

NON-COMMUTATIVE RAYLEIGH–SCHRÖDINGER PERTURBATION THEORY AND ITS APPLICATIONS IN QUANTUM CHEMISTRY

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The review is devoted to development and applications of the so-called non-commutative Rayleigh–Schrödinger perturbation theory (NCRSPT). As opposed to the standard RSPT used for taking into account weak interorbital interactions, the NCRSPT is aimed to account for weak interactions inside and between entire subsets of basis functions of arbitrary dimensions separated by substantial energy gaps. Accordingly, this new PT is formulated in terms of multidimensional (non-commutative) quantities, including row-matrices of basis functions corresponding to individual subsets and the so-called eigenblocks playing the role of eigenvalues. When discussing applications, the principal attention is paid to the perturbative version of the non-canonical theory of molecular orbitals based on the Brillouin theorem.

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1. Introduction

Perturbation theory (PT) is among the most powerful approximate methods in quantum mechanics [1–4]. In particular, the well-known Rayleigh–Schrödinger PT (RSPT) for eigenvalues and eigenfunctions of operators [1–3] and an alternative PT based on the resolvent formalism [4] can be mentioned here.

Various forms of the perturbation theory are widely used in quantum chemistry as well. To obtain the many-electron wave functions of molecules, the so-called Møller–Plesset partitioning of the total Hamiltonian operator is now generally applied [5,6]. The analogous partitioning of localized orbitals [7–9] and its generalization for any type of reference function [6] also are noteworthy. The self-consistent version of the RSPT (the coupled RSPT) [10–13] forms the basis of the perturbed Hartree–Fock (HF) calculations. Self-consistent perturbative approaches for Green’s functions [13] and for density matrices [14–16] instead of the one-electron orbitals also have been developed. It should be additionally noted here that diagonality condition for zero order matrices and/or operators is not imperative in perturbative approaches. Thus, in the resolvent-based PT [4], the zero-order operator is such that its eigenvalues and eigenfunctions can be easily de-

termined. Similarly, the Fock operator of [7–9] is not necessarily diagonal in the orbital space.

Quantum chemistry, however, is far from being only a field of application of quantum mechanics. Moreover, it is an independent branch of science which is based on fundamentals of the classical chemistry along with quantum-mechanical methods [17]. It is no surprise, therefore, that new problems arise in this melting pot of different concepts and thereby new quantum-mechanical formalisms are required to solve them.

The so-called non-commutative RSPT (NCRSPT) discussed in this review is among formalisms of the above-mentioned type. Development of this theory started with its particular cases devoted to the common quantum-mechanical description of saturated molecules [18–24]. (Note that entire classes of the so-called related compounds usually are studied in the classical chemistry instead of individual molecules.) The same theory subsequently acquired a more general form [25,26] that may be applied for solution of the block-diagonalization problem for a definite matrix specified below, as well as of its operator analogue referred to as the eigenblock equation.

The above-mentioned problem is a generalization of the very popular diagonalization (eigenvalue) problem, wherein eigenblocks of arbitrary dimensions are

sought instead of usual (one-dimensional) eigenvalues. In other words, we look for a unitary matrix that transforms the initial matrix \mathbf{H} into a block-diagonal form defined as a direct sum of eigenblocks. Given that subsets of corresponding dimensions may be revealed in the initial basis set so that the intersubset interactions are weak as compared to the intrasubset ones, the perturbation theory may be formulated in terms of entire subsets of basis functions instead of individual orbitals. Accordingly, matrices play the role of usual one-dimensional coefficients in this generalized formalism. In particular, row-matrices of functions arise instead of eigenfunctions in the respective eigenblock equation for operator. As a consequence, non-commutativeness of the eigenblock and of the respective multidimensional eigenfunction and thereby of related terms of power series is the main distinctive feature of this formalism. That is why it has been called the non-commutative RSPT. Allowance for non-diagonal zero-order matrices $\mathbf{H}_{(0)}$ is another feature of the NCRSPT [27] (a block-diagonal constitution of the latter is acceptable).

As opposed to the actual way of development of the NCRSPT, the scheme of this review is based on passing from the most general formalism to its particular cases. Thus, we start with the case of an arbitrary number of interacting subsets of basis functions (Section 2) and subsequently overview the relevant applications (Section 3). The remaining Sections 4, 5, and 6 are devoted to the case of two interacting subsets. The reason why this particular case deserves so much attention consists in the fact that the respective block-diagonalization problem for a Fockian or Hamiltonian matrix is equivalent to the non-canonical HF equation and yields numerous applications including those devoted to chemical reactivity (Section 6).

2. The general operator formalism of the NCRSPT

The standard RSPT is most commonly applied to secular equations for Hamiltonian operators. To be able to compare the NCRSPT to the standard RSPT more easily, an analogous formalism of the former [26] is given in this section.

Let us start with principal definitions. Let us assume that the Hamiltonian matrix of our system \mathbf{H} is determined in the basis $\{\varphi\}$. Let this basis set to be divided into N subsets $\{\{\varphi_1\}, \{\varphi_2\}, \dots, \{\varphi_N\}\}$, each of them containing an arbitrary number of orbitals. In this connection, subscripts i, j, m, \dots here and below will be ascribed to entire subsets (no consideration of

individual basis functions is required in the NCRSPT). Furthermore, basis functions of each subset will be collected into row-matrices that will be designated by ket-vectors $|\Phi_1\rangle, |\Phi_2\rangle, \dots$ and referred to as multiorbitals. Accordingly, the bra-vectors $\langle\Phi_1|, \langle\Phi_2|, \dots$ coincide with column-matrices containing respective complex-conjugate orbitals.

The total Hamiltonian matrix \mathbf{H} will be accordingly divided into submatrices (blocks) that may be alternatively considered as its multidimensional elements and denoted by \mathbf{H}_{ij} . It is evident that elements of intra- and intersubset type may be distinguished. Let us then define the relevant Hamiltonian operator

$$\hat{H} = \sum_{i,j=1}^N |\Phi_i\rangle \mathbf{H}_{ij} \langle\Phi_j|, \quad (1)$$

where multiorbitals meet the orthonormalization condition

$$\langle\Phi_i|\Phi_j\rangle = \mathbf{I}\delta_{ij} \quad (2)$$

and \mathbf{I} stands for the unit matrix of respective dimension.

Let us consider the operator equation of the form

$$\hat{H}|\Psi_a\rangle = |\Psi_a\rangle \mathbf{E}_a, \quad (3)$$

where $|\Psi_a\rangle$ is a row-matrix further referred to as the multieigenfunction. Accordingly, \mathbf{E}_a stands for the respective eigenblock playing the role of a multidimensional eigenvalue. It should be additionally emphasized here that \mathbf{E}_a does not commute with $|\Psi_a\rangle$ in contrast to the usual eigenvalue equation. It may be easily verified that Eq. (3) turns into a block-diagonalization problem for the matrix \mathbf{H} if the multieigenfunction $|\Psi_a\rangle$ is expressed in the form of a linear combination

$$|\Psi_a\rangle = \sum_{p=1}^N |\Phi_p\rangle \mathbf{B}_{pa} \quad (4)$$

containing matrix coefficients \mathbf{B}_{pa} and Eq. (4) is substituted into Eq. (3) with subsequent use of Eq. (2).

Let the operator \hat{H} consist of the zero-order term $\hat{H}_{(0)}$ and of the first-order term \hat{V} , the latter being called the perturbation operator. We will assume also that the zero-order operator $\hat{H}_{(0)}$ complies with the zero-order equation

$$\hat{H}_{(0)}|\Psi_{(0)i}\rangle = |\Psi_{(0)i}\rangle \mathbf{E}_{(0)i} \quad (5)$$

and the zero-order multieigenfunctions are orthonormalized similarly to multiorbitals (see Eq. (2)). Given that Eq. (5) is solved, a block-diagonal zero-order Hamiltonian matrix is evidently obtained for our initial (unperturbed) system.

As in the usual RSPT [1–3], let the multieigenfunction $|\Psi_a\rangle$ of the total operator \hat{H} be represented in the form of a linear combination of zero-order multieigenfunctions, viz.

$$|\Psi_a\rangle = \sum_{i=1}^N |\Psi_{(0)i}\rangle \mathbf{C}_{ia}, \quad (6)$$

where \mathbf{C}_{ia} also are multidimensional coefficients.

The subsequent derivation of the formalism resembles that of the usual RSPT. Thus, we start with substitution of Eq. (6) into Eq. (3) and define multidimensional elements \mathbf{V}_{mp} representing the perturbation operator \hat{V} in the basis $\{\Psi_{(0)}\}$ as follows:

$$\mathbf{V}_{mp} = \langle \Psi_{(0)m} | \hat{V} | \Psi_{(0)p} \rangle. \quad (7)$$

Thereupon, the multidimensional coefficients \mathbf{C}_{ia} along with eigenblocks \mathbf{E}_a are expanded in the form of a power series and terms of the same order are collected to form the equations of PT. The principal difference of this procedure from the standard one [1–3] consists in non-commutativeness of multidimensional factors in respective products. The results may be described as follows.

Some of expressions of the NCRSPT formally resemble those of the RSPT, e. g.,

$$\begin{aligned} \mathbf{E}_{(0)a} &= \mathbf{E}_{(0)r}, & \mathbf{C}_{(0)ra} &= \mathbf{I}\delta_{ra}, \\ \mathbf{E}_{(1)r} &= \mathbf{V}_{rr}, & \mathbf{C}_{(1)rr} &= \mathbf{C}_{(1)rr}^+ = \mathbf{0}, \\ \mathbf{C}_{(2)rr} &= \mathbf{C}_{(2)rr}^+ = \frac{1}{2} \sum_{i(\neq r)} \mathbf{C}_{(1)ir}^+ \mathbf{C}_{(1)ir}, \end{aligned} \quad (8)$$

where the superscript + here and below designates the Hermitian conjugate matrix, \mathbf{V}_{rr} is defined by Eq. (7), and the subscripts contain the order parameter (1 or 2) in their parentheses.

The above-demonstrated similarity of expressions of the NCRSPT to those of the RSPT, however, does not refer to coefficients $\mathbf{C}_{(k)mr}$ for $m \neq r$, where k here and below stands for the order parameter ($k = 1, 2, \dots$). These coefficients are defined by the following matrix equations:

$$\mathbf{E}_{(0)m} \mathbf{C}_{(k)mr} - \mathbf{C}_{(k)mr} \mathbf{E}_{(0)r} + \mathbf{W}_{(k)mr} = \mathbf{0}, \quad (9)$$

instead of usual algebraic expressions in terms of fractions containing elements of the perturbation operator and differences in zero-order eigenvalues in their numerators and denominators, respectively. The first-order

matrix $\mathbf{W}_{(1)mr}$ coincides with \mathbf{V}_{mr} . For higher k values, however, more involved expressions are obtained, e. g.,

$$\mathbf{W}_{(2)mr} = \sum_j \mathbf{V}_{mj} \mathbf{C}_{(1)jr} - \mathbf{C}_{(1)mr} \mathbf{V}_{rr}. \quad (10)$$

Finally, expressions for eigenblocks may be exemplified by the second-order correction $\mathbf{E}_{(2)r}$, which takes the form

$$\mathbf{E}_{(2)r} = \frac{1}{2} \sum_i (1 - \delta_{ri}) (\mathbf{V}_{ir}^+ \mathbf{C}_{(1)ir} + \mathbf{C}_{(1)ir}^+ \mathbf{V}_{ir}). \quad (11)$$

The principal matrix problems of the NCRSPT shown in Eq. (9) belong to well-studied matrix equations of the type $\mathbf{A}\mathbf{X} + \mathbf{X}\mathbf{B} + \mathbf{C} = \mathbf{0}$ [28]. Given that $\mathbf{E}_{(0)m}$ and $-\mathbf{E}_{(0)r}$ are Hermitian and negative-definite matrices, the unique solution of Eq. (9) takes the form of an integral

$$\begin{aligned} \mathbf{C}_{(k)mr} &= - \int_0^\infty \exp[\mathbf{E}_{(0)m} t] \mathbf{W}_{(k)mr} \exp[-\mathbf{E}_{(0)r} t] dt. \end{aligned} \quad (12)$$

It is seen, therefore, that the solution of our principal problem of Eq. (3) is expressed in terms of entire submatrices (blocks) of the initial Hamiltonian matrix without specifying either the structures or dimensions of these submatrices (i. e. of $\mathbf{E}_{(0)m}$ and \mathbf{V}_{mj}), and this is the most essential feature of the NCRSPT.

Before finishing this section, an important particular case of diagonal zero-order matrices $\mathbf{E}_{(0)m}$ and $\mathbf{E}_{(0)r}$ should be mentioned [24–27]. Let these matrices consist of elements $E_{(0)m,\mu}$ and $E_{(0)r,\rho}$, respectively. Separate elements of the matrix $\mathbf{C}_{(k)mr}$ may be then expressed algebraically, viz.

$$C_{(k)mr,\mu\rho} = \frac{W_{(k)mr,\mu\rho}}{E_{(0)r,\rho} - E_{(0)m,\mu}}. \quad (13)$$

Certain resemblance between this formula and the relevant expression of the standard RSPT [1–3] may be noticed. Even for this special case, however, no coincidence of these power series is actually obtained. This fact causes no surprise as the matrix \mathbf{C} made up of coefficients \mathbf{C}_{ia} of Eq. (6) serves to transform the initial matrix \mathbf{H} into a block-diagonal form but not into a diagonal one.

3. Applications of NCRSPT to derive effective Hamiltonian matrices for separate subsystems of molecular systems

In this section we will discuss applications of NCRSPT to investigate molecular systems consisting of weakly interacting subsystems separated by substantial energy gaps. The block-diagonalization procedure is used here as an intermediate step in the way of diagonalization of the respective Hamiltonian matrix \mathbf{H} . Subsets of basis orbitals introduced in Section 2 evidently correspond to individual weakly interacting subsystems in this case.

Traditional ways of investigation of the above-specified systems are based on the quasi-degenerate RSPT [1–3] and consist of an initial diagonalization of the intrasubset blocks of the matrix \mathbf{H} followed by taking into account intersubset interactions. This procedure actually implies passing to the basis of delocalized (canonical) molecular orbitals (MOs) of isolated subsystems from the very outset of solving the problem and a subsequent regard for interactions between these MOs. This approach is usually referred to as the PMO theory [29].

The experience of dealing with eigenvalue equations for matrices shows that it is the decision on the first step when solving the problem that determines the terms in which the final results are expressed and interpreted [30]. It is no surprise, therefore, that the results of the PMO theory are expressed in terms of delocalized MOs of isolated subsystems. This fact is the main origin of difficulties in revealing relations of the final electronic structure characteristics to peculiarities of local constitution of the system.

In this context, application of NCRSPT offers a possibility of an inverted order of operations versus the traditional one, namely, intersubsystem interactions may be taken into account before the intrasubsystem ones. To this end, block-diagonalization of the matrix \mathbf{H} should be initially performed. This approach has been referred to as the alternative one [31, 32].

The final numerical results evidently coincide with one another for both approaches provided that these are obtained at the same level of approximation. The alternative approach, however, offers new possibilities for interpretation of results in terms of local structure as demonstrated below (Sections 3.1 and 3.2).

An essential feature of the alternative approach consists also in the fact that eigenblocks of the Hamiltonian matrix \mathbf{H} resulting from the initial block-diagonalization procedure actually coincide with the

effective Hamiltonian matrices for separate subsystems influenced by the intersubsystem interaction [31]. In this respect, certain analogy may be traced between the approach under discussion and the Löwdin's partitioning technique [33–36]. The principal difference of our procedure from that of [33–36] consists in the eigenvalue-independent nature of the effective Hamiltonian matrix and thereby in the non-iterative character of the respective secular problem. The same refers also to comparison of the present approach to the reduction procedures for Hamiltonian matrices suggested in [30, 37–40].

3.1. Studies of regular quasi-one-dimensional systems. Interpretation of energy bands in terms of local structure

Given that atomic orbitals (AOs) of the elementary cell of a regular quasi-one-dimensional system (polymer) are characterized by substantial energy gaps versus the off-diagonal Hamiltonian matrix elements, weakly interacting subsets of AOs may be revealed in the total basis set. These subsets represent definite subchains of our chain, the latter, in turn, coinciding with the above-defined weakly interacting subsystems. Hence, the alternative approach based on NCRSPT may be applied [31].

Before passing to a more specific discussion, let us note that studies of regular quasi-one-dimensional chains usually are based on concepts and methods of the solid state theory [41, 42]. Delocalized Bloch functions corresponding to subchains play the role of MOs in this case. Accordingly, difficulties arise in establishing the relations between the actual dispersion curves and local interorbital interactions in the system. The alternative approach is especially fruitful in this respect as discussed below.

It should be admitted here that the scope of applicability of the general solid state theory is considerably more extended as compared to that of any perturbative approach. This theory, however, resembles the PMO theory [29] in respect of relative order of taking into account the intra- and intersubset interactions. That is why application of NCRSPT offers a definite conceptual alternative to the solid state theory [31].

Inasmuch as no specifying of the numbers of basis orbitals within separate subsets is required when performing the block-diagonalization procedure by means of the NCRSPT (Section 2), quasi-infinite systems may be treated without additional difficulties. To be able to solve the matrix equations like that of Eq. (9) algebraically, the particular case of diagonal zero-order

blocks $E_{(0)r}$ has been invoked. This assumption evidently implies first-order magnitude of both intra- and intersubchain interactions.

The diagonality requirement for blocks $E_{(0)r}$ and the regular constitution of the chain yield proportionality of these blocks to unit matrices of corresponding dimensions. Then the respective algebraic solutions of Eq. (9) have been substituted into expressions for corrections to eigenblocks (see, e. g., Eq. (11)) and simple formulae for the latter have been derived.

The zero- and first-order intrasubchain blocks ($E_{(0)r}$ and V_{rr}) make the principal contributions to the r th eigenblock E_r (see Eq. (7)). This evidently implies correspondence of this eigenblock to the r th subchain of our chain. Again, the remaining corrections $E_{(k)r}$ ($k > 1$) and thereby the total eigenblock E_r imbibes intersubchain interactions represented by submatrices V_{ir} ($i \neq r$). For example, the second-order correction $E_{(2)r}$ is expressed in terms of products of matrices V_{ir} as follows:

$$E_{(2)r} = \sum_{i(\neq r)} \frac{1}{\varepsilon_{(0)r} - \varepsilon_{(0)i}} V_{ri} V_{ir}, \quad (14)$$

where $\varepsilon_{(0)r}$ and $\varepsilon_{(0)i}$ stand for one-electron energies of AOs of the r th and i th subsets, respectively. It has been concluded on this basis that the eigenblocks E_r are nothing more than effective Hamiltonian matrices for separate subchains influenced by the intersubchain interaction [31].

Analysis of separate elements of the eigenblocks E_r also yields interesting conclusions. Thus, the first-order contribution $E_{(1)r,\mu\nu}$ to the effective interaction between AOs $\varphi_{r,\mu}$ and $\varphi_{r,\nu}$ of the r th subchain coincides with their direct interaction (resonance parameter) $V_{rr,\mu\nu}$ (see Eq. (8)), whereas the relevant second-order correction $E_{(2)r,\mu\nu}$ follows from Eq. (14) and describes the indirect interaction between the same AOs by means of AOs of other subchains playing the role of mediators. Accordingly, an indirect interaction by means of two mediators corresponds to the third-order increment $E_{(3)r,\mu\nu}$. Hence, elements of eigenblocks describe effective interactions between AOs of the given subchain that consist of their initial (direct) interactions and of additional indirect interactions by means of nearest AOs of other subchains.

On the whole, the block-diagonalization procedure allows the initial chain to be divided into M non-interacting effective chains, where M coincides with the number of AOs in the elementary cell. Each of these new chains contains both the initial bonds of the respective subchain and some additional bonds originat-

ing from intersubchain interaction. Experience in dealing with specific examples shows that effective chains of a rather simple constitution actually arise, wherein the most important bonds correspond to neighbouring pairs of equivalent AOs. At the same time, each effective chain gives birth to a definite energy band.

On this basis, dispersion relations for separate energy bands may be derived before the final solution of the problem. Moreover, each of several additive components of such a relation may be traced back to a particular type of effective intrasubchain interaction. Inasmuch as the latter, in turn, are expressible in terms of local interorbital interactions (see Eq. (14)), interpretation of dispersion curves in terms of local structure easily follows from the alternative approach. This important achievement has been illustrated in [31] by several non-trivial examples.

3.2. Expressions for effective energies of bridge-assisted interactions

Let us dwell here on studies of molecules and molecular systems described by the general formula $A-(X)_n-B$, where A and B stand for functional groups and $-(X)_n-$ is a bridge usually consisting of a certain number of similar elementary units X (see [32] and the references cited therein). The groups A and B usually are approximately representable by a single frontier orbital which is sufficiently separated from orbitals of the bridge. That is why the functional groups and the bridge may be considered as two weakly interacting subsystems.

Non-conjugated molecules containing NH_2 , OH or $H_2C=CH$ groups joined with a saturated bridge ($X=CH_2$) or several bridges of the same constitution are among the most well-studied systems of the above-specified type. A pair of splitted energy levels corresponds to terminal groups in the photoelectron spectra of these molecules. Interpretation both of the variable extent of this splitting for related compounds and of relative orders of the two levels is of importance for theoretical spectroscopy.

Further, molecular systems of analogous constitution are assumed to participate in the electron transfer reactions in condensed media. In this case, the system contains an electron-donating subsystem (A) and an electron-accepting one (B) joined with bridges of solvent molecules.

Development of the theory of these important and intriguing systems has been overviewed in a detail in [32]. In our context, applications of the standard PMO

theory [29] may be mentioned [43–45]. So far as electron transfer reactions are concerned, partitioning technique [33–36] and related approaches are most commonly used.

Application of the block-diagonalization procedure based on NCRSPT to the Hamiltonian matrix of a system $A-(X)_n-B$ yields an eigenvalue-independent eigenblock corresponding to the subset of orbitals of terminal groups. For the case of two orbitals φ_a and φ_b representing these groups, a single off-diagonal element of this block describes the effective interaction energy (\mathcal{E}_{ab}) between fragments A and B. As with the quasi-one-dimensional chains (Section 3.1), the energy \mathcal{E}_{ab} was shown to consist of the direct (through-space) interaction of orbitals φ_a and φ_b and of various types of their indirect (bridge-assisted) interactions, as well as of mixed increments. On the whole, the effective interaction energy has been expressed in terms of sums of increments corresponding to various pathways through the bridge from one terminal group to another. As opposed to similar expressions based on partitioning technique [33–36], the formulae of [32] contain the difference $E_{(0)a} - E_{(0)b}$ between one-electron energies of orbitals φ_a and φ_b explicitly. A more detailed comparison of these expressions may be found in [32].

The above-mentioned explicit dependence of \mathcal{E}_{ab} upon the difference $E_{(0)a} - E_{(0)b}$ allowed us to study the case of dissimilar functional groups A and B in detail. Given that the latter are joined with a sufficiently long tightly-bound bridge(s), application of NCRSPT yields a generalization to the case of dissimilar groups A and B of the well-known McConnell formula [46] for the bridge-assisted interaction energy. An analogous extension of the scope of validity of the so-called parity rule [43–45, 47] has also been achieved (the rule consists in opposite signs of \mathcal{E}_{ab} for even and odd numbers of mediating orbitals).

4. Non-commutative RSPT in the framework of the non-canonical method of molecular orbitals. The PNCMO theory

Electronic structures of molecules are most commonly studied in terms of delocalized canonical MOs (CMOs) resulting from the canonical HF (CHF) equation [2, 48]. Since the CMOs are usually sought in the form of linear combination of certain basis functions (usually of AOs), the CHF equation resolves itself into the diagonalization problem for the Fockian matrix.

In contrast to the unique CHF equation, various forms of the non-canonical one-electron problem are possible [2, 48]. As delocalized MOs are more easily obtainable from the CHF equation, the non-canonical problems are usually adapted [49] to look for orbitals localized mostly on separate fragments of molecule. (Orbitals of this type are more closely related to chemical concepts of interatomic bonds, lone electron pairs, etc. [49–51].) Localized pattern of MOs usually is achieved by imposing a certain “external” localization criterion (cf. the criterion of minimal self-energy of an atom in the Adams–Gilbert equation [52–54]).

In our context, the Brillouin theorem [22–24, 26, 48, 49] deserves particular attention. Application of this theorem is equivalent to solution of the non-canonical HF equation [48]. On the other hand, the theorem itself contains no particular localization criterion, and, consequently, it may be used to obtain various types of non-canonical MOs (NCMOs).

Applications of this theorem to derive expressions for NCMOs started with the contribution [55], where the conditions that ensure the existence of non-orthogonal localized MOs (LMOs) containing a single bond orbital and tails consisting of vacant orbitals of other bonds have been explored. Thereupon [56, 57], explicit perturbative expressions for tails have been derived in terms of separate elements of the initial Hamiltonian matrix. A similar iterative approach to the linearized version of the Brillouin theorem for the Fockian operator also may be mentioned here [58].

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 NCMOs being sought [22–24, 26, 55–57]. As a result, the block-diagonalization problem for the Fockian matrix actually arises, where the two eigenblocks correspond to subsets of occupied and vacant NCMOs, respectively. Moreover, basis sets of the so-called fragmental orbitals (FOs) were shown to exist for various classes of molecules (Section 5) that contain two weakly interacting subsets separated by a substantial energy gap. In qualitative investigations, these orbitals may be additionally assumed to be orthonormalized [59]. Finally, the Fockian matrices of molecules can be actually replaced by certain effective one-electron Hamiltonian matrices (e. g., of the Hückel type [17]). That is why a solution of the above-discussed non-canonical prob-

lem proved to be possible by means of the particular case of the NCRSPT corresponding to two eigenblocks and thereby two multidimensional eigenfunctions ($N = 2$).

One-electron density matrices (DMs) are also widely used to represent electronic structures. This matrix is one of the most fundamental quantum-mechanical characteristics describing charge redistributions in a molecule and related to numerous observed properties [2, 36]. Moreover, the DM is a unique characteristic of the given molecule in contrast to NCMOs. The relevant general expressions for the DM were shown to follow from the projector to a single multieigenfunction of the Hamiltonian matrix containing occupied NCMOs (Section 4.2). Finally, the total energy is expressible either as the trace of the occupied eigenblock multiplied by the occupation number 2 or in terms of the DM (Section 4.3). The above-outlined scheme forms the basis of the general perturbative PNCMO theory.

The actual way of formulating the PNCMO theory, however, was different from this rather straightforward scheme. Thus, the particular case of the block-diagonalization problem for two subsets ($N = 2$) [24] has been solved before formulating the general formalism of Section 2. This particular solution was also additionally generalized to the case of two non-orthogonal sets of FOs [25]. (The generalized solution has been accordingly expressed in terms of entire blocks of both Hamiltonian and overlap matrices.) Finally, a direct way of obtaining the DM based on solution of the so-called commutation equation has been applied in the first derivations of this matrix [18–24]. These results will also be discussed briefly in Sections 4.1 and 4.2.

4.1. Analysis of expressions for NCMOs

To discuss the above-indicated expressions, we will turn to more convenient notations used throughout [22–27]. Inasmuch as the principal subsets of FOs usually correspond to initially-occupied (bonding) and initially-vacant (antibonding) orbitals (Section 5), these can be conveniently represented by row-matrices $|\Phi_{(+)}\rangle$ and $|\Phi_{(-)}\rangle$. The zero-order Hamiltonian matrix $\mathbf{H}_{(0)}$ was assumed to take a block-diagonal form containing submatrices $\mathbf{E}_{(+)}$ and $-\mathbf{E}_{(-)}$ in its diagonal positions, where the minus sign in front of $\mathbf{E}_{(-)}$ was introduced for convenience. The relevant first-order matrix $\mathbf{H}_{(1)}$ has been represented in terms of four blocks

\mathbf{T} , \mathbf{R} , and \mathbf{Q} so that the following relations with submatrices \mathbf{V}_{mr} of Section 2 result:

$$\begin{aligned}\mathbf{H}_{(1)11} &= \mathbf{V}_{11} = \mathbf{T}, \\ \mathbf{H}_{(1)22} &= \mathbf{V}_{22} = \mathbf{Q}, \\ \mathbf{H}_{(1)12} &= \mathbf{V}_{12} = \mathbf{R}.\end{aligned}\quad (15)$$

The multieigenfunctions of this Hamiltonian matrix containing occupied and vacant NCMOs, respectively, have been accordingly designated by $|\Psi_{(+)}\rangle$ and $|\Psi_{(-)}\rangle$. From Eq. (6) it is evident that these take the form of simple linear combinations of two multiorbitals $|\Phi_{(+)}\rangle$ and $|\Phi_{(-)}\rangle$ containing matrix coefficients, e. g.,

$$|\Psi_{(+)}\rangle = |\Phi_{(+)}\rangle \mathbf{C}_{11} + |\Phi_{(-)}\rangle \mathbf{C}_{21}. \quad (16)$$

Equation (16) can be considered as the matrix analogue of expressions for MOs of two-level systems as linear combinations of two AOs. The relations like that of Eq. (16) may be rewritten in the following matrix form:

$$\begin{aligned}||\Psi_{(+)}\rangle, |\Psi_{(-)}\rangle| &= ||\Phi_{(+)}\rangle, |\Phi_{(-)}\rangle| \begin{vmatrix} \mathbf{C}_{11} & \mathbf{C}_{12} \\ \mathbf{C}_{21} & \mathbf{C}_{22} \end{vmatrix} \\ &= \Phi \mathbf{C},\end{aligned}\quad (17)$$

where the transformation matrix \mathbf{C} is expressible as a power series. The first three corrections of this series are

$$\begin{aligned}\mathbf{C}_{(0)} &= \mathbf{I}, \\ \mathbf{C}_{(1)} &= \begin{vmatrix} \mathbf{0} & \mathbf{G}_{(1)} \\ -\mathbf{G}_{(1)}^+ & \mathbf{0} \end{vmatrix}, \\ \mathbf{C}_{(2)} &= \begin{vmatrix} -\frac{1}{2}\mathbf{G}_{(1)}\mathbf{G}_{(1)}^+ & \mathbf{G}_{(2)} \\ -\mathbf{G}_{(2)}^+ & -\frac{1}{2}\mathbf{G}_{(1)}^+\mathbf{G}_{(1)} \end{vmatrix},\end{aligned}\quad (18)$$

where the notations $\mathbf{G}_{(k)}$ here and below stand for $\mathbf{C}_{(k)12}$. It should be noted here that $\mathbf{G}_{(k)}$ play the role of the principal matrices of the PNCMO theory, and these are determined by matrix equations

$$\mathbf{E}_{(+)}\mathbf{G}_{(k)} + \mathbf{G}_{(k)}\mathbf{E}_{(-)} + \mathbf{W}_{(k)12} = \mathbf{0} \quad (19)$$

resulting from Eq. (9), where $\mathbf{W}_{(1)12} = \mathbf{R}$ and $\mathbf{W}_{(2)12} = \mathbf{T}\mathbf{G}_{(1)} - \mathbf{G}_{(1)}\mathbf{Q}$. Coincidence between matrices $\mathbf{C}_{(0)}$ and \mathbf{I} seen from Eq. (18) ensures both one-to-one correspondence between NCMOs and basis orbitals (FOs) and a localized nature of the former.

Given that $\mathbf{E}_{(+)}$ and $\mathbf{E}_{(-)}$ are diagonal matrices, Eq. (13) yields the expressions

$$G_{(1)ir}^{(d)} = G_{ri(1)}^{+(d)} = -\frac{R_{ir}}{E_{(+)i} + E_{(-)r}}, \quad (20)$$

$$\begin{aligned} G_{(2)ir}^{(d)} &= G_{(2)ri}^{+(d)} \\ &= \frac{1}{E_{(+)i} + E_{(-)r}} \left\{ \sum_p^{\text{IOFOs}} \frac{T_{ip}R_{pr}}{E_{(+)p} + E_{(-)r}} \right. \\ &\quad \left. - \sum_m^{\text{IVFOs}} \frac{R_{im}Q_{mr}}{E_{(+)i} + E_{(-)m}} \right\}, \quad (21) \end{aligned}$$

where the abbreviations IOFOs and IVFOs stand for initially-occupied and initially-vacant FOs, respectively, and the superscript (d) serves to distinguish this particular case. Interpretation of these elements [24] was based on the concept of direct (through-space) and indirect interactions of orbitals [47, 60–62].

Thus, the first-order term $G_{(1)ir}^{(d)}$ describes the direct (through-space) interaction between orbitals $\varphi_{(+)i}$ and $\varphi_{(-)r}$. Inasmuch as resonance parameters (R_{ir}) decrease rapidly when the interfragmental distance increases, the same refers also to the direct interaction $G_{(1)ir}^{(d)}$. Hence, considerable LMO tails usually are localized on the nearest environment of the given basis orbital. Similarly, the element $G_{(2)ir}^{(d)}$ has been interpreted as indirect interaction of the same basis functions by means of various mediators (either $\varphi_{(+)p}$ or $\varphi_{(-)m}$). This interaction is likely to be of a more long-range nature than the direct one.

4.2. The two ways of derivation of the one-electron DM

As it was mentioned already, the one-electron DM of molecules described by the Hamiltonian matrix of Section 4.1 may be obtained [25] on the basis of a projector to the multieigenfunction $|\Psi_{(+)}\rangle$ of Eq. (16) multiplied by the occupation number 2, that is

$$P(\mathbf{r} | \mathbf{r}') = 2|\Psi_{(+) }(\mathbf{r})\rangle\langle\Psi_{(+) }(\mathbf{r}')|. \quad (22)$$

Substituting Eq. (16) into Eq. (22) yields the following expression for the DM $P(\mathbf{r} | \mathbf{r}')$ in terms of four multidimensional elements of the bond order matrix:

$$P(\mathbf{r} | \mathbf{r}') = \sum_{i,j=1}^2 |\Phi_i(\mathbf{r})\rangle \mathbf{P}_{ij} \langle\Phi_j(\mathbf{r}')|, \quad (23)$$

where i and j coincide with either $(+)$ or $(-)$. This result serves as a generalization of the well-known bilinear form of the DM in terms of individual basis functions [36]. The multidimensional elements \mathbf{P}_{ij} are

$$\begin{aligned} \mathbf{P}_{11} &= 2\mathbf{C}_{11}\mathbf{C}_{11}^+, \\ \mathbf{P}_{22} &= 2\mathbf{C}_{21}\mathbf{C}_{21}^+, \\ \mathbf{P}_{12} &= 2\mathbf{C}_{11}\mathbf{C}_{21}^+. \end{aligned} \quad (24)$$

These expressions demonstrate the analogy of our DM to that of a simple two-level system. Use of Eqs. (17) and (18), in turn, allows us to obtain the four submatrices of the matrix \mathbf{P} in terms of the principal matrices $\mathbf{G}_{(k)}$ defined by Eq. (19). This procedure may be referred to as the indirect way of obtaining the DM (i. e. via NCMOs as an intermediate step).

The direct way of obtaining the same matrix consists in solution of the following system of equations [16]:

$$[\mathbf{H}, \mathbf{Y}]_- = \mathbf{0}, \quad \mathbf{Y}^2 = \mathbf{I}; \quad \text{Tr } \mathbf{Y} = 0, \quad (25)$$

where \mathbf{Y} is the residual charge matrix connected with \mathbf{P} by the relation $\mathbf{Y} = \mathbf{P} - \mathbf{I}$, and the notation $[\dots]_-$ indicates a commutator of matrices. The commutation condition of Eq. (25) is the main physical requirement determining the matrix \mathbf{Y} and thereby the DM \mathbf{P} . This relation results from Dirac's equation for the time-independent Hamiltonian. The remaining relations of Eq. (25) are additional system-structure-independent restrictions following from the idempotence requirement ($\Pi^2 = \Pi$) for the projector $\Pi = (1/2)P$ and the charge conservation condition, respectively.

In [24], the system of matrix equations of Eq. (25) has been solved directly by substituting the matrix \mathbf{Y} in the form of a power series and collecting the terms of the same order. Each correction $\mathbf{Y}_{(k)}$, in turn, has been represented in terms of four multidimensional elements.

It is evident that both ways of obtaining the bond order matrix \mathbf{P} yield coinciding results, viz. the corrections $\mathbf{P}_{(k)}$ of the following form:

$$\mathbf{P}_{(k)} = \begin{vmatrix} \mathbf{P}_{(k)+} & -2\mathbf{G}_{(k)} \\ -2\mathbf{G}_{(k)}^+ & \mathbf{P}_{(k)-} \end{vmatrix}, \quad (26)$$

where the intrasubset blocks $\mathbf{P}_{(k)+}$ and $\mathbf{P}_{(k)-}$ have been expressed in terms of matrices $\mathbf{G}_{(k-1)}$, $\mathbf{G}_{(k-2)}$, etc. as exemplified below:

$$\begin{aligned}\mathbf{P}_{(0)+} &= 2\mathbf{I}, \\ \mathbf{P}_{(0)-} &= \mathbf{0}, \\ \mathbf{P}_{(1)+} &= \mathbf{P}_{(1)-} = \mathbf{0}, \\ \mathbf{P}_{(2)+} &= -2\mathbf{G}_{(1)}\mathbf{G}_{(1)}^+, \\ \mathbf{P}_{(2)-} &= 2\mathbf{G}_{(1)}^+\mathbf{G}_{(1)},\end{aligned}\quad (27)$$

etc. It should be noted, however, that the direct way of obtaining the matrix \mathbf{P} proves to be easier and more convenient when looking for higher order corrections [63, 64] necessary for applications (Section 6). Moreover, feasibility of the direct way demonstrates that the eigenblock equation is not the only problem the NCRSPT is applicable to.

Comparison of corrections $\mathbf{P}_{(k)}$ ($k = 1, 2$) to respective corrections $\mathbf{C}_{(k)}$ of Eq. (18) indicates similarity of their structures. Analysis of direct ways of obtaining these corrections [24] allowed us to conclude that this similarity originates from a deep interrelation between the Brillouin theorem and the commutation condition for the DM in the framework of NCRSPT. Moreover, direct matrix relations between corrections $\mathbf{P}_{(k)}$ and $\mathbf{C}_{(k)}$ have been derived [24].

Similarity of the structures of corrections $\mathbf{P}_{(k)}$ and $\mathbf{C}_{(k)}$ has important implications. First, NCMOs and the respective DM rows (columns) prove to be interrelated and characterized by the same dependence on the structure of the system. Second, diagonal elements of the matrix \mathbf{P} (i. e. occupation numbers of individual FOs) are proportional to extents of delocalization of respective NCMOs, namely, the alterations in occupation numbers versus their initial values (equal to either 2 or 0 for bonding and antibonding FOs, respectively) coincide with the total delocalization coefficients of respective NCMOs (see [23, 24] for definition). As occupation numbers are invariant to unitary transformations, the above relation implies that a certain special choice of NCMOs was actually made when applying NCRSPT, namely, NCMOs, the extents of delocalization of which were related to the unique populations of basis orbitals. Finally, from similarity of corrections $\mathbf{P}_{(k)}$ and $\mathbf{C}_{(k)}$ it follows that the unique bond order matrix belongs to the localized way of representing electronic structures along with LMOs. This conclu-

sion contributes to an increased importance of this alternative representation of electronic structures versus the delocalized (canonical) one.

4.3. Analysis of the total energy

For a system represented by a certain one-electron Hamiltonian matrix \mathbf{H} , the expression

$$\mathcal{E} = \text{Tr}(\mathbf{P}\mathbf{H}) \quad (28)$$

is among alternative definitions of the total energy (\mathcal{E}) [16]. Given that the matrix \mathbf{H} contains a zero-order ($\mathbf{H}_{(0)}$) and the first-order matrices ($\mathbf{H}_{(1)}$) (Section 4.1), two components reveal themselves within any correction $\mathcal{E}_{(k)}$ of the power series for the energy \mathcal{E} , viz.

$$\begin{aligned}\mathcal{E}_{(k)}^{(\alpha)} &= \text{Tr}(\mathbf{P}_{(k)}\mathbf{H}_{(0)}), \\ \mathcal{E}_{(k)}^{(\beta)} &= \text{Tr}(\mathbf{P}_{(k-1)}\mathbf{H}_{(1)}).\end{aligned}\quad (29)$$

Substituting the expressions for $\mathbf{P}_{(k)}$ of Eqs. (26) and (27) along with a definite algebraic procedure based on application of Eq. (19) yields the following general relation [64]:

$$(k-1)\mathcal{E}_{(k)}^{(\beta)} = -k\mathcal{E}_{(k)}^{(\alpha)} \quad (30)$$

for any k . Equation (30), in turn, implies the total correction $\mathcal{E}_{(k)}$ to be alternatively representable as follows:

$$\mathcal{E}_{(k)} = -\frac{1}{k-1}\mathcal{E}_{(k)}^{(\alpha)}, \quad \mathcal{E}_{(k)} = \frac{1}{k}\mathcal{E}_{(k)}^{(\beta)}. \quad (31)$$

Opposite signs of both components of the total correction $\mathcal{E}_{(k)}$ may also be seen from Eq. (30) along with the inequality for their absolute values given below, viz.

$$|\mathcal{E}_{(k)}^{(\beta)}| > |\mathcal{E}_{(k)}^{(\alpha)}|. \quad (32)$$

Therefore, the correction $\mathcal{E}_{(k)}$ of the total energy \mathcal{E} is determined by a difference between two interdependent components, namely, between $\mathcal{E}_{(k)}^{(\beta)}$ of a larger absolute value and $\mathcal{E}_{(k)}^{(\alpha)}$ of a smaller absolute value. Consequently, it is the sign of $\mathcal{E}_{(k)}^{(\beta)}$ that conditions the sign of the total correction $\mathcal{E}_{(k)}$.

In particular, the zero- and first-order corrections take the form

$$\begin{aligned}\mathcal{E}_{(0)} &= \mathcal{E}_{(0)}^{(\alpha)} = 2\text{Tr}\mathbf{E}_{(+)}, \\ \mathcal{E}_{(1)} &= \mathcal{E}_{(1)}^{(\beta)} = 2\text{Tr}\mathbf{T},\end{aligned}\quad (33)$$

and their sum coincides with the total one-electron energy of isolated FOs. Given that one-electron energies

of FOs are entirely included into respective diagonal elements of the matrix $\mathbf{E}_{(+)}$, the equality $\mathcal{E}_{(1)} = 0$ obtained in [65, 66] results.

For the second-order correction $\mathcal{E}_{(2)}$, the following formula has been derived [27, 64]:

$$\mathcal{E}_{(2)} = -\text{Tr}(\mathbf{G}_{(1)}\mathbf{R}^+) \quad (34)$$

on the basis of expression in terms of $\mathcal{E}_{(2)}^{(\beta)}$ shown in Eq. (31). If we recall that a block-diagonal zero-order Hamiltonian matrix ($\mathbf{H}_{(0)}$) corresponds to the power series under discussion (Section 4.1), Eq. (34) can be considered as a generalization of the well-known Dewar formula for total energies of molecules (the latter corresponds to a diagonal form of $\mathbf{H}_{(0)}$ and follows from the standard RSPT). Feasibility of such a generalization, in turn, demonstrates non-trivial consequences of the allowance for a non-diagonal zero-order matrix $\mathbf{H}_{(0)}$ in NCRSPT [27].

Additional possibilities for interpretation of relations of Eqs. (30)–(32) arise in the case of diagonal blocks $\mathbf{E}_{(+)}$ and $\mathbf{E}_{(-)}$ containing the elements $E_{(+)i}$ and $E_{(-)j}$. Thus, the following expressions for $\mathcal{E}_{(k)}^{(\alpha)}$ have been derived in this case [64]:

$$\mathcal{E}_{(k)}^{(\alpha)} = \sum_i^{\text{IOFOs}} \sum_j^{\text{IVFOs}} x_{(+)i,(-)j}^{(k)} (E_{(+)i} + E_{(-)j}), \quad (35)$$

where $x_{(+)i,(-)j}^{(k)}$ coincides with the k th-order partial transferred population between orbitals $\varphi_{(+)i}$ and $\varphi_{(-)j}$. The latter emerge when expressing the occupation numbers of FOs as sums of increments of individual orbitals of the opposite subset, viz.

$$\begin{aligned} \mathbf{P}_{(k)+,ii} &= \sum_l^{\text{IVFOs}} x_{(+)i,(-)l}^{(k)}, \\ \mathbf{P}_{(k)-,jj} &= \sum_m^{\text{IOFOs}} x_{(-)j,(+)m}^{(k)}, \end{aligned} \quad (36)$$

where $x_{(+)i,(-)j}^{(k)} = -x_{(-)j,(+)i}^{(k)}$. For $k = 2$ and 3, simple formulae for partial transferred populations have been derived, viz.

$$\begin{aligned} x_{(+)i,(-)j}^{(2)} &= -2(G_{(1)ij})^2, \\ x_{(+)i,(-)j}^{(3)} &= -4G_{(1)ij}G_{(2)ij}. \end{aligned} \quad (37)$$

On the basis of Eq. (35), the first component of the correction $\mathcal{E}_{(k)}^{(\alpha)}$ (i.e. $\mathcal{E}_{(k)}^{(\alpha)}$) has been interpreted as the charge transfer energy (note that $E_{(+)i} + E_{(-)j}$ coincides with the energy interval between orbitals $\varphi_{(+)i}$

and $\varphi_{(-)j}$). Again, the remaining part of the total correction $\mathcal{E}_{(k)}^{(\beta)}$ ($\mathcal{E}_{(k)}^{(\beta)}$) was shown to describe the effect of formation of new bond orders upon the k th-order energy.

These interpretations along with the general relations of Eqs. (30)–(32) allowed us to conclude that stabilization of the system versus the set of isolated FOs (if any) is entirely due to formation of new bond orders owing to the interorbital interaction, and the subsequent charge redistribution actually reduces this stabilizing effect. On the other hand, the absolute value of the stabilization energy is proportional to the charge transfer energy as Eq. (31) indicates. This principal result formed the basis of substantiation [64] of the popular intuition-based assumption of the theoretical chemistry about a relation between the stabilization energy and the relevant charge redistribution. It should be added finally that a positive charge transfer energy $\mathcal{E}_{(2)}^{(\alpha)}$ and a negative total correction $\mathcal{E}_{(2)}$ has been obtained for $k = 2$. This conclusion gave an additional insight into the content of the Dewar formula [27].

5. Applications of the PNCMO theory to investigate electronic structures of separate classes of molecules

Each of the above-indicated applications may be characterized by a particular choice of basis functions, i.e. of FOs. Thus, let us start with discussing these functions.

Orbitals localized on separate fragments of the system(s) under study usually play the role of FOs. So far as the structures of the fragments themselves are concerned, individual chemical bonds both of saturated [22–24, 27] and conjugated molecules [67] and phenyl rings along with substituents [63, 68] may be mentioned, as well as separate molecules of many-molecular systems (Section 6).

It is noteworthy here that orbitals of the above-specified type are among popular basis sets in quantum chemistry [69]. This especially refers to strictly localized two-centre bond orbitals (BOs) for alkanes and their derivatives [56, 57, 64, 65]. In our applications, BOs have been defined as eigenfunctions of separate two-dimensional Hamiltonian matrix blocks associated with pairs of atomic or hybrid orbitals pertinent to the same bond so that the direct intrabond interaction vanishes. For saturated systems [22–24, 27] and π -electron subsystems of conjugated molecules [67], sp^3 hybrid AOs (HAOs) supplemented by $1s_{\text{H}}$ AOs of hydrogen

atoms and $2p_z$ AOs of carbon atoms were correspondingly used. Eigenfunctions of six-dimensional blocks in the basis of $2p_z$ AOs of carbon atoms were accordingly invoked when studying phenyl rings [63, 68]. Substantial energy gaps between bonding and antibonding orbitals is the main origin of applicability of the NCRSPT in the basis of FOs.

The fact that even particular results of NCRSPT (i. e. those based on a certain choice of FOs) usually embrace entire series or classes of related molecules also deserves emphasizing. Indeed, related compounds usually consist of the same fragments joined in a uniform manner (cf. alkanes containing C–C and C–H bonds). This, in turn, implies FOs of similar structure to represent these compounds. Consequently, a common Hamiltonian operator and/or matrix corresponds to the whole class, where individual representatives (molecules) are characterized by specific structures and dimensions of multidimensional parameters \mathbf{H}_{ij} (see Eq. (1)). Accordingly, a single eigenblock equation refers to the whole class.

Before finishing these introductory remarks, let us distinguish between direct and indirect applications of the PNCMO theory. The former case implies FOs to play the role of the only basis set. Alternatively, we start with the basis of either HAOs or AOs and transform the relevant Hamiltonian matrix into the basis of FOs in order to be able to apply the NCRSPT. Thereupon, retransformation of the results into the initial basis set is carried out. The latter procedure, in turn, may embrace either the entire matrices \mathbf{C} and \mathbf{P} or their particular blocks. (The term local retransformation will be used in the latter case.)

The subsequent overview starts with direct applications of the PNCMO theory in the basis of BOs [22–24, 27, 64, 70] (Section 5.1). These results originally referred to alkanes and their derivatives. Although their applicability to π -electron subsystems of aliphatic conjugated hydrocarbons seems to be rather evident, the relevant extension of the discussion is not undertaken. The main reasons of such a decision are cleared up in Section 5.2, where indirect applications of the PNCMO theory [67, 71, 72] are described. Section 5.3 is devoted to results of local retransformations of expressions of the PNCMO theory [68, 73, 74]. It deserves mentioning here that the contribution [63] devoted to the indirect intersubstituent interaction also belongs to direct applications of the PNCMO theory. However, the relevant results are not discussed separately in this review because of their close resemblance

to those of two interacting molecules overviewed in Section 6.

5.1. Interbond interaction in alkanes and their derivatives

In accordance with the above-introduced definition of BOs, two bond orbitals were ascribed to each chemical bond in a saturated molecule, viz. the initially-occupied bonding BO (BBO) $\varphi_{(+)}i$ and the initially-vacant antibonding BO (ABO) $\varphi_{(-)}i$. Orbitals referring to lone electron pairs (if any) can also be included into the subset $\{\varphi_{(+)}\}$. As a result, a Hamiltonian matrix consisting of four submatrices like that of Section 4.1 has been constructed. The first-order magnitude of interactions (resonance parameters) of the intersubset type (i. e. between a BBO and an ABO) versus the intersubset energy gaps [24] follows from the relevant estimations [19, 21, 75–79]. These ratios between matrix elements, in turn, imply applicability to both alkanes and their derivatives of the NCRSPT and thereby of the results of Section 4. It is also noteworthy here that the above-mentioned ratios have been directly related to the tetrahedral local structure of alkanes [22].

On the whole, a common localized description of saturated molecules follows from the PNCMO theory of Section 4, wherein LMOs and the DM play the role of alternative representations of electronic structures.

So far as the structures of the zero-order blocks $\mathbf{E}_{(+)}$ and $\mathbf{E}_{(-)}$ are concerned, an assumption about their diagonality proved to be a somewhat rough approximation for alkanes [27]. In particular, resonance parameters between nearest-neighbouring (geminal) BBOs were shown to exceed those of the intersubset type considerably [27, 75, 76, 78]. In this connection, two different approximations have been considered, the first one being based on acceptance of diagonal matrices $\mathbf{E}_{(+)}$ and $\mathbf{E}_{(-)}$, and the second one containing a non-diagonal matrix $\mathbf{E}_{(+)}$.

Let us start with the first approximation. Similar energies of all BBOs and of all ABOs may be assumed in this case [80–82]. As a result, matrices $\mathbf{E}_{(+)}$ and $\mathbf{E}_{(-)}$ become proportional to unit matrices and thereby the relevant problem of Eq. (20) may be solved algebraically (see also Section 3.1). Studies of respective expressions for the LMO representation matrix and for the DM showed definite common features to be inherent in these matrices [22]. These have been traced back to the similar spatial constitution of all alkanes, viz. to the constant numbers of the nearest-neighbouring (geminal) bonds for all C–C and for all C–H bonds

equal to six and three, respectively. In particular, similar structures have been obtained for both LMOs and the DM rows (columns) belonging to C–C and C–H bonds. It deserves mentioning here that transferability of LMOs of alkanes has been borne out by numerical calculations, too [50, 51]. In this context, the results of NCRSPT yield a general relation between this transferability and the common local structure of these molecules.

In the framework of the same approximation, application of Eq. (34) to the total energy of alkanes [71] actually yields the Dewar formula [29, 65, 66, 83]. The *a priori* negative sign of the second-order correction of this formula, in turn, indicates an additional stabilization of any molecule versus the relevant set of isolated BOs in line with the observed stability of alkanes. Moreover, any direct interbond interaction was shown to contribute to stabilization of the whole system whatever the actual spatial arrangement of participating bonds [27, 71].

An analogous study of substituted alkanes may be found in [70]. Rules governing the interbond charge transfer originating from the inductive effect of substituent (heteroatom) have been formulated there. On the basis of the general relation between the LMO representation matrix and the DM (Section 4.2) it has been demonstrated that the inductive effect may be interpreted either in terms of a perturbed electron density distribution or in terms of LMOs that have changed shape relative to those of parent alkanes. The latter perturbations, in turn, were shown to be proportional to the extents of delocalization of LMOs in the parent hydrocarbons. Accordingly, the well-known short-range nature of the inductive effect has been concluded to originate from a weak interbond delocalization in alkanes.

Application of the more rigorous second approximation to alkanes has been discussed in [27] in connection with the generalization of the Dewar formula to the case of zero-order intrasubset interactions. No algebraic solution of Eq. (19) is obtained in this case. Thus, a general analysis of LMOs and DM is hardly possible.

Nevertheless, some conclusions concerning total energies of alkanes have been drawn on the basis of studies of signs of the second-order correction $\mathcal{E}_{(2)}$ referring to zero-order blocks $\mathbf{E}_{(+)}$ and $\mathbf{E}_{(-)}$ of arbitrary constitution. Thus, stabilization of the system versus the set of isolated BOs was confirmed for negative-definite matrices $\mathbf{E}_{(+)}$ and $\mathbf{E}_{(-)}$ [28, 84]. Negative signs of eigenvalues of matrices $\mathbf{E}_{(+)}$, in turn, have

been concluded on the basis of studies of their spectra [37, 38, 40]. Hence, the stabilizing effect of the interbond interaction in alkanes was additionally supported. As opposed to the Dewar formula, however, a more profound accounting for stability of alkanes follows from its generalization. Indeed, the above-mentioned negative signs of eigenvalues of matrices $\mathbf{E}_{(+)}$ were related to the asymmetry of their spectra relatively to diagonal elements, which, in turn, is conditioned by the specific spatial arrangement of BOs and thereby of bonds. Consequently, the tetrahedral spatial arrangement of quartets of bonds at the same carbon atom (molecular topology) was considered as the main origin of stability of alkanes.

5.2. Comparative studies of saturated and conjugated hydrocarbons

Bond orbitals are not the optimum basis functions in respect of describing the details of electron density distributions, especially of changes in the intrabond characteristics due to interbond interaction. To this end, the HAO (AO) bases have been used as initial basis sets (cf. the indirect application of the PNCMO theory [67, 71, 72]). Advantages of HAOs (AOs) when comparing the relative rates of convergence of the power series for different types of molecules [67] can also be mentioned.

The HAOs (AOs) of hydrocarbons may be represented by close values of Coulomb and of intrabond resonance parameters, whereas the remaining Hamiltonian matrix elements are relatively small [18–21, 23, 59, 67, 71, 72, 75–79]. This allowed us to reveal a zero-order term $\tilde{\mathbf{H}}_{(0)}$ of a simple and common form in the total Hamiltonian matrix $\tilde{\mathbf{H}}$, which contains unit matrices in its off-diagonal positions. Then the relevant unitary transformation matrix \mathbf{U} (which describes transfer to the basis of BOs and backwards) also consists of unit submatrices and the transformed Hamiltonian matrix ($\mathbf{H} = \mathbf{U}^+ \tilde{\mathbf{H}} \mathbf{U}$) coincides with that referred to as the first approximation for alkanes (Section 5.1).

It is evident that new combinations of the principal matrices $\mathbf{G}_{(k)}$ including their Hermitian-conjugate counterparts ($\mathbf{G}_{(k)}^+$) arise as building blocks of the final DM ($\tilde{\mathbf{P}}$) after retransformation [71, 72]. These combinations were shown to represent new types of intramolecular interactions being expressed in terms of through-space and through-bond ones, namely, intrabond polarization, interbond charge transfer, and redistribution of bond orders (rebonding).

Non-zero intrabond dipole moments in alkanes even for uniform Coulomb parameters of all HAOs and $1s_H$ AOs may be mentioned as a principal result here. Indeed, the second-order intrabond polarization was shown to yield a substantial increment to an intrabond dipole proportional to the self-interaction ($G_{(2)ii}$) between respective BOs $\varphi_{(+i)}$ and $\varphi_{(-i)}$ by means of orbitals of the nearest environment. For C–C bonds in alkanes, the mediating effects of the six geminal neighbours cancel out each other, and, consequently, zero dipoles are obtained. Alternatively, non-zero transferable dipole moments follow for C–H bonds. Their immediate reason was shown to consist in the non-symmetric nearest environment of these bonds. It has been concluded on this basis that non-zero experimental dipole moments of some alkanes [85] are not necessarily related to differences in electronegativities of carbon and hydrogen atoms.

Furthermore, an alternative interpretation of the total energy (versus that in terms of interbond interactions discussed in Section 5.1) was achieved using the HAO (AO) basis [72]. Thus, any correction $\mathcal{E}_{(k)}$ of the energy \mathcal{E} has been expressed as trace of the rebonding matrix $\Omega_{(k)}$, the latter taking the off-diagonal position within the retransformed correction $\tilde{\mathbf{P}}_{(k)}$. As a result, stabilization of hydrocarbons has been related to the so-called rebonding effect, which involves a formation of new bond orders between orbitals of different bonds due to their interaction accompanied by reduction of intrabond bond orders.

Along with the total k th-order energy $\mathcal{E}_{(k)}$, its separate components $\mathcal{E}_{(k)}^{(\alpha)}$ and $\mathcal{E}_{(k)}^{(\beta)}$ also acquired a new interpretation in the HAO (AO) basis [71, 72]. (Note that the relations of Eqs. (29)–(32) are invariant towards the unitary transformations of the basis set.) Thus, the first component $\mathcal{E}_{(k)}^{(\alpha)}$ contains the k th-order corrections to the neighbouring bond orders, whereas the second one ($\mathcal{E}_{(k)}^{(\beta)}$) consists of contributions of non-neighbouring bond orders. As a result of Eq. (30), the relevant effects upon the total k th-order energy are interrelated. In particular, consideration of the second-order term ($k = 2$) allowed us to conclude that lowering in the neighbouring bond orders by itself gives rise to destabilization of the system in accordance to the expectation ($\mathcal{E}_{(2)}^{(\alpha)} > 0$). On this basis, the final stabilization of hydrocarbon versus the respective set of isolated bonds was traced back to the fact that the total stabilizing effect of the newly-formed non-neighbouring bond orders exceeds twice the total destabilizing increment due to reduction of the neighbouring bond orders.

Let us turn now to comparison of saturated and conjugated hydrocarbons [67]. A considerably slower convergence of the power series for both the LMO representation matrix and the DM is peculiar to conjugated molecules versus the saturated ones, and this makes the most important difference between the two classes. Furthermore, substantial individual differences are observed in the relative rates of convergence for separate conjugated hydrocarbons as opposed to the saturated ones. In particular, the convergence rate of linear polyenes decreases gradually when the chain length increases. On the other hand, turning from linear to a cyclic constitution of the chain leads to drastic reduction of the convergence rate. These results, in turn, have been related to different relative values of interbond interactions versus the intrabond energy gaps for conjugated and saturated hydrocarbons (these were evaluated to be 0.25 and 0.1, respectively). It has been concluded on this basis that applicability of the PNCMO theory to conjugated hydrocarbons in general is not self-evident.

Before finishing this subsection, investigation of validity of the basis set orthogonality assumption for alkanes [52] should be mentioned. Let us start with a notation that the above-mentioned assumption seems to be less justified in the HAO basis because of large intrabond overlap integrals. Treatment of this problem is known to be based on transforming the initial Hamiltonian matrix into the symmetrically orthogonalized basis using the Löwdin's transformation matrix $S^{-1/2}$ [86, 87], where S stands for the initial overlap matrix. To obtain a convergent power series for the matrix $S^{-1/2}$ in terms of four submatrices of the matrix S , the NCRSPT has been successfully applied in [59]. This result not only allowed us to justify the basis set orthogonality assumption for alkanes in the HAO basis, but also demonstrated an example of applicability of NCRSPT in dealing with power functions for matrices.

5.3. Electron density redistributions inside hydrocarbon fragments under influence of a heteroatom

As already mentioned, local retransformations of expressions of the PNCMO theory into the HAO (AO) bases are also possible. The relevant matrices \mathbf{U} then embrace orbitals of a certain fragment of the molecule. It is noteworthy that such a procedure refers to all molecules containing the given fragment. Additivity of the PNCMO expressions for elements of the bond order matrix with respect to contributions of separate FOs

(Section 4) allows us to consider the effect of a certain external group (e. g., of a substituent or heteroatom) upon the fragment under interest separately without specifying the structure of the whole compound. The results of just this approach are overviewed in this subsection.

Let us start with a two-dimensional DM block [73, 74] corresponding to two BOs $\varphi_{(+i)}$ and $\varphi_{(-i)}$ of the i th bond defined in terms of HAOs(AOs) χ_1 and χ_2 generally represented by different Coulomb parameters. The diagonal elements of the retransformed DM block describing the occupation numbers of orbitals χ_1 and χ_2 take then the form of sums of several meaningful components, including the zero-order (primary) dipole moment, the increments of the secondary polarization of various orders, the analogous contributions of the so-called depolarization, as well as increments of the population alteration of the whole bond due to interbond charge transfer.

Applications of these results to substituted alkanes [73] allowed us to replenish the early interpretation of the inductive effect in terms of interbond charge transfer (Section 5.1). Thus, alteration in the secondary polarization of a C–C (or C–H) bond under influence of a heteroatom was shown to be among the principal components of the effect. This increment, in turn, has been related to differences in the indirect self-interaction ($G_{(2)ii}$) between BOs $\varphi_{(+i)}$ and $\varphi_{(-i)}$ by means of orbitals of the heteroatom-containing bond before and after substitution.

Further, the so-called *trans*-effect of heteroatom, revealing itself as non-equivalence of the *cis*- and *trans*-arranged C_β – C_γ (C_β –H) bonds with respect to the heteroatom-containing (Z – C_α) bond, has been traced back to the third order increments to occupation numbers of HAOs (AOs) [74]. Moreover, application of the PNCMO theory allowed both the inductive and the *trans*-effect of a heteroatom to be studied on the unified basis. Similarity and differences of the two effects also have been successfully revealed.

Let us turn now to an analogous local retransformation of a six-dimensional Hamiltonian matrix block corresponding to the phenyl ring [68]. The relevant matrix **U** was made up of coefficients of linear combinations of the canonical MOs of benzene in terms of $2p_z$ AOs of carbon atoms. As a result of retransformation, the occupation numbers of AOs of the phenyl ring have been expressed as a sum of five terms, two of them describing the intramolecular charge transfer and the remaining ones representing the secondary dipoles arising within the ring under influence of the heteroatom.

These expressions yielded simple accountings for observed pictures of electron density distributions in substituted benzenes and in pyridine-like heterocycles in terms of direct and indirect interactions of FOs.

6. PNCMO theory as the basis of the semilocalized description of chemical reactivity

Early stages of bimolecular chemical reactions are usually modelled by formation of weak intermolecular bonds. In this connection, various forms of perturbation theory are used in quantum-chemical studies of relative reactivities of alternative routes of a certain process. Passing to the basis of delocalized (canonical) MOs of isolated molecules makes the principal step of these theories and thereby delocalized descriptions of reactivity are obtained. This equally refers both to pioneering contributions based on the simple Hückel theory and to perturbative approaches of a considerably higher level of sophistication developed later (these are overviewed in [88] in detail).

As opposed to the majority of quantum-chemical studies, a local point of view to chemical reactivity is prevalent in the classical chemistry [89–91]. Thus, a definite functional group is regarded as taking part in the given process directly and it is usually referred to as the reaction centre. Again, the remaining parts of molecules are supposed to participate in the same process indirectly by exerting certain electron donating or accepting effects upon the respective reaction centres, and the extents of these effects are usually considered to be quite different at various stages of the reaction [89]. Extinction of the indirect influence when the distance between the given fragment and the reaction centre grows also is among the expectations.

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, a semilocalized approach to chemical reactivity [88] has been developed on the basis of application of the PNCMO theory to the case of two interacting molecules. Orbitals localized on separate elementary fragments of both participants of the process (e. g., the single and double bonds, phenyl rings, etc.) played the role of FOs, and the term “semilocalized” was introduced to distinguish our approach from oversimplified localized models [92], wherein only a few of directly-overlapping orbitals are explicitly considered. Electron density redistribution inside and between two weakly interacting molecules A and B was the principal characteristic under study. The relation between

this redistribution and the total intermolecular interaction energy has been taken from Eq. (35).

To be able to apply the general expressions for the bond order matrix \mathbf{P} shown in Eqs. (26) and (27), the total subset of IOFOs $\{\varphi_{(+)}\}$ has been subdivided into two parts $\{\varphi_{(+) }^{(a)}\}$ and $\{\varphi_{(+) }^{(b)}\}$ referring to molecules A and B, respectively. The subset of IVFOs, in turn, consisted of subsets $\{\varphi_{(-) }^{(a)}\}$ and $\{\varphi_{(-) }^{(b)}\}$. Accordingly, submatrices $\mathbf{E}_{(+)}$ and $\mathbf{E}_{(-)}$ of the zero-order Hamiltonian matrix $\mathbf{H}_{(0)}$ have been assumed to consist of direct sums of matrices referring to separate molecules, viz.

$$\begin{aligned}\mathbf{E}_{(+)} &= \mathbf{E}_{(+)}^{(a)} \oplus \mathbf{E}_{(+)}^{(b)}, \\ \mathbf{E}_{(-)} &= \mathbf{E}_{(-)}^{(a)} \oplus \mathbf{E}_{(-)}^{(b)},\end{aligned}\quad (38)$$

whereas the first-order blocks \mathbf{T} , \mathbf{R} , and \mathbf{Q} contained intermolecular parts of the anti-block-diagonal constitution in addition. Use of these partitions allowed the total principal matrices $\mathbf{G}_{(k)}$ to be represented as follows:

$$\mathbf{G}_{(k)} = \mathbf{G}_{(k)}^{(a)} \oplus \mathbf{G}_{(k)}^{(b)} + \delta\mathbf{G}_{(k)}, \quad (39)$$

where $\mathbf{G}_{(k)}^{(a)}$ and $\mathbf{G}_{(k)}^{(b)}$ are purely monomolecular terms and $\delta\mathbf{G}_{(k)}$ is a correction generally consisting of four non-zero blocks and describing contributions of the intermolecular interaction.

After substituting Eq. (39) into Eqs. (26) and (27), it turned out that any correction $\mathbf{P}_{(k)}$ of the total DM of two interacting molecules also is representable as shown in Eq. (39). This result allowed us to study the respective intermolecular increment $\delta\mathbf{P}_{(k)}$ separately and to derive a general expression for an alteration $\delta\mathbf{P}_{(k)+,ii}$ in the population of a certain IOFO $\varphi_{(+)i}$ of the molecule A due to its contact with the opposite molecule B.

Before going on to an overview of the relevant results, some definitions of [88] should be recalled. Thus, the directly interacting fragments of molecules A and B have been called the reaction centres and denoted by RC(A) and RC(B). Further, the fragments of molecules A and B, the orbitals of which interact directly only with those of reaction centres of their own molecules (but not with orbitals of opposite molecule) have been referred to as the nearest-neighbouring fragments and denoted by NN(A) and NN(B). Analogously, the next-nearest-neighbouring fragments may be defined and so forth.

Let us turn now to the population alteration $\delta\mathbf{P}_{(k)+,ii}$. As with the total populations of FOs shown

by Eq. (36), the alteration $\delta\mathbf{P}_{(k)+,ii}$ consists of a sum of partial populations $\delta x_{(+)i,(-)l}^{(k)}$ of various orders (k). Given that the opposite orbital $\varphi_{(-)l}$ belongs to the same molecule (A), the relevant partial population describes charge redistribution inside the molecule A owing to its contact with the molecule B. Alternatively, an intermolecular increment is obtained.

Analysis of separate contributions to the population alteration $\delta\mathbf{P}_{(k)+,ii}$ showed that the higher is the order of the given increment (k), the more distant fragments are embraced by the relevant charge redistribution. In particular, the second- and third-order increments describe charge redistributions inside and between the reaction centres RC(A) and RC(B). This result indicates the primary role of these centres in chemical processes. Moreover, the above-mentioned local charge redistributions have been considered as the quantum-mechanical analogues of the supposed direct participation of the RC(A) and RC(B) fragments in a certain process.

The fourth-order correction $\delta\mathbf{P}_{(4)+,ii}$ to the total population alteration was shown to contain five meaningful components, three of them describing intramolecular charge redistribution. The first of these components proved to represent an electron-donating or accepting effect of the NN(A) fragment upon the reaction centre RC(A) owing to the indirect participation of orbitals of the opposite molecule B. Accordingly, the second increment described an intramolecular charge redistribution within the RC(A) fragment due to its contact with the molecule B and orbitals of the NN(A) fragment participated in this redistribution indirectly as mediators of a certain interorbital interaction. Finally, the third intramolecular increment represented a charge redistribution inside the same reaction centre RC(A) mediated by orbitals of the opposite reaction centre RC(B).

The remaining two intermolecular components of the fourth-order correction $\delta\mathbf{P}_{(4)+,ii}$ were shown to describe the following effects: (i) an additional charge redistribution between the reaction centres RC(A) and RC(B) under an indirect participation of the NN fragments, and (ii) an indirect charge transfer between one of the two reaction centres (e. g., RC(A)) and the nearest-neighbourhood of the opposite reaction centre (NN(B)), wherein orbitals of the remaining reaction centre (i. e. of the RC(B), respectively) play the role of mediators.

On the whole, the above-discussed fourth-order terms represent additive components of an indirect participation of a certain neighbouring fragment in a

chemical process. In the case of a still more remote fragment, 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 respective reaction centre grows. Moreover, the relative importance of higher order terms may be expected to increase when passing from the early stages of reactions to later ones.

Therefore, the intuition-based hypotheses of the classical chemistry concerning reactivity (see the introductory part of this section) acquired an additional quantum-chemical support. Moreover, the scope of validity of these classical concepts has been related to that of the PNCMO theory. It is also evident that both the local charge redistributions representing consequences of direct participation of the reaction centres in the given process and the above-enumerated principal components of the indirect influence of the nearest-neighbouring fragment (substituent) depend on the spatial arrangement of the reagent with respect to reactant. On this basis, relative efficiencies of alternative routes of reactions may be compared.

Applicability of the above-described general approach to specific chemical problems has been illustrated by several examples. First, the approach formed the basis of the so-called extended model of the S_N2 reaction between a substituted alkane and nucleophile [93]. Application of this model allowed us to distinguish between the efficiencies of the frontal and back attacks of the reagent even if the direct intermolecular interactions between the orbital of the latter and the antibonding orbital of the $Z-C_\alpha$ bond take coinciding absolute values. An analogous model gave us an insight into the origin of the enhanced reactivity of α -halocarbonyl compounds in S_N2 processes [94]. In the case of the Ad_E2 reaction of substituted ethenes [95], different relative reactivities of carbon atoms have been related to dissimilar indirect influences of the substituent for alternative directions of an electrophilic attack.

7. Concluding remarks

As seen from the above review, the NCRSPT is formulated in terms of entire submatrices (blocks) of the initial Hamiltonian matrix. This, in turn, ensures a considerably more general nature of the subsequent results versus those of the standard RSPT. For example, general expressions have been derived for effective Hamiltonian matrices of separate weakly-interacting subsystems of molecular systems and these may be regarded

as the most outstanding result of the NCRSPT in the framework of the usual (canonical) method of MOs.

The principal achievements of NCRSPT, however, refer to the non-canonical method of MOs based on the Brillouin theorem. This fact may be traced back to the more general nature of the NCMO method itself as compared to the CMO method. Moreover, application of the NCRSPT allowed us to formulate the so-called PNCMO theory of molecules that involves the following principal points:

- (1) interrelation between the Brillouin theorem and the commutation equation for the one-electron density matrix;
- (2) expressions for NCMOs that are related to the respective bond order matrix as closely as possible;
- (3) generalization of the Dewar formula for total energies of molecules to the case of substantial intra-subset interactions.

It is no surprise in this context that applications of the PNCMO theory embrace entire classes of related molecules and yields general results concerning chemical reactivity.

Finally, good prospects for further development of NCRSPT in general and of the PNCMO theory in particular may be mentioned. For example, generalization of NCRSPT to the case of non-orthogonal subsets of basis functions seems to be feasible. (Such an expectation is based on an analogous generalization of the standard RSPT [96–99], on the one hand, and of the particular case of two interacting subsets [25], on the other hand.) Moreover, the NCRSPT is likely to be applicable to solution of a wide variety of matrix problems. The latter expectation is based on the successful solution of the commutation equation for the one-electron DM and derivation of a power function for a matrix discussed in this review.

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NEKOMUTATYVI RAYLEIGH'AUS IR SCHRÖDINGER'IO TRIKDŽIŲ TEORIJA IR JOS TAIKYMAI Kvantinėje chemijoje

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Santrauka

Aptarta vadinamoji nekomutatyvi Rayleigh'aus ir Schrödinger'io trikdžių teorija ir jos taikymai. Skirtingai nuo standartinės trikdžių teorijos, įgalinančios atsižvelgti į santykinai mažas sąveikas tarp atskirų orbitalių, nekomutatyvi jos versija skirta sąveikoms tarp ištiesų orbitalių rinkinių ir jų viduje tirti, nenurodant bazinių funkcijų skaičiaus juose. Todėl, pereinant nuo įprastinės prie nekomutatyvios trikdžių teorijos, vienmačiai dydžiai pakeičiami daugiamačiais dydžiais – matricomis, būtent, orbitalės ir tikrinės hamiltoniano funkcijos tampa matricomis-eilutėmis, o tiesinių kombinacijų koeficientai bei tikrinės vertės – kvadratinėmis matricomis. Hamiltono operatoriaus tikrinių verčių lygtis atitinkamai virsta tikrinių blokų lygtimi, kurioje ieškomasis tikrinis blokas nekomutuoja su apibendrinta tikrine funkcija (iš čia ir kyla teorijos pavadinimas). Bendras tokios teorijos formalizmas aptartas 2 skyriuje, o jos pagrindiniai taikymai standartinio

(kanoninio) molekulinio orbitalių (MO) metodo ribose – 3 skyriuje.

Nekomutatyvios trikdžių teorijos panaudojimas pagrindinei nekanoninio MO metodo lygčiai spręsti bei iš to išplaukiantys rezultatai aptarti 4–6 skyriuose. Čia remiamasi Brillouin'o teorema, kurią taikant sudaromas hamiltoniano matricos blokinės diagonalizacijos uždavinys, o jį išsprendus, suformuluojamas vadinamasis perturbacinis nekanoninis MO metodas (4 skyrius). Jo esmę sudaro šie pagrindiniai rezultatai: 1) sąsaja tarp Brillouin'o teoremos nekanoninėms MO gauti ir komutacinės lygties vienelektronei tankio matricai, 2) nekanoninių MO, labiausiai panašių į ryšių eilių matricą, bendros išraiškos ir 3) Dewar'o formulės molekulės energijai apibendrinimas.

Perturbacinio nekanoninio MO metodo taikymai konkrečių molekulių bei jų klasių elektroninės sandaros teorijoje aptarti 5 skyriuje, o cheminio reaktyvumo teorijoje – 6 skyriuje.