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A Molecular Orbital Approach to Electronegativity Equalization

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From the basic premises of Molecular orbital theory it is shown that the various electronegativity equalization theories, at present in the literature, are fundamentally the same, and are expressable in a unified theory, developed herein. General relationships are established for calculating equilibrated electronegativities, electron densities and extra ionic resonance energies. The Equalization method is related to other methods for calculating the properties of *localized bonds* in molecules.

Auf der Grundlage der MO-Theorie werden die verschiedenen bekannten Theorien des Elektronegativitätsausgleichs im Rahmen *einer* Theorie dargestellt. Allgemeine Regeln zur Berechnung ausgeglichener Elektronegativitäten, Elektronendichten und der zusätzlichen ionischen Resonanzenergien werden angegeben. Die Methode des Elektronegativitätsausgleichs wird mit anderen Methoden zur Berechnung der Eigenschaften *lokalisierter Bindungen* in Molekülen verknüpft.

On montre, à partir des fondements de la théorie des orbitales moléculaires, que les diverses théories d'égalisation de l'électronégativité, qui ont actuellement cours, sont essentiellement les mêmes et peuvent être exprimées dans une théorie unifiée développée ci-après. Des relations générales sont établies pour calculer les électronégativités égalisées, les densités électroniques et oes énergies de résonance ionique supplémentaires. La méthode d'égalisation est reliée aux autres méthodes de calcul des propriétés des *liaisons localisées* dans les molécules.

Introduction

There are few methods for estimating the electron density distributions in saturated molecules, other than empirical ionic character versus electronegativity difference relationships. Explicit incorporation of electron repulsions in electronegativity schemes [1, 2], and extension of semi-empirical π-electron methods to σ-electron systems [3] in order to calculate charge distributions in non-conjugated molecules have been attempted. In this paper, the theoretical basis of current Electronegativity Equalization theories is developed, and general relationships for calculating charge densities are derived for the first time, in an attempt to unify the various existing Electronegativity theories.

Theory and Discussion

A. Molecular Orbital Theory of Electronegativity Equalization

The principle *that the electronegativities of all the atomic orbitals in a molecule must be equal* will now be developed from molecular-orbital theory.

Let n_{ui} be the electron density of the u^{th} atomic orbital ϕ_u in the i^{th} molecular orbital ψ_i, then the total electron density of ϕ_u over all the occupied molecular

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orbitals is n_u, where

$$n_u = \sum_{i=1}^{M} n_{ui} \tag{1}$$

and M signifies the highest occupied MO. The molecular electron density of the molecular orbital ψ_i is N_i, where

$$N_i = \sum_{u=1}^{P} n_{ui} \tag{2}$$

and P designates the total number of AO in the MO. N_i is a constant equal to 0, 1 or 2 electrons, whereas n_{ui} and n_u vary between 0 and 2 electrons. Thus the usual assumption of LCAO-MO theory is made that the total electron density of the molecule can be partitioned between the AOs.

If we now assume that the total electronic energy of the molecule E_{MOL}, can be partitioned into a sum of atom energies E_{L} then

$$E_{\mathrm{MOL}} = \sum_{\mathrm{L}} E_{\mathrm{L}}(n_1^{\mathrm{L}}, n_2^{\mathrm{L}} \ldots n_K^{\mathrm{L}}) \tag{3}$$

where E_{L} is a function of the occupancy of all the K atomic orbitals, n_u, on atom L.

In order to find the values of n_{ui} corresponding to the minimum value of E_{MOL}, and subject to the constraints of equation (2)

$$0 = N_i - \sum_{u=1}^{P} n_{ui} \qquad i = 1 \rightarrow M \tag{4}$$

then the Lagrange multiplier method may be used, and a function ε defined so that

$$\varepsilon = E_{\mathrm{MOL}} + \sum_{i=1}^{M} \lambda_i \left(N_i - \sum_{u=1}^{P} n_{ui} \right). \tag{5}$$

Hence

$$\frac{\partial \varepsilon}{\partial n_{ui}} = 0 = \left(\frac{\partial E_{\mathrm{MOL}}}{\partial n_u} \right) \left(\frac{\partial n_u}{\partial n_{ui}} \right) = \frac{\partial \sum_{i=1}^{M} \lambda_i N_i}{\partial n_{ui}} - \frac{\partial \sum_{i=1}^{M} \sum_{u=1}^{P} \lambda_i n_{ui}}{\partial n_{ui}} \tag{6}$$

From Eq. (1), $\left(\frac{\partial n_u}{\partial n_{ui}} \right)$ is equal to 1, and since N_i is a constant the second term in the equation vanishes. Hence

$$\left(\frac{\partial E_{\mathrm{MOL}}}{\partial n_u} \right) = \lambda_i \qquad i = 1 \rightarrow M. \tag{7}$$

Now the orbital ϕ_u is on a particular atom L hence

$$\left(\frac{\partial E_{\mathrm{MOL}}}{\partial n_u^{\mathrm{L}}} \right) = \frac{\partial \left[\sum_{\mathrm{L}} E_{\mathrm{L}}(n_1^{\mathrm{L}} \ldots n_s^{\mathrm{L}}) \right]}{\partial n_u^{\mathrm{L}}}. \tag{8}$$

But $\frac{\partial E_{\mathrm{L}}}{\partial n_u^{\mathrm{L}}}$ has been defined as the *Orbital Electronegativity* X_u^{L} previously [7], and n_u^{L} is particular to atom L, so that from this definition and Eqs. (5) and (6) it follows that

$$X_u^{\mathrm{L}} = \lambda_i \qquad i = 1 \rightarrow M. \tag{9}$$

Since u is a general index for any atomic orbital on atom L, and L is a general index for any atom in the molecule, while i is a general index for any molecular orbital, this equation means that the electronegativities of all the atomic orbitals forming the molecular orbitals are equalized in the molecule.

While it is obvious that E_{L} is dependent on the occupancy of all its atomic orbitals, n_1^{L} to n_s^{L}, only the occupancy of the valence shell atomic orbitals changes when the atom is in the molecule according to usual chemical theory [15]. Hence if n_1^{L} to n_m^{L} are inner shell occupances they remain constant and equal to two electrons; consequently E_{L} and E_{MOL} are unchanged and are then dependent only on n_{m+1}^{L} to n_s^{L}, the valence orbital occupancies. If inner shell orbitals are involved in molecular formation, as considered by Peters [21] then their occupancy must be explicitly considered.

Klopman [1] showed that minimizing the total molecular energy E_{M} of two atomic orbitals ϕ_u and ϕ_v required

$$\frac{\partial E_{\mathrm{M}}}{\partial n_u} = \frac{\partial E_{\mathrm{M}}}{\partial n_v} \tag{10}$$

where n_u represents the total charge of ϕ_u. Thus if the electronegativities were to be identified with the terms $\partial E_{\mathrm{M}}/\partial n_u$, this equation is equivalent to equalizing the electronegativities.

The assumed partitioning of the molecular energy into atom energies cannot be rigorously justified for polyatomic systems; it is valid however for systems involving *localized two-centre* bonds. The electronegativity equalization expressions for two MO-methods which use localized bond concepts are derived below.

B. Expansion of Molecular Energy into Atom Energies

The partition concept will be applied to the simple Hückel method [4]. The energy of a two-centre, two-electron bond is,

$$E_{\mathrm{MOL}} = 2c_u^2\alpha_u + 2c_v^2\alpha_v + 4c_u c_v \beta_{uv} \tag{11}$$

where c_u and c_v are the coefficients of the ϕ_u and ϕ_v in the bonding molecular orbital ψ, α_u and α_v are the AO Coulomb integrals, and β_{uv} is the resonance integral between ϕ_u and ϕ_v. Since overlap is neglected in the simple Hückel method,

$$n_u = 2c_u^2 \tag{12}$$

$$n_v = 2c_v^2 \tag{13}$$

hence

$$(n_u n_v)^{1/2} = 2c_u c_v \tag{14}$$

and

$$n_u + n_v = 2 \tag{15}$$

Consequently within the restraints of the Hückel method it is possible to partition E_{MOL} such that is the sum of two atomic energies.

$$E_{\mathrm{MOL}} = E_u + E_v\,. \tag{16}$$

Where the atomic energies are of the form

$$E_u = n_u\alpha_u + \beta_{uv}(2n_u - n_u^2)^{1/2} \tag{17}$$

evidently a function of n_u alone. From Eqs. (10) and (17), the electronegativity of such an atomic orbital in a molecular orbital can be derived as

$$X_u = \frac{dE_u}{dn_u} = \alpha_u + \frac{\beta_{uv}(1-n_u)}{\sqrt{2n_u - n_u^2}} \tag{17a}$$

X_v is similarly defined in terms of α_v, β_{vu} and n_v. The electronegativities X_u and X_v will be equal within the bond as derived in Eq. (10).

II. Applying the partition concept to Klopman's SCF-LCAO-MO method, where the energy for a two-centre, two-electron bond [5] is:

$$E_{\mathrm{MOL}} = n_u B_u^* + n_v B_v^* + \frac{n_u^2}{4}(A_u^- + \Gamma_{uv}) + \frac{n_v^2}{4}(A_v^- + \Gamma_{uv}) + 2\beta_{uv}(n_u n_v)^{1/2} \tag{18}$$

then E_{MOL} may be partitioned into atomic energies E_u and E_v where

$$E_u = n_u B_u^* + \frac{n_u^2}{4}(A_u^- + \Gamma_{uv}) + \beta_{uv}(2n_u - n_u^2)^{1/2}\,. \tag{19}$$

B_u^* is the interaction energy of an electron in ϕ_u with the nucleus, inner-shell electrons, and other valence-shell electrons in different atomic orbitals on the same atom as ϕ_u. A_u^- is the repulsion energy of two electrons in ϕ of opposite spin, β_{uv} is the resonance integral relative to the core Hamiltonian, and $-\Gamma_{uv}$ is the repulsion energy between an electron in ϕ_u and one in ϕ_v [5]. The equalized orbital electronegativities in the bond can be derived as

$$X_u = \frac{dE_u}{dn_u} = B_u^* + \frac{n_u}{2}(A_u^- + \Gamma_{uv}) + \frac{\beta_{uv}(1-n_u)}{\sqrt{2n_u - n_u^2}}\,. \tag{20}$$

Thus in both the simple Hückel and the SCF-LCAO-MO method E_{MOL} of two-atom molecules can be partitioned into atomic energy terms, and the electronegativity equalization concept of Eq. (10) is valid. Such a partition of E_{MOL} is very complicated in polyatomic molecules, unless these molecules can be treated in terms of localized two-electron, two-centre bonds; that is the molecule is treated by a valence bond approach within the molecular orbital theory. In the SCF-LCAO-MO method for a given AO in a given bond, the effects of other atomic orbitals on the same atom are included in the B_u^*, A_u^-, and Γ_{uv} as effective core integrals.

It is significant that these derivations show that the electronegativities X_u and X_v are equalized in the bond *only* when the resonance integral β_{uv} is included in both the Hückel and SCF-LCAO-MO cases. Pritchard [6] argued that the electronegativities were not equal when β_{uv} was included, because he started from a definition of X which did not include β_{uv}, and in which the X are in equilibrium in the absence of β_{uv}, namely a non-MO theory.

C. General Relationships

It is now possible to derive some new general relations which will be shown to include diverse specific relations already in the literature.

The electronegativity of an atom or orbital can be related to its electron density by the *bond electronegativity* function X_{L} [7], which has generally been assumed to be linear.

Eqs. (17a) and (20) show that in the specific methods considered X_{L} is not a linear function of n_u, since the expression $(1-n_u)/\sqrt{2n_u - n_u^2}$ is non linear. However this expression proves to be almost linear in the range $0.4 < n_u < 1.6$ [1], that is for bonds which are less than 60% ionic; when n_u lies outside this range then the linear assumption attaches *too low* a value of X_{L} to the n_u and consequently exaggerates the ionic character of the bond. Consequently when n_u is within the range quoted a linear relation of the form [8, 9]

$$X_L = F_L + G_L Q_L \tag{21}$$

can be used, where X_L is the electronegativity of the atom or orbital L, Q_L is the electron density of L[1], whether L be an atom or orbital, and F_L and G_L are the bond electronegativity parameters for L. X_L always decreases with increasing Q_L. When there is a molecular charge distribution in which all the X_L have an equilibrium value, X^* then

$$X^* = X_L^* = F_L + G_L Q_L^* . \tag{22}$$

When both sides of (22) are divided by G_L and summed over all L, the equilibrium bond electronegativity becomes:

$$X^* \sum_L \frac{1}{G_L} = \sum_L \frac{F_L}{G_L} + \sum_L Q_L^* . \tag{23}$$

Since the total electron density, $\sum_L Q_L^*$, equals Q^*, then,

$$X^* = \frac{\sum_L F_L/G_L + Q^*}{\sum_L 1/G_L} = \frac{\sum_L F_L/G_L + Q}{\sum_L 1/G_L} . \tag{24}$$

Where $Q^* = Q$ since the total electron density is constant; only the individual Q_L vary.

If the bond electronegativity parameters F_L and G_L are known, X^* may be calculated for any molecule and subsequently the electron density for each atom (or orbital) in the molecule can be calculated:

$$Q_L^* = \frac{X^* - F_L}{G_L} . \tag{25}$$

Extra Ionic Resonance Energy

A general expression will now be derived for the *extra ionic resonance energy* [10] by assuming that the bond electronegativity (Eq. 21) is the first derivative of the atom energy with respect to charge (Eq. 5). The energy E_L for an atom or orbital as a function of the electron density Q_L, in the bond is,

$$E_L(Q_L) = E_L(0) + F_L Q_L + \tfrac{1}{2} G_L Q_L^2 . \tag{26}$$

For the free atom before bond formation E_L would be expressed as

$$E_L^0 = E_L(0) + F_L Q_L^0 + \tfrac{1}{2} G_L (Q_L^0)^2 \tag{27}$$

where Q_L^0 is the charge Q_L before bond formation. The change in energy, ΔE_L, on bond formation is therefore

$$\Delta E_L = E_L^* - E_L^0 = F_L [Q_L^* - Q_L^0] + \tfrac{1}{2} G_L [Q_L^{*2} - (Q_L^0)^2] . \tag{28}$$

Using the general equations for electronegativity and charge Eqs. (21) and (25) gives

(i) the charge difference

$$Q_L^* - Q_L^0 = \frac{X^* - X_L^0}{G_L} \tag{29}$$

and

(ii) the charge sum

$$Q_L^* + Q_L^0 = \frac{X^* + X_L^0 - 2F_L}{G_L} \tag{30}$$

for the free and bonded condition of L.

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[1] Some authors [8] have used the net charge of L, as noted below.

Substituting these Eqs. (29) and (30), into that for the energy change (28) gives a general expression for the energy change in terms of the equilibrium and free electronegativities

$$\Delta E_{\mathrm{L}} = \frac{(X^*)^2 - (X^0_{\mathrm{L}})^2}{2G_{\mathrm{L}}}. \tag{31}$$

Now the *extra-ionic resonance energy* R for the molecule is obviously the sum of the changes in atom energies, (i.e. the change in molecular energy upon bond formation), within the partition condition, hence

$$R = \sum_{\mathrm{L}} (\Delta E_{\mathrm{L}}) = \sum_{\mathrm{L}} \frac{(X^*)^2 - (X^0_{\mathrm{L}})^2}{2G_{\mathrm{L}}}. \tag{32}$$

Thus it has been possible to derive the extra-ionic resonance energy expression within a molecular orbital framework, in terms of the equilibrium bond electronegativity and free atom (or orbital) electronegativity difference.

Extant Electronegativity Equalization Theories

It is now possible to consider how the various extant theories of electronegativity equalization fit into this general theory, despite their being derived outside the molecular orbital theory.

The first theory is one applicable to the molecule as a whole, and not focussing on two centre bonds within the molecule.

I. Sanderson's Method [8]. The bond electronegativity parameters in Sanderson's theory F_{L} and G_{L} are not independent of each other but related by,

$$G_{\mathrm{L}} = (F_{\mathrm{L}})^{1/2} \tag{33}$$

Consequently if this relationship is substituted into the equations for the equilibrium electronegativity and charge these become respectively

$$X^* = \left(\sum_{\mathrm{L}} (F_{\mathrm{L}})^{1/2} + Q\right) \Big/ \sum_{\mathrm{L}} \left(\frac{1}{F_{\mathrm{L}}}\right)^{1/2} \tag{34}$$

and

$$Q^*_{\mathrm{L}} = \left(\frac{1}{F_{\mathrm{L}}}\right)^{1/2} (X^* - F_{\mathrm{L}}). \tag{35}$$

Sanderson defines his Q_{L} as net *atomic* charges, not as populations as has been done above. These formulae were not of course derived by Sanderson, and it is obvious that his assumption that X^* is equal to the geometric mean of all the F_{L} in a molecule [8] is incorrect. The expression for X^* (equation 34) reduces to the geometric mean of the F_{L} *only* in the case of a diatomic molecule with a single bond. But while it is thus a theoretically inaccurate theory, practically the use of the geometric mean for *polyatomics* leads to quite small errors since the geometric mean is usually a good approximation to Eq. (34). Further it is necessary to emphasize that this theory deals with atomic electronegativities, and equalizes these over the whole molecule, so that it cannot describe the properties of bonds.

II. Other Theories. The remaining theories to be considered focus on two centred bonds.

Initially it will be shown that Eqs. (34) and (35) do reduce to the geometric mean for a diatomic molecule, LM, when

$$X^* = \frac{(F_L)^{1/2} + (F_M)^{1/2}}{\left(\frac{1}{F_L}\right)^{1/2} + \left(\frac{1}{F_M}\right)^{1/2}}$$

or $X^* = (F_L F_M)^{1/2}$, as assumed by Sanderson in his derivation [8].

The general expressions for the equilibrium electronegativity and charge for a two-centre bond, whether between atoms or orbitals are:

$$X^* = \frac{F_1 G_2 + F_2 G_1 + Q G_1 G_2}{G_1 + G_2} \tag{36}$$

and

$$Q_1^* = \frac{F_2 - F_1 + Q G_2}{G_1 + G_2}. \tag{37}$$

The ionic character i of the bond can be defined as the *change* in electron density at an atom or in an orbital on bond formation, hence

$$i = |Q_1^* - Q_1^0|. \tag{38}$$

Since, the total electron density $Q = \sum_L Q_L^*$ then

$$Q = Q_1^0 + Q_2^0 = Q_1^* + Q_2^* \tag{39}$$

so that

$$i = \frac{(F_2 + G_2 Q_2^0) - (F_1 + G_1 Q_1^0)}{(G_1 + G_2)} \tag{40}$$

$$= \frac{X_2^0 - X_1^0}{G_1 + G_2} = \frac{\Delta X^0}{G_1 + G_2} \tag{41}$$

since

$$X_L^0 = F_L + G_L Q_L^0. \tag{42}$$

Thus the ionic character of a two-centre bond is proportional to the difference in the free-atom (or orbital) electronegativities, and inversely proportional to the sum of the bond electronegativity G parameters. Thus current Electronegativity equalization methods which assume that the electronegativity is linearly dependent on the charge as in Eq. (21) agree with the intuitive chemical view that the ionic character of a bond is proportional to the electronegativity difference. However, this general theory proves that no unique function relating i to ΔX^0 can be obtained, since the G parameter differs for each atom, and attempts to find such a unique relationship are doomed to failure.

Wilmhurst [11] intuitively derived as an expression for i,

$$i = \frac{|X_M^P - X_L^P|}{X_L^P + X_M^P}. \tag{43}$$

Eq. (41) will only have the form of Eq. (43) if the bond electronegativity function is of the form

$$X_L = F_L + X_L^P Q_L$$

in which the G_L bond electronegativity parameter is replaced by the free neutral atom Pauling electronegativity X_L^P. However, the G_L parameters are all negative, whereas the Pauling electronegativities are always positive, hence the equation must be of the form

$$X_L = F_L - X_L^P Q_L$$

so that the electronegativity will decrease with increasing negative charge on L. In a two-centre bond, atomic neutrality occurs when Q_{L} is unity, and this is when X_{L} must equal the free atom Pauling electronegativity $X_{\mathrm{L}}^{\mathrm{P}}$. Therefore $F_{\mathrm{L}} = 2X_{\mathrm{L}}^{\mathrm{P}}$ and the final form of the equation necessary to generate Wilmhurst's [11] ionic character equation is

$$X_{\mathrm{L}} = 2X_{\mathrm{L}}^{P} - X_{\mathrm{L}}^{P} Q_{\mathrm{L}} \,. \tag{44}$$

This equation has the property that the free atom Pauling electronegativity is X_{L}^{P}, the L^{+} electronegativity is $2X_{\mathrm{L}}^{P}$ and the L^{-} electronegativity is 0. The validity of the theory can only be discussed when there is either of theoretical estimation or empirical estimation of the F_{L} and G_{L} to compare with $2X_{\mathrm{L}}^{P}$ and $-X_{\mathrm{L}}^{P}$. Theoretically F_{L} has the units of electronegativity and G_{L} of electronegativity per unit charge, so that F_{L} should not be equal to $-2G_{\mathrm{L}}$. Empirically [12, 7] the relationship is invalid for the valence states of monovalent atoms in σ-bond formation, for which the valence state electronegativity is equivalent to the atomic electronegativity of Pauling, invalid for atoms forming π-bonds [12] and invalid for tetrahedral carbon [7], all in a quantitative sense; it is qualitatively invalid in that $F_{\mathrm{L}} \neq -2G_{\mathrm{L}}$ even in sign in many cases [12].

The Hinze, Whitehead, and Jaffe bond electronegativity function $X_u(n_u)$ for an *atomic orbital* ϕ_u with occupation number n_u gives [7],

$$i = \frac{|X_v^0 - X_u^0|}{2(c_u + c_v)} \tag{45}$$

since [7]

$$X_u(n_u) = b_u + 2c_u n_u \tag{46}$$

where b_u and c_u are coefficients. In a two-centre bond formed from AOs initially singly occupied

$$X_u^0 = X_u(n_u = n_u^0 = 1) = X_u(1) \tag{47}$$

whence,

$$i = \frac{|X_v(1) - X_u(1)|}{2(c_u + c_v)} \tag{48}$$

in agreement with the general theory developed above.

The expression for the extra ionic resonance energy R is also simplified for two-centre bonds to

$$R = -(X_2^0 - X_1^0)^2/2(G_1 + G_2) \,. \tag{49}$$

Hence R is proportional to the square of the difference in electronegativities of the free atoms before bonding in agreement with Pauling's original ideas [10]. There is no unique dependence of R on $(X_2^0 - X_1^0)^2$ because G_{L} differs for each atom.

The Hinze-Whitehead-Jaffe bond orbital electronegativity function gives for the extra ionic resonance energy

$$R = \frac{-[X_v(1) - X_u(1)]^2}{4(c_u + c_v)} \tag{50}$$

where ϕ_u and ϕ_v are singly occupied valence orbitals [7], which will be identical χ to the χ^0 for monovalent atoms.

D. Bond Electronegativity Functions

The only difficulty in applying the electronegativity equalization conditions to calculate the electron densities, extra ionic resonance energies, and effective group electronegativities in molecular systems lies in evaluating the *bond electronegativity parameters*. Numerous approximate techniques have been used and some of these are briefly considered below in the light of the Partition theory.

Sanderson [8] used a relation

$$X_L^{SR}(Q_L) = X_L^{SR}(Q_L = 0) + Q_L \delta_L \tag{51}$$

to relate X_L^{SR}, the *Stability Ratio definition* of the *Atomic Electronegativity* of atom L, to Q_L the net "partial charge" of an atom, where δ_L is an empirically determined function depending upon the nature of atom L. He assumed that the electronegativities X_L^{SR} of *all* the *atoms* in a molecule should be equalized, in agreement with Eq. (10) except that Eq. (10) is an orbital and not an atom valid theory.

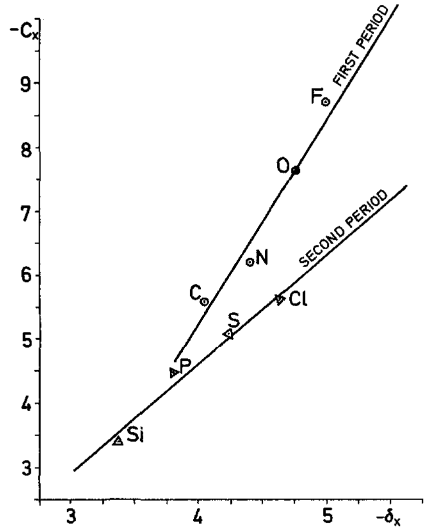

Fig. 1. The plot of δ_L against C_L for specific atoms X of the first and second periods of the periodic table using the results in references [9] and [8]

Element	C_X	δ_X	Element	C_X	δ_X
F	8.70	4.988	Cl	5.65	4.618
O	7.63	4.749	S	5.08	4.216
N	6.21	4.408	P	4.47	3.802
C	5.59	4.050	Si	3.38	3.368

Iczkowski and Margrave [9] developed an *atomic electronegativity* function X^A which varied with partial atomic charge as a method of estimating the electronegativity function parameters here represented is B_L (i.e. F_L) and $2C_L$ (i.e. G_L)

$$X_L^A(Q_L) = B_L + 2C_L Q_L = X_L(Q_L = 0) + 2C_L Q_L\,. \tag{52}$$

The similarity between the definitions of X_L^A and X_L^{SR} suggests that the empirical functions δ_L and C_L should be proportional as shown in Fig. 1. Although the C_L values are available for only eight elements [9], two different pseudo-linear relationships, one for each period of the periodic table, are obtained. Both methods suffer from the fact that they treat atoms as a whole and do not focus in any way on the orbitals on the atoms, but they both fit the general partition theory.

The parameter δ_{L} is evaluated from the empirical relationship [8],

$$\delta_{\mathrm{L}} = 2.08 \sqrt{X_{\mathrm{L}}^{SR}(Q_{\mathrm{L}}=0)} \tag{53}$$

while C_{L} is obtained using atomic energy data; no interatomic energy terms are included in the partitioned atom energy terms E_{L} (Eq. 4) and it is therefore implicitly assumed that the orbital charges obtained by minimizing the sum of the E_{L} are identical to those which would be obtained if the entire molecular energy E_{MOL} were minimized.

Hinze *et al.* [7] defined an orbital *electronegativity* X_u as,

$$X_u(n_u) = \frac{d(E(n_u))}{dn_u} = b_u + 2c_u n_u \tag{54}$$

in which n_u is the electronic charge density of an *orbital* and the dependence of $X_u(n_u)$ on the charge densities of orbitals other than ϕ_u is included in the coefficients b_u and c_u [7]. These coefficients are obtained by using experimentally known $E(n_u)$ for n_u equal to 0, 1, and 2 [12], as,

$$b_u = 1.5\, I_{v_u} - 0.5\, E_{v_u} \tag{55}$$

$$c_u = 0.5(E_{v_u} - I_{v_u})\,. \tag{56}$$

The E_{v_u} and I_{v_u} are *valence state* electron affinities and ionization potentials respectively [13], whence,

$$X_u = 0.5(3\, I_{v_u} - E_{v_u}) + (E_{v_u} - I_{v_u})\, n_u\,. \tag{57}$$

On the other hand, Klopman expressed electronegativity [5] as,

$$X'_u = \frac{\partial(E'_u(n_u))}{\partial n_u} = B_u + \frac{n_u A_u^-}{2} \tag{58}$$

where E'_u is a continuous function of n_u *once the bond is formed* but not when the orbital is non-bonded [1]. In this theory the two parameters B_u, the attraction energy of an electron in orbital ϕ_u for the nucleus and filled inner shells, and A_u^- are required. They can be estimated from the known energies of an isolated, non-bonded atom, with

$$B_u = I_{v_u} \tag{59}$$

the ionization potential of the electron in orbital ϕ_u, and

$$A_u^- = E_{v_u} - I_{v_u}\,. \tag{60}$$

Thus,

$$X'_u = \frac{I_{v_u} + n_u(E_{v_u} - I_{v_u})}{2}\,. \tag{61}$$

X'_u is called the *Molecular orbital bond electronegativity*, since it is derived for use in the Molecular Orbital theory.

The energies and electronegativities in the above theories both fit the general partition theory and are related by

$$\Delta E_u = E_u - E'_u \tag{62}$$

and

$$\Delta X_u = X_u - X'_u\,. \tag{63}$$

Thus

$$\Delta E_u = 0.5\, n_u(I_{v_u} - E_{v_u})\,(1 - 0.5\, n_u) \tag{64}$$

and

$$\Delta X_u = 0.5(I_{v_u} - E_{v_u})\,(1 - n_u)\,. \tag{65}$$

Both the terms ΔE_u and ΔX_u increase as the difference between the ionization potential and electronaffinity increases; ΔE_u is zero at $n_u = 0$ and $n_u = 2$ and a maximum at $n_u = 1$; ΔX_u is zero at $n_u = 1$ when both X_u and X'_u are equal to $I_{v_u} - E_{v_u}$, the Mulliken Electronegativity definition [14], Fig. 2.

The physical significance of the differences can be seen by considering the values at $n_u = 1$; $E'_u(n_u = 1)$ is equal to $(3/4 I_{v_u} + 1/4 E_{v_u})$ while E_u is simply I_{v_u}. Thus the molecular orbital energy E'_u at $n_u = 1$ is equivalent to that for two electrons each spending one-half the time in orbital ϕ_u, with no correlation between the two electrons. On the other hand, E_u at $n_u = 1$, corresponds to complete correlation of the electronic motion such that if the first electron occupies ϕ_u, the second electron is in the other orbital forming the bond. The E'_u function underestimates inter-orbital electron correlation, while the E_u function overestimates it, since electronic motions are only partially correlated [15].

The ionic characters of two-centre, two-electron chemical bonds can be calculated using X_u or X'_u in Eq. (48). Since $X_u(n_u = 1) = X'_u(n_u = 1)$ and since from Eqs. (56) and (61)

$$c_u = 2c'_u \tag{66}$$

then

$$i_{uv} = \tfrac{1}{2} i'_{uv} \,. \tag{67}$$

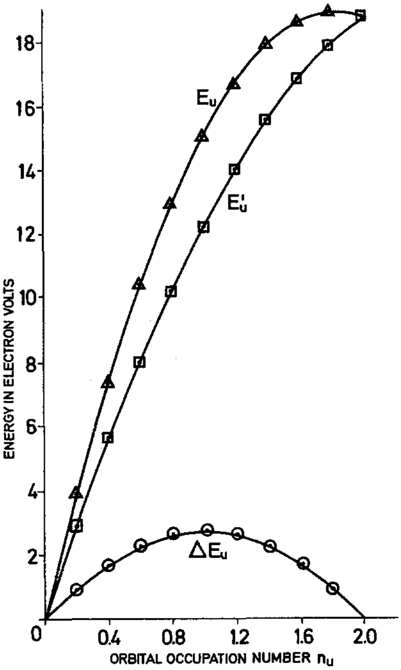

Fig. 2. The plot of the Hinze, Whitehead and Jaffe energy [7] E_u and the Klopman energy [5] E'_u and their difference ΔE_u in electron volts against the number of electrons in the orbital n_u. E_u is always greater than E'_u and ΔE_u is symmetric about $n_u = 1$. The electronegativities χ_u and χ'_u are the same at $n_u = 0$ or 1 but very different at $n_u = 2$. E_u reaches a maximum before $n_u = 2$; E'_u reaches a maximum after $n_u = 2$.

The example used is chlorine $s^2p^2p^2p$ with the $s^2p^2p^2$ as core, whence $I_{V(\mathrm{Cl}p)} = 15.08$ eV and $E_{V(\mathrm{Cl}p)} = 3.73$ eV. Similar curves occur for any other atom or orbital

Thus estimates of the ionic character using these two electronegativity functions, are in the ratio 1 : 2.

Since neither of these extremes is a true representation of the system it may be more accurate to use energy equations which represent the midway point of *partial correlation*. Thus,

$$\begin{aligned} E''_u &= \tfrac{1}{2}(E_u + E'_u) \\ &= (1.25\, I_{v_u} - 0.25\, E_{v_u})\, n_u + n_u^2 (0.375\, E_{v_u} - 0.375\, I_{v_u})\,. \end{aligned} \tag{68}$$

The electronegativity for $n_u = 1$ is,

$$X''_u = \frac{\partial E''_u}{\partial n_u} = 0.5\,(I_{v_u} + E_{v_u}) = X_{\text{Mulliken}} \tag{69}$$

the same as for the individual X_u and X'_u. These three energy relations have maximum energy as given by $\frac{\partial E_u}{\partial n_u} = 0$, namely at $n_u = 1.5$, $n'_u = 2.0$, $n''_u = 1.67$. The ionic characters from this latter theory should be more accurate than those from either the Hinze *et al.* or Klopman theories (see Table), within the limitations of the Partition theory.

Table. *The ionic characters of several diatomics, calculated using $X''_u(1)$ and C''_u (expressed as percentages)*

LiH	31.2	NaH	33.3								
LiF	55.2	NaF	56.7	HF	22.1						
LiCl	52.8	NaCl	54.9	HCl	12.3	FCl	12.9				
LiBr	50.5	NaBr	53.0	HBr	7.3	FBr	18.8	ClBr	6.5		
LiI	48.5	NaI	51.0	HI	5.6	FI	20.5	ClI	8.5	BrI	2.2

These values are calculated assuming pure *s* or *p* orbitals on the combining atoms.

Hinze *et al.* extended their method to saturated polyatomic molecules by using the approximation of localized, two-centre bonds. Repulsions between electrons of the same atom are explicitly considered in this method, and therefore the calculations must be iterated to self-consistency. A simplified version of this theory, the SGOBE method, has been used extensively [17] to calculate electron density distributions in a large number of organic molecules [18] and to derive a bond electronegativity function from the LCAO MO theory [19].

Huheey's method [20] is based on this theory but suffers from the defect of equalizing the X of the initially singly occupied bonding atomic orbitals over the *whole* molecule. It is therefore an orbital version of Sanderson's theory. It would be a valid approach only if Eq. (3) for the partitioning of the molecular energy was valid for a polyatomic system.

Inclusion of Interatomic Terms. Ferriera [2], Jorgenson [16] and others have advocated the use of bond electronegativity functions and including interatomic attractions and repulsions with the free atom energy terms in the definition of the E_L. The effect of this correlation is especially important in considering bonds of high polarity. They will be more fully considered in a later paper, within the theory developed in this paper.

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