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Atomic and Group Electronegativities

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Abstract: A simple equation is presented which can be used to calculate the orbital electronegativity of any atom or group, viz., $\chi_A(\delta_{A,i}) = (1.67G_iz^2/n_e^2 + 0.41)(1 + 1.5\sum^R{}_{l=1}\delta_{A,l})$. $\chi_A(\delta_{A,i})$ is the electronegativity of orbital i on atom A, n_e and Z are Slater's effective principal quantum number and modified screened nuclear charge, G_i is a linear function of the % p character (p_i) of orbital i (i.e., $G_i = 1 - kp_i$, where k is a constant), $\delta_{A,l}$ is the charge on A from orbital l, and R is the number of bonds to atom A. For neutral atoms all $\delta_{A,l} = 0$ and the term in the second parentheses reduces to 1. Values calculated in this case correspond to the usual atomic electronegativities. It is shown that these values correlate very well with commonly accepted values for the whole periodic table. In the case of chemical groups $\delta_{A,l}$ is not in general equal to zero. A simple formalism is presented for calculating the $\delta_{A,l}$ which assumes both charge conservation and electronegativity equalization within each bond. This formalism and the above equation lead to a very simple relation for group electronegativity (χ_G): $\chi_G = (M + 1.5\delta_G)/\sum^M{}_{i=1}(1/\chi^\circ{}_{A_i})$. δ_G is the charge on the group, M is the total nmber of atoms, and $\chi_{A_i}{}^\circ$ is the electronegativity of atom A_i. It is shown that this equation also leads to very reasonable values for group electronegativity.

The concept of electronegativity has been one of the most useful explanatory devices in chemistry. Much of the earlier work in this area centered around the development and evaluation of methods that could be used to estimate specific values for atoms.[1-4] Three of the most popular of these are due to Pauling,[5] Mulliken,[6] and Allred–Rochow.[7] More recently, efforts have been directed toward elucidating and broadening the concept itself.[8-11] In particular the effect of hybridization has been emphasized and delineated as one consequence of an extensive series of calculations based on Mulliken's definition.[8] Also, the relation of electronegativity to the charge on the particular atom or group has been made more explicit.[10,12-14] These developments have increased the versatility and usefulness of the basic concept.[15-17]

The aim of the present paper is to provide an easily used calculational scheme which incorporates the effects of both hybridization and charge and also has a wide range of application. This is done by introducing a simple relation that can be used to calculate electronegativity values for any atom or group and that is consistent with current scales. The relation is based partly on a theoretical analysis by Klopman[9] and utilizes only atomic quantities that can be obtained from modified Slater's rules.

Background Theory

The modern history of electronegativity goes back to the original definition of Pauling as the power of an atom in a molecule to attract electrons to itself.[5] It was initially believed that this power is adequately given by a single values for each atom.[5] This interpretation allows for a simple and easily used scale. It has enjoyed much success as a correlational device.[1] However, it was found that more than one value was required for each atom.[6,8,19] In particular, electronegativity was found to depend on the valence state of the atom in the molecule of interest. Hinze et al. were able to account for the variations in electronegativity by redefining it in terms of atomic orbitals.[8] They argued that electronegativity is most reasonably interpreted as a potential, i.e., in terms of energy per charge, and thus postulated the definition

$$\chi_A(n_{A,i}) = \partial E_A/\partial n_{A,i} \tag{1}$$

where E_A is the energy of atom A and $\chi_A(n_{A,i})$ and $n_{A,i}$ are the electronegativity and occupation of orbital i, respectively. The appropriateness of using the potential point of view has been demonstrated by other investigators as well.[9-11]

In order to assign specific values using (1) it is necessary to express E_A as a function of $n_{A,i}$. This was assumed to be a quadratic function by Hinze in agreement with other work.[10] Thus, in the notation of Hinze et al., $\chi_A(n_{A,i})$ becomes

$$\chi_A(n_{A,i}) = b_A + c_An_{A,i} \tag{2}$$

in which b_A and c_A are constants.

Klopman provided theoretical support as well as clarification of the two constants b_A and c_A.[9] He defined $A_A(i,j)$ and $B_A(i)$ for atom A as

$$B_A(i) \int \phi^*{}_i(1)H_{\text{core}}(1)\phi_i(1) \tag{3}$$

$$A_A(i,j) = \int \phi^*{}_i(1)\phi_j{}^*(2)\phi_i(2)\phi_j(1)/r_{12} \tag{4}$$

where $\phi_i(1)$ refers to electron 1 in atomic orbital i on atom A and $H_{\text{core}}(1)$ is the energy operator acting on electron 1 in the field of the core. He assumed that $A_A(i,j)$ is the same for all electron pairs in the valence shell (i.e., A_A) regardless of the azimuthal quantum number. If it is further assumed that the exchange integral is negligible, the energy of the atom can be calculated very simply as

$$E_A = \sum_k n_{A,k}B_A(k) - (\sum_k n_{A,k} - 1)\sum_k n_{A,k}A_A/2 \tag{5}$$

where the summations are over the valence orbitals. Differentiation of (5) as given in (1) yields

$$\chi_A(n_{A,i}) = \partial E_A/\partial n_{A,i} = B_A(i) - \sum_k n_{A,k}A_A - A_A/2 \tag{6}$$

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For a neutral atom $\sum_k n_{\mathrm{A},k} = N$ (the number of valence shell electrons), and (6) reduces to

$$\chi^\circ_\mathrm{A}(n^\circ_{\mathrm{A},i}) = B_\mathrm{A}(i) - (N-1)A_\mathrm{A} - A_\mathrm{A}/2 \qquad (7)$$

where the superscript on χ and $n_{\mathrm{A},i}$ refers to the fact that the atom has no charge. Note that

$$B_\mathrm{A}(i) = s_i B_\mathrm{A}(\mathrm{s}) + p_i B_\mathrm{A}(\mathrm{p}) + d_i B_\mathrm{A}(\mathrm{d}) + \ldots \qquad (8)$$

where $B_\mathrm{A}(\mathrm{s})$, $B_\mathrm{A}(\mathrm{p})$, and $B_\mathrm{A}(\mathrm{d})$ refer to the core integrals for s, p, and d type orbitals and s_i, p_i, and d_i refer to % *s*, *p*, and *d* character in orbital *i*.

Equation 7 will be used in the present paper to calculate the electronegativity of an atomic orbital *i* of atom A. These values will then be interpreted to correspond to the electronegativity of the atom in any bond in which A uses the orbital *i*. Consistent with Hinze et al.,[12] this electronegativity will be taken as referring to the atomic orbital prior to any electron transfer.

In order for (7) to be useful, A_A and $B_\mathrm{A}(i)$ must be given values for each atom and orbital *i*. Klopman did this by using spectroscopic data.[9] In the present paper relations will be derived which will allow the elimination of explicit reference to $B_\mathrm{A}(i)$ from the equation and the expression of A_A and thus $\chi^\circ_\mathrm{A}(n^\circ_{\mathrm{A},i})$ in terms of a screened nuclear charge (z), an effective principal quantum number (n_e), and the hybridization of the orbital *i*. The following procedure will be used to do this. First results of an analysis of the data in Klopman's paper will be used to relate $B_\mathrm{A}(i)$ and A_A. This will allow the ionization potential of the orbital *i* to be expressed simply in terms of A_A and hybridization (eq 13). The same ionization potential will then also be expressed in terms of z, n_e, and hybridization (eq 18). The equating of these relations will then lead to the expressions for A_A and $\chi^\circ_\mathrm{A}(n^\circ_{\mathrm{A},i})$ (eq 22 and 23).

Atomic Electronegativity

Analysis of the data in ref 9 shows that the following relations hold to a high degree of precision (correlation coefficients >0.999):

$$B_\mathrm{A}(\mathrm{p}) = NA_\mathrm{A} - 0.71 \qquad (9)$$

$$B_\mathrm{A}(\mathrm{p}) = 0.85B_\mathrm{A}(\mathrm{s}) - 0.66 \qquad (10)$$

where again $B_\mathrm{A}(\mathrm{p})$ and $B_\mathrm{A}(\mathrm{s})$ refer to core integrals for p and s type orbitals, respectively.

According to Klopman[9]

$$I_\mathrm{A}(i) = B_\mathrm{A}(i) - (N-1)A_\mathrm{A} \qquad (11)$$

where $I_\mathrm{A}(i)$ is the ionization potential of orbital *i* on atom A. Combination of this with (9) and (10) gives

$$I_\mathrm{A}(i) = A_\mathrm{A}(1 + 0.17Ns_i) - 0.65p_i - 0.06 \qquad (12)$$

for s–p hybridized orbitals.

For the atoms of interest A_A ranges from about 3.6 eV for *K* to 16 eV for *F*. Thus, the 0.06 factor can be neglected in (12). The quantity $0.65p_i$ will also be neglected. This represents about an 18% relative error in the case of *K* which is quite large. In the case of electronegativity this would represent about 0.15 unit (in which *K* is 0.8). Although this is a somewhat large relative error, it is within the accuracy which can be reasonably expected when using the concept of electronegativity since values are typically uncertain by 0.1–0.2 unit.[12] In addition, the largest uncertainties occur in those cases of little chemical interest (i.e., p orbitals of alkali metals). Thus, (12) will be simplified to

$$I_\mathrm{A}(i) = A_\mathrm{A}(1 + 0.17Ns_i) \qquad (13)$$

Substituting (11) and (13) into (7) gives

$$\chi^\circ_\mathrm{A}(n^\circ_{\mathrm{A},i}) = A_\mathrm{A}(1 + 0.17Ns_i) - A_\mathrm{A}/2 \qquad (14)$$

I_A can also be approximated very simply in terms of a screened nuclear charge (z) and effective principal quantum number (n_e)[20]

$$I_\mathrm{A} = z^2/n_\mathrm{e}^2 \qquad (15)$$

where explicit reference to the orbital dependence has been suppressed temporarily.

Table I. Ionization Potential Data[a]

atom	I_A, eV	z^2/n_e^2	z^2/n_e^2 (mod.)
Li	5.39	0.42	0.36
Na	5.14	0.54	0.36
K	4.35	0.35	0.24
F	20.98	6.76	6.5
Cl	15.09	4.13	3.61
Br	13.72	4.22	3.28
I	12.61	3.61	2.81

[a] Data from ref 1. Comparisons of calculated and experimental data is intended to indicate trends.

Values for Z and n_e can be assigned in various ways. In the present case the primary interest is in ionization potential, and, therefore, z and n_e should be chosen with this in mind. If desired a whole set of values could be assigned to maximize the fit between z^2/n_e^2 and experimental I_A values. However, in the present case, it is considered important to be able to obtain z and n_e in a simple manner as well as being able to relate easily to other investigations. For these reasons the simple set of rules suggested by Slater[18] were chosen to estimate both z and n_e. Besides being easy to use the rules have been applied in many areas. As usual z will be calculated by accounting for all electrons except one. It will be necessary to modify these rules in two ways to make them more useful here.

First, it was found necessary to modify Slater's original rules in order to bring the I_A values more in line with experiment in several important cases, i.e., Cl vs. Br and Li vs. Na (see Table I for a comparison of trends). Assuming slightly greater shielding of valence electrons by core electrons was sufficient to rectify the discrepancies. Specifically, a value of 0.9 instead of 0.85 was used for the shielding of s and p type valence electrons by electrons with a principal quantum number less by one.[21] To illustrate consider Cl. Slater's original rules give $z = 17 - 2 - (8)(0.85) - (6)(0.35) = 6.1$ for a valence electron. The modified rules give $z = 17 - 2 - (8)(0.9) - (6)(0.35) = 5.7$. For Br, original and modified rules give $35 - 10 - (18)(0.85) - (6)(0.35) = 7.6$ and $35 - 10 - (18)(0.9) - (6)(0.35) = 6.7$, respectively. Note that this change does not affect the simplicity of the rules, and, since it only deals with valence electrons, it represents a small difference in final atomic energy values.

Second, it is well-known that the ionization potential is dependent on the hybridization of the electron's orbital.[6,8] This is easily seen on theoretical grounds simply because of differences in penetrating abilities of various orbitals. For simplicity it will be assumed that the ionization potential of intermediate hybrids can be obtained by linear interpolation, i.e.

$$I_\mathrm{A}(i) = s_i I_\mathrm{A}(\mathrm{s}) + p_i I_\mathrm{A}(\mathrm{p}) + d_i I_\mathrm{A}(\mathrm{d}) + \ldots \qquad (16)$$

and that

$$z^2/n_\mathrm{e}^2 = I_\mathrm{A}(\mathrm{s}) = K_\mathrm{p} I_\mathrm{A}(\mathrm{p}) = K_\mathrm{d} I_\mathrm{A}(\mathrm{d}) = \ldots \qquad (17)$$

where K_p and K_d are constants. Substituting (16) and (17) into (15) gives

$$I_\mathrm{A}(i) = (s_i + K_\mathrm{p}^{-1}p_i + K_\mathrm{d}^{-1}d_i + \ldots)z^2/n_\mathrm{e}^2 \cdot G_i z^2/n_\mathrm{e}^2 \qquad (18)$$

Both (13) and (18) can be used to calculate $I_\mathrm{A}(i)$. There should then exist a linear relation between them. Thus

$$A_\mathrm{A}(1 + 0.17Ns_i) = K_1 G_i z^2/n_\mathrm{e}^2 + K_2 \qquad (19)$$

where K_1 and K_2 are constants. For $s_i = (1/N)$, (19) is simplified. In the case of nontransition elements, $s_i = (1/N)$ corresponds closely to the % s character of an orbital in the usual valence state of the atom. Thus, the relation

$$1.17A_\mathrm{A} = K_1 G_i z^2/n_\mathrm{e}^2 + K_2 \qquad (20)$$

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[20] Slater, J. C. "Quantum Theory of Atomic Structure"; McGraw-Hill: New York, 1960; Vol. I.

[21] This changes rule 2c in ref 18 to read "If the shell is an s,p shell, 0.9 from each electron with principal quantum number less by one, and an additional 1.00 for each electron further in".

should hold for atoms in their normal valence states. Combining (20) and (14) gives

$$\chi^\circ_A = 0.57K_1G_iz^2/n_e^2 + 0.57K_2 \tag{21}$$

in which specific reference to $n^\circ_{A,i}$ has been suppressed. This will be done until the subject of group electronegativity is treated below. Relation 21 was fit to Pauling's electronegativity values for some elements in their common valence states.[5b] The following relation was obtained

$$\chi^\circ_A = 1.67G_iz^2/n_e^2 + 0.41 \tag{22}$$

This leads to values for K_1 and K_2 in (21) of 2.93 and 0.72, respectively. Putting these into (20) gives

$$A_A = 2.50G_iz^2/n_e^2 + 0.61 \tag{23}$$

The use of z in electronegativity calculations is not new. Two well-known relations that utilize a screened nuclear charge are due to Allred–Rochow[7] and Gordy[2]. These methods utilize the relations (z/r^2_{cov}) and (z'/r_{cov}), respectively, to calculate electronegativity. z is based on Slater's rules, z' utilizes rules devisd by Gordy, and r_{cov} is the covalent radius of the atom. Neither hybridization nor charge is dealt with explicitly in either scale. However, hybridization is implicit in r_{cov}. Recently, efforts have been made to treat charge in the Allred–Rochow framework.[22]

As with the Gordy and Allred–Rochow schemes, the usefulness of eq (22) in calculating electronegativity will depend on its ease of use, versatility, and ability to reproduce the data. The above described derivation is presented in order to relate the present scheme to past work to provide the groundwork for any future refinements as well as to allow it to be related to other investigations.

In obtaining (22) G_i was chosen so as to maximize the fit between (21) and the empirical data while maintaining the relation between the electronegativity of sp^3 hybridized carbon and p hybridized iodine as an approximate equality. This relation was chosen as a constraint because it is consistent with both Pauling's and Mulliken's scales and with the normally assumed hybridization of iodine. In addition it represents elements from two different rows of the periodic chart which helps to assure the applicability of eq (22) to the whole periodic table. It was found that

$$G_i = 1 - (0.56 + 0.11\delta_{2,n})p_i \tag{24}$$

where $\delta_{2,n} = 1$ for $n_e = 2$ and $\delta_{2,n} = 0$ otherwise. It was found necessary to introduce $\delta_{2,n}$ in order to make the electronegativity values for row 1 elements fall in line with the rest of the periodic chart. Relation 22 was also used to calculate electronegativity values for some noncommon s–p orbital hybrids as well as for d orbitals on transition elements.

As an example of the use of (22) consider the chlorine atom. In the calculation of the electronegativity of its s valence orbital $G_i = 1$ since $p_i = 0$ (i.e., $G_i = 1 - (0.56 + (0.11)(0))0 = 1$). z and n_e are 5.7 (i.e., $z = 17 - 2 - (8)(0.9) - (6)(0.35)$) and 3, respectively. Therefore

$$\chi^\circ_{Cl(s)} = 1.67(5.7/3)^2 + 0.41 = 6.45 \tag{25}$$

In the case of the Cl p orbital $p_i = 1$ and, therefore, $G_i = 1 - (0.56 + (0.11)(0)) = 0.44$. Since z and n_e remain the same

$$\chi^\circ_{Cl(p)} = 1.67(0.44)(5.7/3)^2 + 0.41 = 3.06 \tag{26}$$

For carbon sp^3 hybrid orbitals, $p_i = 0.75$. z and n_e are 3.15 $(6-(2)(0.9) - (3)(0.35))$ and 2, therefore,

$$\chi^\circ_{C(sp^3)} = 1.67(1 - (0.56 + 0.11)(0.75))(3.15/2)^2 + 0.41 = 2.47 \tag{27}$$

Table II. Atomic Electronegativities (Pauling Units)

atom	hybrid	$\chi_A^\circ(22)^a$	$\chi_A^\circ(\text{A–R})^b$	$\chi_A^\circ(\text{Paul.})^c$
H	s	2.08	2.10	2.1
Li	s	1.01	0.97	1.0
Be	sp	1.36	1.47	1.5
B	sp^2	1.85	2.01	2.0
C	sp^3	2.47	2.5	2.5
	s	4.55		(4.84)
N	sp^3	3.41		(3.86)
	p	2.40	3.07	3.0
O	s	8.68		(8.98)
	p	3.15	3.50	3.5
F	s	11.27		(10.33)
	p	4.00	4.10	4.0
Na	s	1.01	1.01	0.9
Mg	sp	1.21	1.23	1.2
Al	sp^2	1.55	1.47	1.5
Si	sp^3	1.91	1.74	1.8
P	p	1.99	2.06	2.1
S	p	2.49	2.44	2.5
Cl	s	6.45		(6.25)
	p	3.07	2.83	3.0
K	s	0.80	0.80	0.8
Ca	sp	0.93	1.04	1.0
Sc	d	1.20	1.20	1.3
Ti	d	1.26	1.32	1.5
Fe	d	1.55	1.64	1.8
Co	d	1.62	1.7	1.8
Ni	d	1.70	1.75	1.8
Cu	d	1.78	1.75	1.9
Zn	d	1.86	1.66	1.6
Ge	sp^3	2.01	2.02	1.8
Se	p	2.37	2.48	2.4
Br	s	5.89		(5.96)
	p	2.81	2.74	2.8
Y	d	1.08	1.11	1.2
Ru	d	1.39	1.42	2.2
Rh	d	1.45	1.45	2.2
Pd	d	1.52	1.35	2.2
Ag	d	1.58	1.42	1.9
Cd	d	1.65	1.46	1.7
Sn	sp^3	1.78	1.72	1.8
Te	p	2.09	2.01	2.1
I	s	5.11		(5.06)
	p	2.47	2.21	2.5
La	d	1.02	1.08	1.1
Os	d	1.29	1.52	2.2
Ir	d	1.35	1.55	2.2
Pt	d	1.41	1.44	2.2
Au	d	1.48	1.42	2.4
Hg	d	1.54	1.44	1.9
At	p	2.28	1.90	2.2

[a] Equation 22. [b] From ref 7. [c] From ref 5b. Values in parenthesis are not available in Pauling scale. They were calculated by using Mulliken's method; see ref 8.

When the electronegativity of d and f orbitals for transition elements is calculated, account is taken of the similarity in energy of these orbitals and the s orbital of the row in which they appear in the periodic table, e.g., $E_{A(3d)} = E_{A(4s)}$. z and n_e for these d and f orbitals will thus be taken as being equal to the values for the valence shell s orbital for that atom. In addition K_d and K_f in 18) will be assumed to be equal to 1. Using these assumptions allows the formalism to remain simple for the transition elements as well as being consistent with the data. As an example, consider the d orbital of the Fe atom. In this case z and n_e are 3.05 $(26 - 10 - (14)(0.9) - 0.35)$ and 3.7 which are the values for the outermost 4s shell. Since there is no p character in the orbital, $G_i = 1$. Therefore, $\chi^\circ_{Fe(d)} = 1.67(0.43)(3.05/3.7)^2 + 0.41 = 1.55$.

Results obtained by using (22) are given in Table II and Figure 1. The electronegativities in Figure 1 represent the entire range of values of interest. It can be seen that the overall fit is very good. It should be noted that the values for the d orbitals are also consistent with the other methods. This along with the ability to handle charge effects which will be discussed below should allow the present techniques to be useful in treating transition elements. Thus, relation 22 appears to hold for all hybrids and not only in cases where $s_i = (1/N)$.

This result appears somewhat surprising in light of (19). One possible explanation may lie in the fact that Klopman's analysis

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(22) Zhang, Y. *Inorg. Chem.* **1982**, *21*, 3886.

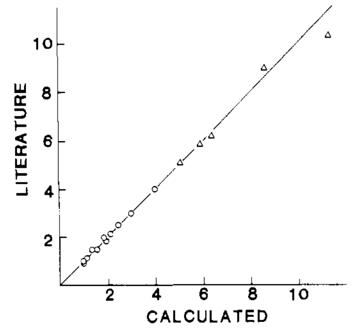

Figure 1. Calculated (see eq 22) vs. literature values of atomic electronegativity in Pauling units. The circles denote the atoms that were used in arriving at the regression parameters in (22). Triangles refer to predicted values.

assumes A_A to be independent of a azimuthal quantum number. The assumption represented by (19) appears to be somewhat better. This is supported by the data, e.g., in ref 13, in which A_A appears to behave more like (20) than a constant.

Note that the hybridization values listed in Table II are only for the orbital of interest. The present method does not account for differences in the other valence orbitals. Data contained in ref 8 show this effect to be of secondary importance. At this point it appears to be unnecessary to account for this effect because of the closeness of fit to literature values.

Group Electronegativity

One important application of the electronegativity concept is in the estimation of the electron-withdrawing ability of chemical groups. This application requires the ability to account for charges on the group. It will be shown that the present formalism can be generalized in a very simple manner to allow the calculation of group electronegativity. As with the atomic electronegativity, no input data will be required besides z, n_e, and p_i.

Upon bond formation between two atoms, charge is transferred from one atom to the other. In the case of a chemical group, charge is transferred to the central atom because of its bonds. In CH_3, for example, the charge is transferred to the C atom because of the CH bonds. The electronegativity of the group will then be the orbital electronegativity of the central atom suitably modified to account for its charge.

Thus, in order to calculate group electronegativity, (7) must be generalized to account for charge transfer that may occur in the bonded orbitals in the group. To do this first reconsider (6). In the ground state of the atom, $n_{A,k}$ of (6) takes the values 0, 1, or 2. In the valence state, some of these orbitals (k_b) are available for bonding and others (k_n) are not. For all of the k_b orbitals, $n_{A,k} = 1$ (i.e., the orbitals are half filled) before bonding occurs. Thus, (6) can be rewritten as

$$\chi_A(n_{A,i}) = B_A(i) - \sum_{k=1}^{k_n} A_A n_{A,k} - \sum_{1=1}^{k_b} A_A + A_A/2 \tag{28}$$

Once bonding occurs charge ($\delta_{A,l}$) is accumulated in the k_b orbitals as follows.

$$\chi(n_{A,i}) = B_A(i) - \sum_{k=1}^{k_n} A_A n_{A,k} - \sum_{l=1}^{k_b} (1 - \delta_{A,l}) A_A + A_A/2 \tag{29}$$

Equation 29 can be rearranged to

$$\chi_A(n_{A,i}) = B_A(i) - NA_A + A_A/2 + \sum_{l=1}^{k_b} A_A \delta_{A,l} \tag{30}$$

or by using (7),

$$\chi_A(n_{A,i}) = \chi_A{}^{\circ}(n_{A,i}{}^{\circ}) + \sum_{l=1}^{k_b} A_A \delta_{A,l} \tag{31}$$

This equation represents the general definition of orbital electronegativity within the approximate scheme used here. Note that it expresses the electronegativity as a linear relation of both atomic (or inherent) electronegativity and of charge. This is consistent with earlier work.[9,13] Substituting (22) and (23) into (31) gives

$$\chi_A(\delta_{A,i}) = (1.67 G_i z^2/n_e{}^2 + 0.41)(1 + \sum_{l=1}^{k_b} 1.5\delta_{A,l}) \tag{32}$$

in which specific functional dependence of χ has now been put in terms of $\delta_{A,i}$.

If atom A is the central atom of the group being considered (e.g., A is C in CH_3), then group electronegativity can be calculated from (32) by assigning one electron to obtial i on A (i.e., the one that is to be bonded) as is done in the case of the neutral atom before bonding (i.e., $\delta_{A,i} = 0$) and by accounting for the charge in the other valence orbitals. The values for the other $\delta_{A,l}$ on the atom can be calculated in a number of ways. In the case of σ bonded $-AB_R$ groups with R equivalent bonds it can be done in an approximate manner by equalizing the electronegativity of each atom in each bond.[13]

As an example consider CH_3. It can be assumed that the C atom will use an sp^3 hybrid orbital for each of its bonds. Thus, its atomic orbital electronegativity in all bonds will be 2.47 as shown in Table II and calculated above. H of course is 2.08. The unbonded orbital on C will be assigned an occupation of one. The other orbitals will have a charge due to the C–H bonding. Since all three are equivalent all of the $\delta_{C,l}$ are equal. Thus, $\delta_{C,l} = \delta_C/3$ for all 1 (where δ_C is the total charge on C), and

$$\chi_C(\delta_C) = 2.47(1 + 1.5\delta_C) \tag{33}$$

If charge conservation is assumed to hold in the C–H bonds, i.e., $\delta_C/3 + \delta_H = 0$, then $\delta_H = -\delta_C/3$ and $\chi_H(\delta_H)$ can be expressed in terms of δ_C as

$$\chi_H(\delta_H) = 2.08(1 - 1.5\delta_C/3) \tag{34}$$

In order to obtain a value for δ_C another constraint is required. For this purpose the electronegativity equalization principle will be used. In the present case this becomes $\chi_H(\delta_H) = \chi_C(\delta_C)$. This principle was first suggested by Sanderson[23] and has been used with good results.[13] Although it is well-known that it neglects electrostatic and resonance energy terms,[24,25] Huheey has shown that it functions quite well for most cases of interest.[13] With this assumption δ_C can be calculated from the relation

$$\chi_C(\delta_C) = 2.47(1 + 1.5\delta_C) = 2.08(1 - 1.5\delta_C/3) = \chi_H(\delta_H) \tag{35}$$

which leads to $\delta_C = -0.081$. The group electronegativity is then equal to the electronegativity of the C orbital to be bonded, i.e.

$$\chi_{CH_3}(\delta_{C,i} = 0) = 2.47(1 - 1.5(0.081)) = 2.17 \tag{36}$$

This procedure can be generalized to cover any group. For the group $-A_1...A_S$ which contains S atoms and m bonds with the atom A_1 as the one to be bonded, the group electronegativity will be calculated in the following manner.

(1) For each bond i between atoms A_k and A_l, the charges $\delta_{A_k,i}$ and $\delta_{A_l,i}$ will be obtained by assuming both charge conservation and electronegativity equalization in i, i.e.

$$\delta_{A_k,i} + \delta_{A_l,i} = 0 \tag{37}$$

and

$$\chi^{\circ}{}_{A_k}(1 + \sum_{p=1}^{P} 1.5\partial_{A_k,p}) = \chi^{\circ}{}_{A_l}(1 + \sum_{q=1}^{Q} 1.5\partial_{A_l,q}) \tag{38}$$

where atom A_k has P bonds and A_l has Q.

(2) The electronegativity of $-A_1...A_S$ will be obtained by using (32) with the calculated values for $\delta_{A_1,k}$ and also the assignment of 0 charge for the orbital to be bonded. If A_1 has R bonds this gives

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(23) Sanderson, R. T. *Science (Washington, D.C.)* **1951**, *114*, 670.
(24) Reed, J. L. *J. Phys. Chem.* **1981**, *85*, 148.
(25) Evans, R. S.; Huheey, J. E. *J. Inorg. Nucl. Chem.* **1970**, *32*, 373.

$$\chi_{-\mathrm{A}_1\ldots\mathrm{A}_S}\ (\delta_{\mathrm{A}_1,i} = 0) = \chi^\circ{}_{\mathrm{A}_1}(1 + \sum_{k=1}^{R} 1.5\delta_{\mathrm{A}_1,k}) \qquad (39)$$

Note that (39) can also be written as

$$\chi_{-\mathrm{A}_1\ldots\mathrm{A}_S} = \chi^\circ{}_{\mathrm{A}_1}(1 + 1.5\delta_{\mathrm{A}_1}) \qquad (40)$$

where δ_{A_l} is the total charge on A_1. In this notation (38) becomes

$$\chi^\circ{}_{\mathrm{A}_k}\ (1 + 1.5\delta_{\mathrm{A}k}) = \chi^\circ{}_{\mathrm{A}_l}(1 + 1.5\delta_{\mathrm{A}_l}) \qquad (41)$$

Since (41) is true for all bonds then all of the atomic orbital electronegativities in $-\mathrm{A}_1\ldots\mathrm{A}_S$ must be equal to the same electronegativity, i.e., $\chi_{-\mathrm{A}_1\ldots\mathrm{A}_S}$. Thus, for all A_i

$$\chi^\circ{}_{\mathrm{A}_l}(1 + 1.5\delta_{\mathrm{A}i}) = \chi_{-\mathrm{A}_1\ldots\mathrm{A}_S} \qquad (42)$$

But this equation cannot in general be satisfied if any atom A_i takes part both in a σ and a π bond (e.g., in C═O). This is because in general $\chi_{\mathrm{A}_{i\sigma}} \neq \chi_{\mathrm{A}_{i\pi}}$ which means that $\delta_{\mathrm{A}i}$ would have to simultaneously satisfy two different equations like (42) which is impossible. Thus, these rules can only be used with groups that contain atoms that use equivalent orbitals in all of their bonds (e.g., CH_2CH_3). This problem is common to other electronegativity schemes of this type.[24,26] The solutions suggested in these references will likewise work in the present formalism. This problem as well as others stemming from the electronegativity equalization postulate[13] will be treated within the present scheme in a separate paper. The approach will be to consider two factors; first, the effect of hybridization of the other valence orbitals, and second, the possibility of charge transfer between bonds.

For the class of groups that can be treated, the above rules lead to the following very simple result,[27]

$$\chi_G = M/\sum_{i=1}^{M}(1/\chi^\circ{}_{\mathrm{A}_i}) \qquad (43)$$

where M is the total number of atoms in the group G. If the unbonded orbital is allowed to have a charge (i.e., if rule 2 above is relaxed) then electron rearrangement will occur in the rest of the bonds so that the whole group can be regarded as having the charge, i.e.

$$\delta_G = \sum_{i=1}^{M}\delta_{\mathrm{A}i} \neq 0 \qquad (44)$$

where δ_G is the charge on the group. In this case rule 1 above leads to[27]

$$\chi_G = (M + 1.5\delta_G)/\sum_{i=1}^{M}(1/\chi^\circ{}_{\mathrm{A}_i}) \qquad (45)$$

To illustrate these results consider $CH_2CH_2CH_3$. Since there are 10 atoms (i.e., 3-C and 7-H), $M = 10$. Using the electronegativity values from Table II gives

$$\chi_{\mathrm{CH_2CH_2CH_3}} = (10 + 1.5\delta_{\mathrm{CH_2CH_2CH_3}})/(7(1/2.08) + 3(1/2.47)) = 2.18 + 0.33\delta_{\mathrm{CH_2CH_2CH_3}} \qquad (46)$$

In the case of CH_3

$$\chi_{\mathrm{CH_3}} = (4 + 1.5\delta_{\mathrm{CH_3}})/((1/2.47)+(3/2.08)) = 2.17 + 0.81\delta_{\mathrm{CH_3}} \qquad (47)$$

For $\delta_{\mathrm{CH_3}} = 0$, this reduces to the neutral group value, i.e., $\chi_{\mathrm{CH_3}} = 2.17$, which was obtained above.

The first term on the right hand side of (4) (which is the same as the term on the right hand side of (43)) can be called the inherent electronegativity of the group. This is simply the reciprocal of the average reciprocal atomic or orbital electronegativity of the atoms comprising the group. Thus, this equation lends support to averaging techniques such as for example, Sanderson's.[23] The coefficient of δ_G is of course the charge coefficient term. Both of these terms are important when interpreting group behavior. This has not always been appreciated with regard to the charge coefficient.[13]

Table III. Group Electronegativities (χ_G) and Charge Coefficients (*b* following Huheey[13]) in Pauling Units

	present work[a]		Huheey[b]	
group	χ_G	*b*	χ_G	*b*
BeF[c]	2.03	1.52	2.16	1.77
BeCl	1.88	1.41	2.02	1.53
BeBr	1.83	1.37	1.94	1.41
BeI	1.75	1.31	1.91	1.39
BeH	1.65	1.24	1.89	1.60
MgF[c]	1.86	1.40	1.87	1.50
MgCl	1.74	1.31	1.79	1.32
MgBr	1.69	1.27	1.73	1.23
MgI	1.63	1.23	1.70	1.22
MgH	1.53	1.15	1.50	1.38
BF_2[d]	2.88	1.44	2.92	1.49
BCl_2	2.51	1.26	2.55	1.17
BBr_2	2.40	1.20	2.38	1.04
BI_2	2.22	1.11	2.30	1.02
BH_2	2.00	1.00	2.09	1.26
CF_3[e]	3.46	1.30	3.46	1.35
CCl_3	2.89	1.09	2.84	0.98
CBr_3	2.72	1.02	2.59	0.85
CI_3	2.47	0.93	2.51	0.83
CH_3	2.17	0.82	2.27	1.09
CH_3CH_2	2.18	0.47	2.28	0.62
CF_3CF_2	3.40	0.73	3.40	0.77
SiF_3[e]	3.14	1.18	3.35	1.30
$SiCl_3$	2.66	1.00	2.78	0.96
$SiBr_3$	2.52	0.95	2.54	0.83
SiI_3	2.31	0.87	2.46	0.81
SiH_3	2.04	0.77	2.21	1.06
GeF_3[e]	3.20	1.20	3.25	1.05
$GeCl_3$	2.71	1.02	2.79	0.82
$GeBr_3$	2.56	0.96	2.58	0.72
GeI_3	2.34	0.88	2.51	0.71
GeH_3	2.06	0.77	2.32	0.88
SnF_3[e]	3.05	1.14	3.11	0.90
$SnCl_3$	2.59	0.97	2.73	0.72
$SnBr_3$	2.46	0.92	2.55	0.65
SnI_3	2.25	0.84	2.49	0.64
SnH_3	2.00	0.75	2.32	0.78
NF_2[e]	3.78	1.89	3.64	1.81
NCl_2	3.17	1.59	3.14	1.35
NH_2	2.39	1.20	2.61	1.50
OF[e]	4.24	3.18	4.14	2.92
OBr	3.46	2.60	3.40	2.09
OH	2.85	2.13	3.51	2.50
SH[f]	2.27	1.70	2.32	1.90

[a] Equation 32. [b] From ref 13. [c] Central atom bonding orbitals all sp hybrids. [d] All sp^2 hybrids. [e] All sp^3. [f] All p.

One illustration of its usefulness which can be easily derived from (45) and the two examples is the following. The more atoms in the group the smaller the charge coefficient. This is easily seen by noting that more atoms make the denominator larger by adding more terms. This in turn reduces the coefficient of δ_G. This result means that the present scheme predicts that larger groups will donate (or absorb) electrons more readily than smaller groups when bonded to atoms or groups with greater (or lesser) inherent electronegativity. This is in agreement both with previous calculational and experimental results.[13,16] In the case of electron donation this is simply the well-known inductive effect. With electron absorption this result (a generalization of the inductive effect) is able to explain acidity data as shown in ref 16.

It should be noted that an equation of the same form as (45) has been derived previously starting from an atomic electronegativity equalization principle rather than the bond orbital electronegativity equalization method used here.[24] If the inherent atomic electronegativity and atomic charge coefficient terms of ref 24 are set at $\chi^\circ{}_{\mathrm{A}}$ and $1.5\chi^\circ{}_{\mathrm{A}}$ as in the present work then exactly the same equation results.

Table III compares both electronegativity and charge coefficient values obtained according to this method with values calculated

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[26] Huheey, J. E. *J. Phys. Chem.* **1966**, *70*, 2086.

[27] Equations 43 and 45 are easily derived by combining (42) and (44). $\delta_G = 0$ leads to (43) and $\delta_G \neq 0$ to (45).

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by using the method developed by Huheey.[13] It can be seen that as in the case of atoms group electronegativity values are also reproduced well. It can also be seen that the charge cofficients are well correlated with Huheey's values. Note, for example, CF_3 vs. CF_2CF_3; even though the electronegativity values are similar for both species the charge coefficients vary. But they do so in exactly the same manner in both schemes. One case in which the two schemes consistently differ is with regard to the charge coefficient of H containing groups. It can be seen that Huheey's values are greater in all cases considered. The reason for the difference lies in the different values for the charge coefficient for the H atom in each scheme (Huheey = 4.32, present method = 3.12). In these cases Huheey's values are expected to correlate better with experimental data since they are based on measured values for ionization potential and electron affinity for H.

Summary

A general relation, i.e., (32), has been derived which can be used to calculate electronegativity of any atomic orbital in any bonding situation. In the case of neutral atoms all $\delta_{A,l}$ of (32) are equal to 0 and (32) reduces to (22). In the case of groups the $\delta_{A,l}$ values are in general not equal to 0 for the bonded orbitals. In order to calculate group electronegativity these $\partial_{A,l}$ values must be evaluated. To do this two constraints must be placed on each bond (since there are two unknowns per A–B bond, i.e., $\delta_{A,l}$ and $\delta_{B,l}$). In the present paper these are chosen as the conservation of charge, i.e., $\delta_{A,l} + \delta_{B,l} = 0$, and the electronegativity equilization principle, i.e., $\chi_A(\delta_{A,l}) = \chi_B(\delta_{B,l})$. Once the $\delta_{A,l}$ values are calculated, they are substituted into (32 along with $\delta_{A,l} = 0$ (i.e., the orbital to be bonded has one electron prior to bonding) to give the group electronegativity. This formalism also leads to a very simple relation (equation 45) that can be used to calculate the electronegativity of groups in which each atom utilizes the same type of orbital for each of its bonds.

With these relations both atomic and group electronegativities are easily calculable in terms of orbital hybridization and modified Slater's screened nuclear charge and effective principal quantum number. Not only is the method simple to use but it is also readily related to theoretical concepts and thus can be made more precise as well as being useful in a wider area.

Carbene and Silylene Insertion Reactions. Ab Initio Calculations on the Effects of Fluorine Substitution

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Abstract: The insertion reactions of CH_2, CHF, CF_2, SiH_2, SiHF, and SiF_2 into hydrogen molecule have been investigated by ab initio molecular orbital methods. Reactants, loose clusters, transition structures, and products were optimized at HF/3-21G and HF/6-31G*. For each structure, relative energies have been calculated at MP4SDQ/6-31G* and vibrational frequencies at HF/3-21G. A dramatic increase in the barrier height is seen with fluorine substitution: 8, 64, and 197 and 51, 130, and 273 kJ mol^{-1} for CH_2, CHF, and CF_2 and SiH_2, SiHF, and SiF_2, respectively, at MP4SDQ/6-31G*//HF/6-31G* plus ΔZPE. An orbital interaction interpretation is given for the trend in barrier heights, and implications for the chemistry of carbenes and silylenes are discussed.

Carbenes have long attracted the attention of experimentalists[1] and theoreticians.[2,3] For silylenes, there has recently been a surge of interest, both as second-row analogues of carbenes and as reactive intermediates in organosilicon chemistry.[4] A wide variety of silylenes can be generated by flash photolysis and vacuum pyrolysis of silanes, halosilanes, and alkylsilanes.[4] Silylenes are also throught to be important constituents in the chemical vapor deposition of amorphous silicon films from SiH_4[5] and possibly also from SiF_4. In addition, silylenes can be formed by rearrangement of unsaturated and/or cyclic organosilicon compounds;[6] because of silicon's reluctance to form multiple bonds, such rearrangement are often thermoneutral or exothermic.[7]

The parent silylene, SiH_2, and simple substituted silylenes (SiHX, X = OH, F, Cl, Br, I, CH_3, SiH_3; SiX_2, X = F, Cl, Br, I) have been studied experimentally in some detail.[8] The ground states are invariably closed shell singlets with sharply bent geometries ($\angle$XSiY ca. 95°); some excited-state singlets and triplets have also been characterized.[8] Vibrational frequencies are available for ground and excited states of SiH_2, SiHF, and SiF_2 (among others) from matrix isolation studies and electronic spectra.[13-15] Schaefer et al.[16] have recently carried out extensive ab initio calculations on these species and obtained excellent agreement with experiment.

Once formed, silylenes can react by abstraction, dimerization, disproportionation, cycloaddition, and insertion.[4] Insertion reactions of SiH_2 have been observed with H_2, Si–H, and Si–Si bonds. In contrast, SiF_2 is surprisingly inert in the gas phase,[9]

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