Terms Representing the Reorganization of Bonding Within Charge-Bond Order Matrices of Reacting Molecules

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ABSTRACT: The usual way of obtaining charge-bond order (CBO) matrices of molecules by summing up the MO LCAO coefficients over occupied molecular orbitals (MOs) is extended to derive terms representing the reorganization of bonding in reacting systems. The CBO matrix of a certain molecule (reactant) under influence of another one (reagent) is expressed in the form of power series with respect to intermolecular interaction. Terms of this series responsible for the internal reorganization of bonding in the reactant are also shown to be representable by sums of MO LCAO coefficients of the relevant isolated compound. As opposed to the case of a single molecule, the new sums embrace all MOs of the reactant and their pairs. This result is conditioned by the fact that the actual occupation numbers of MOs differ from either two or zero in the bimolecular system because of the intermolecular charge transfer, and bond orders arise between pairs of MOs in addition. Partial increments to the final reorganization of bonding related to individual MOs and to their pairs are then studied separately. These increments may be classified on the basis of criteria applied to MOs they originate from. In particular, symmetric and antisymmetric increments are distinguished with respect to any symmetry operation of the isolated reactant lost under influence of an approaching reagent. Increments of the same symmetry are subsequently collected into separate groups representable by specific graphical schemes. Consequently, the final pattern of charge and bond order redistribution in the reactant under influence of an approaching reagent follows from superposition of a few principal schemes. The results are illustrated by consideration of specific examples, in particular of addition of electrophile to the butadiene molecule. © 2009 Wiley Periodicals, Inc. Int J Quantum Chem 110: 1327–1343, 2010

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1. Introduction

Reorganization of bonding is the principal feature of any chemical reaction [1–4]. Thus, revealing of its nature for both specific processes and their types is undoubtedly an important task. In terms of quantum chemistry, the reorganization of bonding is most commonly represented by electron density and bond order redistributions in reacting molecules [2] following from the relevant charge-bond order (CBO) matrices [5]. If we confine ourselves to an early stage of the process characterized by a relatively weak intermolecular interaction, the afore mentioned matrices may be expressed in the form of power series [6, 7]. The problem then resolves itself into derivation and analysis of corrections of this series related to the intermolecular interaction. General properties of these corrections (if any) are of particular interest, as these are able to yield common rules governing the reorganization of bonding in related compounds.

The long history of organic chemistry demonstrates that chemical reactions may be discussed in terms of initial constitutions of participating compounds [1–3, 8]. Moreover, search for relations between relative reactivities of individual molecules and peculiarities of their chemical structures is among the most fundamental approaches of this scientific field. An implicit assumption seems to underlie this approach, namely that the nature of reorganization of bonding during a certain reaction is conditioned by respective initial structures.

Electronic structures of isolated molecules are usually represented in quantum chemistry by respective sets of canonical molecular orbitals (MOs) and their energies [6, 7, 9]. The afore mentioned classical hypothesis then gives us a hint that the reorganization of bonding might be interpretable in terms of MOs of initial compounds too. Such an anticipation is additionally supported by known decisive roles of initial MOs in determining other aspects of chemical reactions, e.g., the allowance of pericyclic processes (cf. the famous Woodward-Hoffmann rule [10–12]), the relative reactivities of alternative routes of organic reactions (cf. the HOMO/LUMO concept [13–17]), etc. If we assume the reorganization of bonding to be conditioned by MOs of initial compounds, these orbitals seem to form the most appropriate basis set for analysis of corrections to CBO matrices of reacting molecules originating from the intermolecular interaction. Finally, the known common properties of MOs (such as symmetry properties [6]) are then likely to determine general rules governing the reorganization of bonding.

Employment of MOs of initial compounds in studies of their chemical reactivities started a long time ago. In the pioneering contribution [18], a simple model has been suggested for S_E2 reactions of aromatic compounds [1–4], wherein the intermolecular charge transfer (intermolecular delocalization) was entirely excluded from consideration. To this end, the influence of the reagent was modelled by an intramolecular perturbation of the Coulomb parameter of the $2p_z$ AO of the atom under attack. As a result, relative reactivities of individual carbon atoms of an alternant conjugated hydrocarbon have been related to the well-known self-polarizabilities π_{rr}. Meanwhile, redistribution of population over the hydrocarbon chain has been represented by other polarizabilities of the atom–atom type (π_{rs}) governed by the rule of the alternating polarity (later, the same rule acquired a graph-theoretical interpretation [19]). Finally, polarizabilities of the atom-bond type ($\pi_{r,st}$) served to describe redistributions of bond orders. It is essential in our context that all polarizabilities proved to be expressible in terms of MO LCAO coefficients of the parent hydrocarbon. This achievement probably is the first demonstration of the relation between the initial structure and its response to the influence of the reagent. The authors of subsequent studies [13, 20–28] focused their efforts on analysis of increments of the intermolecular delocalization to the total energy of the chemical interaction. As a result, the decisive role of the so-called frontier MOs (HOMO and LUMO) has been revealed. Meanwhile, little attention was paid to internal changes in the structures of participating compounds. This especially refers to consequences of the remaining (polarization) increments [20, 21] of the intermolecular interaction energy.

In this study, an attempt is undertaken to unite and generalize the two extreme perturbative concepts as discussed earlier. The new approach to be suggested is aimed at revealing all alterations in electronic structures of reacting systems that follow from their initial constitutions deductively. To this end, we consider both the reactant and the reagent explicitly and address the corrections to CBO matrices of reacting molecules directly instead of starting with the intermolecular interaction energy. The most attention is paid to general properties of these corrections.

CBO matrices of isolated molecules are usually obtained by summing up the MO LCAO coefficients

over occupied MOs [5]. This procedure is equivalent to retransformation into the AO basis of the diagonal representation of the one-electron density matrix (DM) referring to the basis of MOs and containing uniform occupation numbers of the latter equal to either 2 or 0. The essence of the present approach consists in an extension of the same retransformation procedure to the DM of a bimolecular system represented in the composite basis of MOs of respective isolated compounds. Elements of the above-specified initial DM, in turn, follow from the general power series for this matrix [29–31].

The article is organized as follows: We start with an overview of relations the present approach is based on (Section 2). Partial increments of individual MOs and of their pairs to the overall reorganization of bonding are analyzed in Section 3. The role of the initial symmetry of the reactant in determining the subsequent reorganization of bonding is considered in Section 4. Finally, the results are illustrated by analysis of particular examples (Section 5). The most attention is paid here to addition of electrophile to the butadiene molecule.

2. Basic Relations of the Approach

The standard (canonical) MO method consists in passing from the initial basis of atomic orbitals (AOs) $\{\chi\}$ into that of MOs $\{\psi\}$, wherein the Hamiltonian (or Fockian) matrix of our system $\bar{H}$ takes the diagonal form. The respective representation matrix of the one-electron DM $\bar{P}$ is also diagonal in the MO basis and involves occupation numbers of these orbitals equal to either 2 or 0 [5, 32]. This implies no bond orders to arise between MOs. To obtain the usual CBO matrix of the same system P containing populations of AOs and bond orders between the latter, we retransform the matrix $\bar{P}$ into the AO basis again. The relation concerned is as follows [5, 32]

$$P = C\bar{P}C^+, \tag{1}$$

where the matrix C contains the MO LCAO coefficients in its columns, and the superscript $+$ here and below designates the transposed (or Hermitian-conjugate) matrix. This relation along with the above-specified diagonal constitution of the matrix $\bar{P}$ yields the usual expressions for elements of the CBO matrix P in the form of sums of the MO LCAO coefficients over occupied MOs.

The approach of this study is based on an extension of the scope of applicability of the relation of

Eq. (1) and thereby of the above-described common way of obtaining CBO matrices. Two peculiarities of this relation permit such an extension: First, Eq. (1) is actually valid for any pair of basis sets [32]. This implies that the MOs of the whole system $\{\psi\}$ may be replaced by another basis set, provided that the relevant CBO matrix $\tilde{P}$ is known or easily constructable. Second, an algebraic form is allowed for elements of all matrices of Eq. (1). It is just the composite basis of MOs of respective isolated compounds, which is able to replace the basis set $\{\psi\}$ in the case of two interacting molecules. This assertion is based on applicability of the general perturbative expansion for the one-electron DM [29–31] to construct algebraic expressions for elements of the relevant matrix $\tilde{P}$ as demonstrated in detail in the Appendix section. Before exhibiting these expressions, however, let us introduce some notations.

Let our participants of a certain reaction to be denoted A and B. The canonical MOs of respective isolated compounds (φ) also will be correspondingly designated by subscripts A and B. Moreover, the occupied and vacant orbitals will acquire additional subscripts (+) and (−), respectively, e.g. $\varphi_{A(+)i}$, $\varphi_{B(-)n}$, etc., where i and n represent individual orbitals. The composite set of MOs $\{\varphi\}$ will then consist of four subsets, viz.

$$\{\varphi\} = \{\{\varphi_{A(+)}\}, \{\varphi_{A(-)}\}, \{\varphi_{B(+)}\}, \{\varphi_{B(-)}\}\}. \tag{2}$$

In this basis, the zero order Hamiltonian matrix of the whole reacting system is assumed to take the diagonal form containing one-electron energies of MOs correspondingly denoted by $\varepsilon_{A(+)i}$, $\varepsilon_{B(-)n}$, etc. Meanwhile, the first order (perturbation) matrix is supposed to involve intermolecular interactions. The latter will be represented by Hamiltonian matrix elements of four types, viz.

$$M_{is} = \langle \varphi_{A(+)i}|\hat{H}|\varphi_{B(+)s}\rangle, \quad K_{in} = \langle \varphi_{A(+)i}|\hat{H}|\varphi_{B(-)n}\rangle,$$

$$L_{sr} = \langle \varphi_{B(+)s}|\hat{H}|\varphi_{A(-)r}\rangle, \quad T_{rn} = \langle \varphi_{A(-)r}|\hat{H}|\varphi_{B(-)n}\rangle, \tag{3}$$

where bra- and ket-vectors contain the respective basis orbitals. Let us note finally that elements of the matrix $\tilde{P}$ referring to the molecule A suffice to derive the CBO matrix under our interest.

To prove the latter statement, let us accept the relative order of subsets shown in Eq. (2) and

represent the total matrix $\tilde{\mathbf{P}}$ in terms of intra- and intermolecular blocks, viz.

$$\tilde{\mathbf{P}} = \begin{vmatrix} \tilde{\mathbf{P}}^{A(B)} & \tilde{\mathbf{P}}^{AB} \\ \tilde{\mathbf{P}}^{AB} & \tilde{\mathbf{P}}^{B(A)} \end{vmatrix}. \qquad (4)$$

Additional superscripts (B) and (A) of the intramolecular blocks of the matrix $\tilde{\mathbf{P}}$ indicate their indirect dependence on characteristics of the opposite molecule as shown latter in Eqs. (8), (10), and (11).

Because the total basis set of AOs $\{\chi\}$ also consists of subsets of AOs of separate molecules, partition like that of Eq. (4) is allowed also for the final CBO matrix $\mathbf{P}$. Moreover, the total transformation matrix $\mathbf{C}$ takes the form of a direct sum of matrices $\mathbf{C}^A$ and $\mathbf{C}^B$, containing MOs of respective molecules, i.e.

$$\mathbf{C} = \begin{vmatrix} \mathbf{C}^A & 0 \\ 0 & \mathbf{C}^B \end{vmatrix}. \qquad (5)$$

Substituting Eqs. (4) and (5) in Eq. (1) yields the following formula for the CBO matrix of the molecule A under influence of the molecule B, viz.

$$\mathbf{P}^{A(B)} = \mathbf{C}^A \tilde{\mathbf{P}}^{A(B)} \mathbf{C}^{A+} \qquad (6)$$

It is seen that only the submatrix $\tilde{\mathbf{P}}^{A(B)}$ referring to the molecule A is contained within this expression and not the remaining blocks of the total DM $\tilde{\mathbf{P}}$ of Eq. (4). Thus, let us now turn to expressions for separate elements of just this submatrix.

For pairs of orbitals of the molecule A of the same initial occupation (e.g., $\varphi_{A(+)i}$, $\varphi_{A(+)j}$, and $\varphi_{A(-)m}, \varphi_{A(-)r}$), the relevant expressions take the form

$$\tilde{P}^{A(B)}_{(+)i,(+)j} = 2\delta_{ij} + \tilde{P}^{A(B)}_{(2),(+)i,(+)j}, \quad \tilde{P}^{A(B)}_{(-)m,(-)r} = \tilde{P}^{A(B)}_{(2),(-)m,(-)r}, \qquad (7)$$

where 2 represents the initial (zero order) population of an MO $\varphi_{A(+)i}$ or $\varphi_{A(+)j}$ (for MOs $\varphi_{A(-)m}$ and $\varphi_{A(-)r}$, the respective term takes a zero value). Meanwhile, terms of Eq. (7) designated by the subscript (2) coincide with second-order corrections to elements concerned and depend on characteristics of the molecule B, viz.

$$\tilde{P}^{A(B)}_{(2),(+)i,(+)j} = -2\sum_{B(-)n} G^{(K)}_{(1)in} G^{(K)+}_{(1)nj},$$

$$\tilde{P}^{A(B)}_{(2),(-)m,(-)r} = 2\sum_{B(+)s} G^{(L)+}_{(1)ms} G^{(L)}_{(1)sr}, \qquad (8)$$

where sums embrace MOs of subsets $\{\varphi_{B(-)}\}$ and $\{\varphi_{B(+)}\}$, respectively, and

$$G^{(K)}_{(1)in} = -\frac{K_{in}}{\varepsilon_{A(+)i} - \varepsilon_{B(-)n}}, \quad G^{(L)}_{(1)sr} = -\frac{L_{sr}}{\varepsilon_{B(+)s} - \varepsilon_{A(-)r}} \qquad (9)$$

are elements of a certain first-order matrix $\mathbf{G}_{(1)}$ (see Refs. [29–31] and the Appendix section) representing direct intermolecular interactions. Numerators of fractions of these expressions are defined by Eq. (3), whereas denominators contain differences in one-electron energies of respective orbitals. From Eq. (8), it is seen that bond orders arise between MOs of the molecule A if this molecule interacts with the remaining one (B). Corrections to initial occupation numbers of MOs, in turn, follow from Eq. (8) in the cases $i = j$ and $m = r$, respectively. Hence, the actual occupation numbers of MOs are somewhat altered against 2 or 0 for interacting molecules. These alterations evidently are due to the intermolecular charge transfer. In particular, the partial population transferred between orbitals $\varphi_{A(+)i}$ and $\varphi_{B(-)n}$ is determined by square of the direct interaction $G^{(K)}_{(1)in}$ defined by Eq. (9). Given that the Hamiltonian matrix elements K_{in} of Eq. (3) do not differ significantly for various pairs of MOs $\varphi_{A(+)i}$ and $\varphi_{B(-)n}$, a single predominant interaction may be distinguished in the charge transfer-determined diagonal elements of the matrix $\tilde{\mathbf{P}}$ on the basis of relative values of energy gaps $\varepsilon_{A(+)i} - \varepsilon_{B(-)n}$. The famous pair of frontier MOs (i.e., the HOMO of the molecule A and the LUMO of B or vice versa [13–17]) usually plays this role.

For pairs of MOs of opposite initial occupation, the relevant element of the submatrix $\tilde{\mathbf{P}}^{A(B)}$ takes the form

$$\tilde{P}^{A(B)}_{(+)i,(-)r} = \tilde{P}^{A(B)}_{(2),(+)i,(-)r} = -2G^{A(B)}_{(2)ir}, \qquad (10)$$

where $G^{A(B)}_{(2)ir}$ is an element of the second-order matrix $\mathbf{G}_{(2)}$. This element is expressible as follows:

$$G^{A(B)}_{(2)ir} = \frac{1}{\varepsilon_{A(+)i} - \varepsilon_{A(-)r}}$$

$$\times \left\{ \sum_{B(+)s} \frac{M_{is}L_{sr}}{\varepsilon_{B(+)s} - \varepsilon_{A(-)r}} - \sum_{B(-)n} \frac{K_{in}T^+_{nr}}{\varepsilon_{A(+)i} - \varepsilon_{B(-)n}} \right\}, \qquad (11)$$

and represents a newly formed indirect interaction between orbitals of the molecule A ($\varphi_{A(+)i}$ and $\varphi_{A(-)r}$) by means of additional mediators offered by the molecule B. It is seen that intermolecular interaction gives birth to bond orders between MOs of

the molecule A of opposite initial occupation too. As opposed to occupation numbers of MOs, two MOs of the molecule A are necessarily involved within any newly formed bond order. Hence, the HOMO/LUMO concept [13–17] is not applicable here.

In summary, Eqs. (7)–(11) allow the submatrix $\tilde{\mathbf{P}}^{A(B)}$ to be represented in the form

$$\tilde{\mathbf{P}}^{A(B)} = \tilde{\mathbf{P}}^A_{(0)} + \tilde{\mathbf{P}}^{A(B)}_{(2)}, \qquad (12)$$

where the zero-order member ($\tilde{\mathbf{P}}^A_{(0)}$) corresponds to the isolated molecule A and contains the matrix $2\mathbf{I}$ in its first diagonal position referring to the subset $\{\varphi_{A(+)}\}$ and zero matrices elsewhere ($\mathbf{I}$ stands for the unit matrix). Meanwhile, elements of the second-order term $\tilde{\mathbf{P}}^{A(B)}_{(2)}$ are defined by Eqs. (8) and (10) and depend indirectly on the molecule B. Now, no more is required as to substitute Eq. (12) in Eq. (6). The resulting expression for the final CBO matrix of the reacting molecule A ($\mathbf{P}^{A(B)}$) then resembles Eq. (12), where the zero-order member ($\mathbf{P}^A_{(0)}$) coincides with the CBO matrix of the isolated molecule A in accordance with the expectation. The second-order correction ($\mathbf{P}^{A(B)}_{(2)}$), in turn, follows from the relation

$$\mathbf{P}^{A(B)}_{(2)} = \mathbf{C}^A \tilde{\mathbf{P}}^{A(B)}_{(2)} \mathbf{C}^{A+} \qquad (13)$$

and describes charge and bond order redistribution and thereby reorganization of bonding in the molecule A under influence of the molecule B. Thus, we have generalized the relation of Eq. (1) to the case of a reacting molecule A. Equation (13) is the basic expression of the present approach. The decisive role of initial MOs in the formation of the subsequent reorganization of bonding may be easily anticipated on the basis of this expression. Indeed, Eq. (13) indicates the populations of AOs of the reacting molecule A and bond orders describing its chemical bonds to be expressible as linear combinations of elements of the matrix $\tilde{\mathbf{P}}^{A(B)}_{(2)}$, the nature of these combinations being determined by elements of the matrix $\mathbf{C}^A$, i.e. by the structure of MOs of the isolated molecule A. In this connection, the relation of Eq. (13) may be analyzed without specifying the actual intermolecular interaction as demonstrated in Sections 3 and 4.

3. Properties of Partial Increments to the Reorganization of Bonding

Here and latter, we will dwell exclusively on the relation of Eq. (13) referring to the molecule A. Thus,

the superscripts $A(B)$ and A may be omitted for simplicity. The same refers to the subscript (2) too. Let individual AOs of the molecule A to be designated by greek subscripts, e.g. χ_μ, χ_ν, etc. After introducing the following simple notations

$$\tilde{P}^{A(B)}_{(2)kl} = (kl), \quad \mathbf{P}^{A(B)}_{(2)\mu\nu} = p_{\mu\nu} \qquad (14)$$

and reformulating Eq. (13) in terms of separate matrix elements, we obtain

$$p_{\mu\nu} = \sum_{k,l} C_{\mu k} C_{\nu l}(kl). \qquad (15)$$

This relation indicates that any element $p_{\mu\nu}$ consists of a sum of increments of individual MOs and of their pairs. Moreover, these increments are correspondingly proportional to the relevant changes in occupation numbers (kk) and to bond orders (kl). Indeed, the expression of Eq. (13) may be reformulated as follows

$$p_{\mu\nu} = \sum_k p^{(kk)}_{\mu\nu} + \sum_{k>l} p^{(kl)}_{\mu\nu}, \qquad (16)$$

where

$$p^{(kk)}_{\mu\nu} = C_{\mu k} C_{\nu k}(kk), \qquad (17)$$

$$p^{(kl)}_{\mu\nu} = (C_{\mu k} C_{\nu l} + C_{\mu l} C_{\nu k})(kl) \qquad (18)$$

are the partial contributions of the k-th MO φ_k and of the pair φ_k, φ_l, respectively. In the case of a diagonal element $p_{\mu\mu}$, we accordingly obtain

$$p^{(kk)}_{\mu\mu} = (C_{\mu k})^2 (kk), \qquad (19)$$

$$p^{(kl)}_{\mu\mu} = 2 C_{\mu k} C_{\mu l}(kl). \qquad (20)$$

Increments defined by Eqs. (17)–(20) depend on constitutions of respective MOs only and thereby may be studied separately. Moreover, the sets of increments $\{p^{(kk)}_{\mu\nu}, \mu, \nu = 1, 2 \ldots\}$ and $\{p^{(kl)}_{\mu\nu}, \mu, \nu = 1, 2 \ldots\}$ embracing all AOs of the molecule A and their pairs accordingly represent partial reorganizations of bonding originating from the MO φ_k and from the pair φ_k, φ_l, respectively. The final pattern of reorganization of bonding then follows from superposition of these partial redistributions in accordance with Eq. (16).

The above expressions demonstrate the generalized nature of the present approach versus the usual way of obtaining the CBO matrix of an isolated molecule on the basis of Eq. (1). Indeed, occupied MOs only contribute to the CBO matrix in the

standard approach and these contributions are proportional to the uniform number 2. By contrast, all MOs yield increments to an element $p_{\mu\nu}$ in our case and these increments contain nonuniform occupation numbers in addition. Finally, pairs of MOs also make contributions to $p_{\mu\nu}$ owing to nonzero bond orders (kl).

Let us now turn to analysis of separate increments defined by Eqs. (17)–(20). Let us start with $p_{\mu\mu}^{(kk)}$ of Eq. (19). It is seen that the population lost (acquired) by the MO φ_k of the molecule A because of the intermolecular charge transfer becomes distributed among its AOs $\{\chi_{A\mu}\}$ proportionally to squares of the relevant MO LCAO coefficients $C_{\mu k}$. Moreover, the signs of increments $p_{\mu\mu}^{(kk)}$ are uniform and depend on that of (kk). It is evident that $(kk) < 0$ and $(kk) > 0$ for initially occupied and initially vacant MOs [see Eq. (8)]. Thus, negative and positive signs of increments to occupation numbers of AOs correspondingly follow. Taking into account the unitary nature of the matrix $\mathbf{C}^A$ and summing up both sides of Eq. (19) over μ yields

$$\sum_{\mu} p_{\mu\mu}^{(kk)} = (kk), \qquad (21)$$

i.e., the conservation condition for the total distributed population. Contributions of the same terms (kk) to bond orders between AOs are described by Eq. (17). As already mentioned, (kk) is a negative quantity for an initially occupied MO $\varphi_{A(+)k}$. Thus, the bond order between a certain pair of AOs ($\chi_{A\mu}$ and $\chi_{A\nu}$) decreases owing to its deoccupation, if the signs of coefficients $C_{\mu k}$ and $C_{\nu k}$ are uniform, i.e. if the MO is of bonding nature between these AOs. Otherwise, the bond order is predicted to grow.

Let us turn now to partial reorganizations of bonding caused by newly-formed bond orders between MOs and defined by Eqs. (18) and (20). Summing up both sides of Eq. (20) over μ yields a zero result in contrast to that of Eq. (21). Hence, the sum of all increments to occupation numbers of AOs due to a certain bond order (kl) takes a zero value in accordance with the general charge conservation condition (The bond order (kl) cannot create a new population). Turning of the above-specified sum to zero also indicates increments $p_{\mu\mu}^{(kl)}$ of opposite signs necessarily to emerge in the molecule A. Contributions of the plus-minus- like constitution, viz.

$$p_{\mu\mu}^{(kl)}\left[p_{\nu\nu}^{(kl)}\right] = \pm D_{\mu\nu}^{(kl)} \qquad (22)$$

are of particular interest (Section 5), where the upper sign and the lower one correspondingly refer to $p_{\mu\mu}^{(kl)}$ and $p_{\nu\nu}^{(kl)}$, and $D_{\mu\nu}^{(kl)}$ is the absolute value of the increment. Indeed, these changes in populations of AOs may be interpreted as induced dipoles in the molecule A due to its interaction with the compound B.

Contribution of the same element (kl) to the bond order $p_{\mu\nu}$ between AOs $\chi_{A\mu}$ and $\chi_{A\nu}$ is represented by Eq. (18). This expression contains a cross product of the relevant coefficients within MOs φ_k and φ_l. The increments $p_{\mu\nu}^{(kl)}$ also are restricted in respect of their total value. To derive the relevant condition, let us turn to respective energetic increments. The latter will be assumed to be defined in the framework of the Hückel type approximation.

Because MOs of an isolated molecule follow from the diagonality requirement for its Hamiltonian matrix [5–7, 32], off-diagonal elements $H_{kl} = \langle\varphi_{Ak}|\hat{H}|\varphi_{Al}\rangle$ take zero values for any pair of MOs of the molecule A. As a result, the product $H_{kl}\cdot(kl)$ also vanishes. This implies that formation of the bond order (kl) is an energy-free effect. Owing to invariance of energy alterations towards unitary transformations of the basis set, the same conclusion is valid in the basis of AOs too. We then obtain

$$\sum_{\mu} H_{\mu\mu} p_{\mu\mu}^{(kl)} + \sum_{\mu,\nu} H_{\mu\nu} p_{\mu\nu}^{(kl)} = 0, \qquad (23)$$

for any bond order (kl), where $H_{\mu\mu}$ and $H_{\mu\nu}$ stand for the usual Coulomb and resonance parameters of AOs. In the case of conjugated hydrocarbons, the Coulomb parameters $H_{\mu\mu}$ are assumed to be uniform and thereby may be chosen to coincide with zero. Moreover, equalities $H_{\mu\nu} = 1$ and $H_{\mu\nu} = 0$ usually refer to chemically-bound (neighboring) pairs of AOs and to the remaining pairs, respectively. From Eq. (23) we then obtain

$$\sum_{\mu,\nu}^{(neighb)} p_{\mu\nu}^{(kl)} = 0, \qquad (24)$$

where the sum embraces the neighboring pairs of AOs only. Thus, the total alteration in bond orders of chemical bonds originating from the element (kl) takes a zero value in conjugated hydrocarbons. As a result, increments $p_{\mu\nu}^{(kl)}$ of opposite signs also are anticipated to arise, in particular changes of the same absolute value as shown in Eq. (22). Terms of the latter type may be interpreted as a switch of bond order from one bond of the molecule A to another. Let us note finally that the energy-free nature of alterations in the elements of the CBO matrix caused by
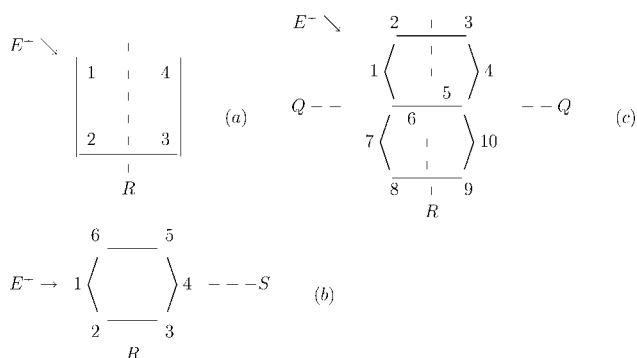
SCHEME 1. Symmetry breakings in the cis butadiene (a), benzene (b), and naphthalene (c) under influence of an approaching electrophile (E$^+$). The reflection planes R and Q represent elements of the total point symmetry group that are lost in the reacting system. The plane S of benzene remains among elements of the group for the reacting system as well.

any bond order (kl) is consistent with the expression for the stabilization energy of a molecular system in terms of charge transfer energy only [31].

Therefore, two distinct types of partial increments to the final pattern of reorganization of bonding reveal themselves from the above analysis, viz. increments caused by the intermolecular charge transfer and those related to newly formed bond orders between MOs. Contributions of the former type are not limited in respect of their total values, and the HOMO/LUMO concept is applicable to them in principle. Opposite to that said above refers to increments of bond orders between MOs.

4. Symmetry Breaking in the Reactant Under Influence of the Approaching Reagent

Reacting molecules usually are characterized by lower symmetry groups when compared with respective isolated compounds. In other words, symmetry of the molecule A breaks with respect to certain operation(s) of the relevant point group after taking into account the intermolecular interaction. The reflection planes R of cis-butadiene and benzene under attack of electrophile [Schemes 1(a) and (b)] serve here as excellent examples.

Canonical MOs of molecules are classified on the basis of irreducible representations of the respective symmetry group (see e.g. [6]). In particular, MOs are either symmetric or antisymmetric with respect to

any operation of the group including the planes R discussed earlier. The same is then likely to refer the individual increments to the reorganization of bonding in reacting molecules.

To show this, let us consider a model system of six AOs of Scheme 2. The AOs χ_μ and χ_ν, as well as χ_ρ and χ_λ, take symmetric positions with respect to the plane R, whereas χ_σ and χ_τ lie on this plane. The bonds $\chi_\mu - \chi_\rho$, $\chi_\nu - \chi_\lambda$, $\chi_\rho - \chi_\sigma$, and $\chi_\sigma - \chi_\lambda$ also accordingly take symmetric positions. For a certain symmetric MO φ_k^S, we then obtain

$$C_{\mu k} = C_{\nu k}, \quad C_{\rho k} = C_{\lambda k}. \tag{25}$$

Given that the MO is antisymmetric, i.e. φ_k^A, the analogue of Eq. (25) is as follows:

$$C_{\mu k} = -C_{\nu k}, \quad C_{\rho k} = -C_{\lambda k}, \quad C_{\sigma k} = C_{\tau k} = 0. \tag{26}$$

Let us now consider separate increments to elements of the CBO matrix of Section 3. Let us start with the increments $p_{\mu\mu}^{(kk)}$ of Eq. (19). Because the right-hand side of this expression contains a square of the coefficient $C_{\mu k}$, we obtain that

$$p_{\mu\mu}^{(kk)} = p_{\nu\nu}^{(kk)}, \quad p_{\rho\rho}^{(kk)} = p_{\lambda\lambda}^{(kk)}, \tag{27}$$

irrespective of the type of symmetry of the MO φ_k. Thus, no symmetry breaking follows in populations of AOs of the molecule A because of the intermolecular charge transfer. An analogous conclusion results also from Eq. (17), viz.

$$p_{\mu\rho}^{(kk)} = p_{\nu\lambda}^{(kk)}, \quad p_{\rho\sigma}^{(kk)} = p_{\sigma\lambda}^{(kk)}, \tag{28}$$

whatever the type of symmetry of the MO concerned. Hence, distribution of bond orders also
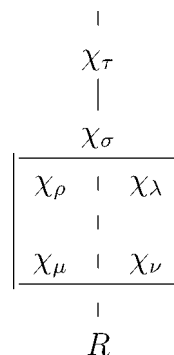
SCHEME 2. Relative positions of AOs with respect to the symmetry plane R in the model system for consideration of the symmetry breaking.

retains its symmetry in spite of changing occupation numbers of MOs.

Let us now turn to increments of newly formed bond orders between MOs. Let us start with contribution of bond orders (*kl*) to populations of AOs described by Eq. (20). For pairs of MOs of the same symmetry (φ_k^S, φ_l^S or φ_k^A, φ_l^A), a relation like that of Eq. (27) easily results along with the equality of population alterations $p_{\sigma\sigma}^{(kl)}$ and $p_{\tau\tau}^{(kl)}$ to zero for pairs of antisymmetric MOs. Hence, pairs of MOs of the same symmetry also yield symmetric changes in the charge distribution. Given that φ_k is a symmetric MO, whereas φ_l is an antisymmetric one, or vice versa, the result is as follows:

$$p_{\mu\mu}^{(kl)} = -p_{\nu\nu}^{(kl)}, \quad p_{\rho\rho}^{(kl)} = -p_{\lambda\lambda}^{(kl)}, \quad p_{\sigma\sigma}^{(kl)} = p_{\tau\tau}^{(kl)} = 0. \quad (29)$$

Hence, antisymmetric alterations in occupation numbers of AOs are predicted to arise owing to newly formed bond orders between pairs of MOs of opposite symmetry (φ_k^S, φ_l^A or φ_k^A, φ_l^S). Moreover, the first two relations of Eq. (29) coincide with that of Eq. (22). Therefore, dipole-like contributions arise to occupation numbers of all symmetrically placed pairs of AOs in this case.

Analogous results also follow from the relation of Eq. (18) for bond orders. Thus, the equality like that of Eq. (28) may be easily derived for any pair of symmetric MOs φ_k^S and φ_l^S. In the case of two antisymmetric MOs, Eq. (28) becomes supplemented with turning of some bond orders between AOs to zero (viz. of those embracing AOs χ_σ and χ_τ). Thus, alterations following from MOs of the same symmetry also are of symmetric nature. For pairs of MOs of opposite symmetry, the result is as follows:

$$p_{\mu\rho}^{(kl)} = -p_{\nu\lambda}^{(kl)}, \quad p_{\rho\sigma}^{(kl)} = -p_{\sigma\lambda}^{(kl)}, \quad p_{\mu\nu}^{(kl)} = p_{\sigma\tau}^{(kl)} = 0 \quad (30)$$

and indicates antisymmetric dipole-like increments to arise to bond orders between AOs. The resulting effect then consists in switches of bond order inside pairs of symmetrically positioned bonds.

Therefore, partial increments to the total reorganization of bonding in the reactant may be classified into symmetric and antisymmetric ones with respect to any symmetry operation lost under influence of the approaching reagent. The symmetric changes arise either from the intermolecular charge transfer or from bond orders between pairs of MOs of the same symmetry, whereas those of the antisymmetric type originate from newly formed bond orders between pairs of MOs of opposite symmetry. Moreover, antisymmetric changes in populations of AOs

always take the form of induced dipoles between individual pairs of symmetrically positioned AOs, whereas antisymmetric alterations in bond orders coincide with their switches from a certain bond to its symmetrically placed counterpart.

5. Illustration of the Results by Consideration of Specific Examples

Let us start with a very simple and illustrative example, viz. with a two-level two-electron system under attack of an electrophile. Thus, our reactant (A) will be represented by two AOs χ_1 and χ_2 and by two MOs $\varphi_{(+)1}$ and $\varphi_{(-)2}$ (Scheme 3). Let us first assume that the AOs are characterized by dissimilar Coulomb parameters ($H_{11} \neq H_{22}$) so that χ_1 is a more electronegative orbital. Just the latter is supposed to be under attack of electrophile (E^+). The energy reference point of our model system will be chosen in the middle of the energy gap between the initially occupied MO ($\varphi_{(+)1}$) and the initially vacant one ($\varphi_{(-)2}$), whereas the energy unit will be assumed to coincide with the internal resonance parameter (H_{12}). One-electron energies of MOs $\varphi_{(+)1}$ and $\varphi_{(-)2}$ will be accordingly denoted by $\varepsilon_{(+)1}$ and $-\varepsilon_{(-)2}$, where $\varepsilon_{(+)1}$ and $\varepsilon_{(-)2}$ are positive parameters. The approaching electrophile (E^+) will be modeled by a single initially vacant orbital $\varphi_{(-)E}$, characterized by a certain one-electron energy $-\varepsilon_{(-)E}$, where $\varepsilon_{(-)E} > 0$. The intermolecular interaction also will be represented by a positive parameter, the latter being denoted by δ, i.e.

$$\delta = \langle \varphi_{(-)E} | \hat{H} | \chi_1 \rangle. \quad (31)$$
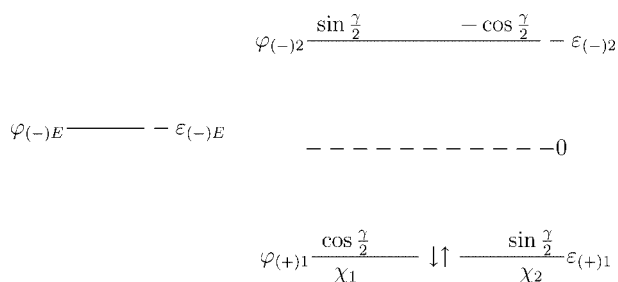
SCHEME 3. Basis orbitals of a two-level two-electron system under attack of an electrophile. The MO LCAO coefficients defined by Eqs. (32) and (33) are shown above the respective energy levels.

Finally, elements of the relevant matrix $\mathbf{C}(\equiv \mathbf{C}^A)$ are expressible as follows [33]:

$$C_{11} = \cos(\gamma/2), \quad C_{12} = C_{21} = \sin(\gamma/2),$$
$$C_{22} = -\cos(\gamma/2), \quad (32)$$

where

$$\gamma = \arctan \frac{2H_{12}}{H_{11} - H_{22}}, \quad 0 \le \gamma \le \frac{\pi}{2}. \quad (33)$$

Two partial reorganizations of bonding may be revealed in our two-level system under influence of the reagent, viz. reorganization related to deoccupation of the initially occupied MO $\varphi_{(+)1}$ because of charge transfer between orbitals $\varphi_{(+)1}$ and $\varphi_{(-)E}$ and that originating from the newly formed bond order (12) between MOs $\varphi_{(+)1}$ and $\varphi_{(-)2}$ owing to their indirect interaction by means of the external orbital $\varphi_{(-)E}$. Consequences of the first reorganization are rather evident and easily followed from constitution of the MO $\varphi_{(+)1}$. The expressions concerned result from Eqs. (17) and (19) after substituting Eq. (32). For the relevant alterations in occupation numbers of AOs and in the bond order between the latter, we obtain

$$p_{11}^{(11)} = (11)\cos^2\frac{\gamma}{2}, \quad p_{22}^{(11)} = (11)\sin^2\frac{\gamma}{2},$$
$$p_{12}^{(11)} = \frac{1}{2}(11)\sin\gamma, \quad (34)$$

where (11) coincides with the extent of deoccupation of the MO $\varphi_{(+)1}$ and is proportional to square of the direct interaction $G_{(1)1E}$ between orbitals $\varphi_{(+)1}$ and $\varphi_{(-)E}$ as Eq. (8) indicates, i.e.

$$(11) = -2(G_{(1)1E})^2 = -2\frac{(K_{1E})^2}{(\varepsilon_{(+)1} + \varepsilon_{(-)E})^2} < 0. \quad (35)$$

Equation (9) is also invoked here. The resonance parameter K_{1E} is defined by Eq. (3) and equals to

$$K_{1E} = \langle \varphi_{(+)1}|\hat{H}|\varphi_{(-)E}\rangle = \delta\cos\frac{\gamma}{2}. \quad (36)$$

Use of Eq. (35) within Eq. (34) shows that both populations of AOs and the internal bond order are predicted to be reduced because of deoccupation of the MO $\varphi_{(+)1}$ in accordance with conclusions of Section 3. The relation of Eq. (21) may also be easily verified by summing up the increments $p_{11}^{(11)}$ and $p_{22}^{(11)}$.

Let us now turn to the second partial reorganization of bonding in our two-level system originating

from the bond order (12). Expressions for the relevant alterations in occupation numbers of AOs and in the internal bond order follow after substituting Eq. (32) in Eqs. (18) and (20). We obtain

$$p_{11}^{(12)}\left[p_{22}^{(12)}\right] = \pm(12)\sin\gamma, \quad p_{12}^{(12)} = -(12)\cos\gamma, \quad (37)$$

where the upper sign of the first relation $(+)$ refers to $p_{11}^{(12)}$, and the lower one $(-)$ corresponds to $p_{22}^{(12)}$. It is seen that an induced dipole of the form shown in Eq. (22) necessarily arises in the two-level system whatever the actual newly-formed bond order between its MOs (12) and whatever the parameter γ. The absolute value of this dipole coincides with (12) $\sin\gamma$. Finally, the relation of Eq. (23) may be easily verified to be met by alterations of Eq. (37).

The newly formed bond order (12) between MOs $\varphi_{(+)1}$ and $\varphi_{(-)2}$ is proportional to the indirect interaction $G_{(2)12}$ as Eq. (10) shows. The orbital of electrophile $\varphi_{(-)E}$ plays here the role of the only mediator. From Eq. (11) we then obtain
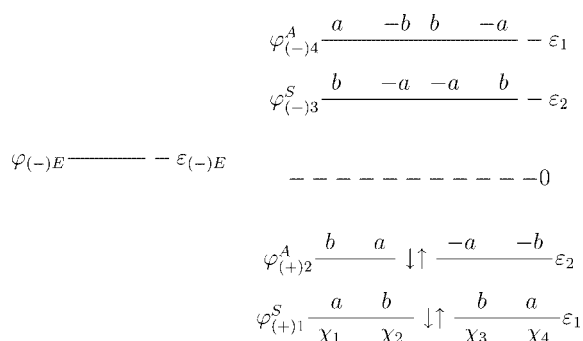
$$(12) = -2G_{(2)12} = \frac{2K_{1E}T_{E2}^+}{(\varepsilon_{(+)1} + \varepsilon_{(-)2})(\varepsilon_{(+)1} + \varepsilon_{(-)E})}, \quad (38)$$

where T_{E2}^+ is defined by Eq. (3) and is expressible as follows:

$$T_{E2}^+ = T_{2E} = \langle \varphi_{(-)2}|\hat{H}|\varphi_{(-)E}\rangle = \delta\sin\frac{\gamma}{2}. \quad (39)$$

The positive sign of the bond order (12) easily results from Eq. (38) after using Eqs. (36) and (39). Hence, the occupation number of the AO under attack (χ_1) grows due to the induced dipole, whereas that of the remaining AO (χ_2) becomes accordingly reduced. This result is in line with the relevant conclusions of the "curly arrow chemistry." Indeed, this classical model predicts that bonds are polarized so that an increase of population is observed at the site of an electrophilic attack [3]. The total pattern of the reorganization of bonding follows after summing up the increments of Eqs. (34) and (37).

Given that the AOs χ_1 and χ_2 are characterized by uniform Coulomb parameters ($H_{11} = H_{22}$), a symmetric two-orbital system follows. This particular case is characterized by the equality $\gamma = \pi/2$ as Eq. (33) indicates. Consequently, the AOs loose uniform populations [see Eq. (34)] and the induced dipole $\pm(12)$ becomes the only increment to the symmetry breaking of our initially symmetric reactant under influence of the approaching reagent. This result is in line with predictions of Section 4 (note that MOs $\varphi_{(+)1}$ and $\varphi_{(-)2}$ are of opposite symmetry in this case).

$$\varphi_{(-)4}^A \, \frac{a \quad -b \quad b \quad -a}{} - \varepsilon_1$$

$$\varphi_{(-)3}^S \, \frac{b \quad -a \quad -a \quad b}{} - \varepsilon_2$$

$$\varphi_{(-)E} \, \rule[2pt]{2cm}{0.4pt} \, - \varepsilon_{(-)E}$$

$$- - - - - - - - - - -0$$

$$\varphi_{(+)2}^A \, \frac{b \quad a}{} \downarrow\uparrow \, \frac{-a \quad -b}{} \varepsilon_2$$

$$\varphi_{(+)1}^S \, \frac{a \quad b}{\underset{\chi_1 \quad \chi_2}{}} \downarrow\uparrow \, \frac{b \quad a}{\underset{\chi_3 \quad \chi_4}{}} \varepsilon_1$$

SCHEME 4. MOs of butadiene along with the orbital of electrophile ($\varphi_{(-)E}$). Numbering of AOs is shown in the lower part of the scheme. Coefficients at these AOs in the MOs of butadiene are shown above the respective energy levels.

Let us now turn to a more involved system, namely to the butadiene molecule under attack of the same reagent (E$^+$). Let the simple Hückel model to be applied to the initial reactant [6, 7, 9, 34]. To this end, we invoke four $2p_z$ AOs of carbon atoms characterized by uniform Coulomb parameters [Scheme 1(a)]. The resonance parameters of chemical bonds C_1–C_2, C_2–C_3, and C_3–C_4 also will be assumed to take uniform values for simplicity. The energy reference point and the energy unit will correspondingly coincide with the afore mentioned parameters. The MOs of butadiene and their one-electron energies [7, 34] are exhibited in Scheme 4. Note that coupled energy levels are present in this scheme, namely $\pm\varepsilon_1$ and $\pm\varepsilon_2$, where $\varepsilon_1 = 1.618$ and $\varepsilon_2 = 0.618$. The standard MO LCAO coefficients of butadiene ($a = 0.372$ and $b = 0.602$) meet the following relations

$$a^2 + b^2 = \frac{1}{2}, \quad b^2 - a^2 = ab. \tag{40}$$

The first relation results from the normalization condition for MOs, whereas the second one follows from transformability of the initial Hamiltonian matrix of butadiene into two blocks representing two similar two-level systems characterized by the relation $\tan \gamma = 2$ [see Eq. (33)] (to show this, passing to symmetric and antisymmetric combinations of pairs of AOs χ_1, χ_4 and χ_2, χ_3 is required).

The reagent (electrophile) will be characterized by the orbital $\varphi_{(-)E}$ and the energy $-\varepsilon_{(-)E}$, as previously. The terminal carbon atoms C_1 and C_4 (the so-called α-position) are known to be much more reactive when compared with the internal atoms C_2 and C_3 (the β-position) in butadiene [1, 3, 4, 17, 35].

Nevertheless, we will consider both directions of the attack for comparison. The reagent will be assumed to approach the respective carbon atom from the above [36]. To be able to compare the relevant alterations in the electronic structure more easily, the resonance parameter between the orbital $\varphi_{(-)E}$ and the AO of the carbon atom under attack will be assumed to take the same value (σ), i.e.

$$\langle \varphi_{(-)E} | \hat{H} | \chi_1 \rangle = \sigma, \quad \langle \varphi_{(-)E} | \hat{H} | \chi_2 \rangle = \sigma \tag{41}$$

for the terminal (α) attack and for the internal (β) one, respectively. To be able to reveal reorganization of bonding of different symmetry (Section 4), the MOs of butadiene are additionally classified into symmetric and antisymmetric ones with respect to the plane R by introducing superscripts S and A.

On the whole, seven partial increments contribute to the final reorganization of bonding in butadiene under attack of electrophile. These originate from deoccupations of two initially occupied MOs [(11) and (22)], as well as from five newly formed bond orders, viz. (13), (24), (14), (23), and (12) [note that no bond order arises between MOs $\varphi_{(-)3}^S$ and $\varphi_{(-)4}^A$ owing to absence of appropriate mediators in Eq. (8)]. These increments, in turn, may be conveniently collected into three groups, namely (i) contributions of deoccupations of MOs, (ii) partial reorganizations originating from newly formed bond orders (13) and (24) between pairs of MOs of the same symmetry (SS and AA, respectively), and (iii) increments resulting from bond orders (14) and (23) between MOs of opposite symmetry (SA and AS). Let us consider the relevant partial reorganizations of bonding separately.

Let us start with contributions of deoccupations of MOs. As with the two-level system studied earlier, changes in occupation numbers of MOs $\varphi_{(+)1}^S$ and $\varphi_{(+)2}^A$ [(11) and (22)] follow from Eq. (8) and are proportional to squares of direct interactions $G_{(1)1E}$ and $G_{(1)2E}$, respectively, the latter being defined by Eq. (9). The consequent alterations in occupation numbers of AOs of butadiene are determined by Eq. (19). Let us define the total increments of deoccupations of MOs as follows:

$$p_{11}^{CT} = p_{44}^{CT} = a^2(11) + b^2(22),$$

$$p_{22}^{CT} = p_{33}^{CT} = b^2(11) + a^2(22), \tag{42}$$

where the superscript CT indicates these changes to originate from the intermolecular charge transfer.

TABLE I _____

Relative numerical values of terms representing the reorganization of charge distribution in butadiene under influence of an approaching electrophile for various values of one-electron energies of the latter (all increments are given in the σ^2 units).

$\varepsilon_{(-)E}$	$p_{11}^{CT,\alpha}$	$p_{22}^{CT,\alpha}, p_{11}^{CT,\beta}$	$p_{22}^{CT,\beta}$	$D^{S\alpha}, -D^{S\beta}$	$D_1^{A\alpha}$	$D_2^{A\alpha}, D_1^{A\beta}$	$D_2^{A\beta}$
0.0	−0.701	−0.300	−0.200	0.200	0.500	−0.500	0.000
0.3	−0.321	−0.146	−0.119	0.143	0.381	−0.323	0.039
0.6	−0.185	−0.088	−0.080	0.113	0.286	−0.235	0.051
0.9	−0.120	−0.059	−0.058	0.094	0.237	−0.184	0.052
1.2	−0.084	−0.043	−0.043	0.080	0.202	−0.150	0.050
1.5	−0.062	−0.033	−0.033	0.070	0.169	−0.126	0.049

The final expressions for these increments take the form

$$p_{11}^{CT,\alpha} = p_{44}^{CT,\alpha} = -2\sigma^2 \left[\frac{a^4}{(\varepsilon_1 + \varepsilon_{(-)E})^2} + \frac{b^4}{(\varepsilon_2 + \varepsilon_{(-)E})^2} \right] < 0,$$

$$p_{22}^{CT,\alpha} = p_{33}^{CT,\alpha} = p_{11}^{CT,\beta} = p_{44}^{CT,\beta}$$

$$= -2a^2b^2\sigma^2 \left[\frac{1}{(\varepsilon_1 + \varepsilon_{(-)E})^2} + \frac{1}{(\varepsilon_2 + \varepsilon_{(-)E})^2} \right] < 0,$$

$$p_{22}^{CT,\beta} = p_{33}^{CT,\beta} = -2\sigma^2 \left[\frac{b^4}{(\varepsilon_1 + \varepsilon_{(-)E})^2} + \frac{a^4}{(\varepsilon_2 + \varepsilon_{(-)E})^2} \right] < 0 \tag{43}$$

where the superscripts α and β of the left-hand sides correspondingly refer to the α- and β-attacks of electrophile. The symmetric nature of these alterations with respect to the plane R is evident. Moreover, all AOs lose their populations under influence of electrophile. The results of numerical calculations on the basis of Eq. (43) are shown in Table I. It is seen that the overall loss of population is approximately two times higher for the α-attack when compared with the β position of the reagent. This result implies a higher stabilization energy of the intermolecular interaction [31] in the former case and thereby it allows us to account for the more significant relative reactivity of the α-position. The above-established ratio between the extents of the charge transfer, in turn, may be traced back to the structure of the HOMO $\varphi_{(+)2}^A$ playing the decisive role in the formation of alterations of Eq. (43).

Let us now turn to influences of the same terms (11) and (22) on bond orders between AOs. The HOMO $\varphi_{(+)2}^A$ is of a bonding nature in the regions of initially double bonds ($C_1=C_2$ and $C_3=C_4$) (Scheme 4). Thus, the orders of these bonds may be expected to be reduced if this MO is deoccupied. Accordingly, the antibonding nature of the same MO in the region

of the remaining bond (C_2-C_3) implies growth of the bond order p_{23}. Such a simple scheme has been discussed in Ref. [20]. It is evident, however, that it may become modified essentially after taking into account the contribution of the lowest MO $\varphi_{(+)1}^S$. To examine this point, let us consider total alterations in bond orders between AOs due to deoccupations of both initially occupied MOs. The expressions concerned result from Eq. (17) and Scheme 4 take the form

$$p_{12}^{CT} = p_{34}^{CT} = ab[(11) + (22)], \quad p_{23}^{CT} = b^2(11) - a^2(22). \tag{44}$$

The final formulae for these alterations are as follows:

$$p_{12}^{CT,\alpha} = p_{34}^{CT,\alpha}$$

$$= -2ab\sigma^2 \left[\frac{a^2}{(\varepsilon_1 + \varepsilon_{(-)E})^2} + \frac{b^2}{(\varepsilon_2 + \varepsilon_{(-)E})^2} \right] < 0,$$

$$p_{23}^{CT,\alpha} = 2a^2b^2\sigma^2 \left[\frac{1}{(\varepsilon_2 + \varepsilon_{(-)E})^2} - \frac{1}{(\varepsilon_1 + \varepsilon_{(-)E})^2} \right] > 0,$$

$$p_{12}^{CT,\beta} = p_{34}^{CT,\beta}$$

$$= -2ab\sigma^2 \left[\frac{b^2}{(\varepsilon_1 + \varepsilon_{(-)E})^2} + \frac{a^2}{(\varepsilon_2 + \varepsilon_{(-)E})^2} \right] < 0,$$

$$p_{23}^{CT,\beta} = 2\sigma^2 \left[\frac{a^4}{(\varepsilon_2 + \varepsilon_{(-)E})^2} - \frac{b^4}{(\varepsilon_1 + \varepsilon_{(-)E})^2} \right]. \tag{45}$$

Signs of the first three changes in bond orders are in accordance with the above expectations, whereas that of the last expression cannot be defined a priori. Numerical calculations (Table II) indicate the term $p_{23}^{CT,\beta}$ to be a negative quantity in a wide range of energies $\varepsilon_{(-)E}$. This result implies reduction of the order of the C_2-C_3 bond under influence of the β-attacking electrophile. The more detailed analysis shows that

TABLE II
Relative numerical values of terms representing the reorganization of bond orders in butadiene under influence of an approaching electrophile for various values of one-electron energies of the latter (all increments are given in the σ^2 units).

$\varepsilon_{(-)E}$	$p_{12}^{CT,\alpha}$	$p_{23}^{CT,\alpha}$	$p_{12}^{CT,\beta}$	$p_{23}^{CT,\beta}$	$F^{S\alpha}, -F^{S\beta}$	F^A
0.0	−0.448	0.224	−0.224	−0.000	0.045	−0.224
0.3	−0.209	0.091	−0.117	−0.026	0.025	−0.127
0.6	−0.122	0.047	−0.075	−0.028	0.017	−0.083
0.9	−0.080	0.028	−0.052	−0.025	0.012	−0.058
1.2	−0.057	0.018	−0.039	−0.022	0.009	−0.044
1.5	−0.042	0.012	−0.030	−0.019	0.007	−0.034

the increment of the lowest MO $\varphi_{(+)1}^S$ predominates in this case.

Let us now turn to increments of the second type (ii) originating from bond orders between MOs of the same symmetry. As already mentioned, two bond orders of this type arise in butadiene, viz. (13) and (24). These bond orders embrace MOs of opposite initial occupation and are determined by Eq. (10). As with the two-level system studied earlier, the relevant indirect interactions $G_{(2)13}$ and $G_{(2)24}$ are mediated by the orbital of electrophile $\varphi_{(-)E}$. We then obtain

$$(13)^\alpha = -(13)^\beta = \frac{2ab\sigma^2}{(\varepsilon_1 + \varepsilon_2)(\varepsilon_1 + \varepsilon_{(-)E})} > 0,$$

$$(24)^\alpha = -(24)^\beta = \frac{2ab\sigma^2}{(\varepsilon_1 + \varepsilon_2)(\varepsilon_2 + \varepsilon_{(-)E})} > 0. \quad (46)$$

It is seen that bond orders (13) and (24) differ in their signs for the α- and β-attacks. Their total increments to populations of AOs follow from Eq. (20), viz.

$$p_{11}^S = p_{44}^S = 2ab[(13) + (24)],$$

$$p_{22}^S = p_{33}^S = -2ab[(13) + (24)], \quad (47)$$

where the superscript S is used here in connection with the anticipated symmetric nature of the alterations (Section 4). Opposite signs of bond orders (13) and (24) for α- and β-attacks ensure opposite directions for respective population alterations of AOs. Moreover, Eq. (47) yields dipole-like increments of the form shown in Eq. (22) for bonds C_1–C_2 and C_3–C_4 symmetrically. In particular, populations of AOs χ_1 and χ_4 grow, whereas those of χ_2 and χ_3 are accordingly reduced if the terminal atom (C_1) is under attack of electrophile.

The relevant increments to bond orders between AOs follow from Eq. (18). After an additional taking into account the second relation of Eq. (40), we obtain

$$p_{12}^S = p_{34}^S = -ab[(24) - (13)], \quad p_{23}^S = 2ab[(24) - (13)]. \quad (48)$$

Constitution of expressions of Eq. (48) indicates symmetric switches of bond order to take place between the terminal bonds (C_1–C_2 and C_3–C_4) and the internal one (C_2–C_3). In particular, the bond order becomes shifted from the former two bonds to the latter under influence of the α-attack and vice versa for the β-attack (note that $(24)^\alpha > (13)^\alpha > 0$ as $\varepsilon_1 > \varepsilon_2$). Condition of Eq. (24) for the total alteration in the orders of chemical bonds is also met by increments of Eq. (48).

On the whole, dipole-like nature of symmetric alterations of Eqs. (47) and (48) may be concluded. Two points serve to account for this unexpected result, the first one consisting in the afore mentioned transformability of the Hamiltonian matrix of butadiene to that of two two-level systems and the second one lying in the above-established dipole-like constitution of relevant alterations referring to the latter. Let us introduce the following notations

$$D^S = 2ab[(13) + (24)], \quad F^S = ab[(24) - (13)] \quad (49)$$

for the induced dipoles of terminal bonds and for switch of bond order defined by Eq. (48). Numerical values of these terms are included into Tables I and II, respectively, while their directions are shown in Scheme 5(a) for both types of the attack. It is seen that the direction of the dipole D^S is such that growth in the electron density is ensured at the site of the attack of electrophile in accordance with predictions of the "curly arrow chemistry" [3]. Meanwhile, the switch of bond order F^S takes an opposite direction versus that of D^S. The latter result implies opposite effects of α- and β-attacking electrophiles on the overall extent of delocalization of π-electrons in butadiene. For comparison, the enhanced delocalization in this hydrocarbon under influence of an electric field of a longitudinal direction established recently [37] deserves mentioning.

Let us finally consider the last type of reorganization of bonding in butadiene originating from bond orders between MOs of opposite symmetry, namely from (14), (23), and (12). The first two bond orders embrace MOs of opposite initial occupation and follow from Eq. (10). The last bond order, viz. (12), refers to initially occupied MOs. Thus, it is determined by
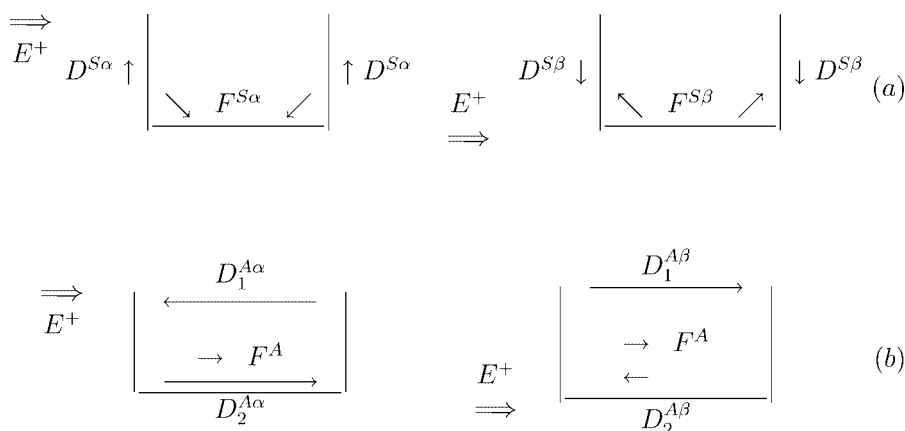
SCHEME 5. Reorganizations of bonding in butadiene under influence of electrophile (E^+) originating from bond orders between MOs. Symmetric shifts of population ($D^{S\alpha}$, $D^{S\beta}$) and of bond orders ($F^{S\alpha}$, $F^{S\beta}$) for the α- and β-attacks of the reagent are shown in the first picture (a). These shifts originate from newly formed bond orders between MOs of the same symmetry. The second picture (b) represents antisymmetric shifts caused by bond orders between MOs of opposite symmetry. The lengths of arrows virtually reflect the relative extents of respective shifts of population and bond order. The cis-form of butadiene is chosen here for convenience.

Eq. (8), where $\varphi_{B(-)n}$ coincides with $\varphi_{(-)E}$. It is essential to note that $(14)^\alpha$ and $(23)^\alpha$ differ from their counterparts $(14)^\beta$ and $(23)^\beta$ not only in signs but also in absolute values. The same then refers to the relevant alterations in occupation numbers of AOs. Let us introduce the following notations for the respective antisymmetric dipoles

$$p_{11}^A = -p_{44}^A = D_1^A, \qquad p_{22}^A = -p_{33}^A = D_2^A. \qquad (50)$$

After using Eq. (20) and Scheme 4, we then obtain

$$D_1^A = 2a^2(14) + 2b^2(23) + 2ab(12),$$

$$D_2^A = -2b^2(14) - 2a^2(23) + 2ab(12). \qquad (51)$$

Substituting the relevant expressions for bond orders (14), (23), and (12) yields the following result

$$
\begin{aligned}
D_1^{A\alpha} &= 2\sigma^2 \left[\frac{a^4}{\varepsilon_1(\varepsilon_1 + \varepsilon_{(-)E})} + \frac{b^4}{\varepsilon_2(\varepsilon_2 + \varepsilon_{(-)E})} - \frac{2a^2 b^2}{(\varepsilon_1 + \varepsilon_{(-)E})(\varepsilon_2 + \varepsilon_{(-)E})} \right], \\
D_2^{A\alpha} &= D_1^{A\beta} = -2a^2 b^2 \sigma^2 \left[\frac{1}{\varepsilon_1(\varepsilon_1 + \varepsilon_{(-)E})} + \frac{1}{\varepsilon_2(\varepsilon_2 + \varepsilon_{(-)E})} + \frac{2}{(\varepsilon_1 + \varepsilon_{(-)E})(\varepsilon_2 + \varepsilon_{(-)E})} \right], \\
D_2^{A\beta} &= 2\sigma^2 \left[\frac{a^4}{\varepsilon_2(\varepsilon_2 + \varepsilon_{(-)E})} + \frac{b^4}{\varepsilon_1(\varepsilon_1 + \varepsilon_{(-)E})} - \frac{2a^2 b^2}{(\varepsilon_1 + \varepsilon_{(-)E})(\varepsilon_2 + \varepsilon_{(-)E})} \right].
\end{aligned}
\qquad (52)
$$

As opposed to the above dipoles, the antisymmetric shifts of bond orders prove to be determined by the term (12) only. Moreover, the equality $(12)^\alpha = (12)^\beta$ ensures an indepence of the switch of bond order F^A on the position of electrophile. From Eqs. (18) and (40), we obtain

$$F^A = p_{12}^A = -p_{34}^A = \frac{1}{2}(12) = -\frac{ab\sigma^2}{(\varepsilon_1 + \varepsilon_{(-)E})(\varepsilon_2 + \varepsilon_{(-)E})}. \qquad (53)$$

Increments of Eqs. (52) and (53) are also shown in Tables I and II and in Scheme 5(b). Positive signs of dipoles $D_1^{A\alpha}$ and $D_2^{A\beta}$ ensure growing populations at the sites of the attack. So far as absolute values are concerned, the α-attack of electrophile is accompanied by considerably larger shifts of population toward the approaching reagent. This result is in line both with the higher relative reactivity of the α-position versus the β one [1, 3, 4, 17, 35] and with the more significant self-polarizability π_{11} versus π_{22}

Numerical values of antisymmetric induced dipoles of naphthalene under influence of electrophile. Superscripts AS and AA are used to denote dipoles of A(R)·S(Q) and A(R)·A(Q) types, respectively, where R and Q stand for reflection planes shown in the Scheme 1(c) (all dipoles are given in the σ^2 units).

$\varepsilon_{(-)E}$	$D_1^{AS\alpha}$	$D_1^{AS\beta}$, $D_2^{AS\alpha}$	$D_2^{AS\beta}$	$D_1^{AA\alpha}$	$D_1^{AA\beta}$, $D_2^{AA\alpha}$	$D_2^{AA\beta}$
0.0	0.140	−0.140	0.056	0.084	−0.084	0.002
0.3	0.104	−0.091	0.055	0.067	−0.058	0.026
0.6	0.085	−0.067	0.052	0.054	−0.044	0.032
0.9	0.070	−0.055	0.050	0.050	−0.038	0.033
1.2	0.060	−0.042	0.045	0.046	−0.030	0.034
1.5	0.054	−0.037	0.040	0.040	−0.026	0.030

in butadiene [7]. Moreover, shifts of electron density of Scheme 5(b) determine an alternating pattern of respective excessive populations, e.g. C_1^+–C_2^-–C_3^+–C_4^- for the α-attack, where $+$ implies an increased population. A growing importance of analogous charge-alternant ionic structures has been revealed recently [38], when studying the responce of cis-butadiene to an electric field of a longitudinal direction. The antisymmetric switch of bond order F^A is directed from the reacting C_1–C_2 bond to the remaining one (C_3–C_4) in accordance with the expectation.

Let us finally turn to a brief consideration of an analogous model of naphthalene under attack of electrophile. The total number of MOs and of their pairs grows significantly when passing from butadiene to naphthalene. Nevertheless, both analysis and conclusions resemble the above ones.

Symmetry of naphthalene breaks under influence of an electrophilic attack with respect to two planes R and Q [Scheme 1(c)]. As a result, the whole manifold of partial reorganizations of bonding may be classified into four types, viz. S(R)·S(Q), A(R)·S(Q), S(R)·A(Q), and A(R)·A(Q). Increments of the first two types (i.e., those symmetric with respect to the plane Q) are largely similar to the relevant partial contributions of butadiene. In particular, this analogy embraces emergence of shifts of electron density and bond orders like those of Scheme 5 in the four fragments of naphthalene, viz. C_1–C_2–C_3–C_4, C_1–C_6–C_5–C_4, C_7–C_6–C_5–C_{10}, and C_7–C_8–C_9–C_{10}. The first three columns of Table III contain relative numerical values of induced dipoles of the A(R)·S(Q) symmetry referring to the fragment C_1–C_2–C_3–C_4 for the α- and β-positions of electrophile (i.e. above the 1st

and the 2nd atom). Although the absolute values of these dipoles (except for $D_2^{AS\beta}$) are reduced considerably versus those of butadiene (see the last three columns of Table I for comparison), the corresponding relative values and signs are similar including the equality $D_1^\beta = D_2^\alpha$. These results may be traced back to the qualitative similarity between the relevant MO LCAO coefficients, as well as to the known extinction of their absolute values when the total number of basis orbitals grows.

It is essential to emphasize here that the afore mentioned alterations embrace both rings of naphthalene symmetrically in accordance with their S(Q) nature. In this context, the role of the remaining increments of the A(Q) type (that are peculiar to the naphthalene only) consists in strengthening of the former changes in the ring under attack and in their neutralization in the remaining ring. Induced dipoles of the A(R)·A(Q) type are also shown in Table III, where D_1^{AA} refers to atoms C_1 and C_7, whereas D_2^{AA} embraces C_2 and C_8. Positive signs of dipoles $D_1^{AA\alpha}$ and $D_2^{AA\beta}$ indicate additional shifts of electron density to take place from atoms C_7 and C_8 to the relevant atoms under attack of the reagent (C_1 and C_2, respectively).

Finally, the analogy between butadiene and naphthalene embraces also the signs and relative values of alterations referring to the α- and β-attacks of electrophile. In particular, the α-attack on naphthalene is accompanied by a larger extent of symmetry breaking in respect of populations of AOs when compared with the β-attack as it was the case in butadiene. The higher absolute values of $D_1^{AS\alpha}$ versus $D_2^{AS\beta}$, as well as of $D_1^{AA\alpha}$ versus $D_2^{AA\beta}$ seen from Table III serve to illustrate the above statement. These results are in line with the enhanced relative reactivity of the α-position of naphthalene (C_1) versus the β one (C_2) [17], as well as with the larger self-polarizability of the 1st carbon atom when compared with the 2nd one [7].

Therefore, the overall reorganization of bonding in both butadiene and naphthalene under influence of electrophile is representable by superposition of several principal contributions of comparable absolute values.

6. Summary

The approach of this study is based on revealing new scopes of applicability for previous achievements. Three principal points deserve to be

mentioned here: (i) the usual retransformation procedure for the one-electron DM from the basis of MOs into that of AOs is extended to the case of a certain molecule (reactant) under influence of another one (reagent), (ii) the general power series for the DM [29–31] is newly applied to the case of two interacting molecules in the composite basis of MOs of respective isolated compounds, and (iii) the standard way of classification of canonical MOs on the basis of irreducible representations of the relevant point symmetry group is extended to partial increments of separate MOs and of their pairs to the total reorganization of charge- and bond-order distribution.

The principal achievement of the study consists in derivation of expressions for corrections to CBO matrices of molecules originating from the intramolecular interaction and in revealing the consequent reorganization of bonding in the reactant under influence of an approaching reagent. Conclusions that may be drawn here are as follows: (1) The overall reorganization of bonding consists of two principal components, the first one originating from the intermolecular charge transfer and governed mostly by frontier MOs, and the second component resulting from newly formed bond orders between MOs of the reactant and meeting certain conservation conditions inside the latter. (2) The charge-transfer component may be further decomposed into increments of separate MOs of the reactant, while that of bond orders contain contributions of separate pairs of these basis orbitals. (3) The above-specified increments may be classified into symmetric and antisymmetric ones with respect to any symmetry operation of the isolated reactant lost under influence of the approaching reagent. (4) Increments of the same symmetry may be joined together, so that the total number of principal contributions to the final reorganization of bonding becomes largely reduced.

With respect to comparison of the approach suggested to related ones, the following points deserve mentioning: (i) Decomposition of the overall reorganization of bonding into several partial schemes underlying the approach suggested resembles the analogous procedure of the classical qualitative version of the resonance theory [3, 4]. The present decomposition, however, is based on the MO method. (ii) An analogy reveals itself between the above-established two principal components of the reorganization of bonding (i.e., the charge transfer component and that of bond orders between MOs) and the two terms of the intermolecular interaction

energy of Refs. [20, 21] (namely, the delocalization term and the polarization one, respectively). (iii) The present approach may be considered as a generalization of that of Ref. [18] to the case of an explicit taking into account both the reactant and the reagent and thereby the charge redistribution between these participants of the reaction. (iv) For specific systems, predictions of the approach suggested are in line with those of the "curly arrow chemistry" [3] and with experimental trends in relative reactivities.

Appendix

EXPRESSIONS FOR THE ONE-ELECTRON DENSITY MATRIX OF TWO INTERACTING MOLECULES IN THE COMPOSITE BASIS OF MOLECULAR ORBITALS

We are about to apply here the general perturbative expansion for the one-electron density matrix (DM) [29–31] to the case of two interacting molecules A and B. Let us first invoke the basic expressions of the original power series.

Let us start with the notation that no specifying of basis orbitals was required when deriving the series. The underlying total basis set $\{\varphi\}$ was only assumed to be divisible into two subsets $\{\varphi_{(+)}\}$ and $\{\varphi_{(-)}\}$ containing the initially occupied orbitals and the initially vacant ones, respectively. Moreover, interactions (resonance parameters) of the intersubset type were supposed to be first-order terms versus the intrasubset ones. As a result, the initial Hamiltonian matrix of the system under study $\tilde{\mathbf{H}}$ has been represented as a sum of the zero-order member $\tilde{\mathbf{H}}_{(0)}$ and of the first-order one $\tilde{\mathbf{H}}_{(1)}$, where

$$\tilde{\mathbf{H}}_{(0)} = \begin{vmatrix} \mathbf{E}_{(+)} & \mathbf{0} \\ \mathbf{0} & \mathbf{E}_{(-)} \end{vmatrix}, \quad \tilde{\mathbf{H}}_{(1)} = \begin{vmatrix} \mathbf{S} & \mathbf{R} \\ \mathbf{R}^+ & \mathbf{Q} \end{vmatrix} \quad (A1)$$

consist of certain submatrices (blocks) $\mathbf{E}_{(+)}$, $\mathbf{E}_{(-)}$, $\mathbf{S}$, $\mathbf{R}$, and $\mathbf{Q}$. The blocks $\mathbf{E}_{(+)} + \mathbf{S}$ and $\mathbf{E}_{(-)} + \mathbf{Q}$ refer to subsets $\{\varphi_{(+)}\}$ and $\{\varphi_{(-)}\}$, respectively, and contain intrasubset interactions along with one-electron energies of individual orbitals. Meanwhile, the only off-diagonal block $\mathbf{R}$ involves intersubset interactions.

The one-electron DM $\tilde{\mathbf{P}}$ corresponding to the above-specified Hamiltonian matrix $\tilde{\mathbf{H}}$ has been obtained in Refs. [29–31] by means of the direct solution of the relevant commutation equation in the form of power series. Accordingly, the matrix $\tilde{\mathbf{P}}$

has been represented as a sum of corrections $\tilde{\mathbf{P}}_{(k)}$ of various orders k, where

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

$$= -2 \begin{vmatrix} \mathbf{G}_{(1)}\mathbf{G}_{(1)}^+ & \mathbf{G}_{(2)} \\ \mathbf{G}_{(2)}^+ & -\mathbf{G}_{(1)}^+\mathbf{G}_{(1)} \end{vmatrix} \quad (A2)$$

and $\mathbf{I}$ stands for the unit matrix. The principal matrices of these expressions $\mathbf{G}_{(k)}, k = 1, 2..$ meet the following matrix equations

$$\mathbf{E}_{(+)}\mathbf{G}_{(k)} - \mathbf{G}_{(k)}\mathbf{E}_{(-)} + \mathbf{W}_{(k)} = \mathbf{0}, \quad (A3)$$

where $\mathbf{W}_{(1)}$ coincides with the matrix $\mathbf{R}$ of Eq. (A1) and

$$\mathbf{W}_{(2)} = \mathbf{S}\mathbf{G}_{(1)} - \mathbf{G}_{(1)}\mathbf{Q}. \quad (A4)$$

Finally, the general solution of Eq. (A3) is representable as an integral [39, 40], viz.

$$\mathbf{G}_{(k)} = \int_0^\infty \exp[\mathbf{E}_{(+)}t] \cdot \mathbf{W}_{(k)} \cdot \exp[-\mathbf{E}_{(-)}t]dt. \quad (A5)$$

Let us now turn to the case of two interacting molecules A and B. Let the composite basis of MOs of the whole system to consist of MOs of respective isolated compounds. These orbitals always may be divided into initially occupied and initially vacant ones. Because the MOs of an isolated molecule follow from the diagonality requirement for the respective Hamiltonian matrix, zero values of interorbital interactions inside separate molecules is also a natural assumption here. So far as intermolecular interactions are conserned, these may be assumed to take sufficiently small values relatively to differences between one-electron energies of MOs of opposite initial occupation, at least for early stages of chemical reactions. This implies the requirements underlying Eq. (A1) to be met by our two-molecular system in the composite basis of initial MOs. Hence, the relations shown in Eqs. (A2)–(A5) may be applied to derive elements of the relevant DM.

To this end, let the basis set $\{\varphi\}$ underlying Eqs. (A1)–(A5) to coincide with the above-defined composite set of MOs. The designation $\tilde{\mathbf{P}}$ will then refer to the respective representation of the DM of the whole reacting system. The subsets $\{\varphi_{(+)}\}$ and $\{\varphi_{(-)}\}$ will accordingly consist of those of individual molecules, e.g. $\{\varphi_{(+)}\}$ will contain a direct sum of $\{\varphi_{A(+)}\}$ and $\{\varphi_{B(+)}\}$. The same subdivision refers also to separate blocks of matrices $\tilde{\mathbf{H}}_{(0)}$ and $\tilde{\mathbf{H}}_{(1)}$ of Eq. (A1). Moreover,

the above-assumed zero intramolecular interactions ensure zero intramolecular sub-blocks within these blocks. As a result, the blocks $\mathbf{S}, \mathbf{R}$, and $\mathbf{Q}$ acquire antiblock-diagonal constitutions, viz.

$$\mathbf{S} = \begin{vmatrix} \mathbf{0} & \mathbf{M} \\ \mathbf{M}^+ & \mathbf{0} \end{vmatrix}, \quad \mathbf{R} = \begin{vmatrix} \mathbf{0} & \mathbf{K} \\ \mathbf{L} & \mathbf{0} \end{vmatrix}, \quad \mathbf{Q} = \begin{vmatrix} \mathbf{0} & \mathbf{T} \\ \mathbf{T}^+ & \mathbf{0} \end{vmatrix},$$
$$(A6)$$

where the subblocks $\mathbf{M}, \mathbf{K}, \mathbf{L}$, and $\mathbf{T}$ contain the intermolecular interactions. The same constitution may be easily shown to refer to the relevant matrix $\mathbf{G}_{(1)}$, viz.

$$\mathbf{G}_{(1)} = \begin{vmatrix} \mathbf{0} & \mathbf{G}_{(1)}^{(K)} \\ \mathbf{G}_{(1)}^{(L)} & \mathbf{0} \end{vmatrix}, \quad (A7)$$

where nonzero subblocks $\mathbf{G}_{(1)}^{(K)}$ and $\mathbf{G}_{(1)}^{(L)}$ also are expressible as integrals, e.g.

$$\mathbf{G}_{(1)}^{(K)} = \int_0^\infty \exp[\mathbf{E}_{(+)}t] \cdot \mathbf{K} \cdot \exp[-\mathbf{E}_{(-)}t]dt. \quad (A8)$$

[Equality $\mathbf{W}_{(1)} = \mathbf{R}$ is used within Eq. (A5) for $k = 1$ when deriving Eqs. (A7) and (A8)]. Use of our specific matrix $\mathbf{G}_{(1)}$ shown in Eq. (A7) within submatrices $-2\mathbf{G}_{(1)}\mathbf{G}_{(1)}^+$ and $2\mathbf{G}_{(1)}^+\mathbf{G}_{(1)}$ of Eq. (A2) allows the blocks of the latter referring to the molecule A to be represented as products $-2\mathbf{G}_{(1)}^{(K)}\mathbf{G}_{(1)}^{(K)+}$ and $2\mathbf{G}_{(1)}^{(L)+}\mathbf{G}_{(1)}^{(L)}$, respectively. This result forms the basis of expressions for elements $\tilde{P}_{(2),(+)i,(+)j}^{A(B)}$ and $\tilde{P}_{(2),(-)m,(-)r}^{A(B)}$ shown in Eq. (8) of Section 2.

Furthermore, substituting the particular blocks $\mathbf{S}, \mathbf{Q}$, and $\mathbf{G}_{(1)}$ from Eqs. (A6) and (A7) into Eq. (A4) followed by invoking the integral of Eq. (A5) for $k = 2$ yields an integral form for the block of the matrix $\mathbf{G}_{(2)}$ referring to the molecule A, viz.

$$\mathbf{G}_{(2)}^{A(B)} = \int_0^\infty \exp[\mathbf{E}_{(+)}t] \cdot \left[\mathbf{M}\mathbf{G}_{(1)}^{(L)} - \mathbf{G}_{(1)}^{(K)}\mathbf{T}^+\right] \cdot$$
$$\exp[-\mathbf{E}_{(-)}t]\,dt. \quad (A9)$$

Given that $\mathbf{E}_{(+)}$ and $\mathbf{E}_{(-)}$ are diagonal matrices consisting of one-electron energies of basis orbitals, fractions for separate elements of matrices being sought easily result from integral solutions shown in Eqs. (A5), (A8), and (A9) [39, 40]. In particular, expressions of Eq. (9) for elements $G_{(1)in}^{(K)}$ and $G_{(1)sr}^{(L)}$ (Section 2) follow instead of Eq. (A8). Similarly, the formula of Eq. (11) for elements $G_{(1)ir}^{A(B)}$ results from Eq. (A9). Diagonality of matrices $\mathbf{E}_{(+)}$ and $\mathbf{E}_{(-)}$ is a natural assumption in the case of two interacting molecules owing to zero values of intramolecular interactions in the composite basis of MOs.

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