The Periodic Electronegativity Table

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The origins and development of the electronegativity concept as an empirical construct are briefly examined, emphasizing the confusion that exists over the appropriate units in which to express this quantity. It is shown how to relate the most reliable of the empirical scales to the theoretical definition of electronegativity in terms of the quantum potential and ionization radius of the atomic valence state. The theory reflects not only the periodicity of the empirical scales, but also accounts for the related thermochemical data and serves as a basis for the calculation of interatomic interaction within molecules. The intuitive theory that relates electronegativity to the average of ionization energy and electron affinity is elucidated for the first time and used to estimate the electron affinities of those elements for which no experimental measurement is possible.

Key words: Valence State, Quantum Potential, Ionization Radius

Introduction

Electronegativity, apart from being the most useful theoretical concept that guides the practising chemist, is also the most bothersome to quantify from first principles. In historical context the concept developed in a natural way from the early distinction between antagonistic elements, later loosely identified as metals and non-metals, and later still as electropositive and electronegative elements, classified as a function of their periodic atomic volumes [1].

Lothar Meyer's atomic volume curve, in its modern form, which shows atomic volume as a function of atomic number, still provides one of the most convincing demonstrations of elemental periodicity and an equally clear exposition of atomic electronegativity.

Atomic volume, computed as $V = M/\rho$ from gram-atomic mass and the density of solid elements, is plotted against atomic number. Instead of connecting all points in sequence of Z, the curve, in Fig. 1, is interrupted at those points where completion of s, p, d and f energy levels are known to occur. By this procedure the curve fragments into regions made up of either 2 or 8 elements, except in the rare-earth domain. Taken together with the preceeding couple of elements, Cs and Ba, a break at Sm divides this domain into two eight-member segments at an obviously special point on the curve. All segmented regions now occur in strict alternation as negatively and positively sloping curves. This is exactly the basis on which electropositive and electronegative elements used to be distinguished traditionally [1].

This theoretical notion, in one form or the other, has survived into the present, where, as will be shown, it provides a precise definition of electronegativity. Electronegativity scales that fail to reflect the periodicity of the L-M curve will be considered inappropriate.

The Pauling Scale

The first known attempt to quantify electronegativity was made by Pauling, who devised an empirical scale, on the basis of thermochemical data [2]. It relies on the simple idea that an *electrovalent* linkage between a pair of electropositive and electronegative atoms results from the transfer of an electron between the two:

$$e.\,g. \quad \text{Na} + \text{Cl} \rightarrow \text{Na}^+\text{Cl}^-$$

whereas a *covalent* linkage between a homopolar pair requires equal sharing of two electrons:

$$e.\,g. \quad \text{Cl} \cdot + \cdot \text{Cl} \rightarrow \text{Cl:Cl}$$
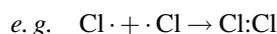
All possible diatomic combinations, AB, correspond to situations between the two extremes. The larger the difference in electronegativity, $|x_A - x_B|$, the larger is the electrovalent component that stabilizes the linkage, and the smaller the covalent contribution. In thermochemical terms [3] – page 88:
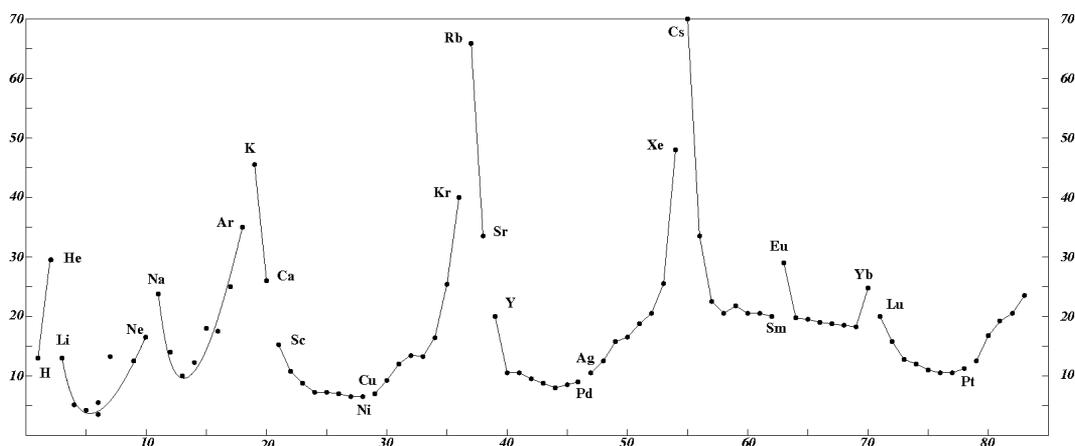
Fig. 1. Modern version of Lothar Meyer's atomic volume curve.

the values of the difference between the energy D(A-B) of the bond between two atoms A and B and the energy expected for a normal covalent bond, assumed to be the arithmetic mean or the geometric mean of the bond energies D(A-A) and D(B-B), increase as the two atoms A and B become more and more unlike with respect to the qualitative property that the chemist calls *electronegativity*, the power of an atom in a molecule to attract electrons to itself.

To hold for both definitions of the covalent mean it is assumed that, ideally

$$\frac{1}{2}\left(D_{AA}+D_{BB}\right)=\sqrt{D_{AA}\cdot D_{BB}}$$

or squared:

$$D_{AA}^2+D_{BB}^2-2D_{AA}\cdot D_{BB}=0 \text{ or } \Delta_{AB}^2$$

such that $\Delta = 0$ for $A = B$, or $\Delta = |x_A - x_B|^2$ for $A \neq B$, defining $(x_A - x_B) = \sqrt{|D_{AA} - D_{BB}|}$. The well-known Pauling scale of electronegativities results from this definition on specifying dissociation energies in units of eV[1].

Some secondary notions, popular in the Pauling era, such as "the extra resonance energy that results from the partial ionic character of the bonds between unlike

atoms", have only clouded the issue, without adding anything to the basic idea.

Alternative Definitions

The intuitive (Mulliken) redefinition of electronegativity [4] as the average of the ionization potential and electron affinity of an atom caused endless confusion in subsequent interpretations and stimulated the development of several alternative scales, in conflict with the central concept.

Although the Mulliken definition

$$\chi_M(A)=\frac{1}{2}\left(I_A+E_A\right)$$

expresses electronegativity as an energy, rather than its square root as in the Pauling definition, it was casually accepted that there is a linear relationship between the two scales, as in [5]:

$$\chi_M=3.15\chi_P$$

Assuming [6], by disregarding dimensional arguments, that the Pauling electronegativity of an atomic species S is specified by $\chi_S = (I_S + A_S)/2 = -\mu$, it is assumed, effectively defined as measuring the escaping tendency of electrons from S. Its negative, $-\mu$, is the chemical potential of the electrons.

Gordy

A more precise definition of an electronegativity energy function, as the surface potential at atomic covalent boundaries, was proposed by Gordy [7]. The

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[1]In later work [3] Pauling used a value of 30 instead of the factor 23 that converts kcal mol^{-1} into eV.

method defined the absolute electronegativity of a neutral atom in a stable molecule as the potential energy $Z_f e/r$, where Z_f is the effective charge of an atomic core acting on a valence electron at a distance equal to the covalent radius from the nucleus. By separating the valence shell from the core, it is assumed that the effective positive charge of the core is equal in magnitude to the electronic charge of the valence shell. On this basis Gordy assumed that any valence electron is screened from the core by a constant factor, k, for each of the other valence electrons. Hence

$$Z_f = n - k(n-1) = k(n+1)$$

where n counts the number of electrons in the valence shell. The formula

$$\chi = 0.31 \left(\frac{n+1}{r} \right) + 0.50$$

produced values to match the Pauling scale. The numerical match may be reasonable, but the meaning of the proportionality constants is unclear.

Dimensionally the quantity Z_f cannot represent an electric charge, which requires $\chi \propto 1/\sqrt{r}$ [8], but rather some empirical factor that defines electronegativity as a function of atomic size, $(1/r)$.

Allred and Rochow

The universally respected, routinely cited [9] and widely used electronegativity scale of Allred and Rochow [10] (AR):

$$\chi = 0.359 \frac{Z_f}{r_{cov}^2} + 0.744$$

is of the same type. In this case Z_f is obtained from the screening factor between the nucleus and an external electron, at the surface of the covalent sphere, calculated with Slater's rules [11]. The two extra constants that seem to convert a force into the square root of energy, are neither explained nor interpreted.

Contrary to popular belief the AR scheme matches the Pauling scale [3] only for the elements Li – C, after which point it becomes increasingly out of register, particularly for the transition series. Up to atomic number 83 there are only 12 (accidental) exact matches and beyond $Z = 54$ there is no recognizable qualitative agreement. The common notion that electronegativities, calculated by the AR formula, define the Pauling scale is therefore not supported by the evidence.

The Pauling scale measures the square root of an energy and the AR scale measures a force. Simple dimensional analysis shows that the two scales are related by a factor K, with dimensions such that:

$$K \cdot M^{1/2} L T^{-1} = M L T^{-2}$$

Charge, measured in coulomb, has dimensions $C = M^{1/2} L^{3/2} T^{-1}$, which means that K has dimensions $C L^{-3/2}$, or in terms of volume (L^3), $C V^{-1/2} = (C^2 V^{-1})^{1/2}$. The quantity in parentheses denotes the product of a charge q_1 and a charge density q_2/V, related to the screening assumption.

Instead of using this relationship to relate the two scales, Allred [12] recalculated all thermochemical electronegativities using an extended data set with comprehensive cross-reference between different diatomic combinations in molecules. This exercise provided ample proof that there is no consistency within the thermochemical scale. As an example, the independently calculated χ values for the elements F, Cl, Br and I fluctuate over the ranges 3.88 – 4.12, 3.04 – 3.36, 2.86 – 3.05, and 2.44 – 2.78 units, respectively; an average spread of 0.27 units. The overall effect is an increased discrepancy between the (AR) force-scale and the thermochemical Pauling scale. The alternative values for gold are 1.4 and 2.54 units.

A Common Scale

Countless efforts to establish a common electronegativity scale have been reported in the literature, without success. As consensus compromise the AR and Pauling scales have been afforded some standing as those which all competing scales are obligated to match [13]. It is hardly surprising that, under this self-imposed constraint, no independent, more logical, definition of electronegativity has emerged.

In reality, both scales are simply too erratic and unreliable to serve as a benchmark to guide theoretical modelling. On Pauling's scale there are too many criteria at play: bond energy or bond dissociation energy; arithmetic mean or geometric mean; different ligands around the central bond of interest; different oxidation states; standard state or valence state; molecular geometry – all of these variables have been implicated as environmental factors that could affect the estimate of atomic electronegativity in molecules. The AR scale, empirically based on variable single-bond covalent radii, is hardly more secure, but somewhat

more regular as a periodic function, compared to the Pauling scale.

The simple truth is that the state of any atom within a molecule depends too critically on its special environment to support the idea of an atom with fixed electronegativity in all molecules. An alternative is to consider the valence state of a free atom as reference; more precisely, the first activated state of a neutral atom, before it enters into chemical interaction with another atom, electron or molecule. To demonstrate the validity of such theory it is not necessary to reproduce any of the empirical scales in exact detail. However, there should be strong qualitative agreement.

The Quantum-Potential Scale

The theoretical basis of electronegativity was identified before [14] as the ground-state energy E_g of a free valence-state electron, confined to its first ionization sphere. In order to avoid dimensional conflict, absolute electronegativity may be defined equally well as the square root, $\sqrt{E_g}$, of the valence-state confinement energy, which, by definition, should relate to AR electronegativities by $\chi_v = \chi_{AR}/K$.

Confinement energies are calculated directly from atomic ionization radii, r_0, obtained by Hartree-Fock-Slater simulation of uniform compression of atoms [15] under the modified boundary condition $\lim_{r \to r_c} \psi = 0$, in which $r_c < \infty$. Increased pressure is simulated by decreasing the critical radius r_c of the impenetrable sphere.

The simulation consists of multiplying all one-electron wave functions by the step function

$$S = \exp\left[-\left(\frac{r}{r_c}\right)^p\right], \text{with } p \gg 1$$

as part of the iterative procedure.

Simulated compression results in raising all electronic energy levels. Interelectronic interaction leads to internal transfer of energy such that a single electron eventually reaches the ionization limit on sustained compression. At this point there is zero interaction between the ionized valence electron and the atomic core, although the valence electron remains confined to a sphere of radius r_0. The ground-state energy of a confined particle amounts to

$$E_g = \frac{h^2}{8mr_0^2}$$

With energies in eV and radii in Å units the numerical value of the operational quantity $\sqrt{E_g} = 6.133/r_0$. The state of such a confined particle is awkward to explain by conventional quantum theory, but is readily understood in the Bohmian interpretation that describes the energy E_g, which derives from compressive work, as pure quantum potential energy [16]:

$$V_q = -\frac{h^2 \nabla^2 R}{8\pi^2 mR}$$

Rearranged into the more familiar form of Schrödinger's amplitude equation:

$$\nabla^2 R + \frac{8\pi^2 m}{h^2} V_q R = 0$$

it correctly describes the confined particle, providing $V_q = E_g = h^2/8mr_0^2$ and R is the zero-order spherical Bessel function with first zero at r_0.

Since r_0 is characteristic of each atom, characteristic energies are predicted for atomic valence-state electrons. It is the atomic equivalent of the Fermi energy of an electron at the surface of the Fermi sea in condensed phases, and in that sense represents the chemical potential of the valence electron for each atom. Electronegativity has been defined [6] in almost identical terms before.

Relating E_g to electronegativity provides the theoretical basis of this concept, derived non-empirically and without assumptions from first principles. It is a function of the electronic configuration of atoms only and emerges naturally as the response of an atom to its environment. It is indeed the tendency of an atom to interact with electrons and the fundamental parameter that quantifies chemical affinity and bond polarity. It is precisely "the average one-electron valence shell energy of a ground-state free atom" that Allen proposed [17] as the third dimension of the periodic table.

Valence-state electronegativity

Two independent sets of ionization radii for all atoms have been calculated [15, 16] using exponential parameters $p = 20$ and 100, respectively. In both cases a clear periodic relationship appears, but the values at $p = 100$ are consistently lower. This difference reflects the steepness of the barrier that confines the valence electron, shown schematically in Fig. 2.

In a chemical environment the barrier is unlikely to be infinitely sharp and there should be some optimum value of p that describes the situation best. The choice
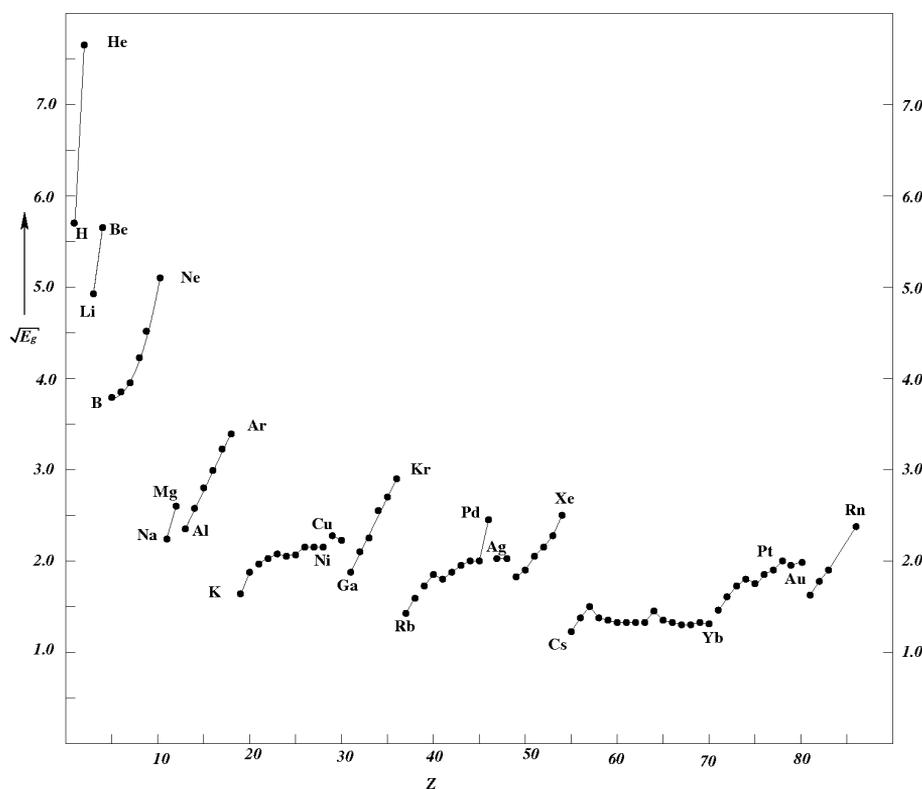
Fig. 3. Periodic variation of $\chi_v = \sqrt{E_g}$ as a function of atomic number.
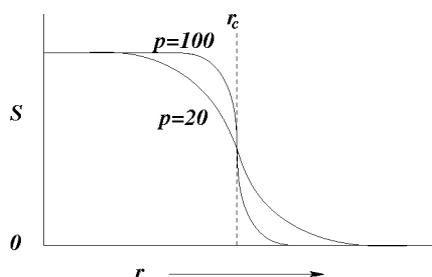

Fig. 2. The schematic representation of the step function $S = \exp[-(r/r_c)^p]$.

of $p = 20$ was established by comparison with independent chemical evidence that relates to ionization radii. A set of atomic radii, derived as an estimate to describe a single valence electron, uniformly spread over a characteristic sphere for each atom, has been known for a long time [18]. These radii were fixed by the assumption that electrostatic interaction between such uniform charge distributions, surrounding monopositive atomic cores, should correspond to the experimental values of binding energy for any pair of atoms.

The agreement between these empirically estimated atomic radii and those calculated by uniform compression ($p = 20$) is quite remarkable, considering the totally unrelated criteria used in the two cases.

The idea of relating E_g to electronegativity is further supported by the interesting correspondence that it shows with atomic first ionization potentials [19]. On average

$$I_P/E_g = 0.42n$$

where n is the number of the row in the periodic table in which the atom occurs. This relationship allows a fair estimate of radii in cases of uncertainty, e. g. for light elements like He.

It is instructive to examine the periodic variation of valence-state electronegativities $\chi_v = \sqrt{E_g}$ shown in Fig. 3. The sequence, as a function of atomic number, fragments spontaneously into the same segments as Lothar Meyer's atomic volume curve[2].

All segments, in this case, have positive curvature, sloping towards the origin on the left and towards closed-shell configurations on the right. The qualitative

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[2]This observed periodicity is best described in terms of the compact periodic table of the elements dictated by simple number theory [20].
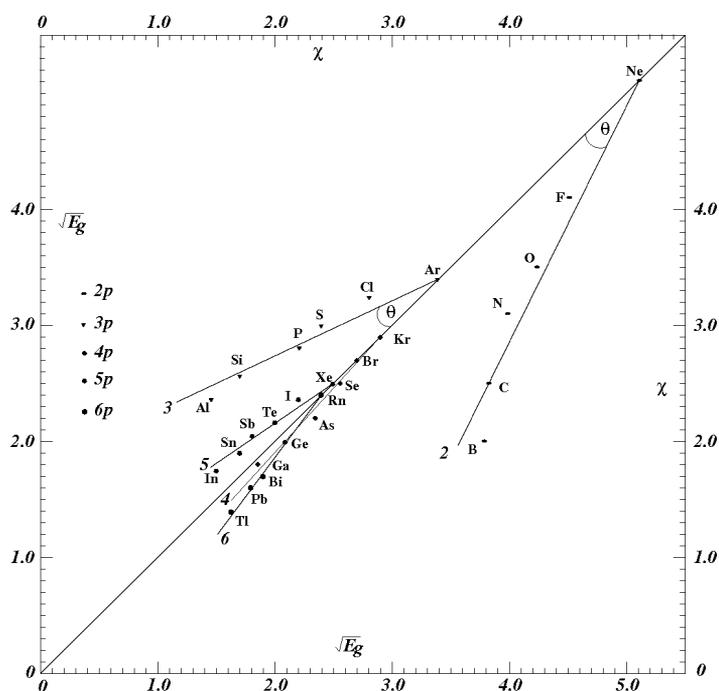
Fig. 4. Relationship between valence-state and Pauling electronegativity for p-block elements. To avoid serious cluttering, the even and odd-numbered periodic rows of elements are plotted separately in two halves of the diagram, by swopping around the coordinate axes. Arranged in this way the only line, which the two half-plots have in common, is the central diagonal. The coordinates of the noble gases are on this diagonal. The same device is used in Fig. 5.

trends are immediately recognized as closely related to the known empirical trends of electronegativity scales. The slope of these curves, at an atomic position, represents the change in energy as a function of atomic number (electron count), and defines the chemical potential of the electrons, $dE/dN = -\mu$, at that point. When the AR scale is plotted on the same graph there is exact agreement with χ_v only at the positions of the closed-shell noble gases.

Derivation of a common scale

Convincing linear relationships between χ_{AR} and χ_v could be demonstrated immediately for all periodic families with p valence shells. In all cases, Fig. 4, graphs of $\sqrt{E_g}$ *vs* χ_{AR} terminate in noble gas positions, on the line $\sqrt{E_g} = \chi_{AR}$, and so provide well-defined fixed points on each straight line.

For s-block[3] sequences, consisting of only two members apiece, linear trends are more difficult to spot. The most convincing straight lines are those that converge on closed-shell arrangements at the origin, rather than noble gas coordinates on the 1 : 1 diagonal, as shown in Fig. 5.

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[3]The metals of periodic groups 11 and 12 do not follow the trend through the transition series and belong better with the s-block groups 1 and 2.

This difference between the s- and p-block members in the same periodic row is equivalent to the difference in slope through electropositive and electronegative elements in Fig. 1.

Divergence angles, of the type θ shown in Fig. 4, depend on the proportionality constant K that relates the quantities $\sqrt{E_g}$ and χ. For periods 1 to 6 θ has the values $25°$, $19°$, $20°$, $3°$, $10°$, and $8°$ respectively. A convenient physical interpretation is to consider K as a valence-electron density, $\rho = 1$ for a closed shell and $\rho = x^{-\mu} < 1$ for non-closed shells with μ vacant sites. The value of x depends on the angle of divergence θ. As an example, $x = 1.1$ for the $2p$ valence shell.

Although it is tempting, and feasible, to scale all calculated values of χ to the AR scale by assigning appropriate values to x, the chemical significance of electronegativity is obscured in the process. Although less regular, the thermochemical Pauling scale [3, 12] better reflects the essence of χ, especially for the transition elements. The correspondence of both empirical scales with the quantum-potential scale is examined in Fig. 6.

All evidence supports the conclusion that $\sqrt{E_g}$ is a good measure of valence-state electronegativity. Not only does it parallel both the AR and Pauling scales convincingly, but it also relates directly to the Mulliken proposal.
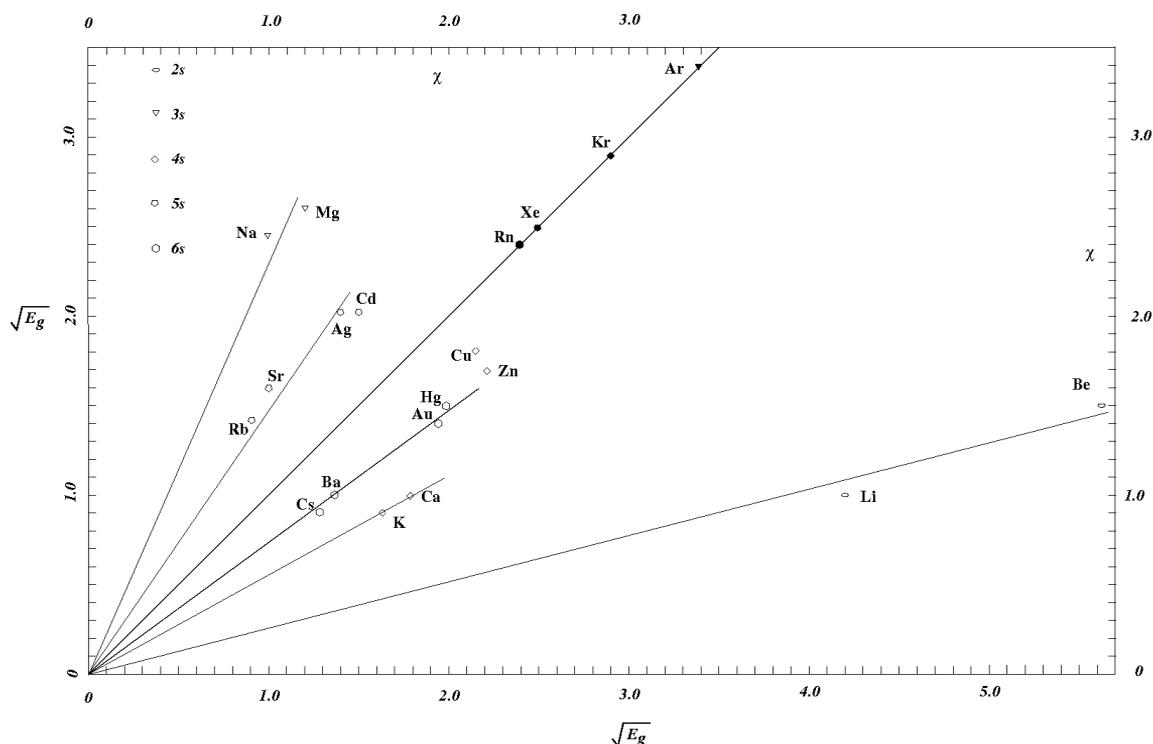
Fig. 5. Electronegativity of *s*-block elements. Coordinate axes are interchanged as explained in the caption to Fig. 4.
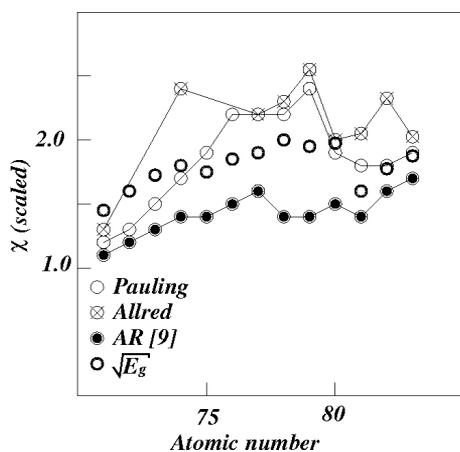

Fig. 6. Comparison of the Pauling [2], Allred [12] and AR [9] empirical electronegativity scales.

Electron Affinity

For $n > 2$ the average formula, $E_g = 2.4I_P/n$ reduces to $E_g \simeq 0.5I_P$, and applies to the majority of elements. Because electron affinities are generally of smaller magnitude than I_P, the Mulliken energy-scale formula is explained directly.

A sufficient number of high-precision atomic electron affinities, to test the Mulliken formula,

$$\chi^2 = E_g = 0.5(I_P + E_A)$$

are known [19]. The variation of $\sqrt{E_g}/\chi_M$ with atomic number is shown in Fig. 7. By scaling the two quantities within periodic families reliable values of unmeasurable electron affinities can be obtained by interpolation. It is noted that electron affinity represents the energy difference between the ground state of a neutral atom and the lowest state of the corresponding negative ion. In many cases the negative-ion state is too unstable to allow experimental measurement of E_A. All noble gases with closed p sub-shells, and many elements with closed s sub-shells belong to this group. With electron affinities for three elements in group 2 unknown, the scaling is complicated and calculations were based on assuming, (from Fig. 7), $\sqrt{E_g}/\chi_M =$ 2.5, 1.4 and 1.5 for Be, N and Ne to yield $E_A = 0.82$, 1.23 and 1.65 eV, respectively. The negative electron affinity for Th may be unexpected, but not unprecedented, noting $E_A(\text{Yb}) = -0.02$ eV [19].

A functional relationship between $\sqrt{E_g}$ and χ_M is clearly evident from Fig. 7, except for Pd, the only
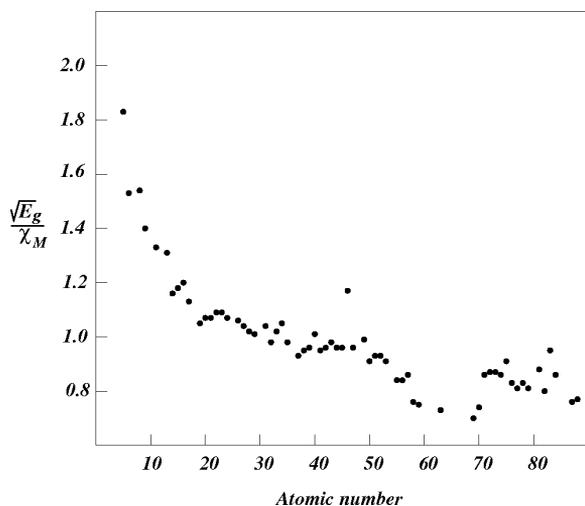
Fig. 7. Diagram to show the relationship between electronegativities based on ionization radii and on Mulliken's formula.

atom with a closed outer d-shell, and for the lanthanides. The calculated $E_A(\text{Hf}) = 0.08$ eV compares well with the reported tentative value, > 0, [19]. The unknown ionization potential of At, calculated from the reported $E_A(\text{At}) = 2.8$ eV, is well in line with that of neighboring elements.

Discussion

Electronegativities on the Mulliken scale, as redefined here, agree remarkably well with the valence-state values calculated from ionization radii, and by inference, also with Pauling electronegativities, once the square-root relationship between the scales is properly recognized.

Other empirical definitions that relate electronegativity to experimental variables such as hardness [6] or atomic polarizability [21] are automatically in line with the new definition.

The various empirical formulae:

$$\chi = 0.313\{(n+2.60)/r^{2/3}\}$$
$$\chi = 0.31\{(n+1)/r\} + 0.50$$
$$\chi \propto (n+1)/\sqrt{2}r$$
$$\chi = 0.359\left(Z_f/r^2\right) + 0.744$$
$$\chi = 1.66(n/\alpha)^{1/3} + 0.37$$

of Liu [22], Gordy [7], Cottrell and Sutton [8], AR [10] and Nagle [21], respectively, and many others, are all different variants of $\chi = \sqrt{E_g}x^{-\mu}$.

The Chinese article [22], completely ignored by western scientists, is one of the more thoughtful assessments of the electronegativity concept. It is based on the principle

> ... that the electronegativity of an element increases with more valence shell electrons and smaller atomic radius.

The equation adopted is:

$$E = \frac{1}{3.2} \times \frac{n+2.6}{r^{2/3}}$$

in which E is the electronegativity, n the number of valence shell electrons and r the atomic radius in Å. Theoretical bases for the constant 2.6 and the 2/3 exponent of r have not been found; but they serve to adjust the effective strengths of the two factors.

The 34 calculated values are correlated in excellent agreement with 31 Pauling and 9 Mulliken electronegativities and used to good effect for "easy and simple systematization" of "the properties of oxides, hydrides and halides...".

The implementation of the various schemes have invariably floundered on how to handle the d-block. The three transition series terminate in the configurations $\text{Ni} - 4s^2 3d^8$, $\text{Pd} - 4d^{10}$ and $\text{Pt} - 6s^1 5d^9$, none of which is a proper closed shell. Convergence formulae are therefore not applicable for these elements. The problem is highlighted in Fig. 6 that compares $\sqrt{E_g}$ with Pauling (Allred) and AR χ's, for the third transition series, as periodic functions. In this instance, where the discrepancy between the empirical scales is at a maximum, it is gratifying to find the absolute values agreeing quite closely with the averages over the two scales. The obvious general solution is to abandon all efforts to scale towards traditional values of χ and to recognize $\chi_v = 6.133/r_0$ as the new electronegativity function.

The ultimate test for any electronegativity scale, by definition, lies in its ability to rationalize the nature and energy of chemical interactions. As noted already, the thermochemical scheme devised for this purpose by Pauling relies on too many variables to be representative of all elements. The quantum-potential valence-state scheme that only depends on atomic ionization radii, like the Mulliken scale, has a clear advantage in this respect, and because of its more fundamental basis

Z	Sy	r_0	χ_v	χ_M	$r_e,(d)$	d/r_x	D_x	D_c	r_x	r_M
1	H	0.98	6.25	6.25	0.741	0.96	436	432	0.77	0.98
2	He	0.30	8.18	(0)						
3	Li	1.25	4.91	1.73	2.673	0.99	110	103	2.70	3.54
4	Be	1.09	5.63	(0.8)	(1.94)	1.14	59	68	1.70	
5	B	1.62	3.79	2.07	1.590	0.86	290	300	1.85	2.96
6	C	1.60	3.83	2.50	1.312	0.71	596	614	1.85	2.45
7	N	1.56	3.93	(1.2)	1.098	0.67	857	947	1.65	
8	O	1.45	4.23	2.75	1.208	0.80	498	496	1.51	2.23
9	F	1.36	4.51	3.23	1.412	1.03	159	162	1.37	1.90
10	Ne	1.20	5.11	(1.7)						
11	Na	2.73	2.25	1.69	3.079	1.03	75	74	3.00	3.63
12	Mg	2.35	2.60	(0)	(2.78)	1.32	9	15	2.10	
13	Al	2.61	2.35	1.79	2.466	0.95	133	139	2.60	3.43
14	Si	2.40	2.56	2.18	2.246	0.75	310	314	3.00	2.91
15	P	2.20	2.79	2.37	1.893	0.67	485	488	2.81	2.59
16	S	2.05	2.99	2.49	1.889	0.71	425	427	2.66	2.46
17	Cl	1.89	3.24	2.88	1.988	0.86	243	241	2.30	2.13
18	Ar	1.81	3.39	(3.0)						
19	K	3.74	1.64	1.56	3.905	1.04	57	56	3.74	3.93
20	Ca	3.26	1.88	1.75	(3.43)	1.18	15	30	2.90	3.50
21	Sc	3.13	1.96	1.83	(2.79)	0.89	163±21	151	3.13	3.35
22	Ti	3.01	2.04	1.86	(2.52)	0.97	118	123	2.60	3.30
23	V	2.95	2.08	1.91	(2.28)	0.81	269	257	2.80	3.21
24	Cr	2.98	2.06	1.93	(2.43)	0.90	155	171	2.70	3.18
25	Mn	2.94	2.09	(0.2)	(3.00)	1.02	81	80	2.95	
26	Fe	2.87	2.15	2.01	(2.16)	1.03	118	109	2.10	3.05
27	Co	2.85	2.15	2.07	(2.18)	0.91	167	183	2.40	2.96
28	Ni	2.86	2.14	2.10	(2.17)	0.87	204	215	2.50	2.92
29	Cu	2.85	2.15	2.12	2.220	0.87	201	206	2.55	2.89
30	Zn	2.78	2.21	(0.2)	(2.32)	1.16	29	34	2.00	
31	Ga	3.29	1.86	1.79	(2.12)	1.01	138	129	2.10	3.43
32	Ge	2.94	2.09	2.14	(2.40)	0.80	274	299	3.00	2.87
33	As	2.62	2.26	2.30	2.103	0.72	382	375	2.92	2.67
34	Se	2.40	2.56	2.43	2.166	0.75	331	325	2.90	2.52
35	Br	2.28	2.69	2.75	2.281	0.88	194	198	2.59	2.23
36	Kr	2.12	2.89	(2.4)						
37	Rb	4.31	1.42	1.53	(4.31)	1.05	46	49	4.10	4.01
38	Sr	3.83	1.60	1.69	(3.74)	1.25	16	14	3.00	3.63
39	Y	3.55	1.73	1.81	(3.09)	0.87	159±21	148	3.55	3.39
40	Zr	3.32	1.85	1.84	(2.50)	0.73	298	277	3.30	3.33
41	Nb	3.30	1.80	1.96	(2.10)	0.63	513	501	3.35	3.13
42	Mo	3.21	1.86	1.98	(2.21)	0.65	436	443	3.40	3.10
43	Tc	3.16	1.94	1.98	(2.35)	0.74	330	316	3.16	3.10
44	Ru	3.13	1.98	2.05	(2.31)					2.99
45	Rh	3.08	1.99	2.07	(2.45)	0.80	236	248	3.08	2.96
46	Pd	2.49	2.46	2.11	(2.39)	0.96	136	135	2.49	2.91
47	Ag	3.04	2.02	2.11	(2.51)	0.90	163	165	2.80	2.91
48	Cd	3.02	2.03	(0)	(2.59)	1.30	11	16	2.00	
49	In	3.55	1.73	1.74	(2.83)	0.98	100	104	2.90	3.52
50	Sn	3.26	1.88	2.06	(2.44)	0.87	195	192	2.80	2.98
51	Sb	3.01	2.04	2.20	(2.52)	0.74	299	293	3.40	2.79
52	Te	2.81	2.18	2.34	2.557	0.77	258	252	3.30	2.62
53	I	2.60	2.35	2.60	2.666	0.91	153	147	2.92	2.36
54	Xe	2.49	2.50	(1.5)						
55	Cs	4.96	1.24	1.48	4.47	1.04	44	48	4.30	4.14
56	Ba	4.48	1.37	1.64						3.74
57	La	4.13	1.48	1.74	(3.00)	0.73	247±21	255	4.10	3.52
58	Ce	4.48	1.37	1,80	(3.18)	0.71	243±21	254	4.48	3.41
59	Pr	4.53	1.35	1.79	(3.17)	0.91	130±29	125	3.50	3.43

Table 1. Summary of ionization radii (r_0), characteristic radii (r_x), and Mulliken radii (r_M) in Å units; valence-state (χ_v) and Mulliken (χ_M) electronegativities in units of $\sqrt{eV}$; interatomic distance (r_e) or its estimate (d); measured (D_x) and calculated (D_c) dissociation energies, in kJmol^{-1}, for diatomic molecules.

Z	Sy	r_0	χ_v	χ_M	$r_e,(d)$	d/r_x	D_x	D_c	r_x	r_M	
60	Nd	4.60	1.33	(1.0)	(3.16)	0.99	84±29	89	3.20		Table 1 (continued).
61	Pm	4.56	1.34	(1.1)							
62	Sm	4.56	1.34	(1.0)							
63	Eu	4.60	1.33	1.81	(3.47)	1.16	34±17	33	3.00	3.39	
64	Gd	4.22	1.45	(0.5)							
65	Tb	4.59	1.34	(0.7)	(3.07)	0.90	131±25	136	3.40		
66	Dy	4.56	1.34	(0.7)							
67	Ho	4.63	1.32	(0.4)	(3.03)	1.01	84±30	85	3.00		
68	Er	4.63	1.32	(0.3)							
69	Tm	4.62	1.33	1.90	(3.00)	1.11	54	52	2.70	3.23	
70	Yb	4.66	1.32	1.76	(3.38)	1.13	21±17	41	3.00	3.48	
71	Lu	4.24	1.45	1.70	(2.99)	0.88	142±33	150	3.40	3.61	
72	Hf	3.83	1.60	(0.1)							
73	Ta	3.57	1.72	1.98	(2.49)	0.67	390±96	372	3.70	3.10	
74	W	3.42	1.79	2.08	(2.16)	0.62	486±96	493	3.50	2.95	
75	Re	3.38	1.81	2.00	(2.38)	0.68	386±96	376	3.50	3.07	
76	Os	3.37	1.82	2.18	(2.33)	0.67	415±77	393	3.50	2.81	
77	Ir	3.23	1.90	2.29	(2.36)	0.73	361±68	324	3.23	2.68	
78	Pt	3.16	1.94	2.35	(2.48)	0.75	308	308	3.40	2.61	
79	Au	3.14	1.95	2.40	2.472	0.81	226	232	3.05	2.56	
80	Hg	3.12	1.97	(0.9)	(2.61)	1.31	17	16	2.00		
81	Tl	3.82	1.61	1.75	(2.96)	1.06	63±17	68	2.80	3.50	
82	Pb	3.47	1.77	2.21	(3.05)	0.98	87	97	3.10	2.78	
83	Bi	3.19	1.92	2.03	2.660	0.83	197	204	3.19	3.02	
84	Po	3.14	2.06	2.27	(2.91)	0.83	186	187	3.50	2.70	
85	At	3.12	2.16	(8.3)*							
86	Rn	3.82	32.31	(1.9)							

it is preferred over the empirical Mulliken scale. Dissociation energies of diatomic molecules and chemical bonds in molecules, calculated from atomic ionization radii, are in agreement with experiment. Details of these calculations are being published elsewhere [23], but for convenient reference some pertinent results and calculated electronegativities are reproduced here in Table 1.

It is of interest to examine the valence-shell electronegativities of those elements, often considered anomalous with respect to other periodic trends [21], for instance in the definition of metalloids. The diagonal line between Si and At in the periodic *p*-block is traditionally considered to separate metals from nonmetals and to contain the metalloids. Classifications that take other factors, such as the amphoteric character of elemental oxides and electrical conductivity into account, demand a more fuzzy distinction and often rely on electronegavity as a guide.

Valence-shell electronegativities of the relevant elements are summarized in Table 2. They provide a clear definition of metalloids on the criterion $2.0 < \chi_v < 2.6$, as shown by the shading.

The variation, within horizontal rows, vertical columns and diagonals, is smooth – virtually without

Table 2. Definition of metalloids, as those elements intermediate to metals and non metals, based on valence-state electronegatvities.

			B	C	N	O	F
			3.79	3.83	3.93	4.23	4.51
			Al	Si	P	S	Cl
			2.35	2.56	2.79	2.99	3.24
Ni	Cu	Zn	Ga	Ge	As	Se	Br
2.14	2.15	2.21	1.86	2.09	2.26	2.56	2.69
Pd	Ag	Cd	In	Sn	Sb	Te	I
2.46	2.02	2.03	1.73	1.88	2.04	2.18	2.35
Pt	Au	Hg	Tl	Pb	Bi	Po	At
1.94	1.95	1.97	1.61	1.77	1.92	2.06	2.16

exception. These trends are in contrast with the assumed alternation within periodic groups B – Tl and C – Pb, which has been claimed [12] to result from transition-metal and lanthanide contractions, although it appears to be out of phase with trends in the *d*-block.

On the metallic side of the shaded region the sense of diagonal variation with increasing atomic number is inverted. On this basis, polonium, an exception on the metalloid diagonal, is placed with the metals.

As a final word of caution it is pointed out that valence-shell electronegativities do not discriminate between, or even relate to, different oxidation states. However, the calculation of ionization radii can be

extended readily to positive ions and converted into electronegativities that should be particularly useful for the definition of parameters such as absolute hardness. Such an exercise would also reduce much of the uncertainty about the electronegativity of the elements of groups 10, 11 and 12, which relates primarily to the assumption [12] of fixed average oxidation states for these elements. The present, valence-state values do not support the previous conclusions [12]. In particular, they reflect the different configurations (d^8, d^{10} and d^9) of the group 10 elements, relative to the uniform s^1 and s^2 configurations of groups 11 and 12. The break between neighboring s and p blocks is as expected.

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