

Electronegativity and Electron Affinity

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Various consequences of the supposition that the value of the resonance integral β_{AB} depends on the nature of the bond are evaluated within the framework of the simple Hückel method. The resulting equation for β_{AB} in function of the polarity I of the AB bond is:

$$\beta_{AB} = (1 - I^2)^{-1/2} [C + (1/2) \int (\alpha_A - \alpha_B) dI]$$

where α_X is the Coulomb integral. A solution is proposed corresponding with $\beta_{AB} = (\beta_{AA} \cdot \beta_{BB})^{1/2}$. Further elaboration then suggests that the simple Hückel method in this form is in favour of the ionic approximation to chemical bonding. The Coulomb integral turns out to be the electron affinity, which must now be considered as the electronegativity of elements when forming chemical bonds.

1. Introduction

Semi-empirical MO methods provide basically simple approximations to the energy of chemical bonds¹. The starting point thereby is the minimization of the total energy, which includes considerable contributions of molecular terms. The minimization process determines the equilibrium contributions of all the terms that can be influenced through the formation of a chemical bond. This latter point is of major importance when a principle such as electronegativity-equalization² is considered as being an equivalent criterion for the determination of these equilibrium contributions. Hence, any definition of electronegativity has to take into account molecular terms in some way in order to be consistent with the principle of total energy minimization^{3–5}. There is however a serious difficulty in that the most important molecular term $4ab\beta_{AB}$, appearing for instance in the simple Hückel approximation for a two-center two-electron heteronuclear bond AB, is difficult to describe. It is indeed frequently suggested, such as for instance by Pearson and Gray⁶, that β_{AB} ought to depend upon the nature of the bond AB. Using the energy minimization method, proposed by these authors, this point is reconsidered in the present report. This analysis results in a rather unusual definition of all the integrals appearing in the simple Hückel MO theory.

2. Total Energy Minimization in the Simple Hückel Method

For a description of heteronuclear two-center two-electron bonds AB, the simple Hückel formalism is particularly suited since it allows one to obtain

bond energy values with the aid of a 2×2 secular determinant. Two approximations for the resonance integral β_{AB} are thereby recommended, i. e.

$$\beta_{AB(M)} = (1/2)(\beta_{AA} + \beta_{BB}) \quad (1a)$$

following Mulliken⁷, and

$$\beta_{AB(PS)} = (\beta_{AA} \cdot \beta_{BB})^{1/2} \quad (1b)$$

according to Pauling and Sherman⁸, the choice between the two being rather arbitrary.

As soon as $\beta_{AA} \neq \beta_{BB}$, the two approximations yield different β_{AB} values. Introducing

$$i = (\beta_{BB} - \beta_{AA}) / (\beta_{AA} + \beta_{BB}) \quad (2)$$

one obtains

$$\begin{aligned} \beta_{AB(PS)} &= \beta_{AB(M)} (1 - i^2)^{1/2} \\ &= (1/2)(\beta_{AA} + \beta_{BB}) (1 - i^2)^{1/2}. \end{aligned} \quad (3)$$

Since, within the framework of the Hückel method, $2\beta_{XX}$ stands for the homonuclear (covalent) bond energy E_{XX} of the bond XX, $\beta_{AB(PS)}$ for an heteronuclear bond AB shows an explicit dependence upon the relative difference in covalent bonding behaviour of the two bonding partners A and B.

According to the Hückel approximation, the total Hückel energy $\mathcal{E}_{AB(H)}$ of a two-center two-electron bond AB is given by:

$$\mathcal{E}_{AB(H)} = 2a^2\alpha_A + 4ab\beta_{AB} + 2b^2\alpha_B \quad (4)$$

where all symbols have their usual meanings and the MO is an LCAO of the form

$$\psi_{AB} = a\psi_A + b\psi_B. \quad (5)$$

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Introducing the charge separation in the AB bond, or its polarity, I , defined as

$$I = b^2 - a^2. \quad (6)$$

Equation (4) may be rewritten as:

$$\mathcal{E}_{AB(H)} = (1 - I) \alpha_A + 2(1 - I^2)^{1/2} \beta_{AB} + (1 + I) \alpha_B \quad (7)$$

since $a^2 + b^2 = 1$.

It can be shown how the equilibrium value of β_{AB} can depend upon I explicitly, and thus, upon some kind of difference in bonding behaviour of the bonding partners, which would be in favour of suggestion (1 b).

Minimization of $\mathcal{E}_{AB(H)}$ with respect to I , which is equivalent with the more commonly used procedure of minimizing with respect to a and b , yields:

$$\partial \mathcal{E}_{AB(H)} / \partial I = 0 = -\alpha_A + \alpha_B + 2(1 - I^2)^{1/2} (\partial \beta_{AB} / \partial I) - 2I \beta_{AB} / (1 - I^2)^{1/2}. \quad (8)$$

It is directly verified that the assumption $\partial \beta_{AB} / \partial I = 0$ leads to an equilibrium $\mathcal{E}_{AB(H)}$ value identical with the one obtained from a solution of the well known secular equations:

$$\mathcal{E}_{AB(H)} = \alpha_A + \alpha_B + [(\alpha_B - \alpha_A)^2 + 4\beta_{AB}^2]^{1/2}. \quad (9)$$

If, however, one tries to evaluate the influence of the dependence of β_{AB} upon bond polarity, by putting $\partial \beta_{AB} / \partial I \neq 0$, one obtains:

$$\beta_{AB} = (1 - I^2)^{-1/2} [C + (1/2) \int (\alpha_A - \alpha_B) dI] \quad (10)$$

whereby C is not dependent upon I .

The validity of Eq. (10) causes certain difficulties as to the construction of a simple 2×2 secular determinant.

Two possibilities now arise for further analysis, depending upon the existence of a relation between $(\alpha_A - \alpha_B)$ and I . If it is firstly assumed that $(\alpha_A - \alpha_B)$ is no function of I at all, one obtains:

$$\mathcal{E}_{AB(H)} = \alpha_A + \alpha_B + C \quad (11)$$

or, there is no particular I value at which the heteronuclear bond energy is at extremum. This assumption is clearly to be rejected upon experimental evidence.

Only one solution is thus retained, i. e. that both $(\alpha_A - \alpha_B)$ and β_{AB} be functions of I , with the implication that the final relationship between $(\alpha_A - \alpha_B)$ and I will fix the one between β_{AB} and I also and vice versa. This is as far as one can go within the constraints of the simple Hückel theory.

As a trial function for further analysis, it is natural to assume:

$$i = I \quad (12)$$

since both i and I (a) should be dimensionless quantities; (b) have the same boundary values with corresponding sign; (c) ought to stand for the difference in chemical behaviour of A and B; and (d) can determine the value of β_{AB} through Equations (3) and (10).

A comparison of these latter equations then yields at once

$$2\beta_{XX} = \alpha_X = E_{XX}. \quad (13)$$

The equilibrium value of β_{AB} is then given indeed by the geometric mean, Eq. (1 b), whereas the equilibrium value of I is obtained by Eq. (2) or by its equivalent forms

$$I = (\alpha_B - \alpha_A) / (\alpha_A + \alpha_B) = (E_{BB} - E_{AA}) / (E_{AA} + E_{BB}). \quad (14)$$

The equilibrium values of the coefficients a and b in the MO approximation (5) can directly be calculated with the aid of experimental E_{XX} values for instance, since

$$a^2 = E_{AA} / (E_{AA} + E_{BB}) \quad \text{and} \quad b^2 = E_{BB} / (E_{AA} + E_{BB}). \quad (15)$$

It is also easily verified that this solution for I is consistent with the requirement that $\partial \mathcal{E}_{AB(H)} / \partial I = 0$.

Moreover, partitioning Hückel $E_{X(H)}$ values can be written within the framework of the Hückel approximation as:

$$E_{X(H)} = n_X \alpha_X + (1/2) (2n_X - n_X^2) \alpha_X \quad (16)$$

if it is reminded that $2a^2$ and $2b^2$ respectively represent the orbital occupancy numbers n_A and n_B of atoms A and B in a bond AB,

Hence, one immediately follows:

$$(\partial E_{A(H)} / \partial n_A) = (\partial E_{B(H)} / \partial n_B) \quad (17)$$

for the bonding partners A and B in a diatomic molecule AB, since derivation of Eq. (16) with respect to n_X leads to

$$\partial E_{X(H)} / \partial n_X = \alpha_X (2 - n_X) \quad (18)$$

yielding a value of α_X when n_X equals unity.

For free atoms on the other hand, it is common practice to represent the orbital energy $O E_X$ in function of the orbital occupancy number by means of the relation⁹:

$$O E_X = A n_X + B n_X^2 \quad (19)$$

wherefrom free atom orbital electronegativities $\chi_{X(\text{free})}$ are defined as:

$$\partial O E_X / \partial n_X = A + 2 B n_X = \chi_{X(\text{free})} \quad (20)$$

With the aid of the experimental $O E_X$ values 0, $I E_X$ and $I E_X + E A_X$ for n_X equal to 0, 1 and 2 respectively, it is easily verified that the orbital electronegativity of a free neutral atom X equals the original Mulliken value for electronegativity¹⁰, i. e.

$$(\partial O E_X / \partial n_X)_{n_X=1} = (1/2) \cdot (I E_X + E A_X) \quad (21)$$

since $I E_X$ and $E A_X$ stand for the ionization energy and the electron affinity respectively.

It is therefore tempting to consider Eq. (18) as the definition of the effective electronegativity of atoms in molecules $e \chi_{X(\text{eff})}$:

$$\partial E_{X(H)} / \partial n_X = \alpha_X (2 - n_X) = e \chi_{X(\text{eff})} \quad (22)$$

which gives the result $e \chi = \alpha_X$ for $n_X = 1$ or $I = 0$. A comparison with Eqs. (14) and (17) shows that this definition:

$$e \chi_X = \alpha_X = 2 \beta_{XX} = E_{XX} \quad (23)$$

for a neutral atom in a bond implicates the concept of electronegativity-equalization in chemical bonds, which now turns out to be a consequence of total energy minimization in the Hückel approximation. The derivation of this concept in its present form was originally based upon slightly different arguments⁵.

The value of the covalent bond energy of an heteronuclear bond AB, i. e. $4 a b \beta_{AB}$, is then given by:

$$\begin{aligned} 4 a b \beta_{AB} &= (1/2) e (\chi_A + \chi_B) (1 - I^2) \\ &= e \chi_{A, B(\text{eff})} \\ &= \partial E_{A(H)} / \partial n_A = \partial E_{B(H)} / \partial n_B \end{aligned} \quad (24)$$

which is clearly in contradiction with Pritchard's argument¹¹ that electronegativity-equalization in a bond AB would not occur for 100% if the resonance integral contribution would be accounted for explicitly. This argument was already rejected by Baird et al.⁴ in their attempt to include molecular terms in the electronegativity-equalization formulae. The condition (see Introduction) that a convenient definition of electronegativity for atoms when forming molecules has to bear some intimate relationship with molecular terms is thus extremely well fulfilled.

As a result of this section, it is seen that the supposition $\partial \beta_{AB} / \partial I \neq 0$ leads to a drastic modification of the bond energy equations. In the next section, the relation between Hückel energy values and the corresponding absolute energies is discussed.

3. Electronegativity and Electron Affinity

The relation $2 \beta_{XX} = \alpha_X (= E_{XX})$ between the two integrals occurring in Hückel's method is of particular importance for the evaluation of the nature of α_X . Indeed, $2 \beta_{XX}$ is a purely molecular characteristic for atom X, whereas, within the constraints of the theory outlined above — and of Hückel's method in general —, α_X is involved into the description of orbital characteristics of atoms in molecules also. For this latter quantity — the eigenvalue of the effective Hamiltonian in Hückel's theory — several values have been suggested. It is often identified with the ionization energy of a free neutral atom, but it is recognized that this can only approximately be true, especially when the identity $2 \beta_{XX} = \alpha_X$ is taken into account. Unless the Hückel one-electron operator is explicitly given, it is impossible to find out to what extent α_X approximates the energy of a valence electron. Hence, a possibly more successful approach might consist in comparing differences in Hückel energy values — such as the resulting bond energies — with experimental values, whereby correction terms, causing the divergence between Hückel approximated and absolute energy values, can be supposed to have cancelled out.

For homonuclear bonds no new results are then obtained, since, by definition, there results

$$2 \beta_{XX} = \alpha_X = E_{XX}.$$

For a completely ionic bond however, the situation is quite different.

Due to the results obtained in the foregoing section, a completely ionic bond A^+B^- , with $I=1$ or $n_B=2$, is obtained, without interference of external forces, only when E_{AA} (or α_A) is equal to zero. Although it is not a necessary condition for $I E_A = 0$ when $E_{AA} = 0$, the reverse argument is valid. This condition $I E_A = 0$ is fulfilled for a free electron in the first place. Hence, one immediately follows $\alpha_B = E A_B$, or in general:

$$\alpha_X = E A_X = 2 \beta_{XX} = E_{XX} = e \chi_X. \quad (25)$$

It is seen that the orbital characteristic $E A_X$ is to be identified with the corresponding molecular one E_{XX} . Several consequences for Hückel energy values follow immediately from these results.

For instance, Hückel's total energy $\mathcal{E}_{AB(H)}$ has to be corrected to yield more absolute energy values. It turns out that $\mathcal{E}_{AB(H)}$ is related to the absolute valence orbital energy of the two atoms A and B

in a bond AB, \mathcal{E}_{AB} , by means of Equation (26):

$$\mathcal{E}_{AB} = \mathcal{E}_{AB(H)} + I E_A - E A_A + I E_B - E A_B \quad (26 \text{ a})$$

$$= I E_A + I E_B + (1/2) (E A_A + E A_B) (1 + I^2) \quad (26 \text{ b})$$

$$= I E_A + I E_B + E_{AB} \quad (26 \text{ c})$$

where E_{AB} is the bond energy.

Absolute partitioning E_X values are obtained through:

$$E_X = E_{X(H)} + I E_X - E A_X \quad (27)$$

$$= I E_X - E A_X + 2 n_X E A_X - (1/2) n_X^2 E A_X \quad (28)$$

yielding the values:

$$E_X^+ = I E_X - E A_X, \quad (29 \text{ a})$$

$$E_X^0 = I E_X + (1/2) E A_X = I E_X + (1/2) E_{XX}, \quad (29 \text{ b})$$

$$E_X^- = I E_X + E A_X. \quad (29 \text{ c})$$

These values for the absolute partitioning energies for atoms in molecules are, by definition, only valid for internuclear separations equal to the actual equilibrium bond lengths r_e of the bonds under consideration. Hence, the limiting value for E_X^+ , i. e. $I E_X - E A_X$ when I approaches unity, is considerably larger than the $O E_X^+$ value of a free ion X^+ , which is actually zero. This must be due to the electrostatic attraction ($I > 0$) at $r = r_e$, which secures that the bonding electron pair is still to some extent under influence of the less electronegativity bonding partner. In the case $I = 1$, $I E_X$ itself tends to zero, wherefrom also E_X^+ tends to zero, since bond equilibrium (polarity) is established without the interference of external forces. As soon as $E_{XX} \neq 0$, this value is never reached in practice. If this E_X^+ value is however taken as a zero point, there results, upon various degrees of interference with the bonding electron pair, for $n_X \alpha_X$: 0, $E A_X$ and $2 E A_X$ when n_X is equal to 0, 1 and 2 respectively, in agreement with the demands for α_X arising from Hückel's theory. It is indeed required in the Hückel formalism that successive addition of electrons yields equal energy increments.

The following bond energy equations are finally obtained

$$E_{AB} = (1/2) (E A_A + E A_B) (1 + I^2) \quad (30 \text{ a})$$

$$= (E A_A^2 + E A_B^2) / (E A_A + E A_B) \quad (30 \text{ b})$$

$$= a^2 E A_A + b^2 E A_B \quad (30 \text{ c})$$

which are all identical. On account of the relation (25) these equations are equivalent with the ones deduced from the principle of electronegativity-equalization^{5, 12}.

Hence the problem of assigning a correct value to the Hückel integrals is transposed to the evaluation of the influence that different chemical environment, i. e. external forces, such as the presence of non-bonding lone electron pairs, ..., may have upon the electron affinity value of a particular element. This is basically a second order effect and, instead of evaluating the influence of these effects a priori through a suited calculation, a very simple device, such as its evaluation through experimental heteronuclear bond energies¹², yields a posteriori adjusted values. It turns out that, in several cases, a practically constant $E A_X = E_{XX}$ value can be used.

4. Discussion

Several authors⁶ have suggested that the resonance integral is dependent upon the nature of the chemical bond and an understanding of this dependence is a sine qua non for any theory of chemical bonding¹³. The evaluation of the consequences of such a dependence, within the framework of the simple Hückel method, as done in the present report, reveals that such relation has rather drastic an impact upon an interpretation of the stability of chemical bonds. Indeed, its introduction into the total energy minimization process (Sect. 2) finally leads to bond energy equations which are definitely in favour of the ionic approximation to account for chemical, e. g. also covalent, bonding. Since this is a rather unexpected result, it is desirable that the nature of this interdependence of β_{AB} and I be examined more closely, for instance through an application of the same method of energy minimization in SCF-LCAO-MO frameworks, whereby molecular terms are also difficult to approximate.

If we restrict ourselves to the present results, obtained within the simple Hückel approximation, the total energy minimization, including minimization of molecular terms, reproduces the principle of electronegativity-equalization rather accidentally as an equivalent form for the description of bond equilibrium.

As a consequence, the computation of heteronuclear diatomic bond energies is extremely simple: no iterative procedure are needed to obtain equi-

librium values. Moreover, only two values have to be known: the E_{XX} (or $E A_X$) value of the bonding partners. Since in all semi-empirical methods, including SCF methods¹⁴, these values are also needed, e. g. to compute reasonable β_{AB} values — and in several cases even more parameters have to be evaluated —, the final gain in simplicity is considerable.

The most important result however is the fact that the simple supposition $\partial\beta_{AB}/\partial I \neq 0$ makes the classical distinction between covalent and ionic types of chemical bonds superfluous, since all types of bonds are stabilized through the same mechanism: the saturation of electron affinity values of both the bonding partners, either to the same or to a different degree, for covalent and ionic bonding respectively. As a result, the theory is still consistent with Lewis's propositions for covalent bonding, although major importance is now attached to $E A_X$ values of elements, rather than to their tendency to acquire a noble gas configuration.

Furthermore, gradual alterations in a^2 and b^2 in Eq. (30c) lead to a very simple illustration of Pauling's definition of electronegativity¹⁵ as the

power of an atom to attract electrons *in a molecule*. Since only electron affinities are involved, the present theory also leads to a classification of bonds intimately connected with the one obtained from the electronegativity concept¹⁶.

Nevertheless, there remain various difficulties to be solved adequately, some of which are inherent with the simple Hückel approximation (e. g. the importance to be attached to ionic structures to account for chemical bonding, the neglect of overlap throughout, the absence of ionization energy values, even for ionic bonds, in the bond energy equation, the verification of the relation $E A_X = E_{XX}$ with the use of experimental values). These will be discussed separately, together with other consequences of the present results.

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