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On a Definition of Bond Energies Based on Localized Molecular Orbitals

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A theoretical model is presented for defining bond energies based on localized molecular orbitals. These bond energies are obtained by rearranging the total SCF energy including the nuclear repulsion term to a sum over orbital and orbital interaction terms and then to total orbital terms, which can be interpreted as the energies of localized orbitals in a molecule. A scaling procedure is used to obtain a direct connection with experimental bond dissociation energies. Two scale parameters are employed, the C–C and the C–H bond dissociation energy in C_2H_6 for A–B and C–H type bonds, respectively. The implications of this scaling procedure are discussed. Numerical applications to a number of organic molecules containing no conjugated bonds gives in general a very satisfactory agreement between experimental and theoretical bond energies.

Key words: Theoretical bond energies – Localized molecular orbitals

1. Introduction

Localized molecular orbitals correspond closely to the classical chemical concepts of inner shells and lone pairs of electrons and bonds connecting the atoms in a molecule and have proved to be very useful in molecular quantum mechanics [1, 2]. The attempts to base a definition of the closely connected concept of bond energies on localized molecular orbitals (LMO's) have been less successful. There is no lack of theoretical models [3–11], but of numerical applications and investigations of the appropriateness and usefulness of these models. The models should be able to explain the approximate constancy of bond energies and other bond properties. Most of the recent investigations are based on the fundamental paper of Ruedenberg [5] such as the work of Ruedenberg *et al.* [12], Moffat and Popkie [13], and Gordon and England [9, 14]. The present article, however, is more closely related in spirit to the work of Hall [3]. A theoretical model is set up for defining bond energies based on LMO's. The total SCF energy of the molecule, where the integrals are over LMO's, is rearranged to obtain energies of the inner shell, lone pair, and bond LMO's and interaction energies between these. By summing the interaction terms on the bond energies and using a scaling procedure a connection with experimental bond dissociation energies is reached. In Section 2 the model is set up and in Section 3 numerical applications to organic molecules are discussed.

2. Theoretical Model

The considerations will be restricted to wave functions for closed shell systems in a one-determinant approximation. The expression for the total SCF energy of the molecular system is

$$E_{\text{tot}}^{\text{SCF}} = \sum_i 2h_i + \sum_{i,j} 2J_{ij} - K_{ij} + \frac{1}{2} \sum_{\lambda \neq \mu} \frac{Z_\lambda Z_\mu}{R_{\lambda\mu}}, \tag{1}$$

where the summations are assumed to be over LMO's. The electronic energy is easily arranged into a summation over energy quantities each one associated with a single LMO and another summation over interaction terms between pairs of different LMO's. This, however, does not lead to a useful definition of bond energies, the internuclear repulsion term has to be incorporated into the energy quantities. This term is not in a useful form for this purpose and has to be rearranged. The definition of nuclear charges per orbital first introduced by England and Gordon [9] will be used here. The nuclear charges per orbital, $Z_{\lambda i}$, are defined by the two equations:

$$\sum_i Z_{\lambda i} = Z_\lambda, \tag{2a}$$

$$\sum_\lambda Z_{\lambda i} = 2 \tag{2b}$$

Equation (2a) expresses the conservation of nuclear charge and Eq. (2b) expresses the fact that a nuclear charge of 2 a.u. is allotted to every doubly occupied orbital. This leads to a partial screening of electronic and nuclear charges. For an inner shell or lone pair LMO φ_i on atom λ, $Z_{\lambda i} = 2$ and all other $Z_{\mu i} = 0$ for $\lambda \neq \mu$. For bond LMO's partial nuclear charges, which are in general not integers, are contributed by several nuclei. The above definition is certainly arbitrary, but any other definition designed for the same purpose will be arbitrary too. The internuclear repulsion term can thus be rearranged to

$$\frac{1}{2} \sum_{\lambda \neq \mu} \frac{Z_\lambda Z_\mu}{R_{\lambda\mu}} = \frac{1}{2} \sum_i \sum_{\lambda \neq \mu} \frac{Z_{\lambda i} Z_{\mu i}}{R_{\lambda\mu}} + \frac{1}{2} \sum_{i \neq j} \sum_{\lambda \neq \mu} \frac{Z_{\lambda i} Z_{\mu j}}{R_{\lambda\mu}}. \tag{3}$$

The total SCF energy takes the form

$$\begin{aligned} E_{\text{tot}}^{\text{SCF}} &= \sum_i \left(2h_i + J_{ii} + \frac{1}{2} \sum_{\lambda \neq \mu} \frac{Z_{\lambda i} Z_{\mu i}}{R_{\lambda\mu}} \right) \\ &\quad + \sum_{i \neq j} \left(2J_{ij} - K_{ij} + \frac{1}{2} \sum_{\lambda \neq \mu} \frac{Z_{\lambda i} Z_{\mu j}}{R_{\lambda\mu}} \right) \\ &= \sum_i \tilde{B}_{ii} + \sum_{i \neq j} \tilde{B}_{ij}. \end{aligned} \tag{4}$$

The first summation involves energy terms of the inner shell, lone pair, and bond LMO's, the second one involves the interaction terms mentioned above. The quantities $\tilde{B}_{ii}$ and $\tilde{B}_{ij}$ define a matrix of bond and bond interaction energies, whose total sum is the energy of the molecule. They are, however, not appropriate for a comparison with experimental quantities, not only because of their magnitude, but because they strongly depend on the molecule as will be seen below in the applications. Larger molecules have more interaction terms and more negative diagonal matrix elements for LMO's of the same type. But one can sum the interaction terms on the diagonal elements:

$$\begin{aligned} E_{\text{tot}}^{\text{SCF}} = \sum_i \Bigg\{ 2h_i + J_{ii} + \frac{1}{2} \sum_{\lambda \neq \mu} \frac{Z_{\lambda i} Z_{\mu i}}{R_{\lambda\mu}} \\ + \sum_{j(\neq i)} \left(2J_{ij} - K_{ij} + \frac{1}{2} \sum_{\lambda \neq \mu} \frac{Z_{\lambda i} Z_{\mu j}}{R_{\lambda\mu}} \right) \Bigg\} = \sum_i B_i \,. \end{aligned} \tag{5}$$

The B_i will be called total bond energies. They are appropriate for a comparison with experimental quantities. The sum of the B_i still gives the total SCF energy of the molecule, the B_i themselves consequently have a magnitude of several atomic units, whereas normal bond energies are of the order of fractions of an atomic unit. To permit a detailed comparison the quantities B_i will be scaled. A theoretical total bond energy will be set equal to an experimental one and all theoretical energies will be scaled accordingly. For bonds involving different atoms different scale parameters are most appropriate, one for each type of bond. The reason for this will be discussed below.

The physical interpretation of the total bond energies, B_i, is aided by a consideration which forms an analogue to Koopmans' theorem for ionization potentials [15]. The total SCF energy of a system of $2n$ electrons is given by Eq. (5). Let two electrons be taken out of a particular LMO, φ_k, without any change in the remaining orbitals and let the nuclear charges $Z_{\lambda k}$ be deleted. The resulting energy expression is similar to Eq. (5) where the sum over orbitals excludes the orbital φ_k. The difference of the two energy expressions is B_k

$$E_{(2n\,\text{electrons})} - E_{(2n-2\,\text{electrons})} = B_k \,.$$

B_k can thus be interpreted to be the energy (including a nuclear repulsion term) of the LMO φ_k (representing e.g. a bond) in the molecule without any electronic rearrangement. In analogue to Koopmans' theorem one can state that the B_k are expected to be quantities which can be correlated with experimental quantities if the change in correlation energy and the electronic reorganization energy approximately cancel or – because of the scaling procedure – have approximately the same magnitude for the molecules which are compared. One further point must be mentioned in this context. Theoretical ionization energies obtained via Koopmans' theorem are compared to vertical ionization energies from experiment. This should also be done for the total bond energies, B_k, which, however, is impossible since all experimental quantities are adiabatic ones. A poor agreement between the theoretical and experimental quantities is expected in cases where the nuclear reorganization is significantly different from the reference compound used in the scaling.

In this connection the question arises with which experimental quantities the B_k should be compared. The traditional bond energies are average quantities whose definition is somewhat problematic (for a discussion see e.g. the book of

Cottrell [16]) and appear thus to be inappropriate. More appropriate for a comparison are the bond dissociation energies, which are characteristic quantities for a particular bond and for the molecule.

3. Applications

To test the usefulness of the model introduced above wave functions have been calculated for a number of organic molecules, which do not contain conjugated bonds. Two different basis sets have been used in the investigations. Basis set I consists of 3 *s*-type functions on the H atom contracted to 2 functions, 6 *s*-type functions on the Li atom contracted to 3 functions, and 6 *s*-type and 3 *p*-type functions on the atoms B to F contracted to 3 *s*-type and 2 *p*-type functions [17]. Basis set II consists of 2 *s*-type functions on the H atom contracted to 1 function and of 5 *s*-type and 2 *p*-type functions on the atoms B to F contracted to 2 *s*-type and 1 *p*-type function [18]. These relatively poor basis sets have been employed because of the exploratory nature of the investigations. Wave functions have been calculated for the following molecules (the basis sets are given in brackets): CH_4, CH_3Li, CH_3OH, CH_3F, CH_2O, HCN, C_2H_6 (staggered and eclipsed conformation), C_2H_4, C_2H_2 (basis set I), C_2H_6 (staggered and eclipsed conformation), C_2H_4, C_3H_8, C_3H_6 (propene), and trans- and *cis*-butene-2 (C_4H_8) (basis set II). The molecular orbitals of these wave functions have been localized according to the method of Edmiston and Ruedenberg [1] and of Boys [2] (from wave functions calculated with basis set II). Because of the similarity of the LMO's calculated by different localization methods [19] no significant differences can be expected. The one-electron-, Coulomb-, and exchange integrals over LMO's were then calculated and the bond energy matrix $\{\tilde{B}_{ij}\}$ set up. Because these bond energy matrices contain too much detailed information only few of these will be given. Table 1 contains the bond energy matrix for CH_4 (basis set I) and Table 2 the bond energy matrices for C_2H_6 in the staggered and eclipsed form (basis set I). The tables give the total interaction terms between any two LMO's, i.e. the lower triangular matrix is added to the upper one. The diagonal elements are negative quantities, whereas the nondiagonal elements are positive, the bond bond interactions are thus repulsive. Bond energy terms are of the order of ten

Table 1. Bond energy matrix of CH_4 (basis set I, all values in a.u.)

	iC	$b\sigma CH_1$	$b\sigma CH_2$	$b\sigma CH_3$	$b\sigma CH_4$
iC	-36.00841	1.75244	1.75244	1.75244	1.75244
$b\sigma CH_1$		-8.76960	1.41544	1.41544	1.41544
$b\sigma CH_2$			-8.76962	1.41544	1.41544
$b\sigma CH_3$				-8.76961	1.41544
$b\sigma CH_4$					-8.76960

Table 2. Bond energy matrix for C_2H_6 (values for the eclipsed conformation are given in brackets below the values for the staggered conformation; basis set I, all values in a.u.)

	iC	iC′	bσCC′	*bσ*CH_1	*bσ*CH_2	*bσ*CH_3	*bσ*$C'H_4$	*bσ*$C'H_5$	*bσ*$C'H_6$
iC	-40.56632 (-40.56639)	1.36489 (1.36489)	1.56721 (1.56719)	1.74881 (1.74965)	1.74881 (1.74965)	1.74886 (1.74970)	1.12500 (1.12474)	1.12500 (1.12474)	1.12501 (1.12475)
iC′		-40.56637 (-40.56636)	1.56721 (1.56719)	1.12500 (1.12474)	1.12500 (1.12474)	1.12501 (1.12475)	1.74882 (1.74964)	1.74882 (1.74965)	1.74886 (1.74970)
*bσ*CC′			-15.84510 (-15.84597)	1.29799 (1.29809)	1.29799 (1.29809)	1.29801 (1.29811)	1.29799 (1.29809)	1.29799 (1.29809)	1.29801 (1.29811)
bσCH_1				-12.58333 (-12.58682)	1.41017 (1.41126)	1.41016 (1.41125)	0.99335 (1.02617)	0.92815 (0.94481)	0.99335 (0.94481)
bσCH_2					-12.58334 (-12.58685)	1.41016 (1.41125)	0.92816 (0.94481)	0.99336 (1.02617)	0.99335 (0.94481)
bσCH_3						-12.58351 (-12.58702)	0.99335 (0.94482)	0.99335 (0.94482)	0.92817 (1.02618)
bσ$C'H_4$							-12.58336 (-12.58683)	1.41017 (1.41126)	1.41016 (1.41125)
bσ$C'H_5$								-12.58336 (-12.58687)	1.41016 (1.41125)
bσ$C'H_6$									-12.58348 (-12.58705)

atomic units (except for inner shell orbitals), the interaction terms are smaller by an order of magnitude, but they are still large quantities. Because the most important contributions to these interaction terms come from the interelectronic Coulomb integrals and the internuclear repulsions these terms cannot be expected to be small or to decrease rapidly with increasing distance between the charge centroids of the LMO's. Since the one-electron integrals contribute only to the diagonal elements, it is not possible in this model to avoid these large interaction terms. The elements of the bond energy matrices can consequently not be compared with experimental quantities. Neither in the scheme of bond energies, nor in the one of bond dissociation energies are bond interaction terms well defined quantities, well defined are only "diagonal" quantities. Further on the bond energy matrices do not exhibit the property of transferability or of constancy of bond energies. The bond energy of the CH bond orbital in CH_4 is approximately 8.5 a.u., whereas in C_2H_6 it is about 12.5 a.u., a difference of nearly 50%. But in C_2H_6 there are more interaction terms. This leads to the definition of total bond energies whose numerical values are to be discussed below. The difference between the staggered and the eclipsed form of ethane shows up in the present model as differences in interaction terms between CH bond LMO's on the two C atoms. All other energy terms are little affected. This is the result one would expect in the present model.

By adding the interaction terms to the diagonal elements one obtains the total bond energies, B_i. In the case of multiple bonds as in C_2H_4 or C_2H_2 the energies of the individual bonds are added to obtain a single bond energy for the multiple bond. The quantities obtained in this way have the following general features. The largest energy terms are those of the inner shell orbitals, which for the C atom are of the order of 29 a.u. Contrary to the above scheme they are approximately constant from molecule to molecule. The relative variation is one to three tenths of one percent for molecules with very different bonding structures. These total bond energies associated with the localized inner shell orbitals are not identical with the Hartree-Fock orbital energies and have different magnitudes, but if one considers only chemical shifts with respect to a reference molecule (taken here to be the staggered form of C_2H_6) then these chemical shifts obtained via differences of Hartree-Fock orbital energies, $\Delta\varepsilon_i$, and those obtained via differences of total bond energies, ΔB_i, have the same magnitude and show the same trends. This can be seen from Table 3 where the present data (ΔB_i) are compared with the results of Basch and Snyder ($\Delta\varepsilon_i$) [20]. The agreement with experimental ESCA chemical shifts [21] is of the same quality for both sets of theoretical values.

The energies of lone pair orbitals are of the same order of magnitude as the energies of the bond orbitals, but as there is too little material on lone pair orbitals only the bond orbitals will be examined further. First the C–X type bonds will be discussed which do not involve a H atom. The reference bond used for scaling the theoretical quantities is the C–C bond in ethane, which according to Cottrell has a bond dissociation energy of 83 kcal/mole [16]. Table 4 lists the theoretical scaled quantities and the experimental bond dissociation energies (whenever known to the author). The experimental quantities are taken only from the tabulation of Cottrell [16]. This has been done to compare the theoretical values with one set of experimental quantities. A significant number of bond dissociation energies is uncertain to such a degree that it would have been easy to obtain a

Table 3. Energy shifts of C atom inner shell orbitals relative to C_2H_6 (all values in e.V.)

Molecule	$\Delta\varepsilon_i{}^a$	$\Delta B_i{}^b$
CH_4	-0.2	-0.4
C_2H_6	0.0	0.0
C_2H_4	0.7	0.5
C_2H_2	1.2	0.8
CH_3Li	-	-4.4
CH_3OH	1.8	1.7
CH_3F	2.7	2.9
CH_2O	3.9	3.4
HCN	2.7	2.5
$C_{(1)}H_3\text{-}C_{(2)}H{=}C_{(3)}H_2$		
$C_{(1)}$	-	0.27
$C_{(2)}$		0.76
$C_{(3)}$		0.08
$C_{(1)}H_3\text{-}C_{(2)}H_2\text{-}CH_3$		
$C_{(1)}$		-0.01
$C_{(2)}$		0.24
$C_{(1)}H_3\text{-}C_{(2)}H{=}CH\text{-}CH_3$		
(tr) $C_{(1)}$		0.16
(tr) $C_{(2)}$		0.38
(cis) $C_{(1)}$		0.15
(cis) $C_{(2)}$		0.35

a: reference 20
b: this work

better agreement between the experimental and theoretical bond energies by selecting appropriate values from different sets of tables. The best agreement between bond dissociation and total bond energies is obtained for the C–C single bonds, where the theoretical values vary only from 82.5 to 83.5 kcal/mole in close agreement with the few available experimental data. Because the change in correlation and reorganization energy is expected to be about the same for all the molecules containing a C–C single bond, which is broken, the bond dissociation energies should differ only by minor amounts. The theoretical quantities reflect this expected constancy in a very satisfactory way. The bond dissociation energies for multiple bonds are experimentally considerably uncertain, this is the case also for the double bond in C_2H_4. The experimental value for the bond dissociation energy of C_2H_4 is 125 kcal/mole (?) according to Cottrell [16], the theoretical value is 145 kcal/mole, closer to the experimental value suggested by Cottrell for general olefinic bonds other than the C–C bond in ethane. Again the constancy of the total bond energies of the C–C double bond in the different molecules is

Table 4. Experimental and theoretical bond energies of A–B-type bonds (reference bond is the C–C bond in C_2H_6, all values in kcal/mole)

Molecule	D_{exp}	$B_{\text{theor.}}$
$CH_3 - CH_3$	83	83
$CH_2 = CH_2$	125 (?)	145 (147[a])
$CH \equiv CH$	230	215
$CH_3 - Li$	30-60 (?)	59
$CH_3 - OH$	90	118
$CH_3 - F$	107	142
$H_2C = O$	166[b]	184
$HC \equiv N$	207[b]	264
$CH_3 - CHCH_2$	90 (?)	83
$CH_3CH = CH_2$		145
$CH_3 - CH_2CH_3$	85 (?)	83
trCH_3-$CHCHCH_3$		82.5
tr$CH_3CH = CHCH_3$		143.5
cis$CH_3 - CHCHCH_3$		83.5
cis$CH_3CH = CHCH_3$		143.5

a: basis set II

b: These values are ΔH values at 298°K

well exhibited by the theoretical quantities, they vary from 143.5 to 147 kcal/mole. The energy of the C–C triple bond is 230 kcal/mole (experiment, ΔH at 298° K) and 215 kcal/mole (theory) in satisfactory agreement with each other. The relative strength of C–C single, double, and triple bonds is thus reproduced by the theoretical model, although only one scale parameter, the energy of the C–C single bond, has been used to scale the theoretical quantities.

The agreement between the theoretical and experimental values deteriorates for the C–X type bonds with X = Li, N, O, and F. For C–Li bonds no experimental values are known to the author. The experimental value given in the table is an estimate based on similar organometallic compounds. The bond dissociation energies for the C–X multiple bonds are uncertain, but nevertheless it is easily seen that the discrepancy between the theoretical and experimental quantities increases with increasing nuclear charge of the atom X. The theoretical quantities are larger than the experimental ones by a factor of about 1.2–1.5. The theoretical bond energies are derived from the total SCF energies of the molecule. This total energy changes in a nonlinear way with the nuclear charge of the constituting atoms.

Table 5. Experimental and theoretical bond energies of CH bonds (reference bond is the CH bond in C_2H_6, all values in kcal/mole)

Molecule	D_{exp}	$B_{theor.}$
$CH_3 - H$	101	99.5
$C_2H_5 - H$	96	96
$C_2H_3 - H$	<121 (?)	96.5 (98^a)
$C_2H - H$	<121	103
$LiCH_2 - H$		90.5
$HOCH_2 - H$		96
$FCH_2 - H$		97
$OCH - H$	76	99.5
$NC - H$	114	105
$CH_2CHCH_2 - H$	77	96
$CH_3\ C\ (CH_2) - H$		94
$CH_3CHCH - H$		96
$CH_3CH_2CH_2 - H$	100	95
$CH_3CH\ (CH_3) - H$	94	92.5
tr$CH_3CHCH\ CH_2 - H$		95
tr$CH_3CHC\ (CH_3) - H$		93.5
cis$CH_3CHCHCH_2 - H$		95
cis$CH_3CHC(CH_3) - H$		91

a: basis set II

This effect of the heavier nuclei on the total energy must be reflected in the theoretical bond energies also after scaling. Since the scale is adjusted to the C–C single bond the C–X bond energies have to be larger in magnitude than the experimental values for X equal to N, O, and F. It would therefore be more appropriate to use a different scale for each type of bond orbital, one for C–C and others for C–N, C–O, and C–F orbitals. Because of the scarcity of both experimental and theoretical data on bond energies this has not been done. But if this same scale (C–C bond energy) would have been used for the C–H bond orbitals rather poor results would have been obtained, a fact which is understandable because of the great difference in nuclear charges of the C and the H atom.

The reference bond used for scaling the theoretical total C–H bond energies is the C–H bond in ethane, which has a bond dissociation energy of 96 kcal/mole [16]. Table 5 contains the theoretical and experimental values for C–H bonds.

Some of the theoretical values (for propane, propene, and butene-2) are average values because the H atoms are not spatially equivalent. The agreement between the two sets of values is in general quite satisfactory. The expected approximate constancy of the bond energies is well demonstrated by the theoretical quantities. On the whole the theoretical values show a variation which is somewhat too small when compared to the experimental ones. But there are some definite disagreements too, which occur for the C–H bond orbitals in the molecules C_2H_4, C_2H_2, H_2CO, and CH_2CHCH_2–H. For the first two molecules the experimental bond dissociation energies are uncertain, they will thus not be commented upon. For propene there is a reason for the disagreement. Abstracting a H atom from the CH_3 group in propene leads to the allyl radical, which has equal C–C bond lengths for both bonds, whereas propene itself contains one single and one double bond with their typical bond lengths. An important nuclear reorganization thus occurs upon abstracting this H atom, which lowers the experimental value with respect to the C–H bond energy in ethane, because this quantity contains the nuclear rearrangement, whereas the theoretical one does not. The discrepancy thus should occur. Why the disagreement occurs in the case of H_2CO is not readily explainable and will not be discussed at present.

4. Conclusions

In the present article a theoretical model has been introduced which leads via bond and bond interaction energies to total bond energies, which can after scaling be very satisfactorily correlated with experimental bond dissociation energies. These total bond energies are based on LMO's and can be interpreted as the energies of particular LMO's in a molecule without any change in correlation or reorganization energy (electronic and nuclear). The scaling procedure, however, somewhat modifies this interpretation. By this scaling procedure which consists in identifying one theoretical bond energy with an experimental one and using this scale parameter to adjust all other theoretical values one introduces the change in correlation and reorganization energy (electronic and nuclear) occurring upon dissociation into the theoretical quantities according to the role they play in the reference molecule. If in other molecules the sum of the changes in correlation and reorganization energy is about the same as in the reference molecule then a good agreement with experimental bond dissociation energies can be expected, if the theoretical model is at all a reasonable model. The model proposed here appears to be such a reasonable model. The approximate constancy of the bond energies is well reproduced and the correlation with experimental values is quite satisfactory in general. There are, however, some discrepancies. In part they may be due to uncertainties in the experimental data. In one case a particularly large nuclear reorganization is expected (propene to allyl radical) which should and does lead to a discrepancy between the theoretical and experimental quantities. In other cases the discrepancies are probably due to shortcomings of the present model (H_2CO). For the larger part of the bonds examined the sum of the changes in correlation and reorganization energy (electronic and nuclear) upon dissociation is consequently probably of the same magnitude. It must be admitted, however, that two different reference bonds have been chosen, the C–C bond in ethane for

A–B-type bonds and the C–H bond in ethane for C–H-type bonds. A single scale parameter would have given good agreement between the theoretical and experimental quantities only for bonds of the same type as the reference bond and poor agreement for all other ones. Even with the two reference bonds selected the agreement deteriorates for C–X-type bonds for X = Li, N, O, and F. It proved to be necessary to take several scale parameters because the theoretical bond energies are derived from the total SCF energy which increases in a nonlinear way with increasing nuclear charge of the atoms. It does not seem possible to set up the present model with only one scale parameter, which would be a great advantage from a theoretical point of view. To obtain the best agreement between experimental and theoretical quantities it would be best to choose for each type of bond (i.e. different atoms and not single or multiple bonds between the same atoms) another scale parameter. For practical purposes this may be advantageous in particular in organic chemistry, where only few different types of bonds occur. The sum of the changes in correlation and reorganization energy is more likely to be the same in the same type of bond, which would render the theoretically defined bond energies more useful and reliable. But there is the danger of ending up in a purely parametric scheme, which can give no conceptual insight.

As mentioned above the theoretically calculated bond energies reproduce the approximate constancy of the bond energies in a very satisfactory way and lead in general to a good correlation with experimental bond dissociation energies for C–C- and C–H-type bonds. They are thus transferable as the LMO's on which they are based. They bridge part of the gap between the theoretical description of molecules by wave functions and the classical chemical concepts, they can be of aid in the interpretation of wave functions and molecular properties, and they can help towards a better understanding of the role of the LMO's and the associated transferability properties in molecular structure.

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