)i}$ and proportional to $X_{(+)i}$ (see Eq.(11.12)) may be traced back to contribution of the LMO $\Psi_{(+)i}$, whilst the remaining ($X_{(-)i}$-containing) parts of the same characteristics result from contributions of occupied LMOs of other bonds extending over the ABO $\varphi_{(-)i}$. Consequently, the hypothesis of the classical chemistry about bond dipoles resulting from shifts of separate pairs of electrons may be proven provided that the dipole concerned originates mainly from the polarization term, i.e. for bonds of relatively low initial polarity.

Similar local retransformation procedures have been developed also for other fragments, e.g. for phenyl rings [106]. The latter evidently are more extended systems as compared to a homopolar bond. In this connection, a few analogues of the polarization dipole $p_{(2)I}$ and of the term $1/2\Delta X_{(2)I}$ arise in the relevant expression for occupation numbers of $2p_z$ AOs of carbon atoms. In particular, three environment-determined secondary (induced) dipoles have been revealed instead of the single one (i.e. of $p_{(2)I}$), namely the so-called ipso-ortho (para-meta), para-ipso and ortho-meta dipoles. Just the latter two moments proved to play the principal role in the formation of the observed picture of the electron density distribution in substituted benzenes.

Applications of analogous retransformation procedures to two weakly- interacting molecules A and B [99,100] also deserve mentioning, where CMOs of isolated compounds play the role of FOs. Explicit algebraic expressions have been derived and analyzed in this case for the reorganization of bonding inside the reactant (say A) under influence of an approaching reagent (B). The crucial role of the initial structure of the substrate (A) in the subsequent reorganization of bonding during the reaction process was the principal conclusion here that is in line with the usual discussions of chemical reactivity of a certain compound in terms of peculiarities of its initial constitution. A detailed overview of the relevant achievements may be found in Ref.[99]. The case of allyle cation (anion) under attack of nucleophile (electrophile) [100] is an especially illustrative example of these studies. Two effects have been revealed to manifest itself inside the allyle ion if a particular terminal carbon atom is attacked by the reagent, namely an induced lengthwise polarization and a partial switch of bond order from one C-C bond to another. As a result, a

trend is observed towards formation of a lone electron pair and of vacancy at the carbon atom under attack for systems anion+ electrophile and cation+ nucleophile, respectively, along with weakening of the nearest C-C bond and strengthening of the remaining bond. This phenomenon has been called the deconjugation effect.

Given that the system under study consists of uniform fragments (as it is the case with simple homogeneous fragmentary molecules defined in Section 5), retransformation procedures of Eqs.(11.4) and (11.6) also are similar. As a result, these may be joined together to embrace total matrices $\mathbf{P}$ and $\mathbf{C}$ instead of their separate blocks ($\mathbf{P}_I$ and $\mathbf{C}_I$). To this end, a certain renumbering of basis orbitals (both of FOs and of AOs (HAOs)) is required. As a result, separate blocks of the retransformed DM start to yield individual intrafragmental effects [107,108]. If we assume, for example, that our system consists of N homopolar bonds, matrix analogues may be constructed for terms $1/2\Delta X_{(k)I}$, $p_{(k)I}$ and $\omega_{(k)I}$ of Eqs.(11.9), (11.11) and (11.15) that accordingly represent the interbond charge redistribution, the intrabond polarization and the so-called rebonding effect [107] [Note that lowering of internal bond orders due to the increment $\omega_{(2)I}$ is related to formation of those between BOs of different bonds as discussed above and this fact serves to justify the term 'rebonding']. Given that our system is supposed to be alternant in addition [this case embraces the aliphatic conjugated hydrocarbons], the matrix analogue of the increment $\omega_{(k)I}$ (denoted by $\Omega_{(k)}$) proved to be the only non-zero submatrix of the retransformed correction $\mathbf{P}'_{(k)}$. Accordingly, the rebonding effect starts to play the decisive role in the formation of the relevant electronic structures [108].

It is seen, therefore, that universal environment-determined intrafragmental effects may be defined and studied for systems containing a certain common fragment. Moreover, the rules of qualitative chemical thinking (viz. additivity, transferability and locality) are applicable in discussions of these effects.

12 The non-canonical MO theory of alternant hydrocarbons

Alternant hydrocarbons (AHs) are among the first and most popular objects of quantum chemistry. Application of the standard HMO theory (based on the Hückel model in the framework of the canonical MO method) was especially fruitful here. These studies resulted into the well-known common rules governing the structures of CMOs of AHs and the relevant one-electron energies that are included nowadays into almost all quantum chemistry textbooks (see e.g. [22, 48]). It also deserves mentioning that CMOs of AHs are delocalized over the whole system and depend on their individual structures as usual. The less-known general form of the relevant CBO matrix $\mathbf{P}$ [31] may be added here as a related achievement and/or as a corollary of the above-mentioned common constitution of CMOs of AHs. Two alternative expressions have been obtained for the matrix $\mathbf{P}$, viz.

$$\mathbf{P} = \begin{vmatrix} \mathbf{I} & \mathbf{RB} \\ \mathbf{B}^{+}\mathbf{R} & \mathbf{I} \end{vmatrix}, \quad \mathbf{P} = \begin{vmatrix} \mathbf{I} & \mathbf{BQ} \\ \mathbf{QB}^{+} & \mathbf{I} \end{vmatrix}, \tag{12.1}$$

where $\mathbf{B}$ is the only non-zero submatrix of the common Hückel type Hamiltonian matrix of AHs shown in Eq.(3.1) and

$$\mathbf{R} = (\mathbf{B}\mathbf{B}^{+})^{-1/2}, \qquad \mathbf{Q} = (\mathbf{B}^{+}\mathbf{B})^{-1/2}. \tag{12.2}$$

[Note that the positive square root is assumed to be chosen here]. Uniqueness of the matrix $\mathbf{P}$ is ensured here by the equality

$$\mathbf{R}\mathbf{B} = \mathbf{B}\mathbf{Q}. \tag{12.3}$$

The common CBO matrix of AHs $\mathbf{P}$ of Eq.(12.1) indicates these systems to resemble a single object. An analogous conclusion about AHs being a class of chemical compounds has been drawn also in Section 3. Thus, existance of the relevant common LMO representation matrix $\mathbf{C}$ is among natural expectations here.

To prove this hypothesis, we should evidently turn to the block-diagonalization problem like that of Eq.(5.1) for the common Hamiltonian matrix of AHs shown in Eq.(3.1). The basis of $2p_z$ AOs $\{\chi\}$ may be assumed to be orthogonal as usual and thereby the unitarity condition of Eq.(5.2) may be imposed on the matrix $\mathbf{C}$ being sought. So far as the standard requirements of perturbation theory are concerned, these are not met by the Hamiltonian matrix of AHs of Eq.(3.1). Thus, we have to look for a non-perturbative solution of the relevant block-diagonalization problem.

Solution of the above-desired type has been found in Ref.[109]. As a result, two alternative forms of the matrix $\mathbf{C}$ like those of Eq.(12.1) have been derived, viz.

$$\mathbf{C} = \frac{1}{\sqrt{2}} \begin{vmatrix} \mathbf{I} & \mathbf{R}\mathbf{B} \\ \mathbf{B}^{+}\mathbf{R} & -\mathbf{I} \end{vmatrix}, \quad \mathbf{C} = \frac{1}{\sqrt{2}} \begin{vmatrix} \mathbf{I} & \mathbf{B}\mathbf{Q} \\ \mathbf{Q}\mathbf{B}^{+} & -\mathbf{I} \end{vmatrix}. \tag{12.4}$$

A large extent of similarity between matrices $\mathbf{C}$ and $\mathbf{P}$ is evident. Moreover, the matrix $\mathbf{P}$ of Eq.(12.1) was shown to follow also from the commutation equation of Eq.(6.1), i.e. without invoking CMOs. Expressions of Eqs.(12.1) and (12.4) form the basis for the non-canonical MO theory of AHs and their derivatives developed in Refs [109-113].

Let us turn now to the principal achievements of this alternative theory and start with properties of NCMOs (LMOs) of AHs [109]. Expressions for these MOs easily follow from Eq.(12.4). In particular, an occupied NCMO ($\Psi_{(+)i}$) and a vacant one ($\Psi_{(-)m}$) take the form

$$\begin{aligned} \Psi_{(+)i} &= \frac{1}{\sqrt{2}}[\chi_i^{*} + \sum_{k=1}^{n} \chi_k^{\circ}(\mathbf{B}^{+}\mathbf{R})_{ki}], \\ \Psi_{(-)m} &= \frac{1}{\sqrt{2}}[-\chi_m^{\circ} + \sum_{j=1}^{n} \chi_j^{*}(\mathbf{B}^{+}\mathbf{R})_{jm}], \end{aligned} \tag{12.5}$$

where sums over k and over j embrace AOs of subsets $\{\chi^{\circ}\}$ and $\{\chi^{*}\}$, respectively. It is seen that each NCMO is attached to an individual AO. Thus, one-to-one correspondence between NCMOs and AOs immediately follows along with the zero intrasubset delocalization of the former. Moreover, occupied and vacant NCMOs originate from different subsets of AOs, i.e. from $\{\chi^{*}\}$ and $\{\chi^{\circ}\}$, respectively.

Furthermore, uniform extents of delocalization are among the most important distinctive features of NCMOs of AHs. Thus, both the relative weights of the principal basis orbitals (AOs) and the respective total intersubset delocalization coefficients are uniform for all NCMOs and equal to 1/2. This result also implies that partial delocalization of NCMOs cannot exceed the relative weight of the principal AO. Hence, NCMOs of AHs are actually of the principal- orbital- and-tail constitution as it was the case with other classes of molecules.

Finally, from similarity of Eqs.(12.1) and (12.4) it follows that the vectors of coefficients of NCMOs of AHs coincide with respective columns (rows) of the CBO matrix $\mathbf{P}$ (up to the normalization factor $1/\sqrt{2}$). Consequently, the shapes of particular NCMOs may be predicted on the basis of bond orders that are formed by the respective principal AO and the AOs of the opposite subset. In particular, the AO of the second subset χ_k° contributes to the NCMO $\Psi_{(+)i}$ if the bond order between AOs χ_k° and χ_i^* takes a non-zero value. Substantial bond orders of conjugated hydrocarbons are known to arise for neighboring pairs of $2p_z$ AOs corresponding to chemical bonds, whilst those for other (non-neighboring) pairs are at least two times smaller. These trends allow us to expect that the shape of a certain NCMO (e.g. of $\Psi_{(+)i}$) depends decisively upon the number of the nearest neighbors for the carbon atom (C_i), the respective principal AO (χ_i^*) is pertinent to and thereby on valency of this atom. Inasmuch as mono-, di- and tri-valent carbon atoms are present in AHs, the relevant NCMOs may be accordingly classified into two-, three- and four-center non-canonical orbitals. As compared to LMOs of the bond-orbital- and- tail constitution of alkanes (Section 5), the above-mentioned NCMOs are generally less localized. This principal conclusion is in line with the well-known hypothesis about the increasing overall extent of delocalization of separate pairs of electrons when passing from saturated hydrocarbons (alkanes) to their unsaturated analogues and especially to aromatic compounds. It deserves adding in this context that the chemical classification of molecules, in general, is based on the presumed different extents of delocalization of these pairs in real space [10,85].

Let us turn now to comparison of NCMOs of AHs shown in Eq.(12.5) to the $\varepsilon-$dependent basis orbitals (GBOs) of the same systems [33] discussed in Section 3 and shown in Eq.(3.5). Let us note first that the eigenblocks ($\mathbf{E}_1$ and $\mathbf{E}_2$) of the common Hamiltonian matrix of AHs of Eq.(3.1) (corresponding to the subsets of occupied and vacant NCMOs, respectively) are as follows

$$\mathbf{E}_1 = \mathbf{R}^{-1} = (\mathbf{B}\mathbf{B}^+)^{1/2}, \quad \mathbf{E}_2 = -\mathbf{Q}^{-1} = -(\mathbf{B}^+\mathbf{B})^{1/2}. \tag{12.6}$$

This implies that the occupied CMOs of AHs are expressible as linear combinations of only occupied NCMOs (LMOs) $\Psi_{(+)i}, i = 1, 2...N$, the coefficients of these combinations coinciding with eigenvectors of the matrix $(\mathbf{B}\mathbf{B}^+)^{1/2}$. [In the case of vacant CMOs(NCMOs), the matrix $(\mathbf{B}^+\mathbf{B})^{1/2}$ playes the same role]. Inasmuch as matrices $\mathbf{B}\mathbf{B}^+$ and $(\mathbf{B}\mathbf{B}^+)^{1/2}$ are characterized by a common set of eigenvectors, we may then conclude both the above-mentioned linear combination and its counterpart in terms of GBOs (see Eq.(3.4) of Section 3) to contain the same set of coefficients. This fact makes the comparison of NCMOs to GBOs even more intriguing.

Similarity between NCMOs of AHs and their GBOs is beyond any doubt. Indeed, both (occupied) NCMOs $\Psi_{(+)i}$ and the relevant GBOs $\varphi_i(\varepsilon)$ are attached to individual AOs χ_i^* as Eqs.(3.5) and (12.5) indicate. Moreover, the overall shapes

of both orbitals are determined by the valency of the respective carbon atom and thereby by the local structure. Thus, the conclusion of Section 3 about the local structures of CMOs of AHs to be determined by local spatial constitutions of these hydrocarbons proves to be additionally supported. Again, significant differences between these orbitals also deserve mentioning. The most important one concernes the way, the influence of the global structure upon the particular orbital is represented by. Indeed, this influence manifests itself via the eigenvalue ε_i and via the bond orders $(B^+R)_{ki}$ in the GBO $\varphi_i(\varepsilon_i)$ of Eq.(3.5) and in the NCMO $\Psi_{(+)i}$ of Eq.(12.5), respectively. Accordingly, the NCMOs of Eq.(12.5) possess tails embracing the remaining AOs of the opposite subset along with their principal parts localized on the nearest neighborhood of the given carbon atom. Meanwhile, GBOs possess no such tails and thereby are more localized. Finally, the NCMOs of the present section are orthogonal and eigenvalue-independent, whereas GBOs represent just the opposite case.

Transformability of the common Hückel type Hamiltonian matrix of Eq.(3.1) into a block-diagonal form by means of the matrix $\mathbf{C}$ of Eq. (12.4) allowed a new and efficient methodology to be developed for solution of block-diagonalization problems and/or commutation equations for more involved Hamiltonian matrices representing various derivatives of AHs [110-113]. In these cases, the total Hamiltonian matrix contains a zero order term $\mathbf{H}_{(0)}$ referring to the respective parent AHs and a first order term $\mathbf{H}_{(1)}$. The overall solution procedure then consists of three principal steps: i) An initial passing to the basis of NCMOs of the parent AHs by applying the transformation of Eq.(12.4) to both terms of the total Hamiltonian matrix, ii) Application of the perturbation theory like that of Sections 5 and 6 to solve the relevant non-canonical problems for the transformed Hamiltonian matrix and iii) The subsequent retransformation of the results of the second step into the basis of AOs $\{\chi\}$ again.

The above-described methodology has been successfully applied to study the so-called perturbed AHs (PAHs) in Ref.[110], including systems characterized by a certain alteration of an individual Coulomb parameter originating from replacement of the respective carbon atom by a more electronegative heteroatom. The first order member $\mathbf{P}_{(1)}$ of the power series for the CBO matrix $\mathbf{P}$ of AHs due to perturbation has been analyzed. The well-known results concerning the consequent charge and bond order redistributions in AHs have been rederived in this study without invoking CMOs (including the famous rule of the alternating polarity). On this basis, the above-mentioned results have been considered as a part of the NCMO theory of PAHs.

Relations between reshapings of NCMOs due to perturbations and the relevant charge redistributions rank among the principal new achievements of the same theory. In particular, reshaping of a single NCMO was shown to reflect the rule of the alternating polarity, namely of that NCMO the principal AO of which coincides with the site of perturbation. Moreover, the overall reshaping pattern of NCMOs proved to be in line with predictions of the simple resonance theory about increased contributions of certain quinoidal structures to the electronic strctures of PAHs due to perturbations.

Obtaining of general algebraic expressions for the second order corrections ($\mathbf{P}_{(2)}$) to the CBO matrix of AHs ($\mathbf{P}$) also is among new achievements [111]. These correc-

tions were shown to determine alterations in bond orders between chemically bound pairs of atoms of AHs under influence of the most popular types of perturbation, as well as to play an important role in the formation of the stabilization energy of PAHs [Invariance of Eqs.(8.4)-(8.7) towards an unitary transformation including the matrix **C** of Eq.(12.4) allows the component $\mathcal{E}_{(2)}^{(\alpha)}$ of AHs to be related to alterations in the neighboring bond orders due to perturbation]. On this basis, an additional insight was given into the content of the well-known formulae for total energies of PAHs in terms of self-polarizabilities of atoms and bonds, viz. an energy correction was shown to be made up of a difference between the primary stabilizing contribution of perturbation (which is twice as large as the final stabilization energy) and the destabilizing increment related to weakening of remaining chemical bonds. Again, the same stabilization energy has been established to be additive with respect to contributions of separate chemical bonds. Finally, a non-trivial and intriguing similarity has been concluded between electronic structures of compounds originating from the same parent hydrocarbon (R) after perturbation of the Coulomb parameter of a certain AO χ_r and after building up a composite AH (R-R') by formation of a new bond between AOs χ_r and $\chi_{r'}$ of two identical AHs R and R' (e.g. pyridine and biphenyl). Besides, this similarity is in line with conclusions of the simple resonance theory too.

Another application of the same methodology concerns the substituted AHs (SAHs) [112]. New rules have been established that govern the effects of substituents upon charge and bond order redistributions in AHs. In particular, two additive components have been revealed within these effects, namely the charge transfer between the AH and the substituent and the intersubset polarization inside the AH, the latter being governed by a second order analogue of the rule of the alternating polarity. As a result, a certain analogy has been concluded between electron density distributions in PAHs and SAHs containing an electron-accepting substituent.

Finally, the latest achievement in the same field [113] concerns relative reactivities of carbon atoms of PAHs vs. those of the parent AHs in the electrophilic substitution (S_E2) reactions. Indeed, replacement of a carbon atom of an AH by a more electronegative heteroatom (e.g. when passing from benzene to pyridine) is known to give rise to suppression of reactivities of the remaining carbon atoms. To prove this experiment-based rule, the reactivities were related to the relevant extents of the intermolecular charge transfer. General algebraic expressions have been derived and analyzed for these extents for various directions of the attack of electrophile, the latter being represented by a single initially-vacant orbital ($\varphi_{(-)E}$) (Section 9). Changes in the intermolecular charge transfer when passing from an AH to a PAH were shown to consist of two components, viz. of an initial-population-dependent component contributing increments of alternating signs for shifting positions of electrophile along the hydrocarbon chain and of an additional negative contribution originating from the increased interval between one-electron energies of orbitals participating in the charge transfer. For soft electrophiles, the negative contribution was shown to predominate over the alternating one. This implies the charge transfer between heteroaromatic reactants (PAHs) and electrophiles to be suppressed vs. the relevant values for hydrocarbon-containing systems. Hence, the above-discussed result of Ref. [81] concerning the suppressed reactivity of pyridine vs. benzene (Section 9) is now generalized to any pair of a PAH and of its parent

13 Applications of the block-diagonalization transformation beyond the limits of the Brillouin theorem

In Section 5, the block-diagonalization problem arose as a matrix representation of the Brillouin theorem (see Eqs.(5.1)-(5.3) and discussion nearby). The initial Hamiltonian matrix (**H**) has been transformed in this case into a specific block-diagonal matrix (**E**), namely into that consisting of two eigenblocks $\mathbf{E}_1^{(n\times n)}$ and $\mathbf{E}_2^{(s\times s)}$, the dimension of the former (n) being unambiguosly determined by the total number of electrons in the given system ($2n$). To formulate and to solve this non-canonical one-electron problem perturbatively, the system under study was additionally assumed to be representable by two weakly-interacting subsets of basis functions $\{\mathbf{\Phi}_1\}$ and $\{\mathbf{\Phi}_2\}$. After partitioning the initial matrix **H** into respective four submatrices (blocks), the intersubset blocks (**R**) have been accordingly supposed to be first order terms vs. the intrasubset ones (see Eq.(5.4)). Solution of the problem has been consequently expressed in terms of entire blocks of the matrix **H** without specifying their internal structures.

It is evident that neither the block-diagonalization problem itself nor its solution of the above-discussed rather general nature are necessarily related to the Brillouin theorem. Indeed, we may look for transformation of our initial matrix (**H**) into a block-diagonal form of any constitution, e.g. into that consisting of N eigenblocks $\mathbf{E}_1^{(m\times m)}$, $\mathbf{E}_2^{(s\times s)}$, $\mathbf{E}_3^{(p\times p)}$ ...$\mathbf{E}_N^{(t\times t)}$ of arbitrary dimensions $m, s, p, ..t$, whatever the total number of electrons. Given that our system is additionally representable by N weakly interacting subsets of corresponding dimensions $\{\mathbf{\Phi}_1\}$, $\{\mathbf{\Phi}_2\}$, $\{\mathbf{\Phi}_3\}$... $\{\mathbf{\Phi}_N\}$, the above-described perturbative way of solution also seems to be accordingly generalizable. It is also obvious that transformations of this type may serve as intermediate steps in the way of diagonalization of the matrix **H**, i.e. as additional procedures inside the canonical one-electron problem.

To clarify what is the good of this extra expenditure, let us dwell on molecules and/or molecular systems consisting of N weakly interacting subsystems. Let the basis functions of individual subsystems to be included into separate subsets $\{\mathbf{\Phi}_1\}$, $\{\mathbf{\Phi}_2\}$, $\{\mathbf{\Phi}_3\}$... $\{\mathbf{\Phi}_N\}$. Suppose that the relevant total Hamiltonian matrix is transformed into a block-diagonal form consisting of N eigenblocks $\mathbf{E}_1^{(m\times m)}$, $\mathbf{E}_2^{(s\times s)}$, $\mathbf{E}_3^{(p\times p)}$ ...$\mathbf{E}_N^{(t\times t)}$ of the appropriate dimensions. These eigenblocks then seem to coincide with effective Hamiltonian matrices for separate subsystems influenced by the intersubsystem interaction. Moreover, elements of these matrices are likely to comply with the rule (principle) of locality just owing to the perturbative nature of expressions for eigenblocks. In this respect, a certain analogy may be expected between the approach under present discussion and the alternative way of dealing with eigenvalue equations outlined in Section 3.

Let us now turn to illustrations of these rather abstract assertions. Let us confine ourselves first to the simplest case of systems containing two weakly interacting subsystems ($N = 2$). The initial Hamiltonian matrix of our system is then repre-

sentable as shown in Eq.(5.4), except for the dimensions of blocks m and s being now determined by sizes of subsystems instead of the total number of electrons. The same evidently refers to dimensions of eigenblocks $\mathbf{E}_1^{(m\times m)}$ and $\mathbf{E}_2^{(s\times s)}$ being sought. The block-diagonalization problem to be considered also coincides with that shown in Eqs. (5.1) and (5.2). Thus, no more is now required as to supplement the solution of Section 5 by expressions for eigenblocks. These are as follows [114]

$$\begin{aligned}\mathbf{E}_1^{(m\times m)} =&\mathbf{E}_{(+)}+\mathbf{T}-\frac{1}{2}(\mathbf{R}\mathbf{G}_{(1)}^{+}+\mathbf{G}_{(1)}\mathbf{R}^{+})-\frac{1}{2}(\mathbf{R}\mathbf{G}_{(2)}^{+}+\mathbf{G}_{(2)}\mathbf{R}^{+})-...,\\ \mathbf{E}_2^{(s\times s)} =&-\mathbf{E}_{(-)}+\mathbf{Q}+\frac{1}{2}(\mathbf{G}_{(1)}^{+}\mathbf{R}+\mathbf{R}^{+}\mathbf{G}_{(1)})+\frac{1}{2}(\mathbf{G}_{(2)}^{+}\mathbf{R}+\mathbf{R}^{+}\mathbf{G}_{(2)})+...,\end{aligned}\quad(13.1)$$

where terms of power series to within the third order inclusive are explicitly shown. Matrices $\mathbf{G}_{(1)}$ and $\mathbf{G}_{(2)}$ coincide with those of Sections 5 and are conditioned by Eq.(5.7) as previously.

As is seen from Eq.(13.1), the zero and first order members of the power series for eigenblocks coincide with respective blocks of the matrix $\mathbf{H}$ of Eq.(5.4) referring to subsets $\{\mathbf{\Phi}_1\}$ and $\{\mathbf{\Phi}_2\}$. Thus, correspondence between the eigenblocks $\mathbf{E}_1^{(m\times m)}$ and $\mathbf{E}_2^{(s\times s)}$, on the one hand, and subsystems of our system, on the other hand, is beyond any doubt. At the same time, the eigenblocks imbibe the intersubsystem interaction as the second and third order terms of the same expressions indicate. Hence, matrices $\mathbf{E}_1^{(m\times m)}$ and $\mathbf{E}_2^{(s\times s)}$ are nothing more than those of effective Hamiltonians of subsystems in accordance with our above statement. Furthermore, expressions of Eq.(13.1) resemble those for diagonal blocks of the CBO matrix $\mathbf{P}$ (see Eq. (6.3)) in the sense that products of matrices of intersubset interaction of lower orders, i.e. $\mathbf{R}, \mathbf{G}_{(1)}, \mathbf{G}_{(2)}, etc.$ are present there. Thus, elements of the eigenblocks $\mathbf{E}_1^{(m\times m)}$ and $\mathbf{E}_2^{(s\times s)}$ seem to comply with the rules of additivity and transferability along with that of locality as it was the case with occupation numbers of basis orbitals and bond orders between the latter (Section 6). To demonstrate these peculiarities of eigenblocks in a more detail, let us turn to the case of diagonal zero order Hamiltonian matrices as shown in Eq.(5.12) and referring to fragmentary systems. Let us also assume that one-electron energies are uniform inside individual subsystems and coincide with certain constants $\varepsilon_{(0)1}$ and $\varepsilon_{(0)2}$ as it was the case with simple homogeneous systems (Section 5). Furher, the energy reference point will be chosen in the middle of the intersubsystem energy gap. Consequently, matrices $\mathbf{G}_{(1)}$ and $\mathbf{G}_{(2)}$ are expressible in terms of entire blocks of the first order Hamiltonian matrix as shown in Eq.(5.15). The same then accordingly refers to eigenblocks $\mathbf{E}_1^{(m\times m)}$ and $\mathbf{E}_2^{(s\times s)}$. As for instance, we obtain

$$\begin{aligned}\mathbf{E}_1^{(m\times m)} =&\varepsilon_{(0)1}\mathbf{I}+\mathbf{T}+\frac{1}{\varepsilon_{(0)1}+\varepsilon_{(0)2}}\mathbf{R}\mathbf{R}^{+}+\frac{1}{(\varepsilon_{(0)1}+\varepsilon_{(0)2})^2}[\mathbf{R}\mathbf{Q}\mathbf{R}^{+}-\\ &-\frac{1}{2}(\mathbf{R}\mathbf{R}^{+}\mathbf{T}+\mathbf{T}\mathbf{R}\mathbf{R}^{+})]+...\end{aligned}\quad(13.2)$$

instead of the first relation of Eq.(13.1). As a result, diagonal and off-diagonal

elements of the first eigenblock are as follows

$$E_{1,ii}^{(m\times m)} = \varepsilon_{(0)1} + T_{ii} + \frac{1}{\varepsilon_{(0)1} + \varepsilon_{(0)2}} \sum_{k}^{(2)} (R_{ik})^2 + ...$$

$$E_{1,ij}^{(m\times m)} = T_{ij} + \frac{1}{\varepsilon_{(0)1} + \varepsilon_{(0)2}} \sum_{k}^{(2)} R_{ik} R_{jk} + ... \qquad (13.3)$$

and contain sums of various types of direct and of indirect interactions of orbitals concerned, i.e. of $\varphi_{1,i}$ and $\varphi_{1,j}$. In particular, the first order increment to the element $E_{1,ij}^{(m\times m)}$ (i.e. T_{ij}) represents the direct (through-space) interaction of the above-mentioned orbitals, whilst the respective second order correction describes the relevant indirect interaction, wherein orbitals of the second subsystem play the role of mediators (sums over k embrace here the basis functions of the second subsystem $\varphi_{2,k}$). It is also seen that second order contributions to elements $E_{1,ii}^{(m\times m)}$ and $E_{1,ij}^{(m\times m)}$ depend on increments of individual orbitals of the opposite subsystem in an additive way [Accordingly, the third order increments contain sums over pairs of basis functions, at least one of them belonging to the opposite subsystem]. If we recall here the known extinction of resonance parameters when the distance between the relevant basis orbitals grows (Section 5), elements of the effective Hamiltonian matrix may be concluded to be determined mainly by that part of the second subsystem which is attached to orbitals underlying the elements concerned (i.e. $\varphi_{1,i}$ and $\varphi_{1,j}$). Given that the above-specified local environments are similar, the relevant elements of the eigenblock $\mathbf{E}_1^{(m\times m)}$ are transferable. Besides, analogous conclusions may be drawn also in the case of non-uniform one-electron energies of basis functions, when elements of matrices $\mathbf{G}_{(1)}$ and $\mathbf{G}_{(2)}$ are expressible as shown in Eqs.(5.13) and (5.14). Therefore, the effective Hamiltonian matrices of separate subsystems are in line with the principles of qualitative chemical thinking.

As the first specific example, let us consider the AMs $\mathbf{B}(G_{Ch}^a)$ of chemical graphs of alkanes in terms of atoms (Section 4). Diagonal elements of these matrices were shown to coincide with 3 and 0 for carbon and hydrogen atoms, respectively. These atoms will be now correspondingly regarded as the first and the second subsystem. Accordingly, parameters $\varepsilon_{(0)1}$ and $\varepsilon_{(0)2}$ of Eq.(13.2) coincide with 3 and 0, respectively. Further, the off-diagonal elements of the AMs $\mathbf{B}(G_{Ch}^a)$ referring to both C-C and C-H bonds were shown to take unit values. This implies the relevant elements of matrices $\mathbf{T}$ and $\mathbf{R}$ to coincide with 1, whilst those of the matrix $\mathbf{Q}$ vanish owing to absence of H-H bonds. Thus, the intersubsystem energy gap (vs. the relevant interaction) coincides with 3 and seems to be sufficient for our illustrative purposes. Equation (13.2) then yields the following formula for the eigenblock $\mathbf{E}_1^{(m\times m)}$ corresponding to the C-skeleton of our alkane, viz.

$$\mathbf{E}_1^{(m\times m)} = 3\mathbf{I} + \mathbf{T} + \frac{1}{3}\mathbf{R}\mathbf{R}^+ - \frac{1}{18}[\mathbf{R}\mathbf{R}^+\mathbf{T} + \mathbf{T}\mathbf{R}\mathbf{R}^+] + ... \qquad (13.4)$$

It is seen that the influence of hydrogen atoms upon the AM of the C-skeleton $(3\mathbf{I} + \mathbf{T})$ is described mainly by the second order term $1/3\mathbf{R}\mathbf{R}^+$. Off-diagonal elements of this term vanish because two carbon atoms usually possess no common hydrogen atoms in alkanes. Meanwhile, diagonal elements of the same correction

are additive with respect to increments of the attached hydrogen atoms and thereby are proportional to the relevant number of the latter. For example, 2/3 and 1 follow from this term for internal and terminal carbon atoms of normal alkanes, respectively. Thus, the terminal atoms prove to be characterized by elements of effective Hamiltonian matrices of higher absolute values as compared to internal atoms. This result seems to be in an excellent aggreement with that following from Eq.(3.8). To make sure this is the case, we should recall here that the notation v of Eq.(3.8) stands for the valency of the given carbon atom in the reduced graph G_{ch}^{a*}. For internal and terminal carbon atoms of normal alkanes, these valencies equal to 2 and 1, respectively. Further, the energy variable ε may be approximately replaced by 3. The second term of Eq.(3.8) then also correspondingly yields corrections 2/3 and 1. Thus, parallelism between the results of Section 3 and those of the present approach is beyond any doubt. It should be emphasized here, however, that a direct application of Eq.(13.2) to the AMs $\mathbf{A}(G_{Ch}^{b})$ of graphs of alkanes in terms of bonds (G_{Ch}^{b}) is hardly possible because the requirements of the perturbation theory are not met in this case. Hence, the overall scope of applicability of the present procedure seems to be narrower as compared to that of the alternative approach of Section 3. Again, Eq.(13.1) provides us with energy-variable- independent expressions for characteristics under interest in contrast to formulae of Section 3.

Our second example belongs to regular quasi-one- dimensional systems defined in Section 3, i.e. to chains of cyclic constitution characterized by translational symmetry. Several chains of this type have been considered in Ref.[115]. Let us confine ourselves here to a regular chain of N uniform atoms each of them contributing two AOs of the s type (e.g. $ns = 1s$ and $n\prime s = 2s$) separated by a substantial energy gap. The overall chain may be then considered as consisting of two weakly- interacting translationally- symmetric subchains embracing the ns ans $n\prime s$ AOs, respectively. The first step of our analysis coincides with transforming the relevant initial Hamiltonian matrix into a block-diagonal form containing two eigenblocks $\mathbf{E}_1^{(N\times N)}$ and $\mathbf{E}_2^{(N\times N)}$ that is equivalent to a direct application of Eq.(13.2) in practice. Thus, we actually start with taking into account the intersubchain interactions. The translational symmetry is automatically preserved during this step and is dealt with later as described below. Hence, the present approach also proves to be an alternative to the standard solid state theory as it was the case with that of Section 3.

Given that the energy reference point is chosen in the middle of the abovementioned gap and the latter coincides with the double negative energy unit, elements of the resulting effective Hamiltonian matrices $\mathbf{E}_1^{(N\times N)}$ and $\mathbf{E}_2^{(N\times N)}$ are uniform over the subchains and take the form [115]

$$\begin{aligned} E_{1,ij}^{(N\times N)} =&(1+\beta^2+\frac{1}{2}\gamma^2)\delta_{ij}+(\sigma+\beta\gamma)(\delta_{i,j+1}+\delta_{i,j-1})+\frac{1}{2}\beta^2(\delta_{i,j+2}+\delta_{i,j-2})+... \\ E_{2,ij}^{(N\times N)} =&-(1+\beta^2+\frac{1}{2}\gamma^2)\delta_{ij}+(\omega-\beta\gamma)(\delta_{i,j+1}+\delta_{i,j-1})-\frac{1}{2}\beta^2(\delta_{i,j+2}+\delta_{i,j-2})+... \end{aligned} \tag{13.5}$$

where ω, σ, β and γ are resonance parameters of different types [ω and σ correspondingly stand for resonance parameters between the neighboring pairs of AOs inside the first and the second subchain, whilst γ and β are intersubchain parameters inside a single atom and for a neighboring pair of atoms, respectively]. The influence of the

intersubchain interaction upon the intrasubchain Hamiltonian matrix elements may be easily seen from Eq.(13.5). Thus, one-electron energies of the ns AOs become increased by

$$\Delta = \beta^2 + \frac{1}{2}\gamma^2 \tag{13.6}$$

under influence of the $n\prime s$ AOs, whereas those of the $n\prime s$ AOs are decreased accordingly. This correction originates from the second order term of Eqs.(13.2) and/or (13.3) and describes the indirect self-interaction of the $ns(n\prime s)$ AOs. Furthermore, the interactions between the first-neighboring AOs of the first subchain becomes increased by $\beta\gamma$ owing to the indirect interaction of these AOs by means of the nearest AOs of the second subchain. The most important peculiarity of elements $E_{1,ij}^{(N\times N)}$ and $E_{2,ij}^{(N\times N)}$, however, consists in the emergence of new effective interactions between the second-neighboring pairs of AOs of the first (second) subchain under influence of the second (first) one. Basis orbitals of the opposite subchain situated in between the interacting AOs play the role of mediators in this case. Effective parameters of these new interactions coincide with $\pm 1/2\beta^2$. [It deserves mentioning here that third and subsequent members of the same power series give birth to new interactions between pairs of more remote AOs that are not exhibited explicitly in Eq.(13.5). The main reason for that consists in their relatively small absolute values (the effective parameters accordingly depend upon products of three and more parent resonance parameters)].

If we recall now the overall block-diagonal constitution of the transformed Hamiltonian matrix (that contains the eigenblocks $\mathbf{E}_1^{(N\times N)}$ and $\mathbf{E}_2^{(N\times N)}$ in its diagonal positions), we may conclude our initial chain to be partitioned into two non-interacting chains of regular and rather simple constitutions that may be subsequently studied separately and independently.

To this end, the well-known methods of obtaining the dispersion relations for simple chains may be applied. After employment of terms of the solid state theory [39-41] (i.e. of $\mathbf{k}$ and $\mathbf{a}$ defined in Section 3), the final dispersion relations for the relevant two energy bands are as follows

$$\begin{aligned}\varepsilon_1(\mathbf{k}) =&(1+\Delta)\delta_{ij} + 2(\sigma+\beta\gamma)\cos(\mathbf{ka}) + \beta^2\cos(2\mathbf{ka}) + ...\\ \varepsilon_2(\mathbf{k}) =&-(1+\Delta)\delta_{ij} + 2(\omega-\beta\gamma)\cos(\mathbf{ka}) - \beta^2\cos(2\mathbf{ka}) + ...\end{aligned} \tag{13.7}$$

Similarity of these relations to those of Eqs.(3.10) and (3.11) is obvious. Moreover, an evident interelation between separate terms of Eqs.(13.5) and (13.7) along with the above-discussed local nature of the former allows an interpretation of individual additive components of dispersion relations of Eq.(13.7) in terms of local structure. Thus, the first $\mathbf{k}-$ independent terms of these relations originate from effective energies of AOs determined by parameter Δ of Eq.(13.6). Similarly, coefficients of the $\cos(\mathbf{ka})-$ like terms are related to effective interactions between the first-neighboring AOs. Finally, the "weights" of the $\cos(2\mathbf{ka})-$ like increments depend on the relative value of the new effective interaction between the second- neighboring AOs. These terms were shown to determine significant changes of the final dispersion curves as compared to the simple $\cos(\mathbf{ka})-$like shape. Hence, the above-concluded parallelism between the results of Section 3 and those of the present procedure is now supported by another example. Besides, some simple chains have been found in Ref.[115], when both approaches yield coinciding results.

The third important specific example may be found in Ref.[114]. The model studied there embraces molecules and molecular systems described by a general formula A-$(X)_n$-B, where A and B stand for some terminal functional groups and -$(X)_n$- is a bridge usually consisting of a certain number of similar elementary units X. The effective interaction between groups A and B was the principal characteristic under interest. In this connection, the terminal groups and the bridge have been considered as separate subsystems. Moreover, each terminal fragment has been represented by a single orbital for simplicity. As a result, the only off-diagonal element of the eigenblock $\mathbf{E}_1^{(2\times 2)}$ has been expected to represent the effective interaction concerned. Besides, the functional groups A and B were assumed to be generally dissimilar so that the overall model served to illustrate the case of non-uniform zero order one-electron energies inside subsets. Explicit algebraic expressions have been derived and analyzed for the above-described decisive matrix element to within the fourth order members of power series inclusive. Additive nature of the effective interaction between groups A and B has been demonstrated. The direct (through-space) interaction between the orbitals concerned and various types of the relevant indirect (bridge-assisted) interactions proved to be among additive components here. In other words, the effective interaction energy has been established to contain sums of increments, each of them corresponding to a certain pathway through the bridge from one terminal group to another. In this respect, a certain analogy reveals itself between the present approach and the so-called partitioning technique [1]. A more detailed discussion of this point may be found in Ref.[114].

Let us return again to the case of systems consisting of an arbitrary number of weakly-interacting subsystems and/or of subsets. A general form of the perturbation theory (PT) suitable for solution of the relevant block-diagonalization problem has been developed in Ref.[53-55]. Comparison of this new PT to the standard Rayleigh-Schrödinger PT (RSPT) [2, 116, 117] showed that we actually have to do with passing from the usual one-dimensional Hamiltonian matrix elements to multidimensional parameters (i.e. submatrices) . Since commutative quantities become replaced by non-commutative ones in this case, the new PT has been called the non-commutative Rayleigh-Schrödinger PT (NCRSPT). Peculiarities of this alternative PT vs. the standard RSPT has been discussed in Ref.[55] in a detail. Let us confine ourselves here to properties of eigenblocks $\mathbf{E}_i (i = 1, 2...N)$.

Let us assume the initial Hamiltonian matrix $\mathbf{H}$ to consist of a certain zero order member $\mathbf{H}_{(0)}$ [being a direct sum of N non-zero blocks $\mathbf{E}_{(0)i} (i = 1, 2...N)$] and of a first order (perturbation) term denoted by $\mathbf{V}$ as usual. The ith eigenblock $\mathbf{E}_i$ takes then the following form [115]

$$\mathbf{E}_i = \mathbf{E}_{(0)i} + \mathbf{V}_{ii} + \frac{1}{2}\sum_j (1 - \delta_{ij})(\mathbf{V}_{ji}^{+}\mathbf{C}_{ji}^{(1)} + \mathbf{C}_{ji}^{(1)+}\mathbf{V}_{ji}) + ... \qquad (13.8)$$

where the sum over j embraces here all the subsets of basis functions. Notations $\mathbf{C}_{ji}^{(1)}$, in turn, are used for blocks of the first order member $\mathbf{C}^{(1)}$ of the power series for the transformation matrix $\mathbf{C}$ as it was the case in Eq.(5.5). These blocks are conditioned by matrix equations like that of Eq.(5.7) as previously. If we recall that $\mathbf{G}_{(1)}$ of Eq.(13.1) coincides with $\mathbf{C}_{12}^{(1)}$ (see Eq.(5.6)), the new formula (13.8) proves to be a direct generalization of Eq.(13.1) to the case of an arbitrary number of subsystems.

In this context, comparison of the present approach to the so-called PMO theory [23] also deserves attention. Let us start with a brief specifying of the latter.

Traditional ways of investigation of systems consisting of weakly interacting subsystems are based on application of the quasi-degenerate RSPT [2, 116, 117]. The overall treatment then starts with diagonalization of the intrasubsystem blocks of the initial Hamiltonian matrix, whilst taking into account the intersubsystem (intersubset) interaction makes up the second step. This procedure actually implies passing to the basis of delocalized (canonical) MOs of isolated subsystems from the very outset of solving the problem and a subsequent regard for interaction between these MOs. Just this approach is usually referred to as the PMO theory [23]. It is evident that application of the NCRSPT offers us a possibility of an opposite order of operations versus that of the PMO theory. Indeed, the intersubsystem interactions are taken into account by means of an initial block-diagonalization procedure, i.e. before regard fot the intrasubsystem ones. Thereupon, the eigenblocks obtained may be diagonalized as usual.

Before finishing this Section, let us return to comparison of the present alternative approach to that of Section 3 and summarize their similarities and differencies. First, both alternative ways of dealing with secular equations are based on an inverted order of the principal operations vs. the usual one. Second, both approaches comply with the classical principles of the qualitative chemical thinking, i.e. with those of locality, additivity and trasferability. Significant differences between these approches also deserve mentioning. First, the eigenvalue- dependent effective Hamiltonian matrices of Section 3 describe the whole system under study and not its separate subsystems. Second, quite extended fragments of the system and not separate AOs correspond to diagonal elements of matrices of Section 3. Finally, no conditions of perturbative nature have been imposed when using the approach of Section 3 in contrast to the present one.

14 Conclusions

The principal achievements of above-overviewed studies are as follows:

1. Common quantum-chemical (algebraic) problems are formulated for extended classes of molecules in analogy with the classical chemistry, where a class of compounds is considered as a single object. The new problems coincide either with eigenblock equations for the relevant common Hamiltonian matrices or with commutation equations determining the one-electron density matrices and thereby find themselves beyond the usual secular (eigenvalue) problems for Hamiltonian matrices of individual compounds. Again, an eigenblock equation is shown to be a generalization of an eigenvalue equation for a definite two-dimensional matrix, wherein multidimensional (non-commutative) quantities (submatrices) play the role of the usual matrix elements. Accordingly, general solutions of these newly-formulated problems are obtained in terms of entire submatrices of the common Hamiltonian matrix of the given class of molecules without specifying either the structures or dimensions of these submatrices.

2. Formations of numerous fundamental quantum-chemical characteristics of molecules are shown to be governed by rules of qualitative chemical thinking, viz.

additivity, transferability and locality. This refers not only to traditionally "semi-classical" characteristics (e.g. total energies, dipole moments, etc.), but also to such "purely quantum-mechanical" quantities as one-electron spectra and canonical MOs. In particular, dispersion relations representing one-electron energy bands of regular quasi-one- dimensional systems are shown to consist of a few additive components, each of them being interpretable in terms of specific peculiarities of local constitutions.

3. Quantum-chemical and thereby algebraic analogues are constructed for numerous qualitative chemical concepts including different roles of the reaction center and of its neighbourhoods in chemical processes, the Lewis perspective on chemical reactions (cf. the so-called "curly arrow chemistry") and others. Accordingly, some known intuition-based verbal relations now acquire rigorous algebraic forms, e.g. the relation between charge redistribution, delocalization and stabilization, the relation between peculiarities of the inductive effect and the extent of delocalization of electrons in the parent hydrocarbon, etc.

4. Scopes of applicability of some classical concepts and/or models are explored and conditions of their validity are formulated explicitly. This primarily refers to various local and semilocal models of chemical reactions, as well as to models based on the "curly arrow chemistry". Moreover, the above-mentioned intuition-based relations also are shown to be of a limited validity.

5. A great cognitive potential of quasi-classical alternatives under developement is demonstrated by defining new generalities and by introducing new concepts and/or rules. Universal environment- determined intrafragmental effects (such as homo- and heterolytic predissociation of bonds) and recently-defined classes of fragmentary and homogeneous molecules may be mentioned as examples of new generalities. Again, the newly- introduced rules may be exemplified by the common selection rule for organic reactions in terms of signs of direct and indirect interorbital interactions. Novel applications of the classical concepts in the "purely quantum-mechanical" fields also may be added here, e.g. interpretation of one-electron spectra in terms of peculiarities of the relevant chemical formulae (molecular graphs).

REFERENCES

1. R. McWeeny, *Methods in Molecular Quantum Mechanics,* 2nd. ed. (Academic Press, London, 1992).

2. L. Zülicke, *Quantenchemie, Bd.1, Grundlagen und Algemeine Methoden* (Deutscher Verlag der Wissenschaften, Berlin, 1973).

3. J. Simons, *An Introduction to Theoretical Chemistry* (Cambridge Univ. Press, Cambridge, 2003).

4. C.J. Cramer, *Essentials of Computational Chemistry, Theories and Models,* 2nd. ed. (John Wiley & Sons, 2004).

5. F. Jensen, *Introduction to Computational Chemistry*, 2nd. ed. (John Wiley & Sons, 2007).

6. E.G. Lewars, *Computational Chemistry: Introduction to the Theory and Applications of Molecular and Quantum Mechanics,* 2nd. ed. (Springer, Heidelberg, 2011).

7. A. Szabo, N.S. Ostlund, *Modern Quantum Chemistry* (McGraw-Hill, 1982).

8. O. Chalvet (Ed.), *Localization and Delocalization in Quantum Chemistry, Atoms and Molecules in the Ground State*, Vol.1 (Reidel, Dordrecht, 1975).

9. V. M. Tatevskii, *Constitution of Molecules* (Khimia, Moscow, 1977) [in Russian].

10. J. March, *Advanced Organic Chemistry, Reactions, Mechanisms and Structure* (Wiley Interscience, New York, 1985).

11. F.A. Carroll, *Perspectives on Structure and Mechanism in Organic Chemistry* (Brooks/Cole, Pacific Grove, CA, 1998).

12. V. Gineityte, J. Mol. Struct. (Theochem) **491**, 205 (1999).

13. C. Yang, J. Mol. Struct. (Theochem) **169**, 1 (1988).

14. G. Del Re, F. Zuccaello, Croat. Chem. Acta, **64**, 449 (1991).

15. M. Edenborough, *Organic Reaction Mechanisms. A Step by Step Approach* (Taylor and Francies, London, 1999).

16. L. Pauling, *The Nature of the Chemical Bond,* 3rd. ed. (Cornell Univ. Press, Ithaca, New York, 1960).

17. A. Streitwieser, Jr., *Molecular Orbital Theory* (John Wiley &Sons, New York, 1961).

18. W. Kutzelnigg, J. Comput. Chem. **28**, 25 (2007).

19. E. Hückel, Z. Phys. **70**, 204 (1931).

20. E. Hückel, Z. Phys. **76**, 628 (1932).

21. R. Zahradnik, R. Polak, *Elements of Quantum Chemistry* (Plenum Press, New York, 1980).

22. N. Trinajstic, *The Hückel Theory and Topology*, in: G.A. Segal (Ed.), Semiempirical Methods in Electronic Structure Calculations, Part A, Techniques (Plenum Press, New York, London, 1977).

23. M.J.S. Dewar, and R.C. Dougherty, *The PMO Theory of Organic Chemistry* (Plenum Press, New York, 1975).

24. J.-P. Malrieu, J. Mol. Struct. (Theochem) **424**, 83 (1998).

25. T.A. Carlson, Ann. Rev. Phys. Chem., **26**, 211 (1975).

26. T.C. Koopmans, Physica, **1**, 104 (1934).

27. G. Bieri, F. Burger, E. Heilbronner, J.P. Maier, Helv. Chim. Acta, **60**, 2213 (1977).

28. G. Bieri, J.D. Dill, E. Heilbronner, A. Schmelzer, Helv. Chim. Acta, **60**, 2234 (1977).

29. E. Heilbronner, Helv. Chim. Acta, **60**, 2248 (1977).

30. E. Heilbronner, *The Photoelectron Spectra of Saturated Hydrocarbons,* In: The Chemistry of Alkanes and Cycloalkanes, Eds. S.Patai, Z.Rappoport (Wiley, New York, 1992), pp. 455-529.

31. G.G. Hall, Proc. Roy. Soc. (London), **A229**, 251 (1955).

32. V. Gineityte, Int. J. Quant. Chem. **60**, 717 (1996).

33. V. Gineityte, MATCH Commun. Math. Comput. Chem. **70**, 119 (2013).

34. V. Gineityte, J. Mol. Struct. (Theochem) **487**, 231 (1999).

35. R.B. Potts, J. Chem. Phys. **21**, 758 (1953).

36. V. Gineityte, Int. J. Quant. Chem. **53**, 245 (1995).

37. V. Gineityte, Croat. Chem. Acta, **71**, 673 (1998).

38. V. Gineityte, Int. J. Quant. Chem. **64**, 481 (1997).

39. R. Hoffmann, *Solids and Surfaces: A Chemist's View of Bonding in Extended Structures* (VCH Publishers, 1988).
40. A.A. Levin, *Introduction to Quantum Chemistry of Solids* (Khimia, Moscow, 1974) [in Russian].
41. Ch. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1977).
42. D. M. Cvetkovic, M. Doob, H. Sachs, *Spectra of Graphs. Theory and Application* (VEB Deutscher Verlag der Wissenschaften, Berlin, 1980).
43. V. Gineityte, Int. J. Quant. Chem. **60**, 743 (1996).
44. I. Mayer, Chem. Phys. Lett. **89**, 390 (1982).
45. P.R. Surjan, I. Mayer, and M. Ketesz, J. Chem. Phys. **77**, 2454 (1982).
46. I. Mayer, and P.R Surjan, J. Chem. Phys. **80**, 5649 (1984).
47. J.P. Daudey, Chem. Phys. Lett. **24**, 574 (1974).
48. S. Huzinaga, *The MO Method* (Mir, Moscow, 1983) [in Russian].
49. V Gineityte, J. Mol. Struct. (Theochem), **288**, 111 (1993).
50. V. Gineityte, J. Mol. Struct. (Theochem), **333**, 297 (1995).
51. V. Gineityte, J. Mol. Struct. (Theochem) **343**, 183 (1995).
52. V. Gineityte, Int. J. Quant. Chem. **72**, 559 (1999).
53. V. Gineityte, Int. J. Quant. Chem. **68**, 119 (1998).
54. V. Gineityte, Lith. J. Phys. **51**, 107 (2011).
55. V. Gineityte, Lith. J. Phys. **44**, 219 (2004).
56. V. Gineityte, J. Mol. Struct. (Theochem) **342**, 219 (1995).
57. P. Lankaster, *Theory of Matrices* (Academic Press, New York, 1969).
58. V. Gineityte, J. Mol. Struct. (Theochem) **680**, 199 (2004).
59. V. Gineityte, D.B. Shatkovskaya, Zh. Strukt. Khim. **25**, 152 (1984).
60. M.M. Mestetchkin, *The Density Matrix Method in Quantum Chemistry* (Naukova Dumka, Kiev, 1977) [in Russian].
61. V. Gineityte, J. Mol. Struct. (Theochem) **585**, 15 (2002).
62. G.N. Lewis, J. Amer. Chem. Soc. **38**, 762 (1916).
63. V. Gineityte, J. Mol. Struct. (Theochem) **364**, 85 (1996).
64. V. Gineityte, Int. J. Chem. Model. **5**, 99 (2013).
65. V. Gineityte, MATCH Commun. Math. Comput. Chem. **72**, 39 (2014).
66. V. Gineityte, Int. J. Quant. Chem. **77**, 534 (2000).
67. V.F.Traven, *Electronic Structure and Properties of Organic Molecules* (Khimia, Moscow, 1989) [in Russian].
68. M. Randic, Chem. Revs. **103**, 3449 (2003).
69. M. Randic, N. Trinajstic, *On Conjugated Chains,* in: R.C. Lacher (Ed.), MATCH/CHEM/COMP, 1987, Elsevier, Amsterdam, 1988, p.p. 109-123.
70. G. Klopman (Ed.), *Chemical Reactivity and Reaction Paths* (John Wiley and Sons Inc., New York, London, Sydney, Toronto, 1974).
71. N.V. Vasiljeva, *Theoretical Introduction into Organic Synthesis* (Prosveshtchenie, Moscow, 1976) [in Russian].
72. K. Fukui, H. Fujimoto, Bull. Chem. Soc. Japan **41**, 1989 (1968).
73. K. Fukui, H. Fujimoto, Bull. Chem. Soc. Japan **42**, 3399 (1969).
74. J.M. Tedder and A. Nechvatal, *Pictorial Orbital Theory* (Pitman, London 1985).
75. V. Gineityte, J. Mol. Struct. (Theochem) **465**, 183 (1999).
76. V. Gineityte, Int. J. Quant. Chem. **94**, 302 (2003).

77. V. Gineityte, J. Mol. Struct. (Theochem) **541**, 1 (2001).
78. V. Gineityte, J. Mol. Struct. (Theochem) **588**, 99 (2002).
79. V. Gineityte, J. Mol. Struct. (Theochem) **663**, 47 (2003).
80. V. Gineityte, J. Mol. Struct. (Theochem) **726**, 205 (2005).
81. V. Gineityte, J. Mol. Struct. (Theochem) **760**, 229 (2006).
82. V. Gineityte, Lith. J. Phys. **49**, 389 (2009).
83. V.Gineityte, Z. Naturforsch. **64A**, 132 (2009).
84. C.K. Ingold, *Structure and Mechanism in Organic Chemistry* (Cornell University Press, Ithaca, 1953).
85. H.G.O. Becker, *Einfürung in die Elektronentheorie Organisch Chemischen Reactionen* (Deutscher Verlag der Wissenschaften, Berlin, 1974).
86. V. Gineityte, J. Mol. Struct. (Theochem) **546**, 107 (2001).
87. R.B. Woodward, R. Hoffmann, J. Amer. Chem. Soc. **87** 395 (1965).
88. R.B. Woodward, R. Hoffmann, *The Conservation of Orbital Symmetry* (Verlag Chemie/ Academic Press, Weinheim, 1971).
89. R. Hoffmann, R.B. Woodward, Acc. Chem. Res. **1,** 17 (1968).
90. M.J.S. Dewar, Tetrahedron Suppl. **8,** 75 (1966).
91. M.J.S. Dewar, Angew. Chem. Int. Ed. **10,** 761 (1971).
92. M.J.S. Dewar, S. Kirschner, H.W. Kollmar, J. Amer. Chem. Soc. **96,** 5240 (1974).
93. E. Zimmerman, Acc. Chem. Res. **4,** 272 (1971).
94. V. Gineityte, J. Mol. Struct. (Theochem) **714**, 157 (2005).
95. V. Gineityte, Int. J. Quant. Chem. **108**, 1141 (2008).
96. V. Gineityte, Int. J. Chem. Model. **4**, 189 (2012).
97. E. Heilbronner, Tetrahedron Lett. **29,** 1923 (1964).
98. A.N. Vereshtchagin, *The Inductive Effect* (Nauka, Moscow, 1987) [in Russian].
99. V. Gineityte, Int. J. Quant. Chem. **110**, 1327 (2010).
100. V. Gineityte, J. Mol. Struct. (Theochem) **766**, 19 (2006).
101. V. Gineityte, Lith. J. Phys. **45**, 7 (2005).
102. V. Gineityte, J. Mol. Struct. (Theochem) **810**, 91 (2007).
103. V. Gineityte, J. Mol. Struct. (Theochem) **434**, 43 (1998).
104. V. Gineityte, J. Mol. Struct. (Theochem) **532**, 257 (2000).
105. V. Gineityte, J. Mol. Struct. (Theochem) **713**, 93 (2005).
106. V. Gineityte, J. Mol. Struct. (Theochem) **507**, 253 (2000).
107. V. Gineityte, J. Mol. Struct. (Theochem) **430**, 97 (1998).
108. V. Gineityte, J. Mol. Struct. (Theochem) **497**, 83 (2000).
109. V. Gineityte, Int. J. Quant. Chem. **101**, 274 (2005).
110. V. Gineityte, Int. J. Quant. Chem. **105**, 232 (2005).
111. V. Gineityte, Int. J. Quant. Chem. **106**, 2145 (2006).
112. V. Gineityte, Croat. Chem. Acta **81**, 487 (2008).
113. V. Gineityte, Croat. Chem. Acta **86**, 171 (2013).
114. V. Gineityte, Lith. J. Phys. **42**, 397 (2002).
115. V. Gineityte, Int. J. Quant. Chem. **81**, 321 (2001); Erratum, **82**, 262 (2001).
116. L.D. Landau, E.M. Lifshits, *Quantum Mechanics. The Non-relativistic Theory* (Nauka, Moscow, 1974).

117. W.H. Flygare, *Molecular Structure and Dynamics* (Prentice-Hall, Englewood Cliffs/ New York, 1978).