

On the role of localized molecular orbitals in the formation of bond dipoles

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Abstract

The hypothesis of the classical chemistry about bond dipoles resulting from shifts of separate pairs of electrons is proved using the non-canonical method of molecular orbitals (MOs). To this end, a relation is sought between the total charge distribution inside an individual chemical bond of a polyatomic molecule and the square of the respective single localized MO (LMO). General expressions for these MOs are obtained directly on the basis of the Brillouin theorem without invoking additional localization criteria. The two characteristics under comparison are presented in an explicit algebraic form in terms of meaningful components. Reshaping of square of the 'own' LMO of the given bond is shown to play the decisive role in the formation of secondary dipoles of initially homopolar bonds (e.g. of C–C and C–H bonds in substituted alkanes), as well as of bonds of relatively low initial polarity. Thus, representability of these dipoles by shifts of the 'own' pairs of electrons of respective bonds is supported. For bonds of a high initial polarity, the secondary dipoles are shown to originate mainly from contributions of LMOs of other bonds extending over the antibonding basis orbital of the given bond. Moreover, the actual secondary bond dipole takes an opposite direction vs. that predicted by the shift of the respective 'own' pair of electrons in this case. The latter result serves to account for the known low nucleofugality of highly electronegative heteroatoms in the S_N2 reactions.

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1. Introduction

Dipole moments are among the principal characteristics of molecules that may be estimated as sums of local increments ascribed to separate chemical bonds, lone electron pairs and/or functional groups [1–3]. Moreover, increments referring to similar bonds are roughly transferable. These facts provided a basis for introducing the concept of the bond dipole [4], as well as for development of additive schemes for total dipole moments of molecules of various degrees of sophistication [4–7]. The non-transferable parts of bond dipoles also are of interest because these serve as a measure of the actual mutual influence of effective bonds and/or atoms in the given compound. For example, emer-

gence of additional (induced) dipole moments of the C–C and C–H bonds in substituted alkanes ($X-CH_2-CH_2\cdots$) [8] reflects the influence of the given heteroatom X upon the hydrocarbon fragment (cf. the inductive effect of heteroatom). In this connection, representation of the actual bond dipole as a sum of the primary increment and of a certain secondary (induced) component is known for a long time [9]. Furthermore, several attempts were undertaken to interpret the bond dipole and its alterations in terms of quantum chemistry. In the pioneering work [10], two components of the bond dipole were distinguished and related to populations of AOs and to overlap populations, respectively. An alternative decomposition into increments originating from the mutual polarization of the neighboring bonds and of the non-neighboring ones also may be mentioned here [11]. Finally, the expression of the bond dipole in terms of three meaningful components [12] should be

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added, namely of the primary increment, of the polarization dipole due to the very presence of the remaining bonds and of the so-called depolarization increment. The latter arises owing to the dipole-like distribution of the population lost (acquired) by the given bond due to the interbond charge transfer.

The concept of an electron pair pertinent to an individual chemical bond also is among prevalent concepts of the classical organic chemistry (it is commonly ascribed to Lewis [13]). In particular, this concept forms the basis of the popular qualitative approach to chemical reactions referred to as the 'curly arrow chemistry' [14]. It is no surprise in this connection that bond dipoles usually are almost automatically assumed to be representable as consequences of shifts of respective pairs of electrons. This hypothesis is implicitly accepted in numerous outstanding theories of the inductive effect (see e.g. [15]). Under these circumstances, a quantum chemical verification of the above-described assumption is highly desirable. The present study addresses just this task. The main reason why such an attempt seems to be not yet undertaken probably lies in the fact that even the one-to-one correspondence between chemical bonds and electron pairs is not self-evident in quantum chemistry.

Distribution of electrons in molecule is described in quantum theory by means of the one-electron density matrix (DM) or, more specifically, by the so-called charge-bond order (CBO) matrix. The latter coincides with the representation of the DM in the basis of AOs or hybrid AOs [16,17]. Elements of the CBO matrix, in turn, are made up of sums of increments of all occupied molecular orbitals (MOs). Inasmuch as each standard (canonical) MO (CMO) generally embraces the entire molecule, there is no one-to-one correspondence between CMOs and chemical bonds and, consequently, between the latter and separate pairs of electrons in this prevalent method of quantum chemistry. As a result, all CMOs and thereby all pairs of electrons actually make significant contributions to any bond dipole.

In contrast to CMOs, the alternative (non-canonical) MOs of molecules are not unique [18,19]. In this connection, the general one-electron problem (see e.g. [19]) is usually adapted to look for orbitals localized mostly on separate bonds and/or lone electron pairs of molecules. MOs of this type proved to be obtainable for the majority of non-aromatic systems [18] and are usually referred to as localized MOs (LMOs). One-to-one correspondence between these alternative orbitals and chemical bonds (and/or lone electron pairs) also is among the natural properties of LMOs. Thus, a certain relation may be expected between a bond dipole and the shape of square of the respective single LMO. Given that the dipole is entirely determined by the respective 'own' LMO of the given bond, a one-orbital model for the former follows. It is evident that the bond dipole is representable as a consequence of a shift of a single pair of electrons in this case. The specific aim of the present study consists in exploration of both

the very feasibility of the above-anticipated one-orbital model and the actual scope of its applicability. The cases of invalidity of the model also are under our interest.

The direct way of obtaining LMOs on the basis of the Brillouin theorem [20–25] is invoked in our study. Three advantages of this approach form the basis of such a choice. The first one consists in the possibility of avoiding the 'external' localization criteria [18] so that the shapes of LMOs depend only on the chemical constitution of the given compound [26]. Second, the direct way yields general results embracing large classes of molecules. The last and the most important attractive feature of the approach lies in the relation between the Brillouin theorem and the commutation equation for the one-electron DM [24,25] and thereby between the representation matrix of LMOs and the relevant CBO matrix. In this connection, we are about to explore whether the principal components of any bond dipole derived previously on the basis of solution of the commutation equation (i.e. the primary dipole along with its polarization and depolarization increments [12]) may be traced back to the partial contribution of the single occupied LMO of the given bond.

The block-diagonalization problem for the initial Fockian (or Hamiltonian) matrix following from the Brillouin theorem [20–25] and determining the LMOs has been solved perturbatively in Ref. [24] along with the commutation equation for the relevant DM. To this end, the basis of bonding and antibonding bond orbitals (BOs) has been used. The BOs were defined as linear combinations of pairs of either AOs or hybrid AOs (HAOs) pertinent to individual chemical bonds. The resulting LMOs then acquired the bond-orbital-and-tail constitution. The above-mentioned principal components of the bond dipole, in turn, resulted from retransformation [12] of the local 2×2 -dimensional block of the original DM of Ref. [24] into the basis of AOs(HAOs) again (the block refers to the two basis orbitals of the given bond). To achieve the above-formulated aim, an analogous retransformation of the LMO representation matrix is undertaken in the present study.

The paper is organized as follows: we start with introducing a model Hamiltonian matrix of a wide scope of applicability and overview the principal definitions required for further study (Section 2). The components of the bond dipole are discussed in Section 3. Section 4 deals with the retransformation procedure for the LMO representation matrix. Thereupon, we find the partial charge distribution originating from the occupied LMO of a separate bond and compare it with the total one. Section 5 contains a discussion of particular cases.

2. Overview of the principal definitions

We will dwell in this study on molecules and molecular systems that obey the Lewis rules and are representable by a single principal Lewis structure. Thus, our molecules will be assumed to contain more or less localized

two-center chemical bonds and lone electron pairs. In terms of the non-canonical method of MOs, this implies a set of LMOs of the bond-orbital-and-tail (or lone-pair-orbital-and-tail) constitution to exist for the given systems(s). This requirement, in turn, was shown to be met [21,24] for molecules representable by sets of weakly interacting bond and lone pair orbitals as compared to differences in one-electron energies of bonding (initially occupied) and antibonding (initially vacant) BOs. The specific definition of BOs is not essential in the above condition.

It deserves mentioning immediately that the actual definition of BOs depends on the structure of the given system. For example, alkanes and their derivatives usually are represented by bonding and antibonding combinations of pairs of $1s_H$ AOs of hydrogen atoms and of sp^3 -hybrid AOs of the remaining atoms pertinent to separate bonds, as well as by lone sp^3 -HAOs for lone pair orbitals (if any). Furthermore, BOs of σ - and π -type are distinguished for unsaturated systems. The former coincide with analogous combinations of $1s_H$ AOs and sp^2 -HAOs referring to separate σ bonds, whilst the latter consist of pairs of $2p_z$ AOs pertinent to formally double bonds [27]. Thus, we may largely formalise our subsequent study by introducing a certain set of BOs $\{\varphi\}$ and a set of HAOs (AOs) $\{\chi\}$ so that the BOs are assumed to be defined as linear combinations of pairs of HAOs (or AOs) irrespective of their actual nature. The orbitals $\{\chi\}$ will be referred to below as HAOs for simplicity. The requirement of the weak interbond interaction then resolves itself into the first order magnitude of the non-neighboring resonance parameters between HAOs of different bonds vs. those of intrabond type between the strongly overlapping (neighboring) pairs of orbitals [12,28,29].

To be able to study the two-center chemical bonds and the lone electron pairs on the unified basis, we will introduce a certain faked initially vacant orbital for any lone pair orbital. The faked orbital will be assumed to overlap strongly with the relevant single lone pair orbital. Moreover, these additional basis functions are presumed to be situated at sufficiently high one-electron energies so as to exert no influence upon final results. It is evident that our basis set $\{\chi\}$ may be assumed to contain an even total number of orbitals ($2N$), where N stands for the total number of bonds and lone electron pairs.

Let the $2N$ -dimensional basis set $\{\chi\}$ to be divided into two N -dimensional subsets $\{\chi'\}$ and $\{\chi''\}$ so that the strongly overlapping pairs of the neighboring orbitals find themselves in the different subsets. Furthermore, let us enumerate the basis functions in such a way that the neighboring pairs of orbitals acquire the coupled numbers i and $N+i$. Finally, orbitals described by larger absolute values of Coulomb parameters (α) will be included into the first subset. The common Hückel type model Hamiltonian matrix of the above-specified systems may be then presented as a sum of zero order ($\mathbf{H}_{(0)}$) and first order terms ($\mathbf{H}_{(1)}$), viz.

$$\mathbf{H} = \mathbf{H}_{(0)} + \mathbf{H}_{(1)} = \begin{vmatrix} \mathbf{A}_{(0)} & \mathbf{B}_{(0)} \\ \mathbf{B}_{(0)} & \mathbf{C}_{(0)} \end{vmatrix} + \begin{vmatrix} \mathbf{A}_{(1)} & \mathbf{B}_{(1)} \\ \mathbf{B}_{(1)}^+ & \mathbf{C}_{(1)} \end{vmatrix}, \quad (1)$$

where submatrices (blocks) correspond to subsets $\{\chi'\}$ and $\{\chi''\}$, and to their interaction. Submatrices $\mathbf{A}_{(0)}$, $\mathbf{C}_{(0)}$ and $\mathbf{B}_{(0)}$ of the zero order term $\mathbf{H}_{(0)}$ are of diagonal constitution consisting of Coulomb parameters of HAOs χ'_i and χ''_{N+i} (α_{I1} and α_{I2} , respectively) and of resonance parameters between the latter (β_I), i.e.

$$A_{(0)ij} = \alpha_{I1} \delta_{ij}, \quad C_{(0)ij} = \alpha_{I2} \delta_{ij}, \quad B_{(0)ij} = \beta_I \delta_{ij}. \quad (2)$$

Again, submatrices $\mathbf{A}_{(1)}$, $\mathbf{C}_{(1)}$ and $\mathbf{B}_{(1)}$ of the first order term $\mathbf{H}_{(1)}$ are square matrices of arbitrary structure. The superscript + is used here and below for Hermitian-conjugate (transposed) matrices.

The energy reference point and the energy unit will be chosen so that the above-enumerated parameters (α_{I1} , α_{I2} and β_I) take positive values for any bond and the inequality $\alpha_{I1} \geq \alpha_{I2}$ is valid (A negative energy unit is actually accepted). Inasmuch as the Coulomb and the intrabond resonance parameters always may be entirely included into the zero order matrix $\mathbf{H}_{(0)}$, the diagonal elements of the first order submatrices $\mathbf{A}_{(1)}$, $\mathbf{C}_{(1)}$ and $\mathbf{B}_{(1)}$ will be assumed to take zero values, i.e. $A_{(1)ii} = C_{(1)ii} = B_{(1)ii} = 0$ for any i .

Let us turn now to the set of BOs $\{\varphi\}$. The bonding and antibonding BOs will be supplemented with subscripts (+) and (−), respectively, e.g. $\varphi_{(+i)}$, $\varphi_{(-i)}$, etc. The bonding BO (BBO) and the antibonding BO (ABO) of the I th bond will be defined as eigenfunctions of the respective 2×2 -dimensional Hamiltonian matrix block in the basis $\{\chi'_i, \chi''_{N+i}\}$, i.e.

$$\varphi_{(+i)} = z_I \chi'_i + v_I \chi''_{N+i}, \quad \varphi_{(-i)} = v_I \chi'_i - z_I \chi''_{N+i}. \quad (3)$$

The expressions for coefficients z_I and v_I take the form [12]

$$z_I = \cos\left(\frac{\gamma_I}{2}\right), \quad v_I = \sin\left(\frac{\gamma_I}{2}\right), \quad (4)$$

where

$$\gamma_I = \arctan\left[\frac{2\beta_I}{\alpha_{I1} - \alpha_{I2}}\right], \quad 0 \leq \gamma_I \leq \frac{\pi}{2}. \quad (5)$$

The lone pair orbitals follow from Eqs. (3)–(5) under an assumption that

$$\alpha_{I1} - \alpha_{I2} \gg 2\beta_I, \quad \gamma_I \rightarrow 0, \quad z_I \approx 1, \quad v_I \approx 0. \quad (6)$$

Substituting Eq. (6) into Eq. (3) yields coincidence between the BO $\varphi_{(+i)}$ and the HAO χ'_i in accordance with the expectation. Accordingly, the upper limit of the γ_I values (i.e. $\gamma_I = \pi/2$) refers to an initially homopolar bond described by the equality $\alpha_{I1} = \alpha_{I2}$.

On the whole, passing from the basis of HAOs $\{\chi\}$ to that of BOs $\{\varphi\}$ will be described by the following unitary (and Hermitian) matrix

$$\mathbf{U} = \mathbf{U}^+ = \begin{vmatrix} \mathbf{Z} & \mathbf{V} \\ \mathbf{V} & -\mathbf{Z} \end{vmatrix}, \quad (7)$$

where \mathbf{Z} and \mathbf{V} are N -dimensional diagonal submatrices consisting of coefficients z_I and v_I of Eq. (4), respectively, i.e. $Z_{ij} = z_I \delta_{ij}$, $V_{ij} = v_I \delta_{ij}$.

The transformed Hamiltonian matrix $\tilde{\mathbf{H}}$ takes then the form

$$\tilde{\mathbf{H}} = \mathbf{U}^+ \mathbf{H} \mathbf{U} = \tilde{\mathbf{H}}_{(0)} + \tilde{\mathbf{H}}_{(1)} = \begin{vmatrix} \boldsymbol{\varepsilon}_{(+)} & \mathbf{0} \\ \mathbf{0} & \boldsymbol{\varepsilon}_{(-)} \end{vmatrix} + \begin{vmatrix} \mathbf{M}_{(1)} & \mathbf{R}_{(1)} \\ \mathbf{R}_{(1)}^+ & \mathbf{N}_{(1)} \end{vmatrix}, \quad (8)$$

where $\boldsymbol{\varepsilon}_{(+)}$ and $\boldsymbol{\varepsilon}_{(-)}$ are diagonal matrices consisting of one-electron energies of BBOs $\varepsilon_{(+)i}$ and of ABOs $\varepsilon_{(-)i}$, respectively. The submatrices $\mathbf{M}_{(1)}$, $\mathbf{R}_{(1)}$ and $\mathbf{N}_{(1)}$, in turn, are expressible in terms of blocks $\mathbf{A}_{(1)}$, $\mathbf{C}_{(1)}$ and $\mathbf{B}_{(1)}$ of Eq. (1), e.g.

$$\mathbf{R}_{(1)} = \mathbf{Z} \mathbf{A}_{(1)} \mathbf{V} + \mathbf{V} \mathbf{B}_{(1)}^+ \mathbf{V} - \mathbf{Z} \mathbf{B}_{(1)} \mathbf{Z} - \mathbf{V} \mathbf{C}_{(1)} \mathbf{Z}. \quad (9)$$

For Hamiltonian matrices containing diagonal (or block-diagonal) zero order members, the relevant DM ($\tilde{\mathbf{P}}$) and the respective LMO representation matrix (\mathbf{T}) have been derived in the form of power series [24] (see also Sections 3 and 4). Members of these series have been expressed in terms of certain principal matrices $\mathbf{G}_{(1)}$ and $\mathbf{G}_{(2)}$. Let us discuss these matrices before finishing this Section.

In the case of the diagonal member $\tilde{\mathbf{H}}_{(0)}$, separate elements of matrices $\mathbf{G}_{(1)}$ and $\mathbf{G}_{(2)}$ have been expressed algebraically in terms of those of particular blocks of the matrix $\tilde{\mathbf{H}}$, viz.

$$G_{(1)jl} = -\frac{R_{(1)jl}}{\varepsilon_{(+)j} - \varepsilon_{(-)l}}, \quad (10)$$

$$G_{(2)jl} = \frac{1}{\varepsilon_{(+)j} - \varepsilon_{(-)l}} \left[\sum_m^{\text{BBOs}} \frac{M_{(1)jm} R_{(1)ml}}{\varepsilon_{(+)m} - \varepsilon_{(-)l}} - \sum_r^{\text{ABOs}} \frac{R_{(1)jr} N_{(1)rl}}{\varepsilon_{(+)j} - \varepsilon_{(-)r}} \right]. \quad (11)$$

Elements $G_{(1)jl}$ of Eq. (10) have been interpreted as direct (through-space) interactions between BOs $\varphi_{(+)j}$ and $\varphi_{(-)l}$. Accordingly, $G_{(2)jl}$ of Eq. (11) represent indirect (through-bond) interactions of the same BOs, where both BBOs ($\varphi_{(+)m}$) and ABOs ($\varphi_{(-)r}$) of other bonds are able to play the role of mediators. The diagonal elements $G_{(1)ii}$ and $G_{(2)ii}$ deserve a separate mentioning. Thus, the above-introduced definition of BOs ensures zero values for intrabond resonance parameters $R_{(1)ii}$ and thereby for first order elements $G_{(1)ii}$. The second order element $G_{(2)ii}$, in turn, describes the indirect intrabond interaction between BOs of the I th bond by means of orbitals of other bonds that will be referred to as the intrabond coupling for simplicity.

3. The algebraic expressions for components of a bond dipole

The first three members of the power series for the DM $\tilde{\mathbf{P}}$ take the form [24]

$$\begin{aligned} \tilde{\mathbf{P}}_{(0)} &= \begin{vmatrix} 2\mathbf{I} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} \end{vmatrix}, & \tilde{\mathbf{P}}_{(1)} &= \begin{vmatrix} \mathbf{0} & -2\mathbf{G}_{(1)} \\ -2\mathbf{G}_{(1)}^+ & \mathbf{0} \end{vmatrix}, \\ \tilde{\mathbf{P}}_{(2)} &= \begin{vmatrix} \mathbf{Q}_{(+)} & -2\mathbf{G}_{(2)} \\ -2\mathbf{G}_{(2)}^+ & \mathbf{Q}_{(-)} \end{vmatrix}, \end{aligned} \quad (12)$$

where \mathbf{I} here and below stands for the unit matrix or submatrix and

$$\mathbf{Q}_{(+)} = -2\mathbf{G}_{(1)} \mathbf{G}_{(1)}^+, \quad \mathbf{Q}_{(-)} = 2\mathbf{G}_{(1)}^+ \mathbf{G}_{(1)}. \quad (13)$$

The initial occupation numbers of BOs follow from diagonal elements of the zero order contribution $\tilde{\mathbf{P}}_{(0)}$ and coincide with 2 and 0 for BBOs and ABOs, respectively. Alterations in these numbers due to interbond interaction, in turn, result from diagonal elements of submatrices $\mathbf{Q}_{(+)}$ and $\mathbf{Q}_{(-)}$. For BOs $\varphi_{(+)i}$ and $\varphi_{(-)i}$, these alterations take the form

$$\begin{aligned} Q_{(+)ii} &= -2 \sum_p^{\text{ABOs}} (G_{(1)ip})^2 < 0, \\ Q_{(-)ii} &= 2 \sum_m^{\text{BBOs}} (G_{(1)mi})^2 > 0 \end{aligned} \quad (14)$$

and depend on squares of direct interactions between BOs under consideration and the remaining BOs. It is seen that BBOs always lose their populations due to interbond interaction, i.e. partial deoccupations of these orbitals take place. Again, ABOs always acquire additional population. Finally, emergence of bond orders between the two BOs of the same (I th) bond may be mentioned among important consequences of the interbond interaction. These particular bond orders are determined by respective intrabond couplings $G_{(2)ii}$ (Note that $G_{(1)ii} = 0$ for any i).

To obtain the actual intrabond charge distribution, the representation of the DM in the basis of HAOs $\{\chi\}$ (i.e. the relevant CBO matrix \mathbf{P}) is required. Members of the respective power series follow after retransforming the matrices $\tilde{\mathbf{P}}_{(k)}$ of Eq. (12) ($k = 0, 1, 2$, etc.) into the HAO basis again using the matrix \mathbf{U} of Eq. (7). Let the occupation numbers of HAOs of the I th bond (i.e. of χ'_i and χ''_{N+i}) to be denoted by X_i and X_{N+i} , respectively. The relevant expressions take the form [12]

$$X_i(X_{N+i}) = 1 \pm \cos \gamma_I + q_{(2)I} \pm d_{(2)I} \pm p_{(2)I}, \quad (15)$$

where

$$q_{(2)I} = \frac{1}{2} (Q_{(+)ii} + Q_{(-)ii}), \quad (16)$$

$$d_{(2)I} = \frac{1}{2} (Q_{(+)ii} - Q_{(-)ii}) \cos \gamma_I \quad (17)$$

and

$$p_{(2)I} = -2G_{(2)ii} \sin \gamma_I. \quad (18)$$

In the case of a lone electron pair, we accordingly obtain

$$X_i = 2 + Q_{(+)ii}, \quad X_{N+i} = 0. \quad (19)$$

The relations of Eq. (6) are taken into consideration here along with the equalities $G_{(2)ii} = 0$ and $Q_{(-)ii} = 0$ originating from the high one-electron energy of the faked HAO χ''_{N+i} attached to our lone pair orbital.

Let us start our discussion with the more simple case of Eq. (19). The HAO χ'_i is initially occupied by two electrons in accordance with its nature, whilst the occupation number of its faked counterpart takes a zero value. Alteration in the population of the lone pair orbital χ'_i due to inter-bond interaction is described by the negative matrix element $Q_{(+)ii}$ (see Eq. (14)). Thus, a partial deoccupation of this orbital is predicted. This effect may be considered as an origin of the molecular-structure-dependent component of the relevant increment to the total dipole moment of molecule (note that increments of lone pair orbitals of heteroatoms are distinguished in some additive schemes for total dipoles of molecules [30] along with increments of individual bonds).

Let us turn now to occupation numbers of HAOs χ'_i and χ''_{N+i} of the I th bond shown in Eq. (15). The zero order dipole-like increment $\pm \cos \gamma_I$ is inherent in the bond under consideration whatever the structure of the whole molecule (γ_I is defined by Eq. (5)). Hence, this increment may be concluded to determine the primary dipole moment of the I th bond. In accordance with the expectation, the population of the HAO χ'_i of the more electronegative atom becomes increased, whereas that of the HAO χ''_{N+i} is accordingly reduced as compared to 1.

The term $q_{(2)I}$ of Eq. (16) represents a half of the total population lost (acquired) by the I th bond owing to inter-bond interaction. This characteristic actually consists of difference between absolute values of population lost by the BBO $\varphi_{(+)i}$ and of that acquired by the ABO $\varphi_{(-)i}$. The increment $q_{(2)I}$ is of the same sign for both occupation numbers X_i and X_{N+i} and thereby it does not contribute to the bond dipole. Hence, the secondary dipole of the I th bond may be expected to be determined by the sum of the remaining increments $d_{(2)I}$ and $p_{(2)I}$. Different origins of these increments also are noteworthy. The term $d_{(2)I}$ originates from the interbond charge redistribution, whilst $p_{(2)I}$ may be traced back to the newly formed internal bond order between BOs $\varphi_{(+)i}$ and $\varphi_{(-)i}$ of the I th bond.

The increment $d_{(2)I}$ contains a sum of absolute values of the population lost by the BBO $\varphi_{(+)i}$ and of that acquired by the ABO $\varphi_{(-)i}$. The *a priori* negative sign of the term $d_{(2)I}$ follows immediately after invoking Eq. (14). This implies that the HAO χ'_i pertinent to the more electronegative atom loses its population owing to formation of the relevant dipole, whereas the HAO χ''_{N+i} acquires an additional population. Therefore, the primary dipole moment of the I th bond becomes reduced owing to this new increment. In this connection, the relevant component of the total bond dipole has been called the depolarization dipole moment [12]. Opposite orientations of the primary dipole and of the depolarization one may be easily accounted for by shapes of BOs $\varphi_{(+)i}$ and $\varphi_{(-)i}$. Thus, the shape of the BBO $\varphi_{(+)i}$ of Eq. (3) ensures the primary reduction of

population of the HAO χ'_i when this BO is deoccupied. Accordingly, the additional population acquired by the ABO $\varphi_{(-)i}$ becomes localized mainly on the HAO χ''_{N+i} . Both of these effects contribute to reduction of the primary dipole moment of our bond.

As opposed to $d_{(2)I}$, the sign of the last increment $p_{(2)I}$ cannot be established *a priori* (i.e. without specifying the structure of the system). Studies of the most popular particular cases showed [31] that $p_{(2)I}$ usually takes a positive value and contributes to growth of the primary dipole. In this connection, the relevant increment has been called the polarization dipole [12].

It deserves mentioning finally that the depolarization dipole $d_{(2)I}$ vanishes for initially homopolar bonds described by uniform Coulomb parameters (Given that $\alpha_{I1} = \alpha_{I2}$, $\gamma_I = \frac{\pi}{2}$ and $\cos \gamma_I = 0$). This result may be traced back to a uniform distribution among HAOs χ'_i and χ''_{N+i} of the population both lost by the BBO $\varphi_{(+)i}$ and of that acquired by the ABO $\varphi_{(-)i}$ due to the equality $z_I = v_I$. The total secondary bond dipole proves to be then determined by the increment $p_{(2)I}$.

4. Analysis of localized molecular orbitals

The block-diagonalization problem consists in obtaining an unitary matrix \mathbf{T} that serves to transform the total matrix $\tilde{\mathbf{H}}$ of Eq. (8) into a block-diagonal form, i.e.

$$\tilde{\mathbf{H}}' = \mathbf{T}^+ \tilde{\mathbf{H}} \mathbf{T} = \begin{vmatrix} \mathbf{E}_{(+)} & \mathbf{0} \\ \mathbf{0} & \mathbf{E}_{(-)} \end{vmatrix}, \quad (20)$$

where $\mathbf{E}_{(+)}$ and $\mathbf{E}_{(-)}$ are the so-called eigenblocks of the Hamiltonian matrix $\tilde{\mathbf{H}}$ referring to subspaces of BBOs and of ABOs, respectively. In accordance with the Brillouin theorem [19–25], the matrix \mathbf{T} coincides with the respective representation matrix of non-canonical MOs. In our case, the representation evidently refers to the basis of bond orbitals. In connection with the non-uniqueness of the non-canonical MOs in general (Section 1) and thereby of the matrix \mathbf{T} , a certain choice of separate corrections $\mathbf{T}_{(k)}$, ($k = 0, 1, 2$) has been made when constructing the relevant power series [24] so as to ensure the resemblance between the matrix \mathbf{T} and the DM $\tilde{\mathbf{P}}$ of Eq. (12) as close as it was possible. The result is as follows

$$\mathbf{T}_{(0)} = \mathbf{I}, \quad \mathbf{T}_{(1)} = \begin{vmatrix} \mathbf{0} & \mathbf{G}_{(1)} \\ -\mathbf{G}_{(1)}^+ & \mathbf{0} \end{vmatrix}, \quad \mathbf{T}_{(2)} = \begin{vmatrix} \frac{1}{4}\mathbf{Q}_{(+)} & \mathbf{G}_{(2)} \\ -\mathbf{G}_{(2)}^+ & -\frac{1}{4}\mathbf{Q}_{(-)} \end{vmatrix}, \quad (21)$$

where the submatrices $\mathbf{G}_{(1)}$, $\mathbf{G}_{(2)}$, $\mathbf{Q}_{(+)}$ and $\mathbf{Q}_{(-)}$ coincide with those of Eq. (12). The zero order contribution $\mathbf{T}_{(0)}$ of the total matrix \mathbf{T} equals to the $2N$ -dimensional unit matrix. This fact ensures the bond-orbital-and-tail structure of the non-canonical orbitals and thereby their localized nature. The remaining corrections of Eq. (21), i.e. $\mathbf{T}_{(1)}$ and $\mathbf{T}_{(2)}$, determine the ‘tails’ of LMOs representing the pattern of their delocalization over the whole molecule.

To represent the functional form of LMOs of Eq. (21), let us define the row-matrices $(\varphi_{(+)})$ and $(\varphi_{(-)})$ containing the subsets of BBOs and of ABOs, respectively. Accordingly, the row-matrices $(\Psi_{(+)})$ and $(\Psi_{(-)})$ will correspondingly consist of the occupied LMOs $\Psi_{(+)i}$ and of the vacant ones $\Psi_{(-)j}$. We then obtain

$$((\Psi_{(+)}, (\Psi_{(-)})) = ((\varphi_{(+)}, (\varphi_{(-)})) \cdot \mathbf{T}. \quad (22)$$

After substituting Eq. (21) into Eq. (22), the occupied LMO of the I th bond may be expressed as follows

$$\begin{aligned} \Psi_{(+)i} = & \varphi_{(+)i} \left[1 + \frac{1}{4} Q_{(+)ii} \right] - \varphi_{(-)i} G_{(2)ii} \\ & + \frac{1}{4} \sum_{j(\neq i)}^{BBOs} \varphi_{(+)j} Q_{(+)ji} - \sum_{m(\neq i)}^{ABOs} \varphi_{(-)m} (G_{(1)mi}^+ + G_{(2)mi}^+). \end{aligned} \quad (23)$$

It is seen that the orbital $\Psi_{(+)i}$ contains contributions of BOs of the I th bond, as well as of all the remaining BBOs and ABOs. Let the increments of the former type to be called the head of the LMO $\Psi_{(+)i}$, whilst those of the latter type will be referred to as the tail of the same LMO as usually. It is also seen that the head of the LMO $\Psi_{(+)i}$ depends on the structure of the whole system under study. In particular, the principal contribution of the BBO $\varphi_{(+)i}$ contains the renormalization increment proportional to the population lost by this BO due to the interbond interaction. Again, the contribution of the ABO $\varphi_{(-)i}$ to the head of the LMO $\Psi_{(+)i}$ is proportional to the intrabond coupling $G_{(2)ii}$.

Derivation of expressions for the representation of LMOs of the same system(s) in the basis of HAOs $\{\chi\}$ may be performed by invoking the matrix \mathbf{U} of Eq. (7). To this end, let us introduce the row-matrices (χ') and (χ'') containing the subsets of HAOs $\{\chi'\}$ and $\{\chi''\}$ defined in Section 2. Passing from the basis of HAOs $\{\chi\}$ to that of BOs $\{\varphi\}$ may be then represented as follows

$$((\varphi_{(+)}, (\varphi_{(-)})) = ((\chi')(\chi''))\mathbf{U}. \quad (24)$$

After substituting Eq. (24) into Eq. (22) it follows that the matrix

$$\mathbf{W} = \mathbf{U}\mathbf{T} \quad (25)$$

is the new LMO representation matrix being sought. As the matrix \mathbf{T} takes the form of power series, the same refers also to the matrix \mathbf{W} , where

$$\mathbf{W}_{(0)} = \mathbf{U}, \quad \mathbf{W}_{(1)} = \mathbf{U}\mathbf{T}_{(1)}, \quad \mathbf{W}_{(2)} = \mathbf{U}\mathbf{T}_{(2)}, \quad \text{etc.} \quad (26)$$

Using Eqs. (7), (21) and (26) we may then express the head of the LMO $\Psi_{(+)i}$ as a linear combination of HAOs χ'_i and χ''_{N+i} , i.e.

$$\Psi_{(+)i} = r_I \chi'_i + s_I \chi''_{N+i} + \dots, \quad (27)$$

where dots stand for the tail of the LMO. The new coefficients r_I and s_I are

$$\begin{aligned} r_I = & z_I - \{ \mathbf{V}\mathbf{G}_{(1)}^+ \}_{ii} + \left\{ \frac{1}{4} \mathbf{Z}\mathbf{Q}_{(+)i} - \mathbf{V}\mathbf{G}_{(2)}^+ \right\}_{ii}, \\ s_I = & v_I + \{ \mathbf{Z}\mathbf{G}_{(1)}^+ \}_{ii} + \left\{ \frac{1}{4} \mathbf{V}\mathbf{Q}_{(+)i} + \mathbf{Z}\mathbf{G}_{(2)}^+ \right\}_{ii}, \end{aligned} \quad (28)$$

where the notation $\{\dots\}_{ii}$ stands for the diagonal element of the total matrix contained within the braces. Employment of the equality $G_{(1)ii} = 0$ within Eq. (28) yields the final expressions for coefficients r_I and s_I , viz.

$$\begin{aligned} r_I = & \left[1 + \frac{1}{4} Q_{(+)ii} \right] z_I - G_{(2)ii} v_I, \\ s_I = & \left[1 + \frac{1}{4} Q_{(+)ii} \right] v_I + G_{(2)ii} z_I. \end{aligned} \quad (29)$$

It is noteworthy that the right-hand sides of these expressions contain the same characteristics as those of Eqs. (16)–(18), i.e. $Q_{(+)ii}$ and $G_{(2)ii}$.

Elements of the CBO matrix are known to be expressible as sums of increments of all occupied MOs of the given system [16]. This rule embraces the basis of LMOs as well [16,17,19]. Hence, the occupation numbers of HAOs χ'_i and χ''_{N+i} are accordingly representable as sums of partial contributions of all occupied LMOs $\Psi_{(+)j}$, $j = 1, 2, \dots, N$, i.e.

$$X_i = \sum_j^{\text{occ}} x_{i,(+)j}, \quad X_{N+i} = \sum_j^{\text{occ}} x_{N+i,(+)j}, \quad (30)$$

where $x_{i,(+)j}$ and $x_{N+i,(+)j}$ correspondingly represent the partial increments of the LMO $\Psi_{(+)j}$. Let us dwell now on the partial contributions of the LMO $\Psi_{(+)i}$ of the own (I th) bond, i.e. on increments $x_{i,(+)i}$ and $x_{N+i,(+)i}$. The latter, in turn, are proportional to twofold squares of coefficients r_I and s_I of Eq. (27). Employment of Eq. (29) and replacing $\cos^2(\gamma_I/2)$ and $\sin^2(\gamma_I/2)$ by $\frac{1}{2}(1 + \cos \gamma_I)$ and $\frac{1}{2}(1 - \cos \gamma_I)$, respectively, yields the following result

$$\begin{aligned} x_{i,(+)i}[x_{N+i,(+)i}] = & 1 \pm \cos \gamma_I + \frac{1}{2} Q_{(+)ii} \pm \frac{1}{2} Q_{(+)ii} \cos \gamma_I \\ & \mp 2G_{(2)ii} \sin \gamma_I, \end{aligned} \quad (31)$$

where terms to within the second order are included. Comparison of these partial increments to the relevant total populations of the same HAOs shown in Eqs. (15)–(18) allows us to reveal the role of the LMO $\Psi_{(+)i}$ in the formation of the bond dipole.

It is seen that the primary increment ($\pm \cos \gamma_I$) is contained within both expressions under comparison. This result causes no surprise if we recall the bond-orbital-and-tail constitution of LMOs. The polarization increment $p_{(2)I}$ defined by Eq. (18) also is present both in Eq. (15) and in Eq. (31). This implies that the polarization dipole of the I th bond may be entirely traced back to the contribution of its own LMO. This non-trivial result follows from proportionality between the increment of the ABO $\varphi_{(-)i}$ within the LMO $\Psi_{(+)i}$ of Eq. (23) (coinciding with $-G_{(2)ii}$) and the bond order between BOs $\varphi_{(+)i}$ and $\varphi_{(-)i}$ (equal to $-2G_{(2)ii}$). This proportionality originates from expressibil-

ity of the off-diagonal blocks of corrections $\tilde{\mathbf{P}}_{(2)}$ and $\mathbf{T}_{(2)}$ via the same matrix $\mathbf{G}_{(2)}$ (see Eqs. (12) and (21)). Finally, this common feature of the DM and of the LMO representation matrix, in turn, results from the fundamental relation between the commutation equation for the former and the Brillouin theorem [24].

Comparison of the remaining terms of Eqs. (15) and (31) shows that increments of the population $Q_{(+ii)}$ lost by the BBO $\varphi_{(+i)}$ also are present in both expressions. This implies that the part of the depolarization dipole originating from the deoccupation of the BBO of the I th bond due to inter-bond interaction also may be traced back to the contribution of its own LMO. So far as increments of the additional occupation of the ABO $\varphi_{(-i)}$ are concerned, these are absent in Eq. (31). Hence, the $Q_{(-ii)}$ -containing part of the depolarization dipole may be expected to result from contributions of occupied LMOs of other bonds extending over the ABO $\varphi_{(-i)}$.

To verify this anticipation, let us note that the population $Q_{(-ii)}$ acquired by the ABO $\varphi_{(-i)}$ may be presented in the form of a sum of partial increments of all BBOs [32], i.e.

$$Q_{(-ii)} = \sum_m^{\text{BBOs}} q_{(-i),(+)m}, \quad (32)$$

where

$$q_{(-i),(+)m} = 2(G_{(1)mi})^2 \quad (33)$$

is the increment of the BBO $\varphi_{(+m)}$ (see Eq. (14)). Inasmuch as $G_{(1)ii} = 0$, no contribution of the BBO $\varphi_{(+i)}$ arises in Eq. (33), i.e. $q_{(-i),(+)i} = 0$. This implies that the ABO $\varphi_{(-i)}$ acquires its population from BBOs of the remaining bonds only. An analogous decomposition of the population $Q_{(+mm)}$ lost by the BBO $\varphi_{(+m)}$ into increments $q_{(+m),(-i)}$ of particular ABOs $\varphi_{(-i)}$ yields the following relation

$$q_{(+m),(-i)} = -2(G_{(1)mi})^2 = -q_{(-i),(+)m}. \quad (34)$$

Eq. (34) implies that the population the ABO $\varphi_{(-i)}$ acquires from the BBO $\varphi_{(+m)}$ coincides with that donated by the latter to the former, i.e. the charge redistribution takes place between separate pairs of orbitals of the opposite initial occupation.

Let us consider now the occupied LMO $\Psi_{(+m)}$ of the M th bond. As with the LMO $\Psi_{(+i)}$ of Eq. (23), the orbital $\Psi_{(+m)}$ involves first order corrections containing all ABOs including the ABO $\varphi_{(-i)}$. The latter increment is proportional to the matrix element $G_{(1)im}^+ = G_{(1)mi}$. As in Refs. [24,29], let us define the partial delocalization coefficient of the LMO $\Psi_{(+m)}$ over the ABO $\varphi_{(-i)}$ as follows

$$d_{(+m),(-i)} = (G_{(1)mi})^2. \quad (35)$$

Comparison of Eqs. (33)–(35) shows that the population donated by the BBO $\varphi_{(+m)}$ to the ABO $\varphi_{(-i)}$ and thereby that acquired by the ABO $\varphi_{(-i)}$ from the BBO $\varphi_{(+m)}$ are proportional to the partial delocalization coefficient of the LMO $\Psi_{(+m)}$ over the ABO $\varphi_{(-i)}$. Just this result sup-

ports our conclusion about the $Q_{(-ii)}$ -dependent part of the depolarization dipole originating from delocalization of LMOs of other bonds over the ABO of the I th bond.

Let us dwell finally on the lone electron pairs. Substituting the equalities $\gamma_I = 0$ (see Eq. (6)) and $G_{(2)ii} = 0$ into Eq. (31) yields the result shown in Eq. (19). Thus, the total population of the lone pair orbital coincides with the partial increment of the relevant LMO. This result causes no surprise as lone pair orbitals are characterized by electron-donating effects only.

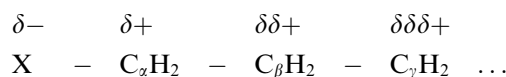
5. Consideration of particular cases

Let us start with the case of an initially homopolar bond described by coinciding Coulomb parameters ($\alpha_{I1} = \alpha_{I2}$) and thereby by zero values both of the primary dipole and of the depolarization increment. The above-obtained results allow us then to conclude that the actual dipole of such a bond coincides with polarization of square of its own LMO. As a result, the secondary bond dipole (if any) is entirely representable by the shift of the respective single pair of electrons. In particular, this conclusion refers to secondary dipoles of C–C and C–H bonds in substituted alkanes ($\text{X}-\text{CH}_2-\text{CH}_2\cdots$) arising under influence of the heteroatom X [8] (Note that C–H bonds also are nearly homopolar in alkanes [28,29]). Thus, let us invoke these systems for a more detailed illustration of our results.

On the basis of the whole complex of experimental data (including chemical reactivities [33] and conformational equilibria [34] of particular compounds, as well as the relevant ESCA spectra [35,36]) it was established that the directions of secondary dipoles of C–C bonds in substituted alkanes coincide with that of the primary polarity of the X–C $_{\alpha}$ bond as shown in the following scheme



where the arrows indicate the directions of the increased electron density. Moreover, the absolute values of these secondary dipoles were found to exhibit a rapid extinction when moving away from the substituent (heteroatom) X so that the anticipated distribution of charge takes the form



The above-described peculiarities of the heteroatom influence in substituted alkanes are considered nowadays as reliable facts [8].

The computational methods of quantum chemistry, however, were really challenged by the problem of signs of population alterations at the farther carbon atoms (C $_{\beta}$, C $_{\gamma}$, etc.) due to substitution. Indeed, the results of calculations proved to depend dramatically on the method applied, and both positive [37–39] and negative [40–43] induced charges on the C $_{\beta}$ atom were obtained. On the basis of Ref. [40], even the concept of the so-called alternating inductive effect was suggested, which was later negated

experimentally [34]. A special study of possible reasons of these discrepant results also has been undertaken [44,45].

In this context, the relevant predictions of the present approach deserve to be considered. To this end, let us take a simple model system $X-C_\alpha-C_\beta$ consisting of two bonds ($N = 2$), the first ($I = 1$) and the second one ($I = 2$) coinciding with $X-C_\alpha$ and $C_\alpha-C_\beta$, respectively. The four sp^3 -HAOs of our system will be enumerated as follows:

$$X \frac{\chi'_1}{1} \quad C_\alpha \quad \frac{\chi''_4}{2} \quad \frac{\chi'_2}{2} C_\beta.$$

Let the Coulomb parameters of these AOs to take zero values for simplicity except for that of the first HAO (χ'_1) referring to the heteroatom X. The latter will be denoted by α_X . The intrabond resonance parameters $\beta_I (I = 1, 2)$ will be chosen to coincide one with another and with the energy unit (i.e. $\beta_1 = \beta_2 = 1$), whilst the only parameter of the interbond type between HAOs χ'_3 and χ''_4 will be denoted by σ . For the secondary polarization of the $C_\alpha-C_\beta$ bond ($p_{(2)2}$), we then obtain

$$p_{(2)2} = -\frac{2}{\varepsilon_{(+2)} - \varepsilon_{(-2)}} \left(\frac{M_{(1)21} R_{(1)12}}{\varepsilon_{(+1)} - \varepsilon_{(-2)}} - \frac{R_{(1)21} N_{(1)12}}{\varepsilon_{(+2)} - \varepsilon_{(-1)}} \right) \quad (36)$$

(see Eqs. (11) and (18)). Parameters of Eq. (36), in turn, are expressible as follows

$$\begin{aligned} M_{(1)21} &= \frac{\sigma}{\sqrt{2}} \sin \frac{\gamma_1}{2}, & R_{(1)12} &= -\frac{\sigma}{\sqrt{2}} \sin \frac{\gamma_1}{2}, \\ R_{(1)21} &= -\frac{\sigma}{\sqrt{2}} \cos \frac{\gamma_1}{2}, & N_{(1)12} &= \frac{\sigma}{\sqrt{2}} \cos \frac{\gamma_1}{2}, \\ \varepsilon_{(+1)} &= \alpha_X \cos^2 \frac{\gamma_1}{2} + \sin \gamma_1, & \varepsilon_{(+2)} &= 1, \\ \varepsilon_{(-1)} &= \alpha_X \sin^2 \frac{\gamma_1}{2} - \sin \gamma_1, & \varepsilon_{(-2)} &= -1, \end{aligned} \quad (37)$$

(see also Refs. [31,45]). Substituting Eq. (37) into Eq. (36) yields the following final expression for $p_{(2)2}$

$$p_{(2)2} = \frac{1}{2} \sigma^2 \left(\frac{\sin^2(\gamma_1/2)}{1 + \sin \gamma_1 + \alpha_X \cos^2(\gamma_1/2)} - \frac{\cos^2(\gamma_1/2)}{1 + \sin \gamma_1 - \alpha_X \sin^2(\gamma_1/2)} \right), \quad (38)$$

where γ_1 coincides with $\arctan(2/\alpha_X)$ in accordance with Eq. (5). Dependence of the secondary polarization $p_{(2)2}$ of Eq. (38) upon parameters of our system α_X and σ is shown in Table 1. Inasmuch as rather different values are recommended for the parameter σ in separate studies (e.g.

0.15–0.20 [44,45], 0.24 [28], 0.30–0.40 [46,47], 0.36 [48]), this parameter is varied from 0.1 to 0.4 inclusive in our calculations. Again, the relative electronegativity of the heteroatom (α_X) lies inside the interval [0;2] [31,45] (Note that $p_{(2)2} = 0$ for $\alpha_X = 0$).

The principal conclusion following from Table 1 consists in negative signs of $p_{(2)2}$ for all values of parameters inside the above-specified intervals. Thus, decrease of population of the HAO χ'_2 is unambiguously predicted by our simple model in accordance with the above-described experimental facts. Furthermore, growing absolute values of $p_{(2)2}$ with increasing parameters α_X and σ also are in line with chemical expectations. Finally, the numerical values of $p_{(2)2}$ coincide with the lost population of the C_β atom obtained in Ref. [39] (0.016) under a reasonable assumption that $\alpha_X = 0.75$ and $\sigma = 0.35$.

As it was mentioned already, the secondary polarization $p_{(2)2}$ represents both the induced dipole of the $C_\alpha-C_\beta$ bond and the acquired polarity of square of the head of the respective occupied LMO. Thus, our results unambiguously indicate a shift of the 'own' pair of electrons of this bond towards the heteroatom X in accordance with the classical hypothesis. Thus, replenishment of the theory of the inductive effect in terms of LMOs [49] follows from the results of the present study.

The inductive effect of a heteroatom upon a hydrocarbon fragment is known to be accompanied by a certain electron-donating effect of its lone electron pair(s) [8]. This additional component of the heteroatom influence also is representable as a shift of the respective pair of electrons towards the hydrocarbon fragment as our results indicate. Moreover, the population donated to the ABO $\varphi_{(-)i}$ of the I th C–C (or C–H) bond is proportional to the partial delocalization coefficient of the LMO of the lone pair over the ABO under consideration. Thus, LMOs prove to be appropriate terms for interpretation of consequences of the overall influence of heteroatom upon a hydrocarbon fragment.

Let us turn now to initially heteropolar bonds. The secondary dipole is now determined by the sum of two terms $p_{(2)I}$ and $d_{(2)I}$ defined by Eqs. (17) and (18), whereas the acquired polarity of square of the LMO $\Psi_{(+i)}$ is conditioned by the former increment only, i.e. by $p_{(2)I}$. Let us assume for simplicity that our bond is characterized by an electron-accepting effect only, i.e. the BBO $\varphi_{(+i)}$ loses no population and $Q_{(+i)i} = 0$. This situation may be

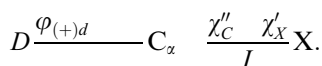
Table 1

Calculated values of the secondary polarization $p_{(2)2}$ of the $C_\alpha-C_\beta$ bond in substituted alkanes ($X-C_\alpha H_2-C_\beta H_2 \dots$) for different Coulomb parameters of the heteroatom X (α_X) and different interbond resonance parameters (σ)

$\downarrow \sigma$	$\alpha_X = 0.1$	$\alpha_X = 0.2$	$\alpha_X = 0.5$	$\alpha_X = 0.75$	$\alpha_X = 1.0$	$\alpha_X = 1.5$	$\alpha_X = 2.0$
0.10	-0.0002	-0.0004	-0.0009	-0.0013	-0.0017	-0.0023	-0.0028
0.15	-0.0004	-0.0008	-0.0020	-0.0030	-0.0038	-0.0052	-0.0063
0.20	-0.0008	-0.0015	-0.0036	-0.0053	-0.0068	-0.0093	-0.0112
0.30	-0.0017	-0.0033	-0.0082	-0.0120	-0.0154	-0.0210	-0.0252
0.35	-0.0023	-0.0045	-0.0111	-0.0163	-0.0209	-0.0285	-0.0343
0.40	-0.0030	-0.0059	-0.0146	-0.0213	-0.0274	-0.0373	-0.0448

exemplified by the C_α–X bond of a substituted alkane influenced by an electron-donating effect of a nucleophilic reagent during an S_N2 reaction [31]. As a result, the relative role of the outside electrons (i.e. of those accepted by the given bond) in the formation of its secondary dipole depends on the relative absolute value of the depolarization increment $d_{(2)I}$ vs. that of $p_{(2)I}$. In this connection, let us consider the ratio between these contributions and its dependence upon the initial polarity of our bond.

Let the I th C_α–X bond of a substituted alkane to be influenced by a certain electron-donating subsystem (D), the latter taking the back position peculiar to the S_N2 reaction [14,30,50]. Moreover, the subsystem D will be modelled by a single initially occupied orbital $\varphi_{(+d)}$ characterized by the Coulomb parameter α_d . The bond itself will be represented by HAOs χ'_X and χ''_C and by the relevant parameters α_X , $\alpha_C = 0$ and $\beta_I = 1$, i.e.



Additivity of expressions for both $p_{(2)I}$ and $d_{(2)I}$ with respect to contributions of the remaining bonds (lone electron pairs) allows us to consider the increments of the orbital $\varphi_{(+d)}$ upon the above-mentioned secondary dipoles separately whatever the structure of the whole molecule. Let these increments to be supplemented by a subscript (D). We then obtain

$$p_{(2)I(D)} = - \frac{2M_{(1)id}R_{(1)di} \sin \gamma_I}{(\varepsilon_{(+i)} - \varepsilon_{(-i)})(\alpha_d - \varepsilon_{(-i)})} > 0, \quad (39)$$

$$d_{(2)I(D)} = - \frac{(R_{(1)di})^2 \cos \gamma_I}{(\alpha_d - \varepsilon_{(-i)})^2} < 0. \quad (40)$$

The above-indicated positive sign of $p_{(2)I(D)}$ follows from the expressions

$$M_{(1)id} = \tau \sin \frac{\gamma_I}{2} < 0, \quad R_{(1)di} = -\tau \cos \frac{\gamma_I}{2} > 0, \quad (41)$$

where τ stands for the resonance parameter between orbitals $\varphi_{(+d)}$ and χ''_C and is a negative quantity in our energy units. (Note that the orbital $\varphi_{(+d)}$ overlaps with the negative lobe of the HAO χ''_C). Hence, the acquired polarity of the LMO $\Psi_{(+i)}$ always corresponds to a shift of the electron pair towards a more electronegative heteroatom X. At the same time, the direction of the total secondary dipole of

our bond cannot be established *a priori* and depends on the ratio under interest.

The expressions for the energy intervals $\varepsilon_{(+i)} - \varepsilon_{(-i)}$ and $\alpha_d - \varepsilon_{(-i)}$ may be derived using the energies of BOs of a heteropolar bond shown in Eq. (37). These take the form

$$\varepsilon_{(+i)} - \varepsilon_{(-i)} = \frac{2}{\sin \gamma_I}, \quad \alpha_d - \varepsilon_{(-i)} = \alpha_d + \frac{1 - \cos \gamma_I}{\sin \gamma_I}, \quad (42)$$

where the first formula results after substituting $2/\tan \gamma_I$ for α_X in accordance with Eq. (5). Using Eqs. (39)–(42) we then obtain

$$\kappa(\alpha_X, \alpha_d) = \frac{|d_{(2)I(D)}|}{|p_{(2)I(D)}|} = \frac{\cot \gamma_I \cot(\gamma_I/2)}{1 + \alpha_d \sin \gamma_I - \cos \gamma_I}. \quad (43)$$

The dependence of the ratio $\kappa(\alpha_X, \alpha_d)$ upon parameters α_X and α_d is exhibited in Table 2. It is seen that this ratio and thereby the relative value of the depolarization component vs. the polarization one decreases with the growing absolute value of the one-electron energy α_d . This result causes no surprise as an increase of α_d implies reduction of the electron-donating ability of the subsystem D . Furthermore, the same ratio $\kappa(\alpha_X, \alpha_d)$ grows with increasing relative electronegativity of the heteroatom X, i.e. with growing α_X values. This result may be traced back to the rising extent of depolarization with the increasing initial polarity of the heteropolar bond [31].

Two extreme cases may be distinguished here:

For bonds of relatively low initial polarity (described by small α_X values) influenced by donors of a low electron-donating ability (represented by large α_d values) we obtain that $\kappa(\alpha_X, \alpha_d) \ll 1$. Hence, the polarization increment predominates over the depolarization one in this case. As a result, the main part of the total secondary dipole of such a bond may be considered as a consequence of reshaping of the head of the respective LMO and thereby of a shift of the relevant pair of electrons.

For bonds of a high initial polarity, however, the ratio $\kappa(\alpha_X, \alpha_d)$ exceeds 1 and thereby the depolarization increment makes the most significant contribution to the total secondary dipole. The latter is then predicted to originate mainly from contribution of the outside (accepted) electrons. Reduction of the primary dipole of the highly polar C–X bond under influence of the electron-donating effect also is among the conclusions. Thus, an intriguing property proves to be peculiar to C–X bonds of a high initial polarity, namely opposite directions of the actual secondary

Table 2

Calculated values of the ratio $\kappa(\alpha_X, \alpha_d)$ between the increments $d_{(2)I(D)}$ and $p_{(2)I(D)}$ to the total secondary dipole of the C–X bond for different parameters of the system α_X and α_d

	$\alpha_d = 0$	$\alpha_d = 0.1$	$\alpha_d = 0.2$	$\alpha_d = 0.5$	$\alpha_d = 1.0$	$\alpha_d = 1.5$	$\alpha_d = 2.0$
$\alpha_X = 0.1$	0.055	0.050	0.046	0.036	0.027	0.021	0.013
$\alpha_X = 0.2$	0.123	0.110	0.100	0.079	0.058	0.046	0.038
$\alpha_X = 0.5$	0.422	0.375	0.336	0.258	0.185	0.145	0.119
$\alpha_X = 1.0$	1.460	1.259	1.105	0.809	0.559	0.427	0.346
$\alpha_X = 1.5$	3.760	3.142	2.693	1.885	1.257	0.943	0.754
$\alpha_X = 2.0$	8.203	6.615	5.539	3.722	2.406	1.778	1.409

dipole and of the respective shift of the ‘own’ pair of electrons. In this connection, a certain lowering of relative rates of the relevant chemical reactions may be expected. The latter anticipation is in line with the experimental fact that highly electronegative heteroatoms (or their groups) are bad nucleofuges in the S_N2 reactions, e.g. the fluorine atoms in alkyl fluorides [14,30,50].

6. Conclusions

The principal achievement of the above study consists in establishing of a general relation between the actual dipole of a certain (I th) bond of a polyatomic molecule (or molecular system) and the shape of square of the respective single occupied LMO. The most important implications of this relation are as follows:

1. Both the primary dipole of the I th bond and its polarization contribution ($p_{(2)I}$) may be entirely traced back to the shape of the head of the respective single occupied LMO. Thus, these two increments of the total bond dipole are representable as consequences of respective shifts of the ‘own’ pair of electrons of the given bond.
2. The depolarization contribution to the total bond dipole ($d_{(2)I}$) is divisible into two distinct components. The first one is related to the shift of the ‘own’ electron pair towards the less electronegative atom of the bond due to deoccupation of the BBO $\varphi_{(+i)}$ as a result of interbond interaction. The second component originates from the partial occupation of the ABO $\varphi_{(-i)}$ by remaining pairs of electrons. This particular component is related to the electron-accepting effect of the I th bond upon the remaining bonds.
3. The molecular-structure dependent increment of a lone electron pair to the total dipole of molecule [30] may be entirely ascribed to reshaping of the head of the respective LMO.

On the whole, the single occupied LMO of the given bond and/or of a lone electron pair proves to play an important role in the formation of the relevant bond dipole.

Application of the above-enumerated results to particular systems yields the following conclusions:

1. The secondary dipoles of initially homopolar C–C and C–H bonds in substituted alkanes are entirely representable by shifts of respective pairs of electrons. The directions of these shifts predicted by the present approach coincide with those following from experimental data.
2. For heteroatom-containing (C–X) bonds influenced by an electron-donating effect of an external orbital, the extent of participation of the outside (accepted) electrons in the formation of the respective secondary dipole depends on the initial polarity of the given bond: The higher is the polarity, the more important is the increment of the additional electrons.

Significance of the results obtained may be summarized as follows:

1. LMOs are demonstrated to reflect not only the existence of more or less localized bonds in molecules, but also the details of intrabond charge distribution. This implies these one-electron orbitals to present a real alternative to the CBO matrix when describing electronic structures.
2. The complementary nature of the non-canonical method of MOs vs. the canonical one [27] is additionally supported. Indeed, an ionization potential of molecule may be traced back to withdrawal of an electron from a single CMO (cf. the Koopmans theorem [17,19]). At the same time, no one-orbital model is possible for the details of electron density distribution in the canonical method of MOs. Again, a bond dipole may be related to a single LMO in the non-canonical method of MOs but not an ionization potential.

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