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Total energies of alkanes in terms of through-space and through-bond interactions. Analysis of the one-electron density matrix

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Abstract

The total energy of alkanes has been expressed in terms of two principal matrices $\mathbf{G}_{(1)}$ and $\mathbf{G}_{(2)}$ introduced previously [V. Gineityte, J. Mol. Struct. (Theochem), 343 (1995)183] and describing the direct (through-space) and indirect (through-bond) interactions of bond orbitals (BOs). As a result, the stabilization energy of an alkane versus the respective set of isolated bonds has been related to sum of squares of the through-space interactions over the whole molecule. The common one-electron density matrix (DM) of alkanes containing the same matrices $\mathbf{G}_{(1)}$ and $\mathbf{G}_{(2)}$ has been transformed into the basis of sp^3-hybrid AOs of carbon atoms and $1s_H$ AOs of hydrogen atoms. Analysis of this new representation of the DM allowed the stabilization energy to be alternatively expressed as spur of the so-called rebonding matrix. This matrix is among the building blocks of the transformed DM and describes redistribution of bond orders when making up an alkane molecule. In this connection, stabilization of alkanes has been concluded to be due to the rebonding effect. The extent of additivity of the stabilization energy with respect to contributions of separate bonds also has been studied. © 1998 Elsevier Science B.V.

Keywords: Bond orbitals; Density matrix; Alkanes

1. Introduction

Total energies are among the most popular quantum-chemical characteristics of molecules. In addition, these are directly comparable to experimental data, viz. to heats of formation and/or atomization (see ref. [1]).

The observed heats of formation of alkanes [2] are known to be expressable as sums of almost transferable bond increments [3,4]. This fact usually serves to substantiate the so-called localized models for these molecules [4]. Moreover, heats of formation of normal alkanes linearly depend on the number of carbon atoms. Finally, the branched isomers (if not overcrowded) are more stable as compared to the respective normal alkanes [2,4].

The Hückel type model along with the usual perturbation theory (the PMO method) [3,4] has been successfully applied for interpretation of the dependence of heats of formation of alkanes upon their structure. Algebraic expressions for total energies also have been studied in the framework of the above-mentioned approach. It has been shown that the first order correction $E_{(1)}$ of the total energy E vanishes, whilst the second one ($E_{(2)}$) contains a sum over pairs of bonds [4]. Given that the resonance parameters are only taken into account between the nearest-neighbour (geminal) bonds, the corrections

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$E_{(2)}$ describe the above-enumerated experimental regularities in the heats of formation of alkanes fairly well.

New possibilities for interpretation of total energies of alkanes are likely to follow from the results of Refs [5–10]. In these contributions a common Hamiltonian matrix (**H**) has been constructed for alkanes and the relevant common expression for the one-electron DM **P** has been obtained by means of perturbations theory (PT) in the general case without specifying the structure of the particular compound. The total energy E of any quantum-mechanical system is known to be related to the respective DM ($E = Spur(\mathbf{PH})$) [11,12]. In this connection, a common expression for the total energy of alkanes becomes feasible, and this energy might be related to definite peculiarities of the common DM. Otherwise, the total energy and the common DM of these molecules are both likely to be interpretable in the same terms.

The most appropriate way of doing this, however, is determined by the choice of the initial basis set. Thus, on the basis of bond orbitals (BOs) the common DM of alkanes ($\mathbf{P}'$) has been expressed [8] in terms of two principal matrices $\mathbf{G}_{(1)}$ and $\mathbf{G}_{(2)}$ describing the direct (through-space) and indirect (through-bond) interactions of BOs. The very concept of these interactions has been suggested in Refs [13–15] and used for interpretation of photoelectron spectra of molecules containing saturated hydrocarbon fragments [13–21] and of localized MOs of saturated organic molecules in general [8,9,22,23]. Application of these terms for interpretation of the total energy of alkanes is among the main aims of this paper.

The sp^3-hybrid AOs (HAOs) of carbon atoms and $1s_H$ AOs of hydrogen atoms make an alternative basis when studying the common peculiarities of the electronic structure of alkanes [5–7]. Use of this basis allows intrabond characteristics (e.g. bond dipoles) to be studied more easily as compared to the basis of BOs. On the whole, the common DM of alkanes in the basis of HAOs (**P**) describes the details of the electron density distribution in a far more convenient way as compared to the DM $\mathbf{P}'$. In this connection, a relation of the total energy of alkanes to certain peculiarities of the DM **P** also seems to be desirable.

The above-mentioned DM of alkanes, $\mathbf{P}'$, may be evidently transformed into the basis of HAOs and $1s_H$ AOs provided that BOs are defined just in this basis. However, new combinations of the principal matrices $\mathbf{G}_{(1)}$ and $\mathbf{G}_{(2)}$ including their complex-conjugate counterparts are likely to arise within the DM of alkanes after this transformation. These combinations, in turn, may be expected to represent new types of intramolecular interactions being expressed in terms of the through-space and through-bond ones. Then, the DM of alkanes **P** and thereby the total energy E are likely to be directly determined just by the above-mentioned composite interactions. In this connection, revealing these new interactions and using them for interpretation of both E and **P** is also an aim of this paper.

2. Algebraic expressions for the common DM and the total energy

Let us start with the common model Hamiltonian matrix of alkanes (**H**) in the basis of HAOs of carbon atoms and $1s_H$ AOs of hydrogen atoms [5–7]. For simplicity let us call them both the HAO basis. To construct the matrix **H**, the Hückel type model based on taking into account the most essential properties of the respective self-consistent Fockians will be used.

In this basis the non-neighboring resonance integrals and the differences between both the various neighboring resonance integrals and between the diagonal elements $\mathbf{H}_{ii}$ of the matrix **H** may be considered [5–7,10,24–26] as first order terms with respect to the mean value (β_0) of the neighboring resonance integrals (see also Section 5). The averaged diagonal element (α_0) and the above-defined parameter β_0 will be used as the reference point and energy unit, respectively; the equalities $\alpha_0 = 0$ and $\beta_0 = 1$ will be accepted.

Let us divide the initial $2n$-dimensional basis set of HAOs $\{\chi\}$ (n stands here for the number of bonds in alkane) 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 $n + i$. Then the initial Hückel type Hamiltonian matrix (**H**) for any alkane in the basis $\{\chi\}$ may be presented as a sum of zero order ($\mathbf{H}_{(0)}$) and first order terms ($\mathbf{H}_{(1)}$), the former containing the averaged neighboring resonance integrals equal to 1 in the positions ($i,n+i$), and the latter involving the remaining terms

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

where **I** is the n-dimensional unit matrix, and **A**, **B** and **C** are $n \times n$-dimensional matrices corresponding to subsets $\{\chi'\}$ and $\{\chi''\}$ and their interaction, respectively. The superscript ' + ' designates the transposed matrix.

Let us define n bonding BOs $\varphi_{(+)k}$ ($k = 1,2\ldots n$) and n antibonding BOs $\varphi_{(-)m}$ ($m = n+1, n+2, \ldots 2n$) as normalized sums and differences of pairs of HAOs belonging to the same chemical bond [9,10]. It is now convenient to transform the matrix **H** of Eq. (1) into the basis of BOs, to write the relevant DM **P**′ in terms of matrices $\mathbf{G}_{(1)}$ and $\mathbf{G}_{(2)}$ [8] and thereupon to retransform the matrix **P**′ into the HAO basis again. The relevant transformation matrix **U** takes the form

$$\boldsymbol{U}=2^{-1/2}\begin{vmatrix}\boldsymbol{I} & \boldsymbol{I}\\ \boldsymbol{I} & -\boldsymbol{I}\end{vmatrix} \tag{2}$$

and the new Hamiltonian matrix $\mathbf{H}' = \mathbf{U}^{+}\mathbf{H}\mathbf{U}$ becomes

$$\boldsymbol{H}'=\boldsymbol{H}'_{(0)}+\boldsymbol{H}'_{(1)}=\begin{vmatrix}\boldsymbol{I} & 0\\ 0 & -\boldsymbol{I}\end{vmatrix}+\begin{vmatrix}\boldsymbol{S} & \boldsymbol{R}\\ \boldsymbol{R}^{+} & \boldsymbol{Q}\end{vmatrix} \tag{3}$$

where

$$\boldsymbol{S}=\frac{1}{2}[(\boldsymbol{A}+\boldsymbol{C})+(\boldsymbol{B}+\boldsymbol{B}^{+})];\boldsymbol{Q}=\frac{1}{2}[(\boldsymbol{A}+\boldsymbol{C})-(\boldsymbol{B}+\boldsymbol{B}^{+})]$$

$$\boldsymbol{R}=\frac{1}{2}[(\boldsymbol{A}-\boldsymbol{C})-(\boldsymbol{B}-\boldsymbol{B}^{+})] \tag{4}$$

The one-electron DM **P**′ corresponding to the Hamiltonian matrix **H**′ has been obtained in Ref. [8] in the form of power series with respect to parameters included into the matrix $\boldsymbol{H}'_{(1)}$. The first three terms of these series are

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

$$\boldsymbol{P}'_{(2)}=-2\begin{vmatrix}\boldsymbol{G}_{(1)}\boldsymbol{G}^{+}_{(1)} & \boldsymbol{G}_{(2)}\\ \boldsymbol{G}^{+}_{(2)} & -\boldsymbol{G}^{+}_{(1)}\boldsymbol{G}_{(1)}\end{vmatrix} \tag{5}$$

The principal matrices $\mathbf{G}_{(1)}$ and $\mathbf{G}_{(2)}$ are

$$\boldsymbol{G}_{(1)}=-\frac{1}{2}\boldsymbol{R};\ \boldsymbol{G}_{(2)}=\frac{1}{4}(\boldsymbol{S}\boldsymbol{R}-\boldsymbol{R}\boldsymbol{Q}) \tag{6}$$

and their elements take the form

$$\boldsymbol{G}_{(1)im}=-\frac{1}{2}\boldsymbol{R}_{im};$$

$$\boldsymbol{G}_{(2)im}=\frac{1}{4}\left(\sum_{j}^{BBOs}\boldsymbol{S}_{ij}\boldsymbol{R}_{jm}-\sum_{r}^{ABOs}\boldsymbol{R}_{ir}\boldsymbol{Q}_{rm}\right) \tag{7}$$

The matrix $\mathbf{G}_{(1)}$ proportional to the matrix **R** contained within Eq. (4) evidently describes the direct (through-space) interactions between bonding BOs (BBOs) and antibonding BOs (ABOs), whereas $\mathbf{G}_{(2)}$ represents the indirect (through-bond) interactions of the same BOs. Both BBOs $\varphi_{(+)j}$ and ABOs $\varphi_{(-)r}$ play the role of mediators in the indirect interaction.

After retransforming Eq. (5) into the HAO basis, we obtain the respective terms of the DM **P**

$$\boldsymbol{P}_{(0)}=\begin{vmatrix}\boldsymbol{I} & \boldsymbol{I}\\ \boldsymbol{I} & \boldsymbol{I}\end{vmatrix};\boldsymbol{P}_{(1)}=\begin{vmatrix}\Pi_{(1)} & 2\boldsymbol{G}^{\circ}_{(1)}\\ 2\boldsymbol{G}^{\circ+}_{(1)} & -\Pi_{(1)}\end{vmatrix}$$

$$\boldsymbol{P}_{(2)}=\begin{vmatrix}\boldsymbol{T}+\boldsymbol{\Pi}_{(2)} & \boldsymbol{M}+2\boldsymbol{G}^{\circ}_{(2)}\\ \boldsymbol{M}+2\boldsymbol{G}^{\circ+}_{(2)} & \boldsymbol{T}-\boldsymbol{\Pi}_{(2)}\end{vmatrix} \tag{8}$$

where

$$\boldsymbol{\Pi}_{(1)}=-2\boldsymbol{G}^{*}_{(1)} \tag{9}$$

$$\boldsymbol{\Pi}_{(2)}=-2\boldsymbol{G}^{*}_{(2)} \tag{10}$$

$$\boldsymbol{T}=[\boldsymbol{G}^{+}_{(1)}\boldsymbol{G}_{(1)}]_{-}=-\frac{1}{8}[(\boldsymbol{A}-\boldsymbol{C}),(\boldsymbol{B}-\boldsymbol{B}^{+})]_{-} \tag{11}$$

$$\boldsymbol{M}=-\boldsymbol{G}_{(1)}\boldsymbol{G}^{+}_{(1)}-\boldsymbol{G}^{+}_{(1)}\boldsymbol{G}_{(1)}=-\frac{1}{8}\{(\boldsymbol{A}-\boldsymbol{C})^{2}-(\boldsymbol{B}-\boldsymbol{B}^{+})^{2}\} \tag{12}$$

and the notation [· ·, · ·] stands for the commutator of matrices. The matrices $\boldsymbol{G}^{*}_{(k)}$ and $\boldsymbol{G}^{\circ}_{(k)}$ ($k = 1,2$) are the symmetric and skew-symmetric parts of the matrices $\mathbf{G}_{(k)}$ defined as follows [27]

$$\boldsymbol{G}^{*}_{(k)}=\frac{1}{2}(\boldsymbol{G}_{(k)}+\boldsymbol{G}^{+}_{(k)}),\ \boldsymbol{G}^{\circ}_{(k)}=\frac{1}{2}(\boldsymbol{G}_{(k)}-\boldsymbol{G}^{+}_{(k)}) \tag{13}$$

Using eqns (4), (6) and (13) we obtain

$$\boldsymbol{G}^{*}_{(1)}=-\frac{1}{4}(\boldsymbol{A}-\boldsymbol{C}),\ \boldsymbol{G}^{\circ}_{(1)}=\frac{1}{4}(\boldsymbol{B}-\boldsymbol{B}^{+}) \tag{14}$$

$$\boldsymbol{G}^{*}_{(2)}=-\frac{1}{8}(\boldsymbol{CB}+\boldsymbol{B}^{+}\boldsymbol{C}-\boldsymbol{AB}^{+}-\boldsymbol{BA}),$$

$$\boldsymbol{G}^{\circ}_{(2)}=\frac{1}{8}\{(\boldsymbol{B}^{+})^{2}-\boldsymbol{B}^{2}-[\boldsymbol{A},\boldsymbol{C}]_{-}\}. \tag{15}$$

The total energy of alkanes E may be defined as [11,12]

$$E=Spur(\boldsymbol{PH}). \tag{16}$$

After substituting the power series for $\mathbf{P}$ and for $\mathbf{H}$ an analogous series for E may be obtained. The first three terms of the latter are

$$E_{(0)}=Spur(\boldsymbol{H}_{(0)}\boldsymbol{P}_{(0)})=2n, \tag{17}$$

$$\begin{aligned}E_{(1)}&=Spur(\boldsymbol{H}_{(0)}\boldsymbol{P}_{(1)}+\boldsymbol{H}_{(1)}\boldsymbol{P}_{(0)})\\&=2Spur\boldsymbol{S}=Spur(\boldsymbol{A}+\boldsymbol{B}+\boldsymbol{B}^{+}+\boldsymbol{C})\end{aligned} \tag{18}$$

and

$$E_{(2)}=Spur(\boldsymbol{H}_{(1)}\boldsymbol{P}_{(1)}+\boldsymbol{H}_{(0)}\boldsymbol{P}_{(2)})= \tag{19a}$$

$$=2Spur(\boldsymbol{G}_{(1)}\boldsymbol{G}^{+}_{(1)}+\boldsymbol{G}^{+}_{(1)}\boldsymbol{G}_{(1)})= \tag{19b}$$

$$=4\sum_{i}^{\mathrm{BBOs}}\sum_{k}^{\mathrm{ABOs}}(\boldsymbol{G}_{(1)ik})^{2}= \tag{19c}$$

$$=\frac{1}{4}Spur\{(\boldsymbol{A}-\boldsymbol{C})^{2}-(\boldsymbol{B}-\boldsymbol{B}^{+})^{2}\}. \tag{19d}$$

Thus, we have derived the expressions for the DM $\mathbf{P}$ and for the total energy of alkanes in terms of matrices $\mathbf{G}_{(1)}$ and $\mathbf{G}_{(2)}$. It is seen that definite combinations of these matrices actually play the role of building blocks of the DM $\mathbf{P}$. These blocks will be analysed separately in the next Section.

3. Interpretation of the one-electron DM of alkanes

The zero order correction $\mathbf{P}_{(0)}$ of the DM $\mathbf{P}$ involves elements equal to 1 in the positions $(i,n+i)$, and these correspond to the neighboring pairs of HAOs. Hence, alkanes resemble a set of n isolated chemical bonds to within the zero order approximation.

The matrix $\mathbf{\Pi}_{(1)}$ of the correction $\mathbf{P}_{(1)}$ may be called the first order polarization matrix. Indeed, dipole-like populations $\pm\,\mathbf{\Pi}_{(1)ii}$ follow from this matrix for strongly interacting pairs of HAOs (χ_i' and χ_{n+i}''). The relevant bond dipoles are determined by the respective local differences in Coulomb integrals ($\mathbf{A}_{\mathrm{ii}}-\mathbf{C}_{\mathrm{ii}}$). Again, the dipole moment $\pm\,\mathbf{\Pi}_{(1)ii}$ of the ith bond is proportional to the direct interaction between BOs of this bond $\varphi_{(+)i}$ and $\varphi_{(-)i}$. It is noteworthy that $\boldsymbol{G}^{\circ}_{(k)ii}=0$ and thereby $\boldsymbol{G}^{*}_{(k)ii}=\boldsymbol{G}_{(k)ii}$ follows from Eq. (13) for both $k=1$ and $k=2$. This also implies zero first order corrections to the neighboring bond orders of HAOs.

Let us turn to the second order correction $\mathbf{P}_{(2)}$. The matrix $\mathbf{\Pi}_{(2)}$ defined by Eq. (10) may be described as the second order intrabond polarization matrix. Thus, elements of this matrix of opposite signs ($\pm\,\mathbf{\Pi}_{(2)ii}$) correspond to HAOs χ_i' and χ_{n+i}'' belonging to the same bond. In contrast to the first order polarization, however, the elements $\mathbf{\Pi}_{(2)ii}$ contain indirect interactions between BOs $\varphi_{(+)i}$ and $\varphi_{(-)i}$ of the ith bond by means of BBOs and ABOs of other bonds. Hence, the second order dipoles are of non-local nature in alkanes.

Any element $\mathbf{\Pi}_{(2)ii}$ is additive with respect to partial increments of separate bonds. Thus, the contribution of the jth bond to the second order dipole of the ith bond ($\pm\,\mathbf{\Pi}_{(2)ii}$) is

$$\mathbf{\Pi}^{(J)}_{(2)ii}=-\frac{1}{2}(\boldsymbol{S}_{ij}\boldsymbol{R}_{ji}-\boldsymbol{R}_{ij}\boldsymbol{Q}_{ji})=\frac{1}{2}(\boldsymbol{C}_{ij}\boldsymbol{B}_{ji}-\boldsymbol{B}_{ij}\boldsymbol{A}_{ji}) \tag{20}$$

The increment of Eq. (20) represents the interaction between the BBO $\varphi_{(+)i}$ and ABO $\varphi_{(-)i}$ of the ith bond by means of either the BBO $\varphi_{(+)j}$ or ABO $\varphi_{(-)j}$ of the jth bond. This interaction depends on the mutual arrangement of the ith and jth bonds only and it is independent of the rest of molecule.

To establish the meaning of the matrix $\mathbf{T}$ defined by Eq. (11), let us turn to Eq. (5). It is seen that the population of the BBO $\varphi_{(+)i}$ lost when making up the molecule and that acquired by the ABO $\varphi_{(-)i}$ are [8]

$$\Delta X_{(+)i}=-2\{\boldsymbol{G}_{(1)}\boldsymbol{G}^{+}_{(1)}\}_{ii},\ \Delta X_{(-)i}=2\{\boldsymbol{G}^{+}_{(1)}\boldsymbol{G}_{(1)}\}_{ii} \tag{21}$$

respectively. Then the diagonal element $\mathbf{T}_{ii}$ of the matrix **T** describes a half of the total population of the ith bond lost (acquired) when building up the alkane molecule. Therefore, the diagonal elements of the matrix **T** describe redistribution of population among bonds, and the matrix **T** may be called the interbond charge transfer matrix (Note that $Spur\mathbf{T} = 0$ and the charge conservation condition proves to be fulfilled).

As with the bond dipole $\pm \mathbf{\Pi}_{(2)ii}$ the element $\mathbf{T}_{ii}$ is additive with respect to partial increments of separate bonds. The contribution of the jth bond to the element $\mathbf{T}_{ii}$ takes the form

$$T_{ii}^{(J)} = \frac{1}{4}\{(\boldsymbol{R}_{ji})^2 - (\boldsymbol{R}_{ij})^2\} = \frac{1}{4}(\boldsymbol{A}_{ij} - \boldsymbol{C}_{ij})(\boldsymbol{B}_{ij} - \boldsymbol{B}_{ji}) \qquad (22)$$

The increment $T_{ii}^{(J)}$ depends on the difference between squares of the direct (through-space) interactions of the BBO $\varphi_{(+)i}$ and ABO $\varphi_{(-)j}$, on the one hand, and that of the BBO $\varphi_{(+)j}$ and ABO $\varphi_{(-)i}$, on the other hand.

Let us dwell now on the matrix **M** defined by Eq. (12). The diagonal elements of this matrix describe alterations in the bond orders between the neighboring pairs of HAOs χ_i' and χ_{n+i}'' after building up the molecule. These elements are

$$\begin{aligned} \boldsymbol{M}_{ii} &= -\sum_j \{(\boldsymbol{G}_{(1)ji})^2 + (\boldsymbol{G}_{(1)ij})^2\} \\ &= -\frac{1}{4}\sum_j \{(\boldsymbol{R}_{ji})^2 + (\boldsymbol{R}_{ij})^2\} < 0 \end{aligned} \qquad (23)$$

It is seen that the correction $\mathbf{M}_{ii}$ to the neighboring bond order of the ith bond is determined by the sum of squares of the direct (through-space) interactions of BOs of this bond with all the remaining BOs of the molecule. In addition, the correction $\mathbf{M}_{ii}$ may be related to the total absolute value of the charge transfer referring to BOs of the ith bond. Lowering of the neighboring bond order against 1 is also seen from both Eq. (8) and the negative sign of $\mathbf{M}_{ii}$.

Furthermore, from Eq. (23) and the expression for the correction $\boldsymbol{P}_{(1)}'$ it follows that the alteration in the order of the ith bond $\mathbf{M}_{ii}$ is proportional to the sum of squares of the non-neighboring bond orders formed by BOs of this bond with the remaining BOs. Thus, the larger the absolute values of the non-neighboring bond orders referring to orbitals of the ith bond become, the more the respective neighboring bond order is lowered. As a result, the diagonal elements of the matrix **M** describe redistribution of bond orders when making up the molecule, and this matrix may be called the rebonding matrix. Additivity of the correction $\mathbf{M}_{ii}$ is evident and the increment of the jth bond

$$\begin{aligned} \boldsymbol{M}_{ii}^{(J)} &= -\frac{1}{4}\{(\boldsymbol{R}_{ji})^2 + (\boldsymbol{R}_{ij})^2\} \\ &= -\frac{1}{8}\{(\boldsymbol{A}_{ij} - \boldsymbol{C}_{ij})^2 + (\boldsymbol{B}_{ij} - \boldsymbol{B}_{ji})^2\} \end{aligned} \qquad (24)$$

depends on the direct interactions between BOs of the ith and jth bond only.

Therefore, separate building blocks reveal themselves within the common one-electron DM of alkanes, each of them representing the definite type of intramolecular interaction, namely, the first order and the second order intrabond polarizations, the interbond charge transfer and redistribution of bond orders (rebonding). Diagonal elements of the second order blocks determining the populations of HAOs and the neighboring bond orders are additive with respect to contributions of individual bonds. Moreover, the increment of certain (jth) bond to an element referring to the ith bond depends on the mutual arrangement of the ith and jth bonds only.

Because of the well-known acute dependence of resonance parameters on the relevant interbond distance, extinction of contributions of the jth bond to the second order characteristics of the ith bond may be expected when the interbond distance (r_{ij}) grows. As a result, these characteristics are likely to be determined by the nearest environment of the ith bond.

If the increments of the nearest-neighboring (geminal) bonds only are taken into account and transferability of resonance parameters for different pairs of geminal bonds is assumed (see e.g. [28–30] and Section 5), transferable second order characteristics follow for all C–H and for all C–C bonds in alkanes. Indeed, three and six similar increments, respectively, determine any of the above-mentioned matrix elements. Again, deviations from transferability of bond characteristics might be due either to differences in resonance parameters for various pairs of geminal bonds or to increments of more distant bonds. These increments are evaluated in Section 5.

4. Analysis of the total energy of alkanes

The zero and the first order terms $E_{(0)}$ and $E_{(1)}$

shown in eqns (17) and (18) contain the sum of the one-electron energies of isolated bonding BOs in accordance with Eq. (3).

The second order correction $E_{(2)}$ of the total energy E shown in Eq. (19a)–(19d) is positive in our negative units β_0. Hence, the actual sign of this correction is negative and $E_{(2)}$ may be interpreted as the stabilization energy of alkanes versus the relevant sets of isolated bonds. The expression for $E_{(2)}$ shown in Eq. (19c) indicates that the stabilization energy consists of a sum of squares of the direct through-space interactions between BBOs and ABOs over the whole molecule. Hence any of these interactions contributes to stabilization of molecule whatever the mutual arrangement of the two involved bonds and the sign of the respective resonance integral.

Alternatively, the correction $E_{(2)}$ may be expressed in terms of the rebonding matrix **M**. Thus, comparison of Eq. (12) and Eq. (19b)–(19d) indicates that

$$E_{(2)} = -2Spur\boldsymbol{M}. \tag{25}$$

Hence, stabilization of an alkane versus the relevant set of isolated bonds may be concluded to be related to the rebonding effect. In this connection $E_{(2)}$ may be called the rebonding energy. Furthermore, both sides of Eq. (25) may be rewritten as sums of contributions of separate bonds, i.e.

$$E_{(2)} = -2\sum_{i}\boldsymbol{M}_{ii} = \sum_{I}E^{(I)}_{(2)}, \tag{26}$$

where

$$E^{(I)}_{(2)} = -2\boldsymbol{M}_{ii}, \tag{27}$$

are the increments of particular bonds. Hence, the total energy of alkanes consists of a sum of contributions of separate bonds to within the second order terms inclusive. The extent of transferability of increments of similar bonds $E^{(I)}_{(2)}$ is directly related to that of $\mathbf{M}_{ii}$ (Section 3).

From Eq. (27) it follows also that each contribution $E^{(I)}_{(2)}$ to the second order correction $E_{(2)}$ is proportional to the respective correction M_{ii} to the neighboring bond order of the ith bond. Owing to the additivity of the elements $\mathbf{M}_{ii}$ (Section 3), a two-fold additivity of the stabilization energy follows from Eq. (27).

Opposite signs of the corrections $E^{(I)}_{(2)}$ and $\mathbf{M}_{ii}$ and thereby of $E_{(2)}$ and *Spur***M** are seen from eqns (27) and (25) and this fact also deserves attention. Thus, stabilization of the system owing to the rebonding effect goes together with lowering of the neighboring bond orders. This result causes no surprise if we take into consideration that two matrix products are contained within the definition of $E_{(2)}$ shown in Eq. (19a), i.e.

$$E_{(2)} = E'_{(2)} + E''_{(2)}, \tag{28}$$

where

$$E'_{(2)} = Spur(\boldsymbol{H}_{(0)}\boldsymbol{P}_{(2)}) = 2Spur\boldsymbol{M} = -\frac{1}{4}\sum_{i,j}\{(\boldsymbol{A}_{ij}-\boldsymbol{C}_{ij})^2+(\boldsymbol{B}_{ij}-\boldsymbol{B}_{ji})^2\} < 0, \tag{29}$$

$$E''_{(2)} = Spur(\boldsymbol{H}_{(1)}\boldsymbol{P}_{(1)}) = -4Spur\boldsymbol{M} = \frac{1}{2}\sum_{i,j}\{(\boldsymbol{A}_{ij}-\boldsymbol{C}_{ij})^2+(\boldsymbol{B}_{ij}-\boldsymbol{B}_{ji})^2\} > 0. \tag{30}$$

The specific structure of the matrix $\mathbf{H}_{(0)}$ seen from Eq. (1) provides for the direct relation between the negative term $E_{(2)}'$ and the sum of the neighboring bond orders. Hence, lowering of these bond orders by itself gives rise to destabilization of the system in accordance with the expectation. The second term $E_{(2)}''$ is positive and it may be related to the formation of the non-neighboring bond orders contained within the correction $\mathbf{P}_{(1)}$. Hence, the final stabilization of alkanes versus the relevant sets of isolated bonds may be accounted for by the fact that the total stabilizing effect of the newly-formed non-neighboring bond orders exceeds twice the total destabilizing effect due to reduction of the neighboring bond orders.

5. Estimations of particular increments to the DM and the total energy of alkanes

To evaluate separate terms of Sections 3 and 4, let us employ the set of parameters of Ref. [31]. The diagonal Hamiltonian matrix elements have been taken equal to negative values of respective ionization potentials.

The ionization potentials for ordinary AOs ($I(2s_C) = 21.3$; $I(2p_C) = 11.5$; $I(1s_H) = 13.6$ eV [32]) have been used to evaluate the respective values for HAOs ($I(sp^3) = (1)/(4)[I(2s_C) + 3I(2p_C)] = 13.95$ eV), as well as the resonance parameter for two HAOs of the same carbon atom [4] ($\beta(\mathrm{sp}^3,\mathrm{sp}^3) = -(1)/(4)[I(2\mathrm{s}_\mathrm{C}) - I(2\mathrm{p}_\mathrm{C})] = -2.45$ eV). Other resonance parameters have been estimated on the basis of the relation $\beta = \beta_0 S/S_0$ where β_0 and S_0 are standard values of resonance and overlap integrals for nearest pairs of $2\mathrm{p}_z$ AOs in conjugated hydrocarbons ($S_0 = 0.247$; $\beta_0 = -2.5$ eV). For C–C and C–H bonds in alkanes we then obtain $\beta_{cc} = -6.55$ eV and $\beta_{CH} = -6.75$ eV, and their mean value is $\beta_0 = -6.65$ eV. It is seen that differences both between β_{CC} and β_{CH} and between $I(\mathrm{sp}^3)$ and $I(1\mathrm{s}_\mathrm{H})$ are first order terms with respect to β_0 as assumed in Section 2.

The above-defined resonance parameter $\beta(\mathrm{sp}^3,\mathrm{sp}^3) = 0.36\ \beta_0$ makes the main part of the through-space interaction ($\mathbf{R}_{ij}$) between geminal pairs of bonds [4]. Let the HAOs of the common carbon atom of the geminal pair of the ith and jth bond to acquire the numbers $n + i$ and $n + j$ (Section 2). Then the resonance parameter $\beta(\mathrm{sp}^3,\mathrm{sp}^3)$ stands for the element $\mathbf{C}_{ij}$ (see Eq. (1)). The remaining contributions to $\mathbf{R}_{ij}$, viz. $\mathbf{A}_{ij}$, $\mathbf{B}_{ij}$ and $\mathbf{B}_{ji}$ (see Eq. (4)) vary in their values for different types of bonds (C–C–C, C–C–H and H–C–H) in the range of 15%. Given that these differences are ignored, the equality $\mathbf{B}_{ij} = \mathbf{B}_{ji}$ follows [5–7] and the contribution of the jth bond to the second order dipole moment of the ith bond equals to $\mathbf{\Pi}^{(J)}_{(2)ii} = 0.014$. As a result, $\mathbf{\Pi}_{(2)ii} = 0.042$ follows for any C–H bond in alkanes. It should be also noted here that contribution of a single *cis*-arranged next-neighbour (vicinal) bond is equal to $\mathbf{\Pi}^{(K)}_{(2)ii} = 0.0022$, whereas the self-contribution of the ith bond is $\mathbf{\Pi}^{(I)}_{(2)ii} = 0.00073$, and these are evidently small corrections only.

The above-established value of $\mathbf{\Pi}_{(2)ii}$ for C–H bonds exceeds the respective absolute value of the relevant first order dipole ($\mathbf{\Pi}_{(1)ii} = -0.026$). Opposite signs of the first and second order dipole moments also are noteworthy. On the whole, these results lead to a conclusion that non-zero experimental dipole moments for C–H bonds in alkanes [33] are not necessarily related to differences in electronegativities of hydrogen and carbon atoms. The observed dipoles should be attributed to the sum of the first and the second order contributions.

Analysis of Eq. (20) in the case of a C–C bond shows that contributions to the element $\mathbf{\Pi}_{(2)ii}$ originating from the geminal neighbors attached to different carbon atoms are of opposite signs and cancel out each other. In this context, the immediate reason of non-zero second order dipole moments for C–H bonds may be concluded to consist in the non-symmetric nearest environment of C–H bonds as opposed to C–C bonds.

If we accept the above-mentioned equality $\mathbf{B}_{ij} = \mathbf{B}_{ji}$, zero interbond charge transfer follows from Eq. (22). This implies the dipole-like nature of total occupation numbers of HAOs in alkanes [5–7]. Furthermore, contributions to $\mathbf{M}_{ii}$ and $E^{(I)}_{(2)}$ originating from a single geminal (jth) and from a single vicinal (kth) bond are determined by eqns (24) and (27). These are −0.0045 and −0.0005 for $\mathbf{M}_{ii}$ and 0.009 and 0.001 for $E^{(I)}_{(2)}$, respectively, the latter two being expressed in β_0 units.

6. Conclusions

The common one-electron DM of alkanes in the basis of BOs and thereby their total energy may be expressed and interpreted in terms of matrices $\mathbf{G}_{(1)}$ and $\mathbf{G}_{(2)}$ describing the direct (through-space) and indirect (through-bond) interactions. As a result, the second order correction $\mathbf{E}_{(2)}$ to the total energy E consists of a sum of squares of the through-space interactions over the whole system and gives rise to stabilization of molecules versus the relevant sets of isolated bonds.

Furthermore, definite combinations of matrices $\mathbf{G}_{(1)}$ and $\mathbf{G}_{(2)}$ and of their complex conjugate counterparts arise within the DM after turning to the basis of HAOs. These new matrices play the role of separate building blocks of the transformed DM and represent new types of intramolecular interaction in alkanes, viz. the intrabond polarization, interbond charge transfer and redistribution of bond orders (rebonding). An alternative interpretation of the total energy follows in this case. Thus, the second order correction $\mathrm{E}_{(2)}$ proves to be expressed as *Spur* of the rebonding matrix. As a result, the total energy of alkanes is additive with respect to increments of separate bonds to within the second order terms inclusive. Moreover, stabilization of alkanes may be concluded to be related to the rebonding effect, which involves a formation of new bond orders between orbitals of different bonds along with reduction of intrabond bond orders.

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