

On the relation between the stabilization energy of a molecular system and the respective charge redistribution

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Abstract

A power series for total energies of molecules is derived using the previously-obtained series for the one-electron density matrix (DM) P [J. Mol. Struct. (Theochem) 343 (1995) 183] and the well-known relation between the energy E and the DM P ($E = \text{Trace}(PH)$, where H is the Hamiltonian matrix). Two components are revealed within any correction $E_{(k)}$ of the new series so that one of them describes the k th order energy alteration due to charge redistribution and the another represents the analogous alteration owing to formation of additional bond orders vs. those of the system underlying the zero order Hamiltonian matrix. Molecular-structure-independent but k -dependent relations are established between the above-specified two components for $k = 0, 1, 2, 3, 4$. These relations allow the total correction $E_{(k)}$ to be expressed in terms of charge transfer energy of respective order and thereby yield a general interdependence between the stabilization energy of a molecular system and the relevant charge redistribution for any number of participating orbitals and for any type of change in the structure of the system. Non-trivial consequences of this principal result of the paper also are revealed, in particular an interrelation between the *trans*-effect of substituent studied recently [J. Mol. Struct. (Theochem) 532 (2000) 257] and the well-known *gauche*- and *cis*-effects describing the most stable conformations of substituted alkanes and alkenes, as well as of related heteroatom-containing compounds. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Implicit and/or explicit assumptions about interdependence between the stabilization energy of certain molecular system and the relevant charge redistribution may be found almost throughout the theoretical organic chemistry. For example, the electron-donating (accepting) effect of a substituent upon a conjugated fragment and the relevant increase of stability of the system are considered as two interdependent aspects of the same mesomeric (resonance) effect [1–4]. This viewpoint is

based on numerous experimental facts, e.g. on comparison of dipole moments of conjugated molecules to those of non-conjugated compounds containing the same substituent, as well as of respective heats of hydrogenization. Analogous two aspects reveal themselves also in the case of the so-called direct conjugation of two substituents in disubstituted benzenes (see Ref. [5] and references cited therein). Furthermore, the well-known assumption about proportionality between relative stabilities of molecular ions and the extents of delocalization of their positive (negative) charge deserves mentioning here [1,4]. Finally, an analogous assumption is invoked when discussing stabilities of the so-called charge transfer

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complexes relatively to respective isolated components [6].

A simple accounting for the interdependence under discussion follows from the valence bond method [1,4,6]. Indeed, the larger is the relative increment ($|C_2|^2$) of the wave function $\Psi_2(D^+ - A^-)$ referring to the ionic resonance structure $(D^+ - A^-)$ in the linear combination for the final wave function of the system Ψ ,

$$\Psi = C_1\Psi_1(D - A) + C_2\Psi_2(D^+ - A^-) \quad (1)$$

the more significant charge transfer is expected between the electron-donating subsystem (D) and the electron-accepting one (A). At the same time, the whole system becomes stabilized more significantly relatively to the energy $E(D - A)$ corresponding to the purely covalent structure $D - A$. In the framework of the one-electron (MO) method, an analogous relation follows from a two-level model where an interaction is considered between an initially-occupied orbital of the electron-donating subsystem (D) and an initially-vacant orbital of the accepting subsystem (A). In some cases, a model of a one-dimensional potential well is invoked for the same purpose [2].

It is evident, however, that the majority of molecules and molecular systems hardly may be described adequately either by two resonance structures or by two one-electron orbitals to say nothing of the one-dimensional potential well. In this context, the main aim of this paper consists in obtaining a general relation between alteration in the total energy and the respective charge redistribution for any number of participating orbitals and for any type of change in the structure of the system.

Total energies of molecules (E) are known to be expressible either in terms of one-electron energies of occupied molecular orbitals or via elements of the one-electron density matrix (bond order matrix) P [7–9]. To achieve the above-specified end, the latter definition will be used. Given that our system may be described by certain one-electron Hamiltonian matrix H (e.g. of the Hückel type), the respective energy is simply expressed as follows

$$E = \text{Trace}(PH) \quad (2)$$

The right-hand side of Eq. (2) evidently contains both diagonal and off-diagonal elements of the matrix P .

Thus, a relation between the total energy E and charge redistribution may be anticipated, if we succeed in eliminating the off-diagonal elements of the matrix P ($P_{ij}, i \neq j$) from the expression of Eq. (2). Feasibility of such an elimination follows from interdependences between separate blocks (submatrices) of the bond order matrix P established previously [10] on the basis of the so-called non-commutative Rayleigh–Schrödinger perturbation theory (NC RSPT) [11]. Thus, we will invoke the power series for the matrix P derived in Ref. [10].

Orbitals localized on separate fragments of the system under study are likely to make up the most appropriate basis set for investigation of intra-and/or intermolecular charge redistribution. As it is shown in Refs. [5,12–15], orbitals of this type comply with the requirements of the NC RSPT and thereby are able to play the role of basis functions underlying the power series for the matrix P (no specifying of basis functions was required when deriving this series in Ref. [10]). So far as the structures of the fragments themselves are concerned, individual chemical bonds both of saturated [12] and of conjugated [13] molecules and phenyl rings along with substituents [5,14] may be mentioned here, as well as separate molecules of many-molecular systems [15]. In this connection, our basis set will be assumed to consist of certain number of fragmental orbitals of any constitution and of any extent of localization.

It should be also mentioned here that members of the power series for the bond order matrix P to within the fourth order inclusive prove to be essential when describing an electron density redistribution among localized orbitals [5,13,16,17] in contrast to the well-studied case of delocalized (canonical) orbitals of two interacting molecules or molecular fragments, where confinement to second order corrections proves to be sufficient [9,18]. Hence, corrections $P_{(k)}$ and $E_{(k)}$ to within $k = 4$ are studied in this paper.

Terms of power series for both the bond order matrix P and the total energy E to within the second order inclusive were derived in Refs. [10,11,19]. On the other hand, Refs. [5,16,17] contain some discussion of the subsequent corrections $P_{(3)}$ and $P_{(4)}$. In this connection, we will confine ourselves to a brief summary of the relevant expressions (Section 2). Thereupon, we will formally define two components within any correction $E_{(k)}$ (denoted by $E_{(k)}^{(\alpha)}$ and $E_{(k)}^{(\beta)}$)

and demonstrate their interdependences for various k values (Section 3). Expressions for total corrections $E_{(k)}$ in terms of either $E_{(k)}^{(\alpha)}$ or $E_{(k)}^{(\beta)}$ follow directly from these interdependences. Section 4 deals with interpretations of components $E_{(k)}^{(\alpha)}$ and $E_{(k)}^{(\beta)}$. It is shown that the first component $E_{(k)}^{(\alpha)}$ coincides with the k th order charge transfer energy under certain conditions. Just this result along with the above-mentioned expression for $E_{(k)}$ in terms of $E_{(k)}^{(\alpha)}$ yields a relation being sought. Applications of the relations obtained are discussed in Section 5.

2. Expressions for the one-electron density matrix and total energy to within the fourth order terms inclusive

Let the total basis set of fragmental orbitals (FOs) $\{\vartheta\}$ to be divided into two subsets $\{\vartheta_{(+)}\}$ and $\{\vartheta_{(-)}\}$ containing the initially-occupied and the initially-vacant basis functions, respectively [10]. The intersubset resonance parameters are assumed to be first order terms vs. the energy differences between orbitals of different subsets [10,11,13–15]. Then the Hückel type one-electron Hamiltonian matrix H of our molecular system may be expressed as a sum of first—and second order matrices, i.e.

$$H = H_{(0)} + H_{(1)} \quad (3)$$

where

$$H_{(0)} = \begin{vmatrix} E_{(+)} & 0 \\ 0 & -E_{(-)} \end{vmatrix}, \quad H_{(1)} = \begin{vmatrix} S & R \\ R^+ & Q \end{vmatrix} \quad (4)$$

The diagonal blocks (submatrices) $E_{(+)} + S$ and $-E_{(-)} + Q$ of the matrix H contain the intrasubset interactions (resonance parameters) along with one-electron energies of FOs, whilst the off-diagonal block R involves the intersubset interactions. The minus sign in front of $E_{(-)}$ is introduced for convenience, and the superscript ‘+’ designates the transposed matrix. It is also seen that zero order intrasubset interactions are allowed in Eq. (4) and these are included into submatrices $E_{(+)}$ and $E_{(-)}$.

The one-electron density matrix (DM) P corresponding to the Hamiltonian matrix H of Eqs. (3)

and (4) has been obtained in the form of power series, i.e.

$$P = \sum_{k=0}^{\infty} P_{(k)} = P_{(0)} + P_{(1)} + P_{(2)} + \dots \quad (5)$$

Separate members of this series may be represented in the form

$$P_{(k)} = -2 \begin{vmatrix} X_{(k)+} & G_{(k)} \\ G_{(k)}^{(+)} & -X_{(k)-} \end{vmatrix} \quad (6)$$

where $X_{(k)+}$ and $X_{(k)-}$ may be called the intrasubset population matrices. These contain the occupation numbers of basis orbitals along with intrasubset bond orders. The off-diagonal blocks $G_{(k)}$ contain intersubset bond orders and may be referred to as intersubset coupling matrices.

The blocks $X_{(k)+}$ and $X_{(k)-}$ have been expressed in Refs. [10,11] in terms of matrices $G_{(k-1)}$, $G_{(k-2)}$, etc. taking the off-diagonal positions in the previous corrections $P_{(k-1)}$, $P_{(k-2)}$, etc. Thus, the first four blocks $X_{(k)+}$ and $X_{(k)-}$ take the form

$$\begin{aligned} X_{(0)+} &= -I, \quad X_{(0)-} = 0, \quad X_{(1)+} = X_{(1)-} = 0, \\ X_{(2)+} &= G_{(1)}G_{(1)}^+, \quad X_{(2)-} = G_{(1)}^+G_{(1)}, \\ X_{(3)+} &= G_{(1)}G_{(2)}^+ + G_{(2)}G_{(1)}^+, \quad X_{(3)-} \\ &= G_{(1)}^+G_{(2)} + G_{(2)}^+G_{(1)}, \\ X_{(4)+} &= G_{(1)}G_{(3)}^+ + G_{(3)}G_{(1)}^+ + G_{(2)}G_{(2)}^+ \\ &+ G_{(1)}G_{(1)}^+G_{(1)}G_{(1)}^+, \\ X_{(4)-} &= G_{(1)}^+G_{(3)} + G_{(3)}^+G_{(1)} + G_{(2)}^+G_{(2)} \\ &+ G_{(1)}^+G_{(1)}G_{(1)}^+G_{(1)} \end{aligned} \quad (7)$$

where I is the unit matrix. The relations of Eq. (7) coincide with those between separate blocks (submatrices) of corrections $P_{(k)}$ mentioned in Section 1.

The intersubset coupling matrices $G_{(k)}$, in turn, meet the matrix equations of the form

$$E_{(+)}G_{(k)} + G_{(k)}E_{(-)} + W_{(k)} = 0 \quad (8)$$

where

$$\begin{aligned} W_{(1)} &= R, & W_{(2)} &= SG_{(1)} - G_{(1)}Q, \\ W_{(3)} &= SG_{(2)} - G_{(2)}Q - (RG_{(1)}^+G_{(1)} + G_{(1)}G_{(1)}^+R), \\ W_{(4)} &= SG_{(3)} - G_{(3)}Q - [R(G_{(1)}^+G_{(2)} + G_{(2)}^+G_{(1)}) \\ &\quad + (G_{(1)}G_{(2)}^+ + G_{(2)}G_{(1)}^+)R] \end{aligned} \quad (9)$$

From Eqs. (2), (3) and (5) it is seen that the total energy E also may be expressed in the form of power series like that of Eq. (5). Moreover, two terms are present within any correction $E_{(k)}$, viz.

$$E_{(k)} = E_{(k)}^{(\alpha)} + E_{(k)}^{(\beta)} \quad (10)$$

where

$$\begin{aligned} E_{(k)}^{(\alpha)} &= \text{Trace}(P_{(k)}H_{(0)}) = -2\text{Trace}(X_{(k)+}E_{(+)} \\ &\quad + X_{(k)-}E_{(-)}) \end{aligned} \quad (11)$$

and

$$\begin{aligned} E_{(k)}^{(\beta)} &= \text{Trace}(P_{(k-1)}H_{(1)}) = -2\text{Trace}(X_{(k-1)+}S \\ &\quad - X_{(k-1)-}Q) \\ &\quad - 2\text{Trace}(G_{(k-1)}R^+ \\ &\quad + G_{(k-1)}^+R) \end{aligned} \quad (12)$$

For the first two members of the power series, we obtain

$$E_{(0)} = E_{(0)}^{(\alpha)} = 2\text{Trace } E_{(+)}, \quad E_{(1)} = E_{(1)}^{(\beta)} = 2\text{Trace } S \quad (13)$$

The sum of these two corrections coincides with the total one-electron energy of isolated FOs. Given that the one-electron energy of any FO is entirely included into the respective diagonal element of the matrix $E_{(+)}$ (this may be evidently done without any restriction), the equality $E_{(1)} = 0$ [20,21] follows. For $k > 1$, however, both components $E_{(k)}^{(\alpha)}$ and $E_{(k)}^{(\beta)}$ take non-zero values and these are studied in Section 3.

3. Interrelations between the two components of the correction $E_{(k)}$

From Eq. (11) it follows that the first component $E_{(k)}^{(\alpha)}$ of the correction $E_{(k)}$ contains only the k th order intrasubset population matrices. Alternatively, the second component $E_{(k)}^{(\beta)}$ depends on both diagonal and off-diagonal blocks of the matrix $P_{(k-1)}$ (see Eq. (12)). Hence, certain interrelations may be expected between $E_{(k)}^{(\alpha)}$ and $E_{(k)}^{(\beta)}$ if we invoke the expressions for $X_{(k)+}$ and $X_{(k)-}$ in terms of $G_{(k-1)}$, $G_{(k-2)}$, etc. shown in Eq. (7).

To derive these relations, let us start with second order terms ($k = 2$). Substitution of expressions for $X_{(2)+}$ and $X_{(2)-}$ from Eq. (7) into Eq. (11) and a subsequent cyclic transposition of matrices inside the Trace sign yields an alternative form of $E_{(k)}^{(\alpha)}$, viz.

$$E_{(2)}^{(\alpha)} = -2\text{Trace}[G_{(1)}(G_{(1)}^+E_{(+)} + E_{(-)}G_{(1)}^+)] \quad (14)$$

After invoking the Hermitian conjugate counterpart of Eq. (8) for $k = 1$, the term of Eq. (14) within the round brackets may be replaced by $-R^+$. Comparison of the obtained expression for $E_{(2)}^{(\alpha)}$ to that for $E_{(2)}^{(\beta)}$ (the latter follows from Eq. (12) after taking into account the equalities $X_{(1)+} = X_{(1)-} = 0$ and $\text{Trace}(G_{(k-1)}R^+) = \text{Trace}(G_{(k-1)}^+R)$) yields the following interrelation between the two components of the second order energy

$$E_{(2)}^{(\beta)} = -2E_{(2)}^{(\alpha)} \quad (15)$$

Using Eqs. (10) and (15), we also obtain a compact expression for the total second order correction

$$E_{(2)} = -2\text{Trace}(G_{(1)}R^+) \quad (16)$$

Let us turn now to the third order terms ($k = 3$). The first component of the correction $E_{(3)}$ takes the form

$$\begin{aligned} E_{(3)}^{(\alpha)} &= -2\text{Trace}[G_{(2)}^+(E_{(+)}G_{(1)} + G_{(1)}E_{(-)}) \\ &\quad + G_{(2)}(G_{(1)}^+E_{(+)} + E_{(-)}G_{(1)}^+)] \\ &= 4\text{Trace}(G_{(2)}R^+) \end{aligned} \quad (17)$$

where the second relation of the right-hand side results after replacing the terms within the round brackets by $-R$ and $-R^+$, respectively.

The second component $E_{(3)}^{(\beta)}$ follows from Eq. (12)

$$E_{(3)}^{(\beta)} = -2\text{Trace}[G_{(1)}^+(SG_{(1)} - G_{(1)}Q)] - 4\text{Trace}(G_{(2)}R^+) \quad (18)$$

The term within the first round brackets of Eq. (18) coincides with the matrix $W_{(2)}$ of Eq. (9). On the other hand, this matrix may be replaced by the sum $-E_{(+)}G_{(2)} - G_{(2)}E_{(-)}$ as Eq. (8) indicates. Thereupon, the matrix $G_{(1)}$ may be eliminated from the expression for $E_{(3)}^{(\beta)}$ using Eq. (8) for $k = 1$.

As a result, the whole component $E_{(3)}^{(\beta)}$ becomes expressed in terms of $\text{Trace}(G_{(2)}R^+)$. After comparing this expression to Eq. (17) we obtain the following relation

$$2E_{(3)}^{(\beta)} = -3E_{(3)}^{(\alpha)} \quad (19)$$

and the compact form of the third order energy

$$E_{(3)} = -2\text{Trace}(G_{(2)}R^+) \quad (20)$$

Let us consider now the fourth order correction $E_{(4)}$. The first component of this correction takes the form

$$E_{(4)}^{(\alpha)} = -2\text{Trace}\left[G_{(3)}^+(E_{(+)}G_{(1)} + G_{(1)}E_{(-)}) + G_{(3)}\left(G_{(1)}^+E_{(+)} + E_{(-)}G_{(1)}^+\right) + G_{(2)}^+(E_{(+)}G_{(2)} + G_{(2)}E_{(-)}) + G_{(1)}^+G_{(1)}G_{(1)}^+(E_{(+)}G_{(1)} + G_{(1)}E_{(-)})\right] \quad (21)$$

As with previous corrections, Eq. (8) allows the terms within the round brackets of Eq. (21) to be replaced by $-R$, $-R^+$, $-W_{(2)}$ and $-R$, respectively. Then the newly-derived term $2\text{Trace}(G_{(2)}^+W_{(2)})$ should be considered separately.

Use of the definition of the matrix $W_{(2)}$ of Eq. (9) allows this term to be expressed as follows

$$2\text{Trace}(G_{(2)}^+W_{(2)}) = 2\text{Trace}[G_{(1)}^+(SG_{(2)} - G_{(2)}Q)] \quad (22)$$

For further remaking of this expression, let us invoke the definition of the matrix $W_{(3)}$ shown in Eq. (9). We then obtain

$$2\text{Trace}(G_{(2)}^+W_{(2)}) = 2\text{Trace}(G_{(1)}^+W_{(3)}) + 4\text{Trace}(G_{(1)}^+RG_{(1)}^+G_{(1)}) \quad (23)$$

Let the matrix $W_{(3)}$ of the right-hand side of Eq. (23) to be replaced by $-E_{(+)}G_{(2)} - G_{(2)}E_{(-)}$. Then the matrix

$-R^+$ may be substituted for $G_{(1)}^+E_{(+)} + E_{(-)}G_{(1)}^+$. We then obtain

$$2\text{Trace}(G_{(2)}^+W_{(2)}) = 2\text{Trace}(G_{(3)}R^+) + 4\text{Trace}(G_{(1)}^+RG_{(1)}^+G_{(1)}) \quad (24)$$

After collecting the terms of the right-hand sides of Eqs. (21) and (24), the following simple expression for $E_{(4)}^{(\alpha)}$ results

$$E_{(4)}^{(\alpha)} = 6\text{Trace}[(G_{(3)} + G_{(1)}G_{(1)}^+G_{(1)})R^+] \quad (25)$$

Finally, the second component of the fourth order correction results from Eq. (12), viz.

$$E_{(4)}^{(\beta)} = -2\text{Trace}\left[G_{(2)}^+(SG_{(1)} - G_{(1)}Q) + G_{(2)}\left(G_{(1)}^+S - QG_{(1)}^+\right)\right] - 4\text{Trace}(G_{(3)}R^+) \quad (26)$$

Matrices $W_{(2)}$ and $W_{(2)}^+$ may be used here instead of the first and second round brackets. Later, the relation of Eq. (24) should be applied. As a result, the correction $E_{(4)}^{(\beta)}$ becomes proportional to $E_{(4)}^{(\alpha)}$ shown in Eq. (25) and their interrelation takes the form

$$3E_{(4)}^{(\beta)} = -4E_{(4)}^{(\alpha)} \quad (27)$$

Consequently, the total fourth order energy may be expressed as follows

$$E_{(4)} = -2\text{Trace}[(G_{(3)} + G_{(1)}G_{(1)}^+G_{(1)})R^+] \quad (28)$$

The relations of Eqs. (15), (19), and (27) may be represented as a single molecular-structure-independent but k -dependent relation

$$(k-1)E_{(k)}^{(\beta)} = -kE_{(k)}^{(\alpha)} \quad (29)$$

which may be assumed to be valid also for $k > 4$. This result implies that the correction $E_{(k)}$ may be expressed either in terms of $E_{(k)}^{(\alpha)}$ or in terms of $E_{(k)}^{(\beta)}$ as follows

$$E_{(k)} = -\frac{1}{k-1}E_{(k)}^{(\alpha)}, \quad E_{(k)} = \frac{1}{k}E_{(k)}^{(\beta)} \quad (30)$$

Opposite signs of both components of the total correction $E_{(k)}$ also may be seen from Eq. (29) along with the following inequality for their absolute values

$$|E_{(k)}^{(\beta)}| > |E_{(k)}^{(\alpha)}| \quad (31)$$

After recalling Eq. (10) we may then conclude that the

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

Before finishing this section, let us also note that all the above-obtained results are as general as the power series for the DM P (the latter was shown to be valid for an extended class of molecules and molecular systems described by the Hamiltonian matrix of Eqs. (3) and (4) [4,12–15]). Thus, the compact expressions for corrections $E_{(k)}$ (Eqs. (13), (16), (20), and (28)) make up a power series for total energies of the same scope of validity. It is also seen that the very possibility of deriving these compact formula is largely based on the principal relations between the two components $E_{(k)}^{(\alpha)}$ and $E_{(k)}^{(\beta)}$.

4. Interpretation of separate components of the corrections $E_{(k)}$. The charge transfer energy

A simple interpretation of separate components of the corrections $E_{(k)}$ proves to be possible if we turn to the particular case of diagonal zero order blocks $E_{(+)}$ and $E_{(-)}$ [10] containing elements $E_{(+)i}$ and $E_{(-)j}$, respectively. This implies that both intra- and intersubset resonance parameters are required to be first order terms as compared to the intersubset energy differences.

Let the energy reference point to be chosen in the middle of the intersubset energy gap so that the elements $E_{(+)i}$ and $E_{(-)j}$ both are negative and the sum $E_{(+)i} + E_{(-)j}$ represents the respective energy interval.

Owing to the above-assumed particular form of matrices $E_{(+)}$ and $E_{(-)}$, only diagonal elements of the intrasubset population matrices $X_{(k)+}$ and $X_{(k)-}$ are actually present within the definition of $E_{(k)}^{(\alpha)}$ shown in Eq. (11). These elements, in turn, determine the k th order corrections to occupation numbers of basis orbitals as Eqs. (5) and (6) indicate.

Let the populations of an initially-occupied FO (IOFO) $\vartheta_{(+)i}$ and of an initially-vacant FO (IVFO) $\vartheta_{(-)j}$ to be expressed as follows

$$P_{(+)i} = 2 + \sum_{k=2}^{\infty} P_{(k)+,ii}, \quad P_{(-)j} = 2 \sum_{k=2}^{\infty} P_{(k)-,jj} \quad (32)$$

where

$$P_{(k)+,ii} = -2X_{(k)+,ii}, \quad P_{(k)-,jj} = 2X_{(k)-,jj} \quad (33)$$

are the relevant k th order corrections. Then the first component $E_{(k)}^{(\alpha)}$ of the k th order energy takes the form

$$E_{(k)}^{(\alpha)} = \sum_i^{\text{IOFOs}} P_{(k)+,ii} E_{(+)i} - \sum_j^{\text{IVFOs}} P_{(k)-,jj} E_{(-)j} \quad (34)$$

As it is seen from Eq. (7), the intrasubset population matrices $X_{(k)+}$ and $X_{(k)-}$ consist of sums of products, each of them containing two intersubset coupling matrices of lower orders. This implies that the elements $X_{(k)+,ii}$ and $X_{(k)-,jj}$ and thereby the corrections $P_{(k)+,ii}$ and $P_{(k)-,jj}$ may be represented as sums of increments of individual orbitals of the opposite subset, viz.

$$P_{(k)+,ii} = \sum_l^{\text{IVFOs}} q_{(+)i,(+)l}^{(k)}, \quad P_{(k)-,jj} = \sum_m^{\text{IOFOs}} q_{(-)j,(-)m}^{(k)} \quad (35)$$

(the fact that the subscripts i and j of any element $G_{(k)ij}$ correspond to an IOFO $\vartheta_{(+)i}$ and to an IVFO $\vartheta_{(-)j}$, respectively, should be taken into consideration here). Moreover, the relation

$$q_{(+)i,(+)l}^{(k)} = -q_{(-)j,(-)m}^{(k)} \quad (36)$$

may be easily established on the basis of Eq. (7), where

$$q_{(+)i,(+)l}^{(2)} = -2(G_{(1)ij})^2 \quad (37)$$

$$q_{(+)i,(+)l}^{(3)} = -4G_{(1)ij}G_{(2)ij} \quad (38)$$

$$q_{(+)i,(+)l}^{(4)} = -4G_{(1)ij}G_{(3)ij} - 2G_{(1)ij}(G_{(1)ij}G_{(1)ij}^+G_{(1)ij}) - 2(G_{(2)ij})^2 \quad (39)$$

The expression for $P_{(k)+,ii}$ of Eq. (35) indicates that the increment $q_{(+)i,(+)l}^{(k)}$ describes the k th order partial population donated by the IOFO $\vartheta_{(+)i}$ to the IVFO $\vartheta_{(-)l}$. Similarly, $q_{(-)j,(-)m}^{(k)}$ represents the partial k th order population acquired by the IVFO $\vartheta_{(-)j}$ from the IOFO $\vartheta_{(+)m}$, whereas Eq. (36) is nothing more than the charge conservation condition. Using Eqs.

(34)–(36) we then obtain

$$E_{(k)}^{(\alpha)} = \sum_i^{\text{IOFOs}} \sum_j^{\text{IVFOs}} q_{(+i,(-j)}^{(k)} (E_{(+i)} + E_{(-j)}) \quad (40)$$

It is seen that $E_{(k)}^{(\alpha)}$ consists of partial increments, each of them corresponding to a pair of basis orbitals of different initial occupation. Moreover, the increment referring to the pair of FOs $\vartheta_{(+i)}$ and $\vartheta_{(-j)}$ is proportional to the partial population transferred between these basis functions and to the relevant energy interval $E_{(+i)} + E_{(-j)}$.

Therefore, the first component $E_{(k)}^{(\alpha)}$ of the total k th order correction $E_{(k)}$ may be interpreted as the charge transfer energy.

Let us consider now the second component of the total energy $E_{(k)}^{(\beta)}$. One-electron energies of basis orbitals may be entirely included into the zero order elements $E_{(+i)}$ and $E_{(-j)}$ without any restriction. As a result, the equalities $S_{ii} = 0$ and $Q_{jj} = 0$ may be accepted. This implies that the increment $E_{(k)}^{(\beta)}$ does not contain populations of basis orbitals (see Eq. (12)) and thereby it describes the effect of formation of new bond orders upon the k th order energy.

Therefore, $E_{(k)}^{(\alpha)}$ is the only contribution to the total correction $E_{(k)}$ describing charge redistribution. Moreover, the first relation of Eq. (30) indicates that the absolute value of the correction $E_{(k)}$ is proportional to that of the k th order charge transfer energy $E_{(k)}^{(\alpha)}$. On the other hand, it is the sign of the bond order energy $E_{(k)}^{(\beta)}$ that determines the actual sign of the total correction $E_{(k)}$, i.e. whether the k th order correction $E_{(k)}$ contributes to stabilization or to destabilization of the system.

For a more detailed interpretation of the above-obtained relations, let us dwell on the second order terms ($k = 2$). From Eq. (37) it is seen that the partial transferred population $q_{(+i,(-j)}^{(2)}$ and thereby the total second order correction $P_{(2)+,ii}$ to the population of the IOFO $\vartheta_{(+i)}$ are negative quantities. Such a result causes no surprise as the total population of an initially double-occupied orbital necessarily decreases as a result of charge redistribution.

Furthermore, negative signs of both $q_{(+i,(-j)}^{(2)}$ and $E_{(+i)} + E_{(-j)}$ imply a positive sign of $E_{(2)}^{(\alpha)}$. Hence, the charge redistribution in itself gives rise to destabilization of the system. This conclusion is in line with the fact that charge is transferred from orbitals of lower

energies (IOFOs) to those of higher energies (IVFOs). On the other hand, a negative sign of the total second order energy $E_{(2)}$ results from Eq. (30) and it implies the system being stabilized vs. the set of isolated FOs.

It is seen, therefore, that stabilization of the system is entirely due to formation of new bond orders owing to interaction, and the subsequent charge redistribution actually reduces this stabilizing effect. Nevertheless, the absolute value of the final correction $E_{(2)}$ coincides with the positive charge transfer energy $E_{(2)}^{(\alpha)}$.

As opposed to the second order term $q_{(+i,(-j)}^{(2)}$, the signs of the third and fourth order partial transferred populations defined by Eqs. (38) and (39) are not evident *a priori*. Hence, both negative and positive third and fourth order increments are possible (see Ref. [17] and Section 5.2).

Let any partial charge transfer taking place from an initially-occupied basis orbital to an initially-vacant one and described by a negative increment $q_{(+i,(-j)}^{(k)}$ to be called a normal one. Accordingly, a charge transfer of an opposite direction represented by a positive increment $q_{(+i,(-j)}^{(k)}$ will be referred to as an abnormal partial charge transfer. In the latter case, a negative contribution to the charge transfer energy and a positive one to the total correction $E_{(k)}$ will be obtained. Thus, such a pair of orbitals yields a destabilizing increment to the total energy.

To summarize the above results, let the stabilization energy ΔE_{stab} to be defined as a difference between the total energy E and the sum of one-electron energies of isolated basis orbitals (FOs), the latter coinciding with the sum $E_{(0)} + E_{(1)}$ shown in Eq. (13). Then the first relation of Eq. (30) yields an expression for the total ΔE_{stab} in terms of charge transfer energy, viz.

$$\Delta E_{\text{stab}} = - \sum_{k=2}^{\infty} \frac{1}{k-1} E_{(k)}^{(\alpha)} \quad (41)$$

where $E_{(k)}^{(\alpha)}$ is shown in Eq. (40).

5. Applications of the relations obtained

Let us start with a notation that elements $G_{(k)ij}$ of matrices $G_{(k)}$ also acquire simple interpretation under an assumption about diagonal structure of zero order matrices $E_{(+)}$ and $E_{(-)}$ [10]. Thus, the first order

element $G_{(1)ij}$ takes the form

$$G_{(1)ij} = -\frac{R_{ij}}{E_{(+i)} + E_{(-j)}} \quad (42)$$

and describes the direct (through-space) interaction between the IOFO $\vartheta_{(+i)}$ and the IVFO $\vartheta_{(-j)}$. It is seen that a non-zero value of the resonance parameter R_{ij} is required for a non-zero direct interaction to arise. Accordingly, the second and third order elements ($G_{(2)ij}$ and $G_{(3)ij}$) represent the indirect interactions of the same orbitals by means of one and two mediators, respectively [4], and a zero value of the resonance parameter R_{ij} is allowed in this case. From Eqs. (37)–(39) it also follows that a second (and higher order) partial charge transfer takes place between two directly interacting orbitals (i.e. when $G_{(1)ij} \neq 0$), whilst only a fourth order charge transfer is peculiar to pairs of directly non-interacting orbitals (when $G_{(1)ij} = 0$). The non-local nature of the partial transferred populations $q_{(+i),(-j)}^{(k)}$ for $k = 3$ and $k = 4$ also deserves mentioning here. Indeed, these partial increments contain indirect interactions of orbitals $\vartheta_{(+i)}$ and $\vartheta_{(-j)}$ and thereby depend implicitly on the whole set of FOs.

Now we are about to exemplify the relations of Sections 3 and 4 for $k = 2, 3$, and 4 separately.

5.1. The mesomeric effect in mono-substituted benzenes

Let us start with demonstrating a simple relation between the electron density redistribution in mono-substituted benzenes due to substitution [14] and the relevant stabilization energy [18]. Let us dwell first on the case of an electron-donating substituent D, which may be represented by a single initially-occupied orbital $\vartheta_{(+d)}$ [14].

It is evident that the orbital $\vartheta_{(+d)}$ interacts directly with the initially-vacant orbitals of the phenyl ring (benzene). Hence, the electron-donating effect of the substituent D upon this ring is described by second order terms of the power series.

The first order matrix elements $G_{(1)ij}$ representing the above-mentioned direct interactions follow from Eq. (42), viz.

$$G_{(1)d5} = -\frac{\sigma b}{\epsilon + 1}, \quad G_{(1)d6} = -\frac{\sigma a}{\epsilon + 2} \quad (43)$$

where the subscripts 5 and 6 refer to the initially-vacant MOs of benzene $\vartheta_{(-)5}$ and $\vartheta_{(-)6}$ of the appropriate symmetry (which ensures non-zero values for resonance parameters R_{d5} and R_{d6}). The positive constants σ and ϵ represent the resonance parameter of the C_{Ar} -D bond and the one-electron energy of the orbital $\vartheta_{(+d)}$, respectively, whereas the coefficients $a = 0.408$ and $b = 0.577$ coincide with those of the standard MOs of benzene at the site of substitution.

The direct interactions shown in Eq. (43) determine the relevant partial transferred populations in accordance with Eq. (37), viz.

$$q_{(+d),(-)5}^{(2)} = -2\frac{\sigma^2 b^2}{(\epsilon + 1)^2}, \quad q_{(+d),(-)6}^{(2)} = -2\frac{\sigma^2 a^2}{(\epsilon + 2)^2} \quad (44)$$

Thereupon, Eq. (40) may be used to obtain the expression for the charge transfer energy

$$\begin{aligned} E_{(2)}^{(\alpha)} &= q_{(+d),(-)5}^{(2)}(E_{(+d)} + E_{(-)5}) + q_{(+d),(-)6}^{(2)}(E_{(+d)} \\ &\quad + E_{(-)6}) \\ &= 2\sigma^2 \left[\frac{b^2}{(\epsilon + 1)} + \frac{a^2}{(\epsilon + 2)} \right] > 0 \end{aligned} \quad (45)$$

which coincides with the absolute value of the stabilization energy $|\Delta E_{\text{stab}}|$.

It is seen that both ΔE_{stab} and $E_{(2)}^{(\alpha)}$ are additive with respect to contributions of IVFOs $\vartheta_{(-)5}$ and $\vartheta_{(-)6}$ and inversely proportional to the electronegativity of the substituent D. At the same time, positive bond orders

$$P_{d5} = -2G_{(1)d5} > 0, \quad P_{d6} = -2G_{(1)d6} > 0 \quad (46)$$

are formed between pairs of orbitals ($\vartheta_{(+d)}, \vartheta_{(-)5}$) and ($\vartheta_{(+d)}, \vartheta_{(-)6}$) as Eq. (6) indicates and these also are determined by the same direct interactions $G_{(1)d5}$ and $G_{(1)d6}$.

It is evident that an electron-accepting substituent (A) may be treated similarly [14]. The relevant IVFO $\vartheta_{(-)a}$ along with IOFOs of benzene make up the appropriate basis set in this case.

Therefore, an interdependence may be concluded between the three principal manifestations of the substituent influence upon the phenyl ring, viz. between the intramolecular charge redistribution, the newly-formed bond orders and the stabilization

energy. This result contributes to substantiation of the classical concept of the single mesomeric effect being described by the above-enumerated three aspects.

5.2. Interdependence between the third order *trans*- and *gauche*-effects

A predominant influence of a substituent (D or A) upon the *trans*-arranged vicinal bonds ($C_{\beta}-C_{\gamma}$ or $C_{\beta}-H$) (the so called *trans*-effect) has been established both experimentally [22–25] and theoretically [17,26–29] in substituted alkanes and alkenes. Moreover, different populations of orbitals of the $C_{\gamma}(H)$ atoms in the *cis*- and *trans*-arranged $C_{\beta}-C_{\gamma}$ ($C_{\beta}-H$) bonds [26,30,31] proved to be among the principal manifestations of this effect.

Application of the power series for the bond order matrix [10] to investigation of the *trans*-effect [17] showed that different extents of the total intramolecular charge transfer between pairs of orbitals of *cis*- and *trans*-arranged $D(A)-C_{\alpha}$ and $C_{\beta}-C_{\gamma}$ ($C_{\beta}-H$) bonds are peculiar to substituted alkanes and alkenes. Moreover, this dissimilarity has been traced back to different signs of the relevant third order increments to partial transferred populations. (Absolute values of direct interactions $G_{(1)ij}$ between orbitals of the above mentioned pairs of bonds and thereby the second order increments to the partial transferred populations were shown to fall close together).

In the case of an electron-donating substituent D, the partial charge transfer between its electron-donating orbital and the antibonding orbital of the $C_{\beta}-C_{\gamma}$ ($C_{\beta}-H$) bond proved to be of primary importance. For molecules containing an electron-accepting substituent (A), the partial charge transfer between the bonding orbital of the $C_{\beta}-C_{\gamma}$ ($C_{\beta}-H$) bond and the antibonding orbital of the $A-C_{\alpha}$ bond played the decisive role. In both cases, however, a normal (negative) third order partial charge transfer corresponds to *trans*-arranged pairs of the $D(A)-C_{\alpha}$ and $C_{\beta}-C_{\gamma}$ ($C_{\beta}-H$) bonds and an abnormal (positive) increment of the same absolute value refers to *cis*-arranged pairs of the same bonds.

These results along with the relations of Eqs. (30) and (40) allow us to conclude that the third order interactions of the *trans*-arranged pairs of the above-specified vicinal bonds contribute to stabilization of the system, whereas the analogous interactions of the

cis-arranged pairs yield destabilizing increments to the total energy. This, in turn, promotes an expectation that molecule will adopt that conformation which is described by the maximum number of *trans*-arranged pairs of bonds $D(A)-C_{\alpha}$ and $C_{\beta}-C_{\gamma}$ ($C_{\beta}-H$) and by the minimum number of analogous *cis*-arranged pairs. For 1,2-disubstituted ethanes and ethylenes containing either two electron-donating substituents or two electron-accepting ones, it is the *gauche*- and the *cis*-conformations, respectively, that meet the above condition best of all. As a result, we arrive at the well-known *gauche*- and *cis*-effects describing the most stable conformations of disubstituted ethanes and ethylenes [1,5,32–41] (the *gauche*-arrangements of the two lone electron pairs established experimentally in molecules N_2H_2 [5,32,35,36] and H_2O_2 [32] may be mentioned as examples of the *gauche*-effect. Similarly, the two vicinal $C_{\alpha}-D_1$ and $C_{\beta}-D_2$ bonds adopt a *gauche*-arrangement in the most stable conformations of 1,2-difluoroethane [5,34,37] and of 1,2-dimethoxyethane [38]. The related *cis*-effect may be exemplified by a greater stability of *cis*-1,2-disubstituted ethylenes vs. respective *trans*-isomers [5,34,39,40]).

It is seen, therefore, that a relation between the *trans*-effect of substituent and the well-known *gauche*- and *cis*-effects is among non-trivial consequences of the above-established interdependence between stabilization energy and charge redistribution. Moreover, the obtained relation yields a simple accounting for the increased stability of *gauche*- and *cis*-conformations: it is the latter that offer better conditions for the normal charge redistribution.

5.3. The intersubstituent interaction in (D,A)-disubstituted benzenes as an example of the fourth order effects

As with the mesomeric effect of a single substituent upon the phenyl ring (Section 5.1), the intersubstituent interaction in (D,A)-disubstituted benzenes (the so-called direct conjugation of substituents) also manifests itself as both an additional charge transfer [4] and an extra stabilization relatively to respective mono-derivatives [18]. Search for an interrelation between these two aspects also may be carried out similarly as it was done in Section 5.1. The only difference between the two cases consists in different

orders of terms of our power series (k) that serve to describe them.

Indeed, no direct interaction was assumed to take place between substituents D and A in (D,A)-disubstituted benzenes [4]. As a result, the inter-substituent interaction proves to be determined by the fourth order terms of our power series. Then Eqs. (39)–(41) yield the following expression for the stabilization energy of a (D,A)-disubstituted benzene

$$\Delta E_{\text{stab}} = -\frac{1}{3}E_{(4)}^{(\alpha)} = -\frac{1}{3}\left[q_{(+d,(-)5)}^{(4)}(E_{(+d)} + E_{(-)5}) + q_{(+2,(-)a)}^{(4)}(E_{(+2)} + E_{(-)a}) + q_{(+d,(-)a)}^{(4)}(E_{(+d)} + E_{(-)a}) \right] \quad (47)$$

where the subscripts (+)2 and (–)5 stand for the highest-occupied and lowest-vacant MOs of benzene, whilst (+) d and (–) a refer to orbitals of substituents D and A, respectively [4]. Analysis of expressions for the fourth order transferred populations contained in Eq. (47) for various isomers [4] showed that both $q_{(+d,(-)5)}^{(4)}$ and $q_{(+2,(-)a)}^{(4)}$ are negative quantities for *para*- and *ortho*-(D,A)-disubstituted benzenes and thereby contribute to a greater stability of these molecules. Alternatively, the same partial transferred populations are positive for *meta* isomers and a destabilizing energy increment follows. The remaining term $q_{(+d,(-)a)}^{(4)}$ always is of a negative sign but its absolute values meet the following relation

$$\left| q_{(+d,(-)a)}^{(4)para} \right| > \left| q_{(+d,(-)a)}^{(4)ortho} \right| \gg \left| q_{(+d,(-)a)}^{(4)meta} \right| \quad (48)$$

On the whole, these results are in line with a greater stability of *para*- and *ortho*-disubstituted benzenes as compared to respective *meta* isomers [18].

Summarizing all the results of Section 5, we may conclude that there is a possibility of classification of various effects on the basis of the order parameter k . Moreover, it is seen that the influence of the given effect upon the total energy decreases when the order parameter grows even if the relevant charge redistributions are of comparable extents.

6. Concluding remarks

The principal result of the above study lies in obtaining the relation between stabilization energy of a molecular system and the relevant charge redistribution in an explicit algebraic form. This achievement yields a substantiation for an intuition-based assumption about validity of such a relation for molecules and molecular systems of an involved constitution.

Conclusions about the nature of the relation that may be drawn on the basis of our results are as follows:

First, the relation involves two additive characteristics with respect to contributions of pairs of orbitals of different initial occupation, namely the stabilization energy and the charge transfer energy. The above-mentioned contributions, however, generally contain indirect interactions of the respective two orbitals and thereby depend on the structure of the whole system. Thus, an additive but non-local nature of the relation under study may be concluded.

Second, the relation under discussion is by no means of a straightforward nature. Indeed, charge redistribution in itself usually gives rise to destabilization of the system. Moreover, the final stabilization energy originates from the difference between the stabilizing effect of the newly-formed bond orders and the above-mentioned destabilizing increment. Under these circumstances, however, the above-established proportionality between absolute values of the stabilization energy and the charge transfer energy is an even more surprising result.

Good prospects for further applications of the obtained relations also deserve mentioning, in particular in studies of chemical reactions. Indeed, the direction of the attack of the reagent which is described by larger normal transferred populations between orbitals of interacting molecules may be expected to be accompanied by a more efficient stabilization of the whole system and thereby by an increased relative reactivity as compared to other directions (cf. the so-called back attack of nucleophile vs. its frontal attack during the S_N2 reaction of substituted alkanes [16]).

The scope of validity of the relation between stabilization energy and charge redistribution also follows from the above-performed derivation. Thus,

the relation is valid when the basis set of the system under study may be divided into two subsets containing the initially-occupied and the initially-vacant basis functions so that all the resonance parameters are first order terms vs. the energy differences between orbitals of different subsets (This requirement is met for an extended class of molecules and molecular systems [4,12–15]). At the same time, no specifying either of the number of orbitals participating in the charge redistribution or of the extent of their localization is required for derivation of our relation. The same also refers to the actual structure of the system and the nature of its alteration.

Given that zero order intrasubset resonance parameters are additionally allowed, the relation under study turns into an interdependence of a more involved nature wherein the energy of formation of intrasubset bond orders also is present in the expression for the total energy alteration along with the charge transfer energy (see Eq. (11) for the case when $E_{(+)}ij(i \neq j)$ or $E_{(-)}kl(k \neq l)$ take non-zero values). This fact indicates a direction for further extending the relation studied in this paper.

References

- [1] J. March, *Advanced Organic Chemistry, Reactions, Mechanisms and Structure*, Wiley-Interscience, New York, 1985.
- [2] H.G.O. Becker, *Einführung in die Elektronentheorie Organisch Chemischen Reaktionen*, Deutscher Verlag der Wissenschaften, Berlin, 1974.
- [3] A.S. Dnieprovskii, T.I. Temnikova, *Theoretical Fundamentals of Organic Chemistry*, Khimia, Leningrad, 1991 in Russian.
- [4] V.F. Traven, *Electronic Structure and Properties of Organic Molecules*, Khimia, Moscow, 1989 in Russian.
- [5] V. Gineityte, *J. Mol. Struct. (Theochem)* 546 (2001) 107.
- [6] J.N. Murrell, S.F.A. Kettle, J.M. Tedder, *The Chemical Bond*, Wiley, New York, 1978.
- [7] R. McWeeny, B.T. Sutcliffe, *Methods of Molecular Quantum Mechanics*, Academic Press, London, 1969.
- [8] R. McWeeny, *Methods in Molecular Quantum Mechanics*, 2nd ed, Academic Press, London, 1992.
- [9] R. Zahradník, R. Polák, *Elements of Quantum Chemistry*, Plenum Press, New York, 1980.
- [10] V. Gineityte, *J. Mol. Struct. (Theochem)* 343 (1995) 183.
- [11] V. Gineityte, *Int. J. Quant. Chem.* 68 (1998) 119.
- [12] V. Gineityte, *J. Mol. Struct. (Theochem)* 430 (1998) 97.
- [13] V. Gineityte, *J. Mol. Struct. (Theochem)* 487 (1999) 231.
- [14] V. Gineityte, *J. Mol. Struct. (Theochem)* 507 (2000) 231.
- [15] V. Gineityte, *J. Mol. Struct. (Theochem)* 465 (1999) 183.
- [16] V. Gineityte, *J. Mol. Struct. (Theochem)* 541 (2001) 1.
- [17] V. Gineityte, *J. Mol. Struct. (Theochem)* 532 (2000) 257.
- [18] M.J.S. Dewar, R.C. Dougherty, in: Rosetta (Ed.), *The PMO Theory of Organic Chemistry*, Plenum Press, New York, 1975.
- [19] V. Gineityte, *Int. J. Quant. Chem.* 77 (2000) 534.
- [20] M.J.S. Dewar, R. Pettit, *J. Chem. Soc.* (1954) 1625.
- [21] M.J.S. Dewar, *J. Am. Chem. Soc.* 106 (1984) 669.
- [22] F. Bohlman, *Chem. Ber.* 90 (1958) 2157.
- [23] H.B. Schlegel, S. Wolf, F. Bernardi, *J. Chem. Phys.* 67 (1977) 4181.
- [24] J.B. Lambert, R.G. Keske, *J. Am. Chem. Soc.* 88 (1966) 620.
- [25] M.W. Mackenzie, *Spectrochim. Acta* 40 (1984) 279.
- [26] D.B. Shatkovskaya, V.L. Gineityte, A.B. Bolotin, *Theoreticheskaya i Eksp. Khimia* 22 (1986) 168.
- [27] V.L. Gineityte, *Zhurn. Strukt. Khim.* 29 (1988) 164.
- [28] V.L. Gineityte, D.B. Shatkovskaya, *Lithuan. J. Phys.* 30 (1990) 658.
- [29] D. Satkovskiene, V. Gineityte, *Int. J. Quant. Chem.* 58 (1996) 453.
- [30] V. Bachler, G. Olbrich, *Theoret. Chim. Acta* 57 (1980) 329.
- [31] I.A. Shlygina, V.Z. Gabdrakipov, *Zhurn. Fizicheskoi Khimii* 57 (1983) 2618.
- [32] S. Wolfe, *Acc. Chem. Res.* 5 (1972) 102.
- [33] N.C. Zefirov, *Tetrahedron* 33 (1977) 3193.
- [34] L.V. Vilkov, V.S. Mastryukov, N.I. Sadova, *Determination of the Geometrical Structure of Free Molecules*, English ed, Mir, Moscow, 1983.
- [35] M. Klessinger, P. Rademacher, *Angew. Chem.* 91 (1979) 885.
- [36] A. Veillard, *Chem. Phys. Lett.* 33 (1975) 15.
- [37] D. Friesen, K. Hedberg, *J. Am. Chem. Soc.* 102 (1980) 3987.
- [38] S. Patai (Ed.), *The Chemistry of Ethers, Crown Ethers, Hydroxyl Groups and their Sulfur Analogues* Wiley, New York, 1980.
- [39] F. Bernardi, A. Bottoni, N.D. Epiotis, M. Guerra, *J. Am. Chem. Soc.* 100 (1978) 6017.
- [40] N.D. Epiotis, S. Shaik, J.R. Larson, *Tetrahedron* 33 (1977) 327.
- [41] A. Domenicano, I. Hargittai (Eds.), *Accurate Molecular Structures Their Determination and Importance*, Oxford University Press, Oxford, 1992.