On an Ionic Approximation to Chemical Bonding

G. Van Hooydonk

Centrale Bibliotheek, Rijksuniversiteit Gent, België

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It is shown how previously reported bond energy equations (Van Hooydonk, 1973) can be regenerated starting from the assumptions (i) that the valence-orbital energy of an element in a bond can be expressed as a function of its occupancy number (Iczkowski-Margrave, 1961) and (ii) that the potential around an atom in a bond vanishes as soon as its valence orbital is doubly occupied (Ferreira, 1963). The results are consistent with an ionic approximation to chemical bonding. A comparison of the approximations involved in the present theory with those in a semi-empirical LCAO–MO method (Klopman, 1964) is advanced.

1. Introduction

One of the greatest difficulties in most semi-empirical bonding theories is the evaluation of the off-diagonal core integrals (the molecular terms). The usual procedure consists in either introducing a suited parameterization, e. g. with the aid of overlap-integrals and suited scaling, or in simply recalling on the Pauling-Yost[1] or Pauling-Sherman[2] approximation, for which, however, a satisfactory justification can not be given. Nevertheless, it was recently shown[3] that a particular interpretation of the Pauling-Sherman approximation for molecular terms leads to the rather unexpected result that bonding might be explained by considering ionic structures only. Since this has always been a controversial hypothesis, we have now constructed a semi-empirical bonding theory, in which it is not necessary to introduce the Pauling-Sherman approximation. However, the results of the present approach are again consistent with an ionic approximation to chemical bonding. Moreover, this theory is based upon the Iczkowski-Margrave relation[4] for the orbital energy of elements, which, as a particularity, is known to regenerate the Mulliken-definition of electronegativity[5], at least under certain conditions. The starting point of the theory is that also the energy of atoms when forming a chemical bond can be approximated by the general polynomial, first suggested by Iczkowski and Margrave for free atoms and their ions. By then imposing the supplementary condition, taken from the analysis of Ferreira[6], that the derivative of the orbital energy with respect to the occupancy number should vanish when the orbital is doubly occupied, the equations become soluble completely and yield our previously introduced electronegativity-equalization theory[7]. Furthermore, it is possible to compare the present approach with Klopman's semi-empirical LCAO-MO bonding theory[8].

2. Theory

2.1. The Iczkowski-Margrave Procedure[4]

According to Iczkowski and Margrave, the valence orbital energy ε_X of an atom X may be expressed as a function of its occupancy number n_X $(0 \leqq n_X \leqq 2)$:

$$\varepsilon_X(n_X) = a_X + b_X n_X + c_X n_X^2 + \dots \qquad (1)$$

where a, b and c are constants to be determined for each X. For free atoms and ions, Eq. (1) may be reduced to

$$\varepsilon_X(n_X) = b_X n_X + c_X n_X^2 . \qquad (2)$$

Indeed, this equation is capable of reproducing the values $\varepsilon_X(0) = 0$, $\varepsilon_X(1) = \mathrm{IE}_X$ and $\varepsilon_X(2) = \mathrm{IE}_X + \mathrm{EA}_X$ (whereby IE_X and EA_X are the valence-state-ionization energy and -electron affinity of element X) on the condition that $b_X = (1/2)(3\,\mathrm{IE}_X - \mathrm{EA}_X)$ and $c_X = (1/2)(\mathrm{EA}_X - \mathrm{IE}_X)$. With these values, the Mulliken electronegativity definition[5]

$$\chi_X(\mathrm{M}) = (1/2)(\mathrm{IE}_X + \mathrm{EA}_X) \qquad (3)$$

may be considered as the potential around atom X when its valence orbital is occupied by one electron, since obviously

$$(\partial\varepsilon_X/\partial n_X)_{n_X=1} = b_X + 2\,c_X = (1/2)(\mathrm{IE}_X + \mathrm{EA}_X) . \qquad (4)$$

The works of Hinze, Whitehead and Jaffé[9] and of Klopman[8, 10] clearly illustrate the usefulness of

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Reprint requests to Dr. G. Van Hooydonk, Rijksuniversiteit te Gent, Centrale Bibliotheek, Rozier 9, *B-9000 Bent*/België.

these empirical relations suggested by Iczkowski and Margrave.

However, it seems strange that a quantity such as electronegativity, which originally entered the chemical literature as a property of atoms "in molecules" [11], can be defined, as in Eq. (4), in the complete absence of any reference to molecular interactions. Only when chemical interactions are governed by the quantities appearing in Eq. (1), this state of affairs can be justified, at least if one agrees that the concept of electronegativity should retain the context in which it was formerly introduced. Hence, it is important, as widely recognized [12, 13], to trace the interference of molecular terms with the quantities involved in the Iczkowski-Margrave procedure and with the free-atom-electronegativity, defined in Equation (4).

2.2. *The Iczkowski-Margrave Relation for Atoms in Molecules*

In order to establish a general expression for the partitioning energies of atoms in molecules, it is useful to examine some specific examples. A partitioning based upon the Hückel method involves only terms in n_X and a molecular term. A similar procedure based upon another LCAO-MO procedure however involves terms in n_X, n_X^2 and a molecular term also, as to be seen from Klopman's semi-empirical bonding theory [8]. We will correspondingly assume that the partitioning energies of atoms in molecules can, to a fair degree of approximation, be represented by a polynomial of the form originally introduced by Iczkowski and Margrave, i. e. Equation (1). The two states $\varepsilon_X(0) = 0$ and $\varepsilon_X(2) = \mathrm{IE}_X + \mathrm{EA}_X$ will retain their validity, even for atoms in molecules. Indeed, complete ionization can only take place, without interference of external forces, if the ionization energy of one of the bonding partners is zero, a condition that applies for a free electron for instance upon combining with an element X to form the ion X^-.

The state $\varepsilon_X(1)$ however will have to be corrected with respect to the free atom, where its energy is IE_X. Indeed, a mean occupancy number equal to unity for elements in homonuclear bonds for instance refers to a bonded atom, whence the corresponding energy $\varepsilon_X(1)$ should account for the bond energy.

For atoms in molecules, the boundary conditions for Eq. (1) are;

$$\varepsilon_X(0) = a_X , \tag{5 a}$$

$$\varepsilon_X(1) = \mathrm{IE}_X + x_X = a_X + b_X + c_X , \tag{5 b}$$

$$\varepsilon_X(2) = \mathrm{IE}_X + \mathrm{EA}_X = a_X + 2\, b_X + 4\, c_X . \tag{5 c}$$

We have left the term a_X in these expressions since it is not a priori certain that it has to be zero. In fact, since $\varepsilon_X(0) = 0$ only occurs when IE_X itself is zero, the possibility that a_X be related to IE should not be ruled out. x_X is the correction introduced to account for the molecular environment of X.

Before proceding with the solution of these equations, it seems useful to remind that the three energy differences (per electron) of the free atoms energies, i. e. IE_X, $(1/2)(\mathrm{IE}_X + \mathrm{EA}_X)$ and EA_X respectively, have thus far all three been defined as the one-electron energies for atoms when forming molecules, and as such, appear in the diagonal matrix elements of various quantummechanical bonding theories. This situation is most unsatisfactory and it seems appearently difficult to reconcile the three proposals. At this stage of the present method, it is however irrelevant which one of these three one chooses as a starting point, since always the various constants and the molecular term x_X can be adapted in function thereof.

Defining $\varepsilon_X'(n_X)$ as $\varepsilon_X(n_X) - a_X$ and solving Eq. (5) for b_X and c_X, one obtains

$$\begin{aligned}\varepsilon_X(n_X) = a_X + n_X [\,(3/2)\,\mathrm{IE}_X \\ - (3/2)\,a_X + 2\,x_X - (1/2)\,\mathrm{EA}_X] \\ + n_X^2 [\,(1/2)\,\mathrm{EA}_X - (1/2)\,\mathrm{IE}_X - x_X + (1/2)\,a_X] .\end{aligned} \tag{7}$$

With the identity $n_A = 1 - I$ and $n_B = 1 + I$, wherein I is the bond polarity, the valence electron energy of a bond AB, ε_{AB}, may be written as:

$$\begin{aligned}\varepsilon_{AB} = \varepsilon_A(n_A) + \varepsilon_B(n_B) \\ = (\mathrm{IE}_A + \mathrm{IE}_B) + (1/2)\ (1 - I^2)\ (x_A + x_B) \\ + (1/2)\, I\, [\,(\mathrm{EA}_B - \mathrm{EA}_A) + I(\mathrm{EA}_A + \mathrm{EA}_B)\,] \\ + (1/2)\, I\, [\,(\mathrm{IE}_B - \mathrm{IE}_A) - I(\mathrm{IE}_A + \mathrm{IE}_B)\,] \\ - (1/2)\, I\, [\,(a_B - a_A) \ - I(a_A + a_B)\,] .\end{aligned} \tag{8}$$

When it is reminded that the bond energy $E_{AB} = \varepsilon_{AB} - (\mathrm{IE}_A + \mathrm{IE}_B)$ and that the condition $I = 0$ defines x_X as $(1/2)\,E_{XX}$, one obtains a bond energy

$$\begin{aligned}E_{AB} = (1/2)\ (1 - I^2)\ (E_{AA} + E_{BB}) \\ + (1/2)\, I\, [\,(\mathrm{EA}_B - \mathrm{EA}_A) + I(\mathrm{EA}_A + \mathrm{EA}_B)\,]\end{aligned} \tag{9}$$

for relatively low I-values, since the 4th and the 5th term in Eq. (8) will then be negligible and, in this case, the supposition $a_X = 0$ does not influence the bond energy value.

Only by imposing a further condition, it is possible to reduce the above expressions. This will be done in the next section, but it is first recognized that on the supposition that $a_X = 0$ the bond energy (9) for low I-values is based on the Mulliken-electronegativity. Indeed, differentiation of Eq. (7) then yields ($a_X = 0$):

$$(\partial \varepsilon_X(n_X)/\partial n_X)_{n_X=1} = (1/2)\,(\mathrm{IE}_X + \mathrm{EA}_X)$$

2.3. The Condition $(\partial \varepsilon_X(n_X)/\partial n_X)_{n_X=2} = 0$

Ferreira[6] has pointed out that for the saturation processes under discussion at present, i. e. those leading to IE_X and EA_X values, it may be assumed that (i) the potential varies linearly with charge, as in the Iczkowski-Margrave formalism, and that (ii) the potential vanishes as soon as the saturation is completed.

Since the latter condition does not apply to the Iczkowski-Margrave potential-definition, unless the identity $3\,\mathrm{EA}_X = \mathrm{IE}_X$ would be valid, we shall now impose that for atoms in molecules

$$(\partial \varepsilon_X/\partial n_X)_{n_X=2} = 0 .$$

With the use of Eq. (7) this leads to

$$\varepsilon_X(n_X) = \mathrm{IE}_X + 2\,E_{XX} - \mathrm{EA}_X + n_X\,(4\,\mathrm{EA}_X - 2\,E_{XX}) - n_X^2(\mathrm{EA}_X - E_{XX}/2) \quad (10)$$

since under this condition a_X should be given by

$$a_X = \mathrm{IE}_X + 2\,E_{XX} - 3\,\mathrm{EA}_X . \quad (11)$$

It is now readily verified that in order to reproduce the conditions (5) with the aid of one of the three possible one-electron energies, given in Section 2.2., substituted in Eq. (10), only one solution can be retained, i. e.

$$\mathrm{EA}_X = E_{XX} \quad (12)$$

for the one-electron energy involved in chemical interactions. This answers some questions raised in Section 2.2. but, more generally, Eq. (12) has rather important consequences for the validity of the ionic approximation to chemical bonding, as pointed out earlier for the case of homonuclear bonds[14]. More specifically, it is now evident that atomic valence state energies should be used to compute molecular constants[14]. Moreover, the equations describing heteronuclear bond formation are now markedly simplified, as to be seen from the following recapitulation:

$$\varepsilon_X(n_X) = \mathrm{IE}_X - \mathrm{EA}_X + 2\,n_X\,\mathrm{EA}_X - (1/2)n_X^2\,\mathrm{EA}_X , \quad (13)$$

$$(\partial \varepsilon_X/\partial n_X) = \mathrm{EA}_X(2 - n_X) = \mathrm{EA}_X(1 \pm I) , \quad (14)$$

$$\varepsilon_{AB} = \mathrm{IE}_A + \mathrm{IE}_B + (1/2)\,n_A\,\mathrm{EA}_A + (1/2)\,n_B\,\mathrm{EA}_B , \quad (15)$$

$$\begin{aligned} E_{AB} &= (1/2)\,(\mathrm{EA}_A + \mathrm{EA}_B)(1 + I^2) \\ &= (1/2)\,(E_{AA} + E_{BB})\;(1 + I^2) , \end{aligned} \quad (16)$$

$$\begin{aligned} I &= (E_{BB} - E_{AA})/(E_{AA} + E_{BB}) \\ &= (\mathrm{EA}_B - \mathrm{EA}_A)/(\mathrm{EA}_A + \mathrm{EA}_B) . \end{aligned} \quad (17)$$

It must be realized indeed that these equilibrium bond properties may easily be obtained on minimizing the total valence electron energy, or equivalently[3], on assuming that the potential acting on the bonding electrons in a bond AB must be the same around A as around B (Sanderson's electronegativity-equalization principle[15], as it was applied earlier[3]), which leads to the equilibrium occupancy numbers $n_A = 2\,E_{AA}/E_{AA} + E_{BB}$ and $n_B = 2\,E_{BB}/E_{AA} + E_{BB}$, used in the calculation of the bond energy (15), (16) and the polarity (17).

It is seen finally that the solution (12) is incompatible with an assumption $a_X = 0$.

Before continuing the discussion on the ionic approximation to bonding, we will first compare the present semi-empirical bonding theory with the semi-empirical LCAO-MO procedure, advanced by Klopman, in order to discuss the approximations involved in both methods. It should be reminded indeed that we originally retained equation (1) as a starting point on the basis of the bond energy equation deduced by Klopman.

2.4. Comparison with Klopman's LCAO-MO Bonding Theory[8]

A few years after the Iczkowski-Margrave relation was proposed, Hinze, Whitehead and Jaffé introduced their now standard concept of orbital electronegativity. Klopman very soon thereafter proposed his very interesting bonding theory, which however, as he himself pointed out clearly, lacked a satisfactory approach to the molecular terms (off diagonal matrix elements) but the theory very smoothly introduced the free-atom electronegativities into the diagonal matrix elements.

After the usual approximations, as the formal neglect of differential overlap and of non-bonded interactions, the ground state of any diatomic molecule AB can be represented as [8]:

$$\begin{aligned}\varepsilon_{\mathrm{AB}} = {} & n_{\mathrm{A}}(\mathrm{IE}_{\mathrm{A}} + \Sigma \Gamma_{\mathrm{a}}) + n_{\mathrm{B}}(\mathrm{IE}_{\mathrm{B}} + \Sigma \Gamma_{\mathrm{b}}) \\ & + n_{\mathrm{A}}^2(\mathrm{A}_{\mathrm{A}} - + \Gamma_{\mathrm{ab}})/4 + n_{\mathrm{B}}^2(\mathrm{A}_{\mathrm{B}} - + \Gamma_{\mathrm{ab}})/4 \\ & + 2(n_{\mathrm{A}} n_{\mathrm{B}})^{1/2} \beta_{\mathrm{AB}} \end{aligned} \qquad (18)$$

and this equation can only be simplified with the aid of several approximations, to be discussed below.

At this stage, Eq. (18) should be compared with the unsimplified valence-electron energy expression (8) which may be rewritten as follows:

$$\begin{aligned}\varepsilon_{\mathrm{AB}} = {} & n_A[\mathrm{IE}_{\mathrm{A}} + (1/2)(\mathrm{IE}_{\mathrm{A}} - \mathrm{EA}_{\mathrm{A}}) - a_{\mathrm{A}} + (1/2) a_{\mathrm{B}}] \\ & + n_{\mathrm{B}}[\mathrm{IE}_{\mathrm{B}} + (1/2)(\mathrm{IE}_{\mathrm{B}} - \mathrm{EA}_{\mathrm{B}}) - a_{\mathrm{B}} + (1/2) a_{\mathrm{A}}] \\ & + n_{\mathrm{A}}^2(\mathrm{EA}_{\mathrm{A}} - \mathrm{IE}_{\mathrm{A}} + a_{\mathrm{A}})/2 + n_{\mathrm{B}}^2(\mathrm{EA}_{\mathrm{B}} - \mathrm{IE}_{\mathrm{B}} \\ & + \mathrm{a}_{\mathrm{B}})/2 + (1/2) n_{\mathrm{A}} n_{\mathrm{B}} (E_{\mathrm{AA}} + E_{\mathrm{BB}}) . \end{aligned} \qquad (19)$$

In order to reduce the number of Γ-terms in Eq. (18), Klopman uses the identity $\Sigma \Gamma = 0$, introduced by Pople [16], where from the remaining Γ-term can be treated as a parameter. As a second approximation, the Pauling-Sherman relation is used for the molecular term, since there is, as stated by Klopman [8], "not really any possibility to determine the best approximation for β_{AB}". This assumption however has drastic consequences. Indeed, upon comparing the molecular terms in Eqs. (18) and (19), one obtains:

$$\beta_{\mathrm{AB}} = (1/2)(\beta_{\mathrm{AA}} + \beta_{\mathrm{BB}})(1 - I^2)^{1/2} \qquad (20)$$

since $E_{\mathrm{XX}} = 2\beta_{\mathrm{XX}}$ and $n_{\mathrm{A}} n_{\mathrm{B}} = (1 - I^2)$. Requiring that the Pauling-Sherman relation [2] $\beta_{\mathrm{AB}} = (\beta_{\mathrm{AA}} \cdot \beta_{\mathrm{BB}})^{1/2}$ is valid then corresponds with a solution (17) for the bond polarity, and such solution requires that $a_{\mathrm{X}} \neq 0$ and that it be given by Equation (11). It is then seen that the simple fact of retaining the Pauling-Sherman approximation for the molecular term, implies the solution $a_{\mathrm{X}} = \mathrm{IE}_{\mathrm{X}} - \mathrm{EA}_{\mathrm{X}}$ for Equation (19). Now, this corresponds to the well-known Pariser-approximation [17] for electron repulsion. This is only valid if the term Γ_{ab} reduces to $\mathrm{A}_{\mathrm{X}}^{-}$, i. e. when the two electrons are in the valence orbital of one and the same bonding partner. Obviously, this calls for a general solution in terms of an ionic approximation to bonding. It is exactly this Γ_{ab}-term that remains in the final bond energy expression of Klopman, after the Pople approximation has been applied. Although it seems interesting to compare the Eqs. (18) and (19) in detail, it is difficult to evaluate all the integrals occuring in the LCAO-MO theory in such a way that an ionic approximation comes out automatically, as in the present semiempirical theory. This is due to the presence of molecular terms in the first place, and, moreover, to the fact that such a solution imposes rather severe coditions on the Γ-terms (as in the Pople approximation), in which integrals of different kinds appear (such as nucleus-nucleus interactions, core integrals and electronic repulsion integrals [8]). Nevertheless, Pariser's definition of electron-repulsion comes in smoothly through the term a_{X}, as in Eq. (13) for instance. This is in agreement with the fact that, taking EA_{X} as a one-electron energy for the two-electron problems under consideration, means that electron repulsion is counted twice. In this way the appearance of the term $\mathrm{IE}_{\mathrm{X}} - \mathrm{EA}_{\mathrm{X}}$ in Eq. (13) is completely justified and this confirms our earlier results in connection with the correction to be applied on the energies deduced from a simple Hückel approximation [3].

3. The Ionic Approximation to Chemical Bonding

Although the same bond energy was obtained, i. e. Eq. (16), as the one extensively discussed and applied elsewhere [18], the present method has so far not given the same weight to ionic structures in comparison for instance with our discussion of homonuclear bonds [14]. When however Eq. (15) is rewritten as

$$\begin{aligned}\varepsilon_{\mathrm{AB}} = {} & (1/2) n_{\mathrm{A}}(\mathrm{IE}_{\mathrm{A}} + \mathrm{EA}_{\mathrm{A}} + \mathrm{IE}_{\mathrm{B}}) \\ & + (1/2) n_{\mathrm{B}}(\mathrm{IE}_{\mathrm{B}} + \mathrm{EA}_{\mathrm{B}} + \mathrm{IE}_{\mathrm{A}}) \end{aligned} \qquad (21)$$

the energy of separate ionic structures $\mathrm{A}^{+}\mathrm{B}^{-}$ and $\mathrm{A}^{-}\mathrm{B}^{+}$ is easily introduced. Indeed, the coefficients of n_{X} in this equation can be interpreted as the energies of ionic structures $\mathrm{A}^{-}\mathrm{B}^{+}$ and $\mathrm{A}^{+}\mathrm{B}^{-}$, on the condition that, respectively $\mathrm{IE}_{\mathrm{B}} = e^2/r_{\mathrm{BB}}$ and $\mathrm{IE}_{\mathrm{A}} = e^2/r_{\mathrm{AA}}$. On this condition, similar to the one discussed in our ionic approximation to homonuclear bonding [14], one obtains:

$$\begin{aligned}\varepsilon_{\mathrm{AB}} &= a^2(\mathrm{IE}_{\mathrm{A}} + \mathrm{EA}_{\mathrm{A}} + e^2/r_{\mathrm{BB}}) \\ &\quad + b^2(\mathrm{IE}_{\mathrm{B}} + \mathrm{EA}_{\mathrm{B}} + e^2/r_{\mathrm{AA}}) && (22) \\ &= a^2 \varepsilon_{\mathrm{A}^{-}\mathrm{B}^{+}} + b^2 \varepsilon_{\mathrm{A}^{+}\mathrm{B}^{-}} && (23)\end{aligned}$$

if $n_{\mathrm{A}} = 2a^2$ and $n_{\mathrm{B}} = 2b^2$.

As a result, Eq. (23) has some important consequences for the bond distance of heteronuclear bonds, as to be shown elsewhere. Finally, it seems worthwhile to partition the valence electron energy after equilibrium in the bond is established. Eqation (15) then leads to

$$\varepsilon_{\mathrm{X}}(n_{\mathrm{X}}) = \mathrm{IE}_{\mathrm{X}} + (1/2)\, n_{\mathrm{X}} \cdot \mathrm{EA}_{\mathrm{X}} \qquad (24)$$

which is the final result of the effects leading to bond formation, according to the ionic approximation. Hence, the equilibrium partitioning energies increase "linearly" with the amount of charge transferred between the bonding partners and the bond energy depends on the extend one bonding partner interfers with the valence electron of the other $(0 \leqq \frac{1}{2} n_{\mathrm{X}} \leqq 1)$!

4. Conclusion

The present results tend to confirm those deduced earlier with the aid of Sanderson's principle of electronegativity-equalization. In this work however, more attention was paid to the ionic approximation to chemical bonding, which is now seen to be the guiding principle throughout. Particularly interesting seems the result of the present semi-empirical approach to partitioning energy values of atoms in molecules in comparison with the semi-empirical LCAO-MO method used by Klopman. Further investigation of these points might be useful, especially in view of the starting wave function to be used to account for chemical interactions. In general, an ionic approximation most certainly has several advantages and remains a challenging hypothesis, in spite of the fact that it is usually disregarded either completely or in part.

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