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Ionic Character

By

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The concept of ionic character in σ and π bond systems is considered in the light of recent definitions of orbital electronegativity [*6*, *14*].

Le caractère ionique des liaisons σ et π est discuté en tenant compte des définitions récentes de l'électronégativité des orbitales.

Das Konzept des ionischen Charakters in σ und π Bindungen wird im Lichte neuerer Definitionen von Orbitalelektronegativitäten diskutiert.

Hinze, Whitehead and Jaffe [*6*] used the Principle of the Equalization of Orbital Electronegativities [*1*, *6*, *7*, *12*] for two atomic orbitals forming a covalent σ bond to define the ionic character of the bond as

$$i = \left| \frac{\chi_A^0 - \chi_B^0}{2\,(c_A + c_B)} \right| \tag{1}$$

in which χ^0 represents the atomic orbital electronegativity of the atom prior to bonding. c_A and c_B are constants.

The orbital electronegativities are expressed as a linear function of the number of electrons n in an orbital. Thus for the bonding atomic orbital of atom A:

$$\chi_A^0 = b_A + 2c_A n_A \tag{2}$$

and likewise for atom B.

This applies to the formation of a covalent σ bond, a co-ordinate covalent σ bond and a π bond [*5*]. The energy of an orbital j, occupied by n_j electrons is given by [*5*, *6*, *7*].

$$E\,(n_j) = a + b n_j + c n_j^2 . \tag{3}$$

The orbital electronegativity defined by:

$$\chi_j^0 = \frac{\partial E}{\partial n_j} = b + 2 c n_j \tag{4}$$

is a property of the atom before bond formation, and hence can only have $n_j = 0$, 1 or 2. The combination of $n_j^A = 0$ and $n_j^B = 2$ defines a co-ordinate σ bond, and $n_j^A = 1$ with $n_j^B = 1$ a normal covalent σ bond. In the case of π bonded systems both n_j^A and n_j^B can be 0, 1 or 2 independently.

The two electrons in the bond, formed by the overlap of two atomic orbitals, must be in equilibrium and each electron sees the same potential, χ, on atoms A and B. Thus the equilibrium occupation numbers n_A^* and n_B^* [*2*, *6*, *9*] are defined from

$$\chi^*(n_A^*) = \chi^*(n_B^*)\,. \tag{5}$$

The sum of n_A^* and n_B^* is 2 for a σ bond (covalent or co-ordinate) but may be 1, 2, 3 or 4 for a π bond.

Thus a plot of $\chi_A(n_A)$ against n_A and similarly for n_B gives Fig. 1, where the intersection of the two lines gives the equilibrium values n_A^* and n_B^*.

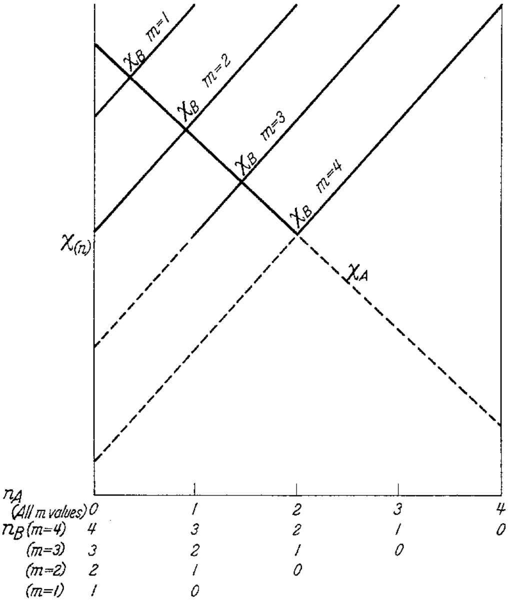

Fig. 1. The electronegativities of atoms A and B in an AB bond as a function of n_A and n_B. The lines are designated by m where $m = n_A + n_B$. The significance of the parameters is discussed in the text

The case where n_A varies from 0 to 2 as n_B goes from 2 to 0 is the normal σ covalent or co-ordinate bond [*6*]. The dotted lines for n_A equal to 3 or 4 are of course hypothetical since the Pauli Principle would be violated, and in all actual cases the lines are found to cross where neither n_A nor n_B actually exceeds 2.

Since ionic character is the amount by which transfer of charge must occur to equalize the orbital electronegativities,

$$i = |n_A^* - n_A| = |n_B^* - n_B| \tag{6}$$

which is the ionic character for a σ or π bond depending on the values of the n^* and n. Since the electronegativities are equal [equ. (5)], then

$$b_A + 2c_A n_A = b_B + 2c_B n_B \tag{7}$$

and n_A and n_B are related by

$$n_A + n_B = m \tag{8}$$

where m can have all possible values of one through four. In a π bond system with $n_A = n_B = 0$ there is of course no bond; with $n_A = n_B = 2$ the σ bond electronegativity changes result in equalization of the p electronegativities such that the two p orbitals retain two electrons each; but for all other combinations of n_A and n_B, π ionic bond character occurs. Combining equations 7 and 8

$$b_A + 2c_A n_A = b_B + 2c_B(m - n_A)$$

from which the occupation number for orbital A may be found to be

$$n_A = \frac{b_B - b_A + 2c_B m}{2(c_A + c_B)}\,. \tag{9}$$

The ionic character is given by $|n_A^* - n_A|$. Substituting for n_A,

$$i = \left| \frac{(b_A + 2c_A n_A^*) - (b_B + 2c_B[m - n_A^*])}{2(c_A + c_B)} \right|. \tag{10}$$

The equilibrium values for n_A^* can vary from 0 to 2 and m from 1 to 4. In all possible combinations of n_A^* and m this equation reduces to

$$i = \left| \frac{\chi_A^0 - \chi_B^0}{2(c_A + c_B)} \right| \tag{11}$$

which demonstrates that ionic character may be defined for both σ and π bonds of the covalent and coordinate type [*9*], in terms of the electronegativity difference.

When the ionic character of a σ bond was defined as in equation 1 [*6*, *14*], evaluation of the constants c_A and c_B was not deemed possible. However knowledge of the ionization potentials, I_v, and electron affinities, E_v, of the orbitals on the atoms of interest, permits both the constants c_A and c_B, and b_A and b_B [of eq. (2)] to be tabulated. From equation (3) the energies of the orbitals containing one, E (1), two, E (2) or zero electrons, E (0) can be defined:

$$E\ (0) = a;\ E\ (1) = a + b + c;\ E\ (2) = a + 2b + 4c\,.$$

By definition, the ionization potential of an orbital is

$$I_v = E\ (1) - E\ (0) \qquad (12)$$

while the electron affinity is

$$E_v = E\ (2) - E\ (1)\,. \qquad (13)$$

Therefore $E_v = b + 3c$ and $I_v = b + c$, and the constants are given by

$$c = (E_v - I_v)/2 \qquad (14)$$

$$b = (3\,I_v - E_v)/2 = \chi\,(0)\ . \qquad (15)$$

These constants have been evaluated for the elements from hydrogen to chlorine in the periodic table, for the valence states of the atoms for which the I_v and E_v were available [*5*]. They are shown in Tab. 1 in Mulliken electron volt units for the normal valence states of the monovalent atoms, since equation (1) is immediately applicable to these.

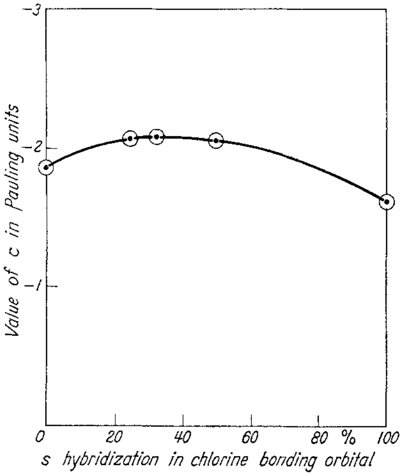

Fig. 2. The variation of the parameter c of equation (2) against the percentage s character of the σ bonding orbital of the chlorine atom

The parameter c* has a slight parabolic dependence on the s character of the bonding orbital on the atom under consideration; for most atoms the value of c is always negative and the parabolic dependence so slight that it can be treated as a constant not dependent on hybridization, (Fig. 2).

As values of the parameters c_A and c_B were not available, HINZE et al. [*6*] and subsequently WHITEHEAD and JAFFE [*14*] assumed that $|c_A + c_B| = 1$ in the case of ionic σ bonding, for all the cases treated in their papers, using Pauling units for χ. We have found that the individual values of c for orbitals combining as σ bonds range from -0.7 to -3.3 and that in all cases $|c_A + c_B| \gg 1$. This is also true of π bonding where the values of c range from -0.19 to -3.62. The

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* all values used for χ, b, c in the text are in Pauling units which are obtained from the Mulliken units given in the tables using

$$\chi_{\text{Pauling}} = 0.336\ (\chi_{\text{Mulliken}} - 0.615)\ ,$$

$$b_{\text{Pauling}} = 0.336\ (b_{\text{Mulliken}} - 0.615)\ ,$$

and

$$c_{\text{Pauling}} = 0.336\ c_{\text{Mulliken}}$$

See HINZÉ, J., and H. H. JAFFÉ: Can. J. Chem. **41**, 1315 (1963).

ionic characters calculated with the correct values of $|c_A + c_B|$ are therefore substantially lower than those using $i_\sigma = 1/2\,|\chi_A - \chi_B|$ which is the equation resulting from equation (1) with $|c_A + c_B| = 1$, and identical with that due to Gordy [*3*]. A comparison between the values of i_σ calculated from equation (1) with c_A and c_B from Tab. 1, and other assessments of i_σ for diatomic molecules is shown in Tab. 3. The values of χ used by Pauling [*9*] and Hannay and Smyth [*4*] are naturally Pauling's original *atomic* electronegativities and not the orbital electronegativities used in this paper. The results obtained by the above theory (Tab. 3) are in marked disagreement with those calculated with the same, or

Table 1

b and c values for the valence state orbitals of the monovalent atoms in σ bond formation

The orbital being considered has no superscript designation of its occupation since occupation numbers of 0, 1 and 2 are used to calculate I_v and E_v (see reference [*5*]).

Atom	Valence state	Ionization Potential I_v (e.v.)	Electron Affinity E_v (e.v.)	$b^\star$ (e.v.)	$c^\star$ (e.v.)
H	s	13.60	0.75	20.02	−6.42
Li	s	5.39	0.82	7.67	−2.28
Na	s	5.14	0.47	7.47	−2.33
F	$s^2\,p^2\,p^2\,p$	20.86	3.50	29.54	−8.68
Cl	$s^2\,p^2\,p^2\,p$	15.08	3.73	20.75	−5.67
Br	$s^2\,p^2\,p^2\,p$	13.10	3.70	17.80	−4.70
I	$s^2\,p^2\,p^2\,p$	12.67	3.52	17.25	−4.57

★ Mulliken Scale

Table 2

b and c values for the valence state orbitals of selected atoms forming π bonds

The orbital being considered has no superscript designation of its occupation since occupation numbers of 0, 1 and 2 are used to calculate I_v and E_v (see reference [*5*]). *di* is a *sp* hybridized orbital and *tr* a sp^2 hybrid orbital while π designates the p orbital used in π bonding independent of its occupation number. In Be and B the π orbital is empty, in C and $N^{(1)}$ singly occupied and in $N^{(2)}$, F and Cl doubly occupied in the atom.

Atom	Valence state	Ionization Potential I_v (e.v.)	Electron Affinity E_v (e.v.)	$b^\star$ (e.v.)	$c^\star$ (e.v.)
Be^-	$di^1di^1\pi$	+0.16	−0.99	−0.25	−0.58
B^-	$tr^1tr^1tr^1\pi$	+1.06	−5.32	−1.07	−3.19
C	$di^1di^1\pi^1\pi$	+11.19	+0.10	+16.73	−5.54
C	$tr^1tr^1tr^1\pi$	+11.16	+0.03	+16.72	−5.56
$N^{(1)}$	$tr^2tr^1tr^1\pi$	+14.12	+1.78	+20.29	−6.17
$N^{+(2)}$	$tr^1tr^1tr^1\pi$	+28.71	+11.95	+37.09	−8.38
F^+	$s^2p^2p^1\pi$	+39.67	+18.11	+50.45	−10.78
Cl^+	$s^2p^2p^1\pi$	+26.36	+13.38	+32.86	−6.49

★ Mulliken Scale

Table 3

Ionic character in some diatomic molecules

The orbitals on Li, Na and H are assumed to be pure s and on the halogens pure p. The results from this paper and for the Gordy equation used orbital electronegativities χ^0, whereas Hannay and Smyth were using atomic electronegativities. The C di^1 di^1 π^1 π and C tr^1 tr^1 tr^1 π show slightly different values of I.P, E.A and χ since they are different valence states: see for instance C. A. Coulson "Valence" O.U.P 1961 page 206.

Molecule	i This Paper %	i Gordy %	i Hannay and Smyth %
LiH	23.4	68.5	21.8
NaH	24.8	73.5	24.2
HF	16.6	84.5	43.0
HCl	8.9	37.0	17.2
HBr	8.2	30.5	12.9
HI	6.9	25.5	7.0
FCl	9.9	47.5	19.5
BrCl	1.9	6.5	3.3

Pauling electronegativities, using the Gordy relationship. This is due to the fact that the relationships would be identical if $| c_A + c_B | = 1$ in the denominator of equation (11). For the cases considered, the calculated values of $| c_A + c_B |$ range from 2.9 to 5.1. It is concluded that in most cases, estimation of the ionic character of σ bonds using the Gordy equation results in values which are too high.

Somewhat better agreement is noted between the values calculated by the Hannay and Smyth relationship of ionic character and electronegativity (atomic) and our values. This is not surprising since at low values of electronegativity difference their relationship

$$i = 0.16 \, | \chi_A - \chi_B | + 0.035 \, | \chi_A - \chi_B |^2 \tag{16}$$

reduces to

$$i = 0.16 \, | \chi_A - \chi_B | \, . \tag{17}$$

The range of $| 1/ [2 \, (c_A + c_B)] |$ for the cases considered, is 0.10 to 0.17, which explains why the results of Hannay and Smyth approximate to ours. Of course the assessment of the constant 0.16 of Hannay and Smyth was made using atomic electronegativities and if the orbital electronegativities of this paper are used in their formula the agreement between the i from equations (11) and (16) becomes very much worse.

This is because the χ_A and χ_B of Hannay and Smyth, being derived from bond dissociation energies, include any hybridization present in the orbitals of the atoms in the bond dissociated, whereas the χ^0 used are the pure s or p orbital electronegativities. The disagreements are worst for the ionic characters of HF and HCl. These are precisely the cases where any hybridization on the halogen would increase the χ^0_{halogen} and raise the value of i_σ from equation (11) toward the value from equation (16) using $\chi_{\text{Pauling atomic}}$. In the case of Cl, Br and I such hybridization can be roughly estimated from nuclear quadrupole resonance data; preliminary calculations on HCl using this data show that s hybridization of the bonding chlorine orbital would give i_σ as 22%, in closer agreement with Hannay and Smyth at 17%. The factor $0.035 \, | \chi_A - \chi_B |^2$ in equation (16) is a factor necessary to correct for the fact that the value of $1/[2\,|c_A + c_B|]$ is not a constant, and that the χ^0_{hybrids} used in equation (11) differ from compound to compound, neither of which is taken into account explicitly in equation (16). Thus the method of HANNAY and SMYTH is almost equivalent to ours for the diatomic molecules considered.

The present approach has the advantage that changes in the electronegativity of the bonding orbital of an atom in different molecules (such as carbon in ethane, ethylene and acetylene) can be accounted for, since χ, b and c can all be calculated for any normal valence states (*s*, *p*, *di*, *tr* and *te*) for the atoms under consideration, and for all intermediate hybridizations, readily estimated [*6*]. Whereas the Pauling χ are only valid for atoms whose bonding orbitals are of exactly the same hybridized character as in the molecules from whose dissociation energy the χ were derived.

The second advantage is that equation (11) is applicable to polyatomic and π-bonded systems. HINZE et al. [*6*] demonstrated that the effects of the groups A, B and C upon the electronegativity of the bonding orbital of atom R in ABCR- can be taken into account and equation (13) applied. The technique of handling polyatomic molecules has been generalized and simplified and the results for these together with π bonded systems will be given in the next paper. In general, it is concluded that the factor $|c_A + c_B|$ varies from molecule to molecule, substantiating previous qualitative arguments [*1*, *6*, *8*] that there can be no unique curve relating ionic character to electronegativity difference.

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