A local point of view to intermolecular bonding of saturated organic molecules

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Abstract

The general expression for the common one-electron density matrix (DM) of saturated organic molecules obtained previously in the framework of the Hückel type model [V. Gineityte, J. Mol. Struct. (Theochem) 343 (1995) 183] has been applied to investigate intermolecular bonding. To this end, the total DM of two interacting molecules has been expressed as a sum of two matrices, the first one coinciding with the direct sum of DMs of isolated molecules and the second one being a correction describing the intermolecular bonding. As a result, additive intra- and intermolecular contributions have been revealed both within occupation numbers of basis orbitals and within the total energy of interacting molecules, and an internal additivity of intermolecular terms with respect to increments of pairs of bonds has been established. These results have been used to substantiate the local models of intermolecular bonding commonly used when studying the early stages of chemical reactions between two saturated molecules. Conditions for which the local model is adequate have been formulated explicitly. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Studies of chemical reactions are among the main goals of quantum chemistry [1–5]. As with electronic structures of isolated molecules [6], chemical processes may be investigated from both quantitative and qualitative points of view. In the former case the relevant results (if sufficiently accurate) allow certain predictions to be made about the reaction path and transition states [7]. It should be noted, however, that extremely involved numerical calculations of potential energy surfaces are required for quantitative studies of most reactions.

Alternatively, simple approaches and models are usually used when looking for qualitative rules governing chemical processes. In contrast to numerical results, these rules commonly embrace certain type of reactions instead of an individual process. In this case, qualitative rules serve to provide classification and interpretation of the entire information about chemical reactions.

The so-called PMO theory [1] of chemical reactivity of organic compounds based on the perturbation theory in the framework of the Hückel model is among the most popular qualitative approaches. An early stage of reaction is usually studied using this method. In particular, bimolecular processes are modelled by formation of an intermolecular bonding represented by respective resonance parameters.

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Intramolecular interactions, i.e. resonance parameters between pairs of basis orbitals inside isolated molecules, are taken into account from the very outset of applying the PMO theory. This step coincides with diagonalization of two separate Hamiltonian matrices and obtaining two sets of delocalized (canonical) MOs of individual molecules. Taking into account the intermolecular resonance parameters constitutes the second step of this theory. A perturbative approach is applied there for diagonalization of the total model Hamiltonian matrix in the basis of delocalized MOs of individual molecules.

Turning to the basis of delocalized MOs creates an impression that whole molecules participate in the reaction under study even if local fragments actually come into contact. Local characteristics of interacting molecules, e.g. charges on atoms, coefficients of highest occupied and/or lowest vacant MOs, etc. also may be obtained and studied in the framework of the PMO theory. Nevertheless, the above-described impression remains because the canonical MOs, which these local characteristics are based on, depend on the structure of the whole system.

The above-described standard PMO theory was especially successful in studying chemical reactions of conjugated hydrocarbons and their derivatives. This fact allows us to believe that the concept of a non-local intermolecular interaction taking place between entire molecules is actually adequate for conjugated systems.

So far as reactions of saturated molecules are concerned, an opposite approach is applied here [1,2,4,8]. The essence of this approach is as follows:

Intermolecular interaction is studied directly in the basis of localized orbitals with no regard for intramolecular interactions. For example, a local interaction between the lone pair orbital of nucleophile and the antibonding orbital of the Z–C bond of the substituted alkane (Z is a heteroatom) is considered when investigating an S_N2 process instead of numerous interactions between delocalized MOs of both molecules.

The above-described local model may be traced back to respective modification of the PMO theory for saturated molecules where delocalized MOs are replaced by localized two-center bond orbitals [1]. When applied to intermolecular bonding, however, this local model seems to be based on an implicit assumption that the intermolecular bonding may be studied independently of the intramolecular one. In other words, the above two types of interactions are assumed to be additive. Moreover, the consequences of the intermolecular interaction are supposed to depend mainly on the structure of the directly contacting fragments.

In this paper we are about to substantiate the above-mentioned implicit assumptions and hence bear out the local models for intermolecular bonding of saturated organic molecules. In addition, we will reveal the conditions for which this model is adequate.

To this end, we will consider the extent of additivity of inter- and intramolecular contributions both to the total one-electron density matrix (DM) and its particular elements and to the energy of two interacting molecules. Thereupon, we will study the internal structure of the intermolecular terms.

The additivity of electronic structure characteristics obtained using the standard PMO theory is known to be rather low (except of the trivial additivity of the first order corrections) [1]. Furthermore, the delocalized (canonical) MOs are hardly the most appropriate terms for substantiation of the local model. Hence, it would be advisable to avoid turning to the basis of the canonical MOs at all.

Therefore, we are about to employ the direct way of obtaining the one electron DM and the total energy of any saturated system [9] based on the solution of the commutation equation [10] by means of a perturbative approach. Thus, the general algebraic expression for the DM of any saturated system obtained in [9] will be applied here to the case of two interacting molecules. Additivity of the total DM will be studied in Section 2, whilst that of occupation numbers and of the total energy is discussed in Section 3. The case when only two bonds of interacting molecules come into contact is considered separately in Section 4.

2. Intra- and intermolecular contributions to the one-electron DM of two saturated molecules

The basis of bonding and antibonding bond orbitals (BOs) along with lone pair orbitals (if any) has been used in [9] when deriving the general algebraic expressions for the DM of any saturated system. In
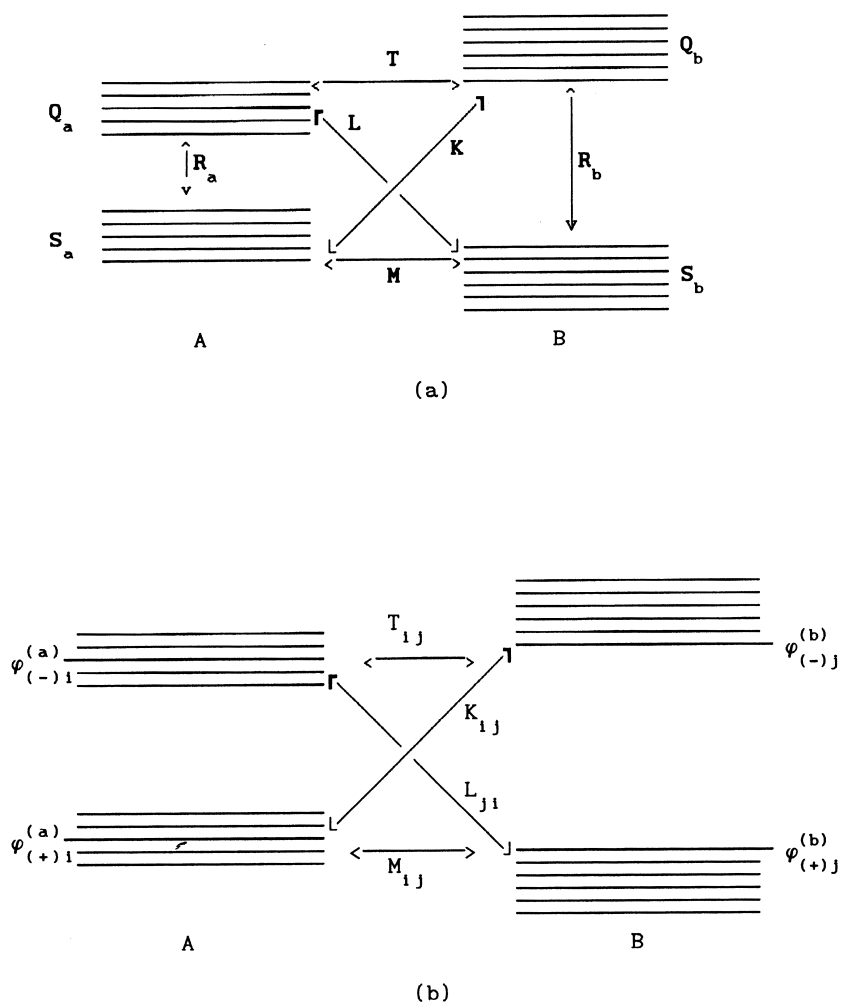
(a)

(b)

Fig. 1. A diagram representing the intra- and intermolecular interactions between the molecules *A* and *B*. Matrices containing resonance parameters between various subsets of basis orbitals are shown in the upper part (a). The case of a local intermolecular contact is displayed in the lower part of the diagram (b).

addition, the total basis set $\{\phi\}$ has been divided into two subsets $\{\phi_{(+)}\}$ and $\{\phi_{(-)}\}$ containing the bonding BOs (BBOs) along with lone pair orbitals and the antibonding BOs (ABOs), respectively. Furthermore, the intersubset interactions have been assumed to be first order terms vs. the energy differences between BBOs and ABOs.

As a result, the common Hückel type Hamiltonian matrix of saturated molecules $\mathbf{H}$ has been expressed as a sum of first- and second order matrices, i.e.

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

where

$$\mathbf{H}_{(0)} = \begin{vmatrix} \mathbf{E}_{(+)} & 0 \\ 0 & -\mathbf{E}_{(-)} \end{vmatrix}, \ \mathbf{H}_{(1)} = \begin{vmatrix} \mathbf{S} & \mathbf{R} \\ \mathbf{R}^{+} & \mathbf{Q} \end{vmatrix} \tag{2}$$

The diagonal blocks (submatrices) $\mathbf{E}_{(+)} + \mathbf{S}$ and $-\mathbf{E}_{(-)} + \mathbf{Q}$ of the total matrix $\mathbf{H}$ contained the intra-subset interactions (resonance parameters), whilst the off-diagonal block $\mathbf{R}$ involved the intersubset reso-nance parameters. The minus sign in front of $\mathbf{E}_{(-)}$ has been introduced for convenience, and the super-script + designates the transposed matrix. It is also

seen that zero order intrasubset interactions are allowed in Eq. (2), and these are included into submatrices $\mathbf{E}_{(+)}$ and $\mathbf{E}_{(-)}$.

The one-electron DM (bond order matrix) corresponding to the Hamiltonian matrix $\mathbf{H}$ has been obtained in [9] in the form of power series. The first three terms of this series are

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

$$= -2 \begin{vmatrix} \mathbf{G}_{(1)}\mathbf{G}_{(1)}^{+} & \mathbf{G}_{(2)} \\ \mathbf{G}_{(2)}^{+} & -\mathbf{G}_{(1)}^{+}\mathbf{G}_{(1)} \end{vmatrix} \tag{3}$$

where $\mathbf{I}$ is the unit matrix. The matrices $\mathbf{G}_{(1)}$ and $\mathbf{G}_{(2)}$ have been expressed in the form of integrals

$$\mathbf{G}_{(1)} = \int_{0}^{\infty} \exp(\mathbf{E}_{(+)}t)\mathbf{R}\exp(\mathbf{E}_{(-)}t)\mathrm{d}t,$$

$$\mathbf{G}_{(2)} = \int_{0}^{\infty} \exp(\mathbf{E}_{(+)}t)\mathbf{V}\exp(\mathbf{E}_{(-)}t)\mathrm{d}t \tag{4}$$

where

$$\mathbf{V} = \mathbf{S}\mathbf{G}_{(1)} - \mathbf{G}_{(1)}\mathbf{Q} \tag{5}$$

Let us introduce the following simplified notations for integrals shown in Eq. (4)

$$\mathbf{G}_{(1)} = (\mathbf{E}_{(+)}|\mathbf{R}|\mathbf{E}_{(-)}), \ \mathbf{G}_{(2)} = (\mathbf{E}_{(+)}|\mathbf{V}|\mathbf{E}_{(-)}) \tag{4a}$$

The above-described form of the DM may be easily applied to the case of two interacting saturated molecules A and B. To this end, the subset of BBOs $\{\phi_{(+)}\}$ will be further subdivided into two parts $\{\phi_{(+)}^{(a)}\}$ and $\{\phi_{(+)}^{(b)}\}$ referring to molecules A and B, respectively. Similarly, the subset of ABOs will consist of two parts $\{\phi_{(-)}^{(a)}\}$ and $\{\phi_{(-)}^{(b)}\}$. As a result, the total basis set may be represented in terms of four subsets, i.e. $\{\phi\} = \{\{\phi_{(+)}^{(a)}\}, \{\phi_{(+)}^{(b)}\}, \{\phi_{(-)}^{(a)}\}, \{\phi_{(-)}^{(b)}\}\}$.

The blocks (submatrices) of matrices $\mathbf{H}_{(0)}$ and $\mathbf{H}_{(1)}$ will be subdivided accordingly, viz.

$$\mathbf{E}_{(+)} = \begin{vmatrix} \mathbf{E}_{(+)}^{(a)} & 0 \\ 0 & \mathbf{E}_{(+)}^{(b)} \end{vmatrix}, \ \mathbf{E}_{(-)} = \begin{vmatrix} \mathbf{E}_{(-)}^{(a)} & 0 \\ 0 & \mathbf{E}_{(-)}^{(b)} \end{vmatrix}, \ \mathbf{S}$$

$$= \begin{vmatrix} \mathbf{S}_{a} & \mathbf{M} \\ \mathbf{M}^{+} & \mathbf{S}_{b} \end{vmatrix}, \ \mathbf{R} = \begin{vmatrix} \mathbf{R}_{a} & \mathbf{K} \\ \mathbf{L} & \mathbf{R}_{b} \end{vmatrix}, \ \mathbf{Q} = \begin{vmatrix} \mathbf{Q}_{a} & \mathbf{T} \\ \mathbf{T}^{+} & \mathbf{Q}_{b} \end{vmatrix} \tag{6}$$

The blocks of Eq. (6) denoted by superscripts (a) and (b) contain interactions (resonance parameters) inside the molecules A and B, respectively, whilst the blocks $\mathbf{M}$, $\mathbf{K}$, $\mathbf{L}$ and $\mathbf{T}$ consist of the intermolecular interactions as shown in Fig. 1a. Eq. (6) also involves an additional assumption that intermolecular resonance parameters are first order terms comparable to those contained within the matrices $\mathbf{R}_{a}$ and $\mathbf{R}_{b}$.

The block-diagonal structure of matrices $\mathbf{E}_{(+)}$ and $\mathbf{E}_{(-)}$ resulting from the above-mentioned assumption implies that matrices $\exp(\mathbf{E}_{(+)}t)$ and $\exp(\mathbf{E}_{(-)}t)$ are block-diagonal too. As a result, the total matrix $\mathbf{G}_{(1)}$ may be represented in terms of four blocks, viz.

$$\mathbf{G}_{(1)} = \begin{vmatrix} \mathbf{G}_{(1)}^{(a)} & \mathbf{G}_{(1)}^{(\mathbf{K})} \\ \mathbf{G}_{(1)}^{(\mathbf{L})} & \mathbf{G}_{(1)}^{(b)} \end{vmatrix} \tag{7}$$

where the blocks $\mathbf{G}_{(1)}^{(a)}$ and $\mathbf{G}_{(1)}^{(b)}$ taking the diagonal positions within the matrix $\mathbf{G}_{(1)}$ contain intramolecular interactions only. Using the notations shown in Eq. (4a) we obtain

$$\mathbf{G}_{(1)}^{(a)} = (\mathbf{E}_{(+)}^{(a)}|\mathbf{R}_{a}|\mathbf{E}_{(-)}^{(a)}), \ \mathbf{G}_{(1)}^{(b)} = (\mathbf{E}_{(+)}^{(b)}|\mathbf{R}_{b}|\mathbf{E}_{(-)}^{(b)}) \tag{8}$$

The off-diagonal blocks of the matrix $\mathbf{G}_{(1)}$, in turn, depend on the intermolecular resonance parameters, viz.

$$\mathbf{G}_{(1)}^{(\mathbf{K})} = (\mathbf{E}_{(+)}^{(a)}|\mathbf{K}|\mathbf{E}_{(-)}^{(b)}), \ \mathbf{G}_{(1)}^{(\mathbf{L})} = (\mathbf{E}_{(+)}^{(b)}|\mathbf{L}|\mathbf{E}_{(-)}^{(a)}) \tag{9}$$

It is seen that these blocks turn into zero matrices if the intermolecular resonance parameters contained within the blocks $\mathbf{K}$ and $\mathbf{L}$ vanish. Hence the submatrices $\mathbf{G}_{(1)}^{(\mathbf{K})}$ and $\mathbf{G}_{(1)}^{(\mathbf{L})}$ may be referred to as the intermolecular subblocks of the matrix $\mathbf{G}_{(1)}$.

Using Eqs. (3) and (7), the first order correction $\mathbf{P}_{(1)}$ of the DM $\mathbf{P}$ may be obtained in terms of intra- and intermolecular subblocks.

The above-described structure of the matrix $\mathbf{G}_{(1)}$ proves to be essential also in the formation of the second order correction $\mathbf{P}_{(2)}$ of the DM $\mathbf{P}$. Thus, sums of intra- and intermolecular contributions arise within the diagonal positions of products $\mathbf{G}_{(1)}\mathbf{G}_{(1)}^{(+)}$ and $\mathbf{G}_{(1)}^{(+)}\mathbf{G}_{(1)}$ owing to the above-described constitution of the matrix $\mathbf{G}_{(1)}$, e.g. the sum $\mathbf{G}_{(1)}^{(a)}\mathbf{G}_{(1)}^{(a)+} + \mathbf{G}_{(1)}^{(\mathbf{K})}\mathbf{G}_{(1)}^{(\mathbf{K})+}$ stands for the first diagonal block of the matrix $\mathbf{G}_{(1)}\mathbf{G}_{(1)}^{+}$. An analogous additivity proves to be inherent in the matrix $\mathbf{V}$ defined by Eq. (5) and thereby in the matrix $\mathbf{G}_{(2)}$. As a consequence, the total DM $\mathbf{P}$ of

the interacting molecules A and B may be represented in the form of a sum

$$\mathbf{P} = \mathbf{P}_{\text{isol}} + \delta\mathbf{P} \tag{10}$$

to within second order terms inclusive.

Let us consider the terms of Eq. (10) separately.

The first three corrections making up the matrix $\mathbf{P}_{\text{isol}}$ take the form

are the second order intramolecular terms, and

$$\mathbf{V}_a = \mathbf{S}_a\mathbf{G}_{(1)}^{(a)} - \mathbf{G}_{(1)}^{(a)}\mathbf{Q}_a, \ \ \mathbf{V}_b = \mathbf{S}_b\mathbf{G}_{(1)}^{(b)} - \mathbf{G}_{(1)}^{(b)}\mathbf{Q}_b \tag{13}$$

It is seen that the matrix $\mathbf{P}_{\text{isol}}$ actually contains the direct sum of DMs of isolated molecules. In particular, $\mathbf{P}_{(1)\text{isol}}$ involves intramolecular bond orders between occupied and vacant BOs of molecules A and B separately, whereas $P_{(2)\text{isol}}$ contains intramole-

$$\mathbf{P}_{(0)\text{isol}} = \begin{vmatrix} 2\mathbf{I} & 0 \\ 0 & 0 \end{vmatrix}, \ \ \mathbf{P}_{(1)\text{isol}} = -2 \begin{vmatrix} 0 & 0 & \mathbf{G}_{(1)}^{(a)} & 0 \\ 0 & 0 & 0 & \mathbf{G}_{(1)}^{(b)} \\ \mathbf{G}_{(1)}^{(a)+} & 0 & 0 & 0 \\ 0 & \mathbf{G}_{(1)}^{(b)+} & 0 & 0 \end{vmatrix} \tag{11a}$$

$$\mathbf{P}_{(2)\text{isol}} = -2 \begin{vmatrix} \mathbf{G}_{(1)}^{(a)}\mathbf{G}_{(1)}^{(a)+} & 0 & \mathbf{G}_{(2)}^{(a)} & 0 \\ 0 & \mathbf{G}_{(1)}^{(b)}\mathbf{G}_{(1)}^{(b)+} & 0 & \mathbf{G}_{(2)}^{(b)} \\ \mathbf{G}_{(2)}^{(a)+} & 0 & -\mathbf{G}_{(1)}^{(a)+}\mathbf{G}_{(1)}^{(a)} & 0 \\ 0 & \mathbf{G}_{(2)}^{(b)+} & 0 & -\mathbf{G}_{(1)}^{(b)+}\mathbf{G}_{(1)}^{(b)} \end{vmatrix} \tag{11b}$$

where

$$\mathbf{G}_{(2)}^{(a)} = (\mathbf{E}_{(+)}^{(a)}|\mathbf{V}_a|\mathbf{E}_{(-)}^{(a)}), \ \ \mathbf{G}_{(2)}^{(b)} = (\mathbf{E}_{(+)}^{(b)}|\mathbf{V}_b|\mathbf{E}_{(-)}^{(b)}) \tag{12}$$

cular diagonal blocks in addition. Diagonal elements of the latter evidently describe the intramolecular charge transfer.

The first three corrections of the second term $\delta\mathbf{P}$ of the DM $\mathbf{P}$ take the form

$$\delta\mathbf{P}_{(0)} = 0, \ \ \delta\mathbf{P}_{(1)} = -2 \begin{vmatrix} 0 & 0 & 0 & \mathbf{G}_{(1)}^{(\mathbf{K})} \\ 0 & 0 & \mathbf{G}_{(1)}^{(\mathbf{L})} & 0 \\ 0 & \mathbf{G}_{(1)}^{(\mathbf{L})+} & 0 & 0 \\ \mathbf{G}_{(1)}^{(\mathbf{K})+} & 0 & 0 & 0 \end{vmatrix} \tag{14a}$$

$$\delta\mathbf{P}_{(2)} = -2 \begin{vmatrix} \mathbf{G}_{(1)}^{(\mathbf{K})}\mathbf{G}_{(1)}^{(\mathbf{K})+} & \mathbf{F}_{(2)}^{(ab)} & \mathbf{G}_{(2)}^{(ab)} & \mathbf{C}_{(2)}^{(ab)} \\ \mathbf{F}_{(2)}^{(ab)+} & \mathbf{G}_{(1)}^{(\mathbf{L})}\mathbf{G}_{(1)}^{(\mathbf{L})+} & \mathbf{D}_{(2)}^{(ab)} & \mathbf{G}_{(2)}^{(ba)} \\ \mathbf{G}_{(2)}^{(ab)+} & \mathbf{D}_{(2)}^{(ab)+} & -\mathbf{G}_{(1)}^{(\mathbf{L})+}\mathbf{G}_{(1)}^{(\mathbf{L})} & \mathbf{N}_{(2)}^{(ab)} \\ \mathbf{C}_{(2)}^{(ab)+} & \mathbf{G}_{(2)}^{(ba)+} & \mathbf{N}_{(2)}^{(ab)+} & -\mathbf{G}_{(1)}^{(\mathbf{K})+}\mathbf{G}_{(1)}^{(\mathbf{K})} \end{vmatrix} \tag{14b}$$

where the subblocks of the second order correction $\delta \mathbf{P}_{(2)}$ are

$$\mathbf{G}_{(2)}^{(ab)} = (\mathbf{E}_{(+)}^{(a)}|\mathbf{V}_{ab}|\mathbf{E}_{(-)}^{(a)}), \ \ \mathbf{G}_{(2)}^{(ba)} = (\mathbf{E}_{(+)}^{(b)}|\mathbf{V}_{ba}|\mathbf{E}_{(-)}^{(b)})$$

$$(15a)$$

$$\mathbf{C}_{(2)}^{(ab)} = (\mathbf{E}_{(+)}^{(a)}|(\mathbf{W}_{ab} + \mathbf{Y}_{ab})|\mathbf{E}_{(-)}^{(b)}), \ \ \mathbf{D}_{(2)}^{(ab)}$$

$$= (\mathbf{E}_{(+)}^{(b)}|(\mathbf{X}_{ba} + \mathbf{U}_{ba})|\mathbf{E}_{(-)}^{(a)}) \qquad (15b)$$

$$\mathbf{F}_{(2)}^{(ab)} = \mathbf{G}_{(1)}^{(a)}\mathbf{G}_{(1)}^{(L)+} + \mathbf{G}_{(1)}^{(K)}\mathbf{G}_{(1)}^{(b)+}, \ \ \mathbf{N}_{(2)}^{(ab)}$$

$$= \mathbf{G}_{(1)}^{(a)+}\mathbf{G}_{(1)}^{(K)} + \mathbf{G}_{(1)}^{(L)+}\mathbf{G}_{(1)}^{(b)} \qquad (16)$$

and

$$\mathbf{V}_{ab} = \mathbf{M}\mathbf{G}_{(1)}^{(L)} - \mathbf{G}_{(1)}^{(L)}\mathbf{T}^{+}, \ \ \mathbf{V}_{ba} = \mathbf{M}^{+}\mathbf{G}_{(1)}^{(K)} - \mathbf{G}_{(1)}^{(L)}\mathbf{T}$$

$$(17a)$$

$$\mathbf{W}_{ab} = \mathbf{S}_{a}\mathbf{G}_{(1)}^{(K)} - \mathbf{G}_{(1)}^{(K)}\mathbf{Q}_{b}, \ \ \mathbf{Y}_{ab} = \mathbf{M}\mathbf{G}_{(1)}^{(b)} - \mathbf{G}_{(1)}^{(a)}\mathbf{T}$$

$$(17b)$$

$$\mathbf{X}_{ba} = \mathbf{S}_{b}\mathbf{G}_{(1)}^{(L)} - \mathbf{G}_{(1)}^{(L)}\mathbf{Q}_{a}, \ \ \mathbf{U}_{ba} = \mathbf{M}^{+}\mathbf{G}_{(1)}^{(a)} - \mathbf{G}_{(1)}^{(b)}\mathbf{T}^{+}$$

$$(17c)$$

The first order correction $\delta \mathbf{P}_{(1)}$ shown in Eq. (14a) contains intermolecular bond orders between occupied and vacant BOs proportional to intermolecular resonance parameters $\mathbf{K}_{ij}$ and $\mathbf{L}_{ij}$. Analogously, diagonal elements of the second order correction $\delta \mathbf{P}_{(2)}$ describe the intermolecular charge transfer. It is also seen that both $\delta \mathbf{P}_{(1)}$ and $\delta \mathbf{P}_{(2)}$ turn into zero matrices if $\mathbf{L} = \mathbf{K} = \mathbf{M} = \mathbf{T} = 0$. Hence, the correction $\delta \mathbf{P}$ may be entirely associated with intermolecular interaction.

Therefore, the total DM of two interacting molecules consists of a sum of two matrices, the first one containing the direct sum of DMs of isolated molecules and the second one being a correction originating from the intermolecular interaction.

3. Additivity of occupation numbers of basis orbitals and of the total energy

Additivity of occupation numbers of BOs with respect to intra- and intermolecular contributions follows directly from the results of Section 2. Indeed, any alteration in occupation number vs. that of an isolated BO (equal to 2 and 0 for BBOs and ABOs,

respectively) contains a sum of two terms describing the intra- and intermolecular contributions as it is seen from Eqs. (10)–(17c). For example, the occupation number of the BBO $\phi_{(+)i}^{(a)}$ of the molecule A takes the form

$$x_{(+)i}^{(a)} = 2 + \Delta x_{(+)i}^{(a)} = 2 + \Delta x_{(+)i}^{(a)\text{intra}} + \Delta x_{(+)i}^{(a)\text{inter}} \qquad (18)$$

where $\Delta x_{(+)i}^{(a)}$ is the total alteration consisting of intra- and intermolecular contributions equal to

$$\Delta x_{(+)i}^{(a)\text{intra}} = -2 \sum_{p}^{\text{vac}(A)} (\mathbf{G}_{(1)ip}^{(a)})^{2} \qquad (19a)$$

$$\Delta x_{(+)i}^{(a)\text{inter}} = -2 \sum_{m}^{\text{vac}(B)} (\mathbf{G}_{(1)im}^{(K)})^{2} \qquad (19b)$$

respectively, where the sums embrace the vacant BOs of molecules A and B.

Each of the contributions shown in Eqs. (19a) and (19b), in turn, is additive with respect to increments of separate bonds (lone pairs).

On the whole, the above results show that the intermolecular contributions to occupation numbers may be considered independently from the intramolecular ones. Thus, the intermolecular increment to occupation number of an *ABO*, $\phi_{(-)i}^{(a)}$ is

$$\Delta x_{(-)i}^{(a)\text{inter}} = 2 \sum_{l}^{\text{occ}(B)} (\mathbf{G}_{(1)li}^{(L)})^{2} \qquad (20)$$

To consider the influence of the intermolecular interaction on the internal characteristics of bonds (e.g. dipole moments), occupation numbers of sp^{3}-hybrid AOs (HAOs) and 1s AOs of hydrogen atoms ($1s_{H}$ AOs) are required, and these result from the above-described DM $\mathbf{P}$ after transforming it into the HAO basis [11,12]. The bond orbitals (BOs) are assumed to be defined as linear combinations of pairs of HAOs and $1s_{H}$ AOs belonging to separate bonds in this case.

Let us consider the *I*-th Z-C bond containing two HAOs χ_{Z} and χ_{C}. Then the occupation numbers of these orbitals (χ_{Z} and χ_{C}) may be expressed as follows [12]

$$x_{Z}(x_{C}) = 1 \pm \cos \gamma_{I} + \frac{1}{2} \Delta x_{I} \pm p_{I} \pm d_{I} \qquad (21)$$

where $\gamma_{I} = \text{arctg}(2/\alpha)$, and $\alpha = \alpha_{Z} - \alpha_{C}$ is the relevant

difference in the Coulomb parameters of HAOs χ_Z and χ_C. The third term of Eq. (21) is the total alteration in the population of the I-th bond ($\Delta x_I = \Delta x_{(+)i} + \Delta x_{(-)i}$). The forth term ($p_I$) is the secondary dipole moment of the I-th bond equal to

$$p_I = -2\mathbf{G}_{(2)ii} \sin \gamma_I \tag{22}$$

where $-2\mathbf{G}_{(2)ii}$ coincides with the bond order between the BBO $\phi_{(+)i}$ and ABO $\phi_{(-)i}$. And finally, d_I is the so-called depolarization dipole moment equal to

$$d_I = \frac{1}{2}(\Delta x_{(+)i} - \Delta x_{(-)i})\cos \gamma_I \tag{23}$$

and containing the alterations of the occupation numbers of the BBO $\phi_{(+)i}$ and ABO $\phi_{(-)i}$ and thereby being directly related to the charge transfer.

Let us assume now that the I-th bond belongs to the molecule A. Then additivity of the total alteration in the population of this bond (Δx_I) with respect to intra- and intermolecular contributions is evident.

For the dipole moments p_I and d_I we obtain

$$p_I = p_I^{\text{intra}} + p_I^{\text{inter}}, \quad d_I = d_I^{\text{intra}} + d_I^{\text{inter}} \tag{24}$$

where

$$p_I^{\text{intra}} - 2\mathbf{G}_{(2)ii}^{(a)} \sin \gamma_I, \quad p_I^{\text{inter}} = -2\mathbf{G}_{(2)ii}^{(ab)} \sin \gamma_I \tag{25}$$

$$d_I^{\text{intra}} = -\left\{ \sum_{p}^{\text{vac}(A)} (\mathbf{G}_{(1)ip}^{(a)})^2 + \sum_{j}^{\text{occ}(A)} (\mathbf{G}_{(1)ji}^{(a)})^2 \right\}\cos \gamma_I \tag{26a}$$

$$d_I^{\text{inter}} = -\left\{ \sum_{m}^{\text{vac}(B)} (\mathbf{G}_{(1)im}^{(K)})^2 + \sum_{l}^{\text{occ}(B)} (\mathbf{G}_{(1)li}^{(L)})^2 \right\}\cos \gamma_I \tag{26b}$$

These results imply that the total second order corrections within the occupation numbers x_Z and x_C are additive with respect to contributions of intra- and intermolecular bonding (the initial values of occupation numbers are $1 \pm \cos \gamma_I$).

Let us turn now to the total energy of two interacting molecules.

Given that the one-electron DM of the system under study is represented by Eq. (3), the relevant total energy may be defined as [10]

$$\mathbf{E} = \mathbf{Spur}(\mathbf{PH}) \tag{27}$$

and expressed in the form of power series. The first two terms of this series take the form

$$\mathbf{E}_{(0)} = 2\mathbf{Spur}\mathbf{E}_{(+)}, \quad \mathbf{E}_{(1)} = 2\mathbf{Spur}\mathbf{S} \tag{28}$$

and contain the sum of one-electron energies corresponding to doubly-occupied BOs. The second order correction $\mathbf{E}_{(2)}$ is

$$\mathbf{E}_{(2)} = \mathbf{Spur}(\mathbf{H}_{(1)}\mathbf{P}_{(1)} + \mathbf{H}_{(0)}\mathbf{P}_{(2)}) \tag{29}$$

Substituting Eqs. (1)–(3) into Eq. (29) and invoking Eq. (27) of [9] in addition, we finally obtain

$$\mathbf{E}_{(2)} = -\mathbf{Spur}(\mathbf{G}_{(1)}\mathbf{R}^+ + \mathbf{R}\mathbf{G}_{(1)}^+) \tag{30}$$

Let us consider now the case of two interacting molecules. To this end, the expressions for $\mathbf{R}$ and $\mathbf{G}_{(1)}$ in terms of four submatrices as shown in Eqs. (6) and (7) should be substituted into Eq. (30). We then obtain

$$\mathbf{E}_{(2)} = \mathbf{E}_{(2)}^{(a)} + \mathbf{E}_{(2)}^{(b)} + \mathbf{E}_{(2)}^{(\text{inter})} \tag{31}$$

where

$$\mathbf{E}_{(2)}^{(a)} = -\mathbf{Spur}(\mathbf{G}_{(1)}^{(a)}\mathbf{R}_a^+ + \mathbf{R}_1\mathbf{G}_{(1)}^{(a)+}), \quad \mathbf{E}_{(2)}^{(b)}$$
$$= -\mathbf{Spur}(\mathbf{G}_{(1)}^{(b)}\mathbf{R}_b^+ + \mathbf{R}_b\mathbf{G}_{(1)}^{(b)+}) \tag{32}$$

are the increments of intramolecular bonding. The last term of Eq. (31) takes the form

$$\mathbf{E}_{(2)}^{\text{inter}} = -\mathbf{Spur}[(\mathbf{G}_{(1)}^{(K)}\mathbf{K}^+ + \mathbf{K}\mathbf{G}_{(1)}^{(K)+}) + (\mathbf{G}_{(1)}^{(L)}\mathbf{L}^+$$
$$+ \mathbf{L}\mathbf{G}_{(1)}^{(L)+})] \tag{33}$$

and describes the intermolecular interaction energy. The expression of Eq. (33) may be represented in an alternative form, i.e.

$$\mathbf{E}_{(2)}^{\text{inter}} = -2 \sum_{i}^{\text{occ}(A)} \sum_{m}^{\text{vac}(B)} \mathbf{G}_{(1)im}^{(K)}\mathbf{K}_{im}$$
$$- 2 \sum_{l}^{\text{occ}(B)} \sum_{j}^{\text{vac}(A)} \mathbf{G}_{(1)li}^{(L)}\mathbf{L}_{li} \tag{34}$$

It is seen that the intermolecular interaction energy is additive with respect to contributions of various pairs of bonds.

We may conclude, therefore, that occupation numbers of basis orbitals of two interacting molecules and the relevant total energy both contain zero order

terms corresponding to isolated basis functions and two additive second order corrections describing the contributions of intra- and intermolecular bonding separately. Hence, intermolecular contributions to the above-mentioned characteristics may be studied independently of intramolecular ones.

An internal additivity of the intermolecular contributions also follows from the above-described results. Thus, occupation numbers of HAOs contain sums of three terms describing the intermolecular charge transfer, polarization and depolarization of bonds, respectively. Moreover, both the total intermolecular contributions and their separate components are additive with respect to increments of pairs of bonds.

The above conclusions, in turn, may be regarded as a consequence of additivity of the one-electron DM described in Section 2.

4. The case of a local intermolecular contact. Substantiation of the local models for intermolecular bonding

Let us suppose now that only two bonds (lone pairs) of molecules A and B (the Ith and the Jth one) come nearer when these molecules contact. As a result, four intermolecular resonance parameters shown in Fig. 1b, i.e.

$$\mathbf{M}_{ij} = \langle \phi_{(+)i}^{(a)} | \hat{\mathbf{H}} | \phi_{(+)j}^{(b)} \rangle, \ \mathbf{T}_{ij} = \langle \phi_{(-)i}^{(a)} | \hat{\mathbf{H}} | \phi_{(-)j}^{(b)} \rangle, \ \mathbf{K}_{ij}$$

$$= \langle \phi_{(+)i}^{(a)} | \hat{\mathbf{H}} | \phi_{(-)j}^{(b)} \rangle, \ \mathbf{L}_{ji} = \mathbf{L}_{ij}^{+} = \langle \phi_{(+)j}^{(b)} | \hat{\mathbf{H}} | \phi_{(-)i}^{(a)} \rangle$$

$$(35)$$

may be assumed to take considerable values, whereas the remaining resonance parameters may be neglected. In other words, local nature of the intermolecular overlap (resonance) parameters will be assumed. However, this does not necessarily ensure an analogous local nature of consequences of this interaction.

Thus let $\mathbf{E}_{(+)}^{(a)}$, $\mathbf{E}_{(+)}^{(b)}$, $\mathbf{E}_{(-)}^{(a)}$ and $\mathbf{E}_{(-)}^{(b)}$ be arbitrary matrices. Then non-zero elements arise within the intermolecular matrices $\mathbf{G}_{(1)}^{(\mathbf{L})}$ and $\mathbf{G}_{(1)}^{(\mathbf{K})}$ not only between pairs of orbitals $(\phi_{(+)i}^{(a)}, \phi_{(-)j}^{(b)})$ and $(\phi_{(+)j}^{(b)}, \phi_{(-)i}^{(a)})$ but also between the remaining orbitals.

For example, the element $\mathbf{G}_{(1)kl}^{(\mathbf{K})}$ equals to

$$\mathbf{G}_{(1)kl}^{(\mathbf{K})} = \int_0^\infty [\exp(\mathbf{E}_{(+)}^{(a)}t)]_{ki} \mathbf{K}_{ij} [\exp(\mathbf{E}_{(-)}^{(b)}t)]_{jl} dt \qquad (36)$$

and it does not vanish also for $k \neq i$ and $l \neq j$.

Let us consider now the particular case when $\mathbf{E}_{(+)}^{(a)}, \mathbf{E}_{(+)}^{(b)}, \mathbf{E}_{(-)}^{(a)}$ and $\mathbf{E}_{(-)}^{(b)}$ are diagonal matrices containing one-electron energies of BOs, i.e.

$$\mathbf{E}_{(+)ik}^{(a)} = \mathbf{E}_{(+)i}^{(a)}\delta_{ik}, \ \mathbf{E}_{(+)jm}^{(b)} = \mathbf{E}_{(+)j}^{(b)}\delta_{jm}, \ \mathbf{E}_{(-)ir}^{(a)}$$

$$= \mathbf{E}_{(-)i}^{(a)}\delta_{ir}, \ \mathbf{E}_{(-)js}^{(b)} = \mathbf{E}_{(-)j}^{(b)}\delta_{js} \qquad (37)$$

Eq. (37) corresponds to an assumption that intra- and intermolecular resonance parameters are of comparable values, and both are first order terms vs. the differences in the one-electron energies. The electronic structure characteristics (e.g. occupation numbers) referring to the above-mentioned approximation will be further designated by ~.

The elements of the first order matrices $\tilde{\mathbf{G}}_{(1)}^{(a)}, \tilde{\mathbf{G}}_{(1)}^{(b)}, \tilde{\mathbf{G}}_{(1)}^{(\mathbf{K})}$ and $\tilde{\mathbf{G}}_{(1)}^{(\mathbf{L})}$ describe the direct (through-space) interactions between the respective pairs of BOs. For example, the element $\tilde{\mathbf{G}}_{(1)ij}^{(\mathbf{K})}$ takes the form

$$\tilde{G}_{(1)ij}^{(\mathbf{K})} = -\frac{\mathbf{K}_{ij}}{\mathbf{E}_{(+)i}^{(a)} + \mathbf{E}_{(-)j}^{(b)}} \qquad (38)$$

Substitution of expressions like that of Eq. (38) into Eqs. (19b) and (20) allows the intermolecular contributions to occupation numbers of BOs $\phi_{(+)i}^{(a)}$ and $\phi_{(-)i}^{(a)}$ of the Ith bond to be expressed as follows

$$\tilde{\Delta} x_{(+)i}^{(a)\mathrm{inter}} = -2\frac{(\mathbf{K}_{ij})^2}{(\mathbf{E}_{(+)i}^{(a)} + \mathbf{E}_{(-)j}^{(b)})^2}, \ \tilde{\Delta} x_{(-)i}^{(a)\mathrm{inter}}$$

$$= 2\frac{(\mathbf{L}_{ji})^2}{(\mathbf{E}_{(+)j}^{(b)} + \mathbf{E}_{(-)i}^{(a)})^2} \qquad (39)$$

It is seen that the corrections to occupation numbers shown in Eq. (39) depend only on squares of the direct (through-space) interactions between BOs of the two directly contacting bonds. Further, the respective contributions for BOs $\phi_{(+)j}^{(b)}$ and $\phi_{(-)j}^{(b)}$ of the Jth bond are related to those of Eq. (39), viz.

$$\tilde{\Delta} x_{(+)j}^{(b)\mathrm{inter}} = -\tilde{\Delta} x_{(-)i}^{(a)\mathrm{inter}}, \ \tilde{\Delta} x_{(-)j}^{(b)\mathrm{inter}} = -\tilde{\Delta} x_{(+)i}^{(a)\mathrm{inter}} \qquad (40)$$

whilst other orbitals $\phi_{(+)k}, k \neq i,j$ and $\phi_{(-)m}, m \neq i,j$

are characterized by zero intermolecular corrections to occupation numbers.

Therefore, non-zero intermolecular contributions to occupation numbers of BOs arise for directly contacting bonds only and these are determined by the nature and spatial arrangement of these bonds and are independent of the remaining fragments of molecules.

The total populations lost (acquired) by the Ith and Jth bonds meet the relation

$$\tilde{\Delta} x_I^{(a)\text{inter}} = -\tilde{\Delta} x_J^{(b)\text{inter}} \tag{41}$$

Hence, a local interbond charge transfer between the Ith and Jth bonds actually takes place as a result of the above-described local intermolecular contact.

Similar conclusions refer also to the internal dipole moments of bonds. Thus, the intermolecular contribution to depolarization dipole moment of the Ith bond equals to

$$\tilde{d}_I^{\text{inter}} =$$
$$- \left\{ \frac{(\mathbf{K}_{ij})^2}{(\mathbf{E}_{(+)i}^{(a)} + \mathbf{E}_{(-)j}^{(b)})^2} + \frac{(\mathbf{L}_{ji})^2}{(\mathbf{E}_{(+)j}^{(b)} + \mathbf{E}_{(-)i}^{(a)})^2} \right\} \cos \gamma_I \tag{42}$$

whilst the relevant expression for $\tilde{d}_J^{\text{inter}}$ resembles Eq. (42) only $\cos \gamma_J$ stands for $\cos \gamma_I$ and a plus sign arises before the braces instead of minus of Eq. (42). Other bonds ($K \neq I,J$) prove to be described by zero depolarization dipole moments. Hence, local nature of the depolarization effect may be concluded as well.

Given that the Ith and Jth bonds contain the same types of atoms ($\gamma_I = \gamma_J$), depolarization of these bonds proves to be of similar values and of opposite signs. In the general case, the following ratio may be established between the depolarization dipole moments

$$\frac{|\tilde{d}_I^{\text{inter}}|}{|\tilde{d}_J^{\text{inter}}|} = \frac{\cos \gamma_I}{\cos \gamma_J} \tag{43}$$

To study the secondary dipole moments $\tilde{p}_I^{\text{inter}}$ originating from the intermolecular interaction, the elements $\mathbf{G}_{(2)ii}^{(ab)}$ under conditions of Eqs. (35) and (37) are required. An element of this type takes the

form

$$\tilde{\mathbf{G}}_{(2)ii}^{(ab)} = \frac{1}{\mathbf{E}_{(+)i}^{(a)} + \mathbf{E}_{(-)i}^{(a)}} \left(\frac{\mathbf{M}_{ij}\mathbf{L}_{ji}}{\mathbf{E}_{(+)j}^{(b)} + \mathbf{E}_{(-)i}^{(a)}} - \frac{\mathbf{K}_{ij}T_{ji}^+}{\mathbf{E}_{(+)i}^{(a)} + \mathbf{E}_{(-)j}^{(b)}} \right) \tag{44}$$

and it describes the indirect interaction between the BOs $\phi_{(+)i}^{(a)}$ and $\phi_{(-)i}^{(a)}$ of the Ith bond by means of either $\phi_{(+)j}^{(b)}$ or $\phi_{(-)j}^{(b)}$ of the Jth bond. This element depends on the spatial arrangement of the Ith and Jth bonds only. The relevant secondary polarization $\tilde{p}_I^{\text{inter}}$ equals to

$$\tilde{p}_I^{\text{inter}} = - \frac{2 \sin \gamma_I}{\mathbf{E}_{(+)i}^{(a)} + \mathbf{E}_{(-)i}^{(a)}} \left(\frac{\mathbf{M}_{ij}\mathbf{L}_{ji}}{\mathbf{E}_{(+)j}^{(b)} + \mathbf{E}_{(-)i}^{(a)}} - \frac{\mathbf{K}_{ij}\mathbf{T}_{ji}^+}{\mathbf{E}_{(+)i}^{(a)} + \mathbf{E}_{(-)j}^{(b)}} \right) \tag{45a}$$

Similarly, the intermolecular contribution to the secondary polarization of the Jth bond of the molecule B takes the form

$$\tilde{p}_J^{\text{inter}} = - \frac{2 \sin \gamma_J}{\mathbf{E}_{(+)j}^{(b)} + \mathbf{E}_{(-)j}^{(b)}} \left(\frac{\mathbf{M}_{ji}\mathbf{K}_{ij}}{\mathbf{E}_{(+)i}^{(a)} + \mathbf{E}_{(-)j}^{(b)}} - \frac{\mathbf{L}_{ji}\mathbf{T}_{ij}}{\mathbf{E}_{(+)j}^{(b)} + \mathbf{E}_{(-)i}^{(a)}} \right) \tag{45b}$$

whereas secondary polarizations of other bonds keep unchanged, i.e. $\tilde{p}_K^{\text{inter}} = 0$ unless $K = I,J$.

Therefore, non-zero intermolecular contributions to secondary dipole moments of bonds also arise for directly contacting bonds only, and these are determined by the nature and spatial arrangement of these bonds. The same conclusion evidently refers to total occupation numbers $x_Z(x_C)$ of HAOs of interacting bonds.

Let us turn now to the energy of the intermolecular interaction $\mathbf{E}_{(2)}^{\text{inter}}$ shown in Eq. (34). If we substitute the expressions for $\mathbf{G}_{(1)im}^{(\mathbf{K})}$ and $\mathbf{G}_{(1)li}^{(\mathbf{L})}$ like that of Eq. (38) into Eq. (34), we obtain

$$\tilde{\mathbf{E}}_{(2)}^{\text{inter}} = 2 \left[\frac{(\mathbf{K}_{ij})^2}{\mathbf{E}_{(+)i}^{(a)} + \mathbf{E}_{(-)j}^{(b)}} + \frac{(\mathbf{L}_{ji})^2}{\mathbf{E}_{(+)j}^{(b)} + \mathbf{E}_{(-)i}^{(a)}} \right] \tag{46}$$

It is seen that the intermolecular interaction energy $\tilde{\mathbf{E}}_{(2)}^{\text{inter}}$ turns into a local interbond interaction energy between the two directly contacting bonds whatever the structure of the remaining fragments of molecules. Hence, the remaining fragments of molecules A and B may be ignored when studying the intermolecular

interaction, and a two-bond four-orbital model becomes adequate.

Therefore, we have substantiated a local model for investigation of the intermolecular interaction.

5. Conclusions

1. Adequacy of the local model for investigation of the intermolecular bonding of saturated organic molecules may be traced back to the above-established high extent of additivity of the one-electron DM and of the total energy of interacting molecules with respect to intra- and intermolecular contributions. Hence, validity of this model has nothing to do with relative values of intra- and intermolecular resonance parameters (comparable values of these parameters are allowed).
2. Two conditions providing for adequacy of the local model may be mentioned:

    i) Relatively insignificant values of intermolecular resonance parameters for orbitals of all bonds except for several directly contacting bonds, i.e. a local intermolecular contact;
    ii) First order magnitude of both intra- and intermolecular resonance parameters as compared to differences in one-electron energies of bonding and antibonding BOs.

3. Substantiation of the local model of the intermolecular bonding carried out in this paper is based on application of the direct way of obtaining the DM. No need arises here for diagonalization of the Hamiltonian matrix and thereby for turning to the basis of delocalized MOs. In addition, no distinguishing of the degenerate and non-degenerate case is required in contrast to the standard PMO theory [1,4,5].
4. Similarity between the intra- and intermolecular

interactions in saturated systems also deserves attention. Thus, investigation of the heteroatom influence in saturated molecules [12] showed that intramolecular charge transfer, as well as polarization and depolarization of bonds are the additive components of this intramolecular effect. The same contributions make up the intermolecular bonding as established above. Additivity of both intra- and intermolecular interactions with respect to increments of separate bonds also may be mentioned among their common features. These, in turn, may be traced back to similar structures of intra- and intermolecular contributions both to occupation numbers of basis orbitals and to their separate terms as it is seen from Eqs. (19a), (19b), (25), (26a) and (26b).

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