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Relation Between an Atomic Electronegativity Scale and the Work Function

Abstract: Recently compiled data for the first electron affinity and the first ionization potential are used to obtain values for an atomic electronegativity scale, based on the Mulliken relation. From this scale and a new compilation of work function data, a linear equation is obtained which includes a parameter for any given element, depending on its subgroup in the periodic table. Data are plotted for 51 elements, including simple metals, transition metals, and semiconductors. These data fit the straight-line equation better than 10 percent. Data for the transition metals deviate within the same limits as those for elements having simpler electronic configurations. The electronegativity scale differs significantly from the Pauling scale and is shown to be a useful guide to preferred values of the work function for elements.

Introduction

Various forms of an empirical relation between electronegativity χ and electron work function ϕ have been proposed [1–8] in recent years. Such a relation may be expected because both quantities are defined in terms of the energy of valence electrons:

1. *Electronegativity* is the power of an atom in a molecule to attract electrons to itself [9], and
2. The *work function* is the minimum work that must be done to remove an electron from a metal at 0 K [10].

In the empirical equations, most investigators have used Pauling's χ_P and the experimental values ϕ_{exp} available at the time. Good correlation between these two quantities has been obtained, particularly for alkali metals, alkaline earths, and noble metals.

The χ_P scale is a macroscopic concept based on the heats of formation of ionic compounds. A somewhat different definition, given by Mulliken [11, 12], is a microscopic concept based on atomic spectra,

$$\chi_M = (I + EA)/2, \tag{1}$$

where I is the ionization potential and EA the electron affinity.

This paper makes an exploratory test of the relation between χ_M and ϕ_{exp}. It is clear that the electronic properties of atoms need not be identical to the electronic properties of elemental solids because in atoms the charging effects are large and nonlinear, whereas in solids they are linear. Obviously, in a free atom the wave functions of valence electrons differ from those of an atom in a solid.

It follows, then, that in the periodic table the systematic changes of the properties of isolated atoms may not coincide with those properties of atoms in elemental solids. For electron energies, however, the atomic periodicity may well be related empirically to the solid-state periodicity. This possibility is explored in the test of the Mulliken relation by using published data for ϕ_{exp} for 51 elements. The relative periodicities are further confirmed by using interpolations between nearest neighbors in the table of the elements.

The electronegativity scale

There have been several different approaches to the construction of electronegativity scales. Most, like Pauling's, describe the power of an atom to attract electrons as it is modified *in the bonded condition*. The Mulliken scale, however, is based on the ionization energies and electron affinity energies of valence states of free atoms. Mulliken pointed out that it could be more readily applied to monovalent atoms. To deal with the various states of multivalent atoms, some rather complex correction factors are required.

The use of the Mulliken scale in the present paper does not deal with the complexities of several possible valence

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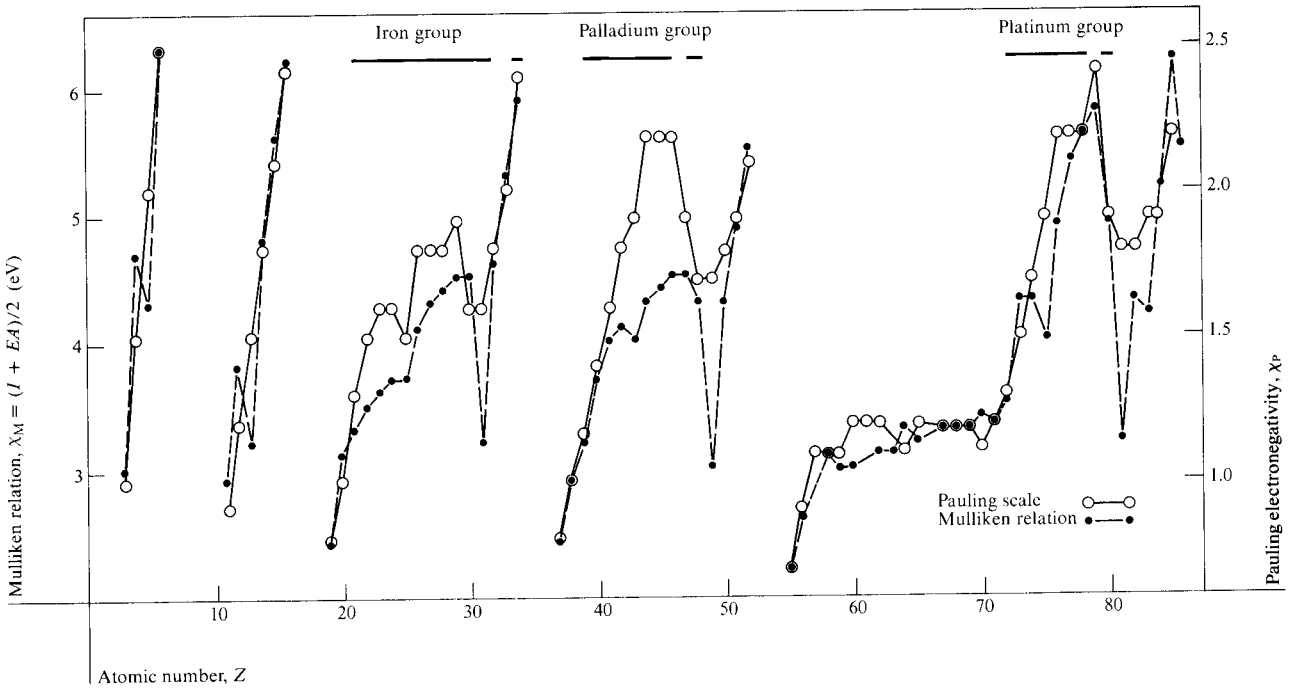

Figure 1 Superposition of Pauling and Mulliken electronegativities, scaled proportionately.

states in the chemical bond, such as in ionic, covalent, or homopolar bonding. It deals instead with one class of bond—the metallic bond, in which we assume that a single valence state exists for any metal in the form used in work function measurements.

Because other scales have been used in correlations with the work function, a brief description is included here of the various electronegativity concepts.

Allred-Rochow scale [13]: Uses the same quantities as those in Gordy's equation, but in the form $\chi_A = (Z_{eff})e/r^2$.

Gordy scale [14]: Defines χ_G as $(Z_{eff})e/r$, where Z in a bonded atom is the effective nuclear charge acting on a valence electron when the electron is at a distance from the nucleus equal to the covalent radius r. (Several other scales were derived by Gordy [15, 16].)

Mulliken relation [11]: Defines a relation that depends on the orbital characteristics of an atom in a molecule; χ_M is the numerical average of the ionization potential and the electron affinity.

Pauling scale [17]: Obtains values by a thermochemical method in which the extra ionic resonance energy of chemical bonds in a highly ionic compound is obtained from its heat of formation.

Phillips scale [18]: Defines electronegativity χ_{Ph} based on the dielectric properties of the atoms in a given valence state.

Sanderson scale [19]: Takes χ_S as the ratio of the average electron density of an atom to that of a hypothetical "inert" atom having the same number of electrons. This ratio is a measure of the relative compactness of the atom.

Walsh scale [20]: Relates χ_W to the stretching force constants of the bonds of an atom to a hydrogen atom.

The relative merits of most of these scales are discussed at length by Pritchard and Skinner [21] and by Iczkowski and Margrave [22].

Table 1 Values of periodicity parameter P in Eq. (10) for chemical elements in each of the columns in the periodic table.

Subgroup								*P* (eV)	*Elements*
		VIA						0.3	Se, Te
					IB & IIB			0.2	Cu, Ag, Au, Zn, Cd, Hg
IA	&	VA						0.1	Li, Na, K, Rb, Cs, As Sb, Bi
IIA								0	Be, Mg, Ca, Sr, Ba
		IVA			IIIB			−0.2	Si, Ge, Sn, Pb Sc, Y, La
							VB	−0.3	V, Nb, Ta
				VIII				−0.4	Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt
					IVB	&	VIB	−0.6	Ti, Zr, Hf, Cr, Mo, W
							VIIB	−0.7	Mn, Tc, Re
IIIA								−1.0	Al, Ga, In, Tl

Most of the scales are not a fundamental measure of electronegativity but instead are correlations between physically unrelated quantities, based on their similar periodicities in the table of the elements.

The Mulliken relation, specified by the two kinds of electron energy I and EA, has not been reported in the form of a scale for a large number of elements. One reason is that prior to 1970 the only definitive measurements of EA were those on H, F, Cl, Br, I, C, O, and S. Recent improvements of the laser photodetachment method and the surface ionization technique for determining atomic electron affinities have now produced a large number of precise determinations.

The advances in the theoretical and experimental aspects of the binding energies in atomic negative ions were critically reviewed in 1975 by Hotop and Lineberger [23], who have provided an authoritative list for 85 elements. Uncertainties for several of these elements are identified, and 11 elements are listed as having an unspecified small, negative value for EA [23]. However, their summary of our present knowledge of electron affinities does provide a comprehensive list that is probably the best evaluation now available. The values for the first electron affinity (also called the "zeroth ionization potential"), together with Moore's data [24] for the first ionization potential, now permit calculation of a χ scale based on Eq. (1). Values of χ_M are plotted as a function of atomic number Z in Fig. 1 and are superimposed for comparison with a plot of the Pauling electronegativity. The two curves are scaled to equate the range 2.2 to 6.3 eV of the Mulliken potential with the range 0.7 to 2.5 units of the Pauling scale.

Figure 1 shows how the two curves deviate in the three series of the transition metals. This comparison is of special interest. The discrepancies in these portions of the curves are due to the fact that the Pauling scale was derived from molecular data for *compounds*. These bond energies are not related to metallic bond energies in the pure transition metals. A similar difficulty arises when Gordy's formulas are used for transition metals. For these reasons, the direct relation of χ_M to electron energies in the atom and in the solid, as indicated in Fig. 2, may make the new scale for χ more useful for all elements, including the transition metals. That possibility is explored later in this paper in connection with the work function.

In regard to the χ_M scale, it should be noted that a recent finding [25] on the formation of negative ions in sputtered alloys has been interpreted in terms of the Mulliken relation.

The electron work function

Prior to the analysis reported in this paper, a compilation was made of the work functions of the elements [26]. The preferred list of data was based on a search of *Physics Abstracts* and *Chemical Abstracts*, 1969–1976. A few older data for those elements not reported in the literature of that eight-year period were added to provide as complete a list as possible, comprising 63 elements. Included were ϕ_{exp} data for polycrystalline samples and single crystal directions.

The selection of ϕ_{exp} data was based on

1. the validity of the experimental technique (e.g., vacua of 10^{-9} or 10^{-10} torr (1.33×10^{-7} Pa or 1.33×10^{-8} Pa), clean surfaces, and identification of crystal-face distribution and other surface conditions), and
2. best agreement with preferred values and theoretical values of the "true" work function (given variously by Fomenko [27], Rivière [28], Trasatti [29], and Lang and Kohn [10]).

Several elements in the source list [26] have been omitted here. These include the actinides because Hotop and Lineberger do not cite data for the elements above $Z =$

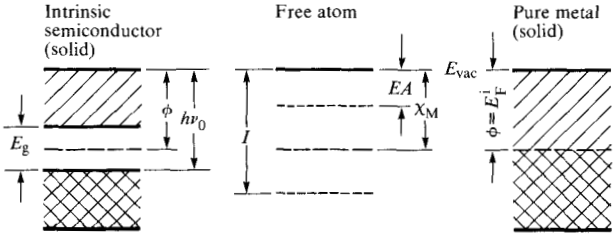

Figure 2 Energy level diagram showing quantities discussed in the text: ϕ = work function, I = first ionization potential, EA = first electron affinity, E_F^i = intrinsic Fermi energy level, E_{vac} = vacuum level, E_g = energy gap, $h\nu_0$ = photoelectric threshold, and χ_M = Mulliken electronegativity = $(I + EA)/2$.

86. The rare earths are omitted because the data do not fit clearly into the column groupings discussed in the next section. In addition, the high-energy-gap elements C and B are omitted. Work functions of these are not adequately substantiated in the literature. Polycrystalline data for the remaining 51 elements from [26] are used here.

The work function is defined in Fig. 2 as the energy difference between the intrinsic Fermi level E_F^i and the vacuum level. Photoelectric measurements of semiconductors require a correction factor for the band gap $h\nu_0 \approx E_F^i + E_g/2$.

The work function data are cited here with the number of significant figures originally reported in the literature. These indicate the precision of an author's experiment, which is frequently as high as ±0.01 eV. However, the accuracy and reproducibility of data for a given element of specified surface condition, as reported by different workers, ranges from about ±0.1 to ±0.2 eV. For this reason the calculations of χ and ϕ in this paper are given with only two significant figures.

Prior research on relation of ϕ_{exp} to χ

Probably the first attempt to relate χ and ϕ_{exp} was published by Gordy and Thomas [2]. For this purpose a composite scale was used, a compromise between the Pauling and the Gordy electronegativities. The empirical equation was of the form

$$\chi_{PG} = 0.44\,\phi_{exp} - 0.15. \qquad (2)$$

The Gordy-Thomas results were an important contribution and inspired others to find a closer correlation. The work function data used in [2] were Michaelson's 1950 compilation [30] of published values. Many of those old data, however, are now known to be inaccurate by as much as 0.5 eV because of surface contamination of the specimens. Moreover, many transition elements were omitted from the plot in Fig. 1 of [2]. The authors ac-

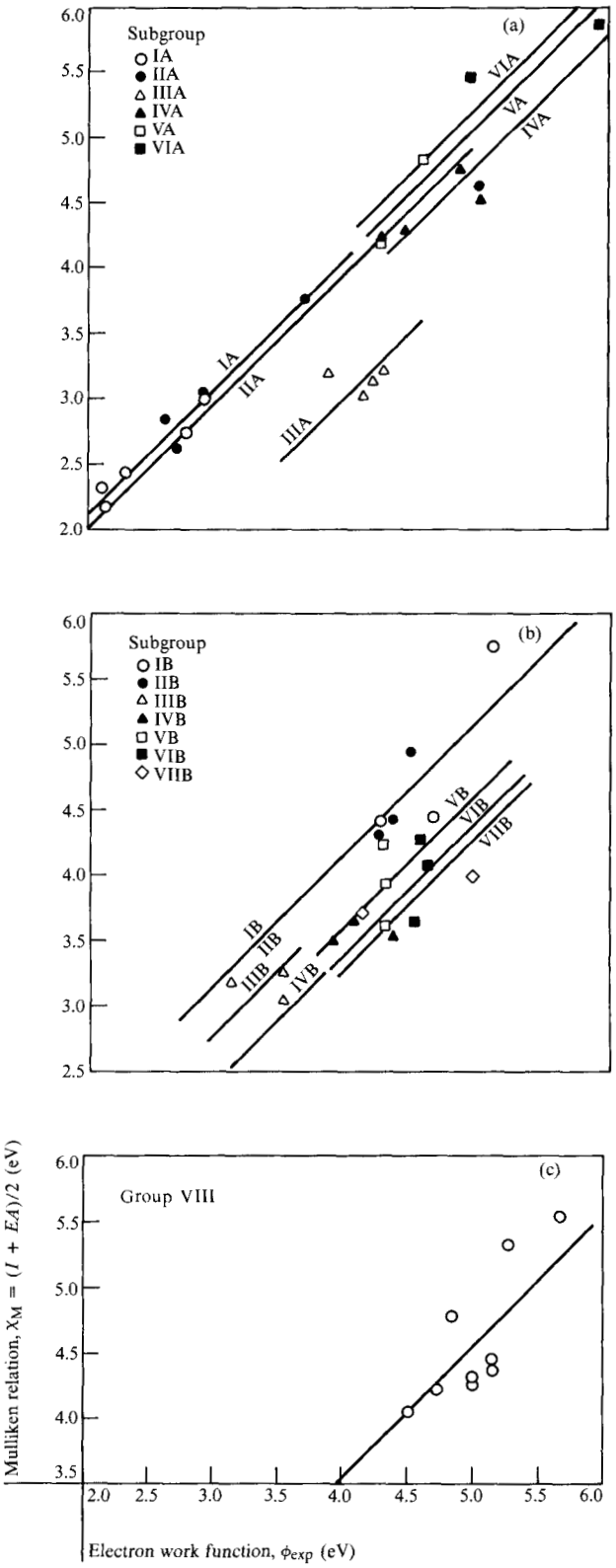

Figure 3 Plots of χ_M calculated from the values of I and EA in Table 3 vs data from a recent compilation of preferred values of the work function [26]. (a) Best fit at slope 1.0 for elements in the A subgroups of the periodic table. (b) Data for the B subgroups. (c) Data for elements in group VIII.

Table 2 Comparison of ϕ, interpolated from nearest neighbors, with the corresponding points in Fig. 3 and with ϕ_{calc} from (10).

Subgroup	*Element*	*Points in Fig. 3* ϕ_{exp} (eV)	ϕ_{calc} *from Eq. (10)* (eV)	ϕ *interpolated from nearest neighbors* (eV)
IIIA	Tl	3.84	4.2	4.37
VA	Sb	4.55	4.8	4.68
IIIB	La	3.5	3.3	3.3
VIIB	Tc	none	4.7	4.65
VIIB	Mn	4.1	4.4	4.5
VIIB	Re	4.96	4.7	4.7

knowledged the difficulty of fitting the Gordy equations to transition metals, because nuclear screening constants were hard to estimate.

Subsequently, Conway and Bockris [1] obtained a similar relation for 19 metals,

$$\chi_P = 0.40\ \phi_{exp} - 0.3, \tag{3}$$

and Miedema et al. [4], in a paper on the role of electronegativity in alloy formation, obtained from data for 24 metals the equation

$$\phi_{exp} = 2.6\ \chi_P + 0.3,$$

or

$$\chi_P = 0.39\ \phi_{exp} - 0.12. \tag{4}$$

Later some interesting research was reported by Trasatti [8]. He analyzes a much larger number of elements and uses a more refined list of work functions, including measurements made as late as 1971. These, however, do not include a number of more accurate measurements of ϕ_{exp} reported since that time and made with an ultrahigh vacuum technique.

Trasatti, in plotting the Pauling χ_P vs the ϕ_{exp} data for 52 metals, found a rather wide spread of data, and divided them into four groups defined by the following straight-line equations:

$$\chi_P = 0.50\ \phi_{exp} - 0.55 \quad \text{for transition metals,} \tag{5}$$

$$\chi_P = 0.50\ \phi_{exp} - 0.29 \quad \text{for } sp \text{ metals,} \tag{6}$$

$$\chi_P = 0.23\ \phi_{exp} + 0.28 \quad \text{for alkaline earths, and} \tag{7}$$

$$\chi_P = 0.23\ \phi_{exp} + 0.36 \quad \text{for alkali metals.} \tag{8}$$

At first, this would seem to be a logical separation into four sets of chemical elements. The grouping for (7) and (8) is, in fact, consistent. The division of the remaining metals into (5) and (6), however, seems not as consistent because seven transition metals are included in the (6) grouping, and some of the (5) metals are *sp* metals. Although there was some speculation [8] about the role of *d* electrons, there was no clear explanation of the separation into the main groups (5) and (6).

A more recent study was reported by Poole et al. [7] to relate the work function to the Sanderson electronegativity for 15 elements by the equation

$$\phi_{exp} = 2.69\,(0.21\ \chi_S + 0.77)^2. \tag{9}$$

Only two of the elements are transition metals.

Hodges and Stott [5] also found an approximate correlation between E_F^i and χ_P, but only for non-transition metals.

Equations (2) to (9), then, are approximations that apply mainly to simple metals.

Recognizing the need for clarifying the special case of the transition metals, Miedema [31] developed an electronegativity parameter for those elements. It should be noted that his scale, unlike the various χ scales described here, was derived from the work function itself (and modified by a study of phase diagrams) and gave a useful relation with the heat of formation of binary alloys.

The relation of χ_M to ϕ_{exp}

The present study is an attempt to find a good linear fit between the best available data on χ_M and ϕ_{exp} for a large number of metallic elements and also for semiconductor elements. The basis of this linear fit is the relation between the electron transition energy in an atom (χ_M) and the electron transition energy in an elemental metal (ϕ).

Data for the first ionization potential [24] and the electron affinity relative to the ground state of atoms [23] were used to calculate χ_M from Eq. (1). The values of χ_M vs ϕ_{exp} are plotted in Fig. 3.

Because the Mulliken equation is linear, one would expect the points to fall on a straight line. Inspection of the points in Figs. 3(a) and 3(b) showed that several straight lines could be drawn for separate families of data according to subgroups in the table of the elements.

The slope 1.0 for each of these lines was chosen by the following line of reasoning. One study of theoretical work functions [3] showed that the quantity ϕ for a metal surface equals the neutral electronegativity of the surface atoms, i.e., $\phi = (I + EA)/2$, where I and EA are the ioni-

Table 3 Data (eV) for the electronegativity scale and the work function calculated from Eq. (10) compared with preferred values of the experimental work function.

Element	*Sub-group*	*First ionization potential I* [24]	*First electron affinity EA* [23]	*Mulliken relation* $\chi_M = (I + EA)/2$	*Work function* ϕ_{calc} *from Eq. (10)*	*Preferred value of work function* ϕ_{exp} [26]	*Percent deviation of* ϕ_{exp} *from* ϕ_{calc}
Ag	IB	7.576	1.3	4.5	4.3	4.26	0
Al	IIIA	5.986	0.46	3.2	4.2	4.28	−2.4
As	VA	9.81	0.80	5.3	5.2	—	—
Au	IB	9.225	2.3086	5.8	5.6	5.1	8.9
Ba	IIA	5.212	<0	2.6	2.6	2.7	−3.9
Be	IIA	9.322	<0	4.7	4.7	4.98	−6.4
Bi	VA	7.289	1.1	4.2	4.1	4.22	−2.4
Ca	IIA	6.113	<0	3.1	3.1	2.87	6.5
Cd	IIB	8.993	−0.333	4.3	4.1	4.22	−2.4
Co	VIII	7.86	0.7	4.3	4.7	5.0	−6.4
Cr	VIB	6.766	0.66	3.7	4.3	4.5	−4.7
Cs	IA	3.894	0.47	2.2	2.1	2.14	0
Cu	IB	7.726	1.226	4.5	4.3	4.65	−9.3
Fe	VIII	7.870	0.25	4.1	4.5	4.5	0
Ga	IIIA	5.999	0.3	3.2	4.2	4.2	0
Ge	IVA	7.899	1.2	4.6	4.8	5.0	−4.2
Hf	IVB	7.0	<0	3.5	4.1	3.9	4.9
Hg	IIB	10.437	−0.63	4.9	4.7	4.49	4.3
In	IIIA	5.786	0.3	3.0	4.0	4.12	−2.5
Ir	VIII	9.1	1.6	5.4	5.8	5.27	8.6
K	IA	4.341	0.50	2.4	2.3	2.30	0
La	IIIB	5.577	0.5	3.1	3.3	3.5	−6.1
Li	IA	5.392	0.62	3.0	2.9	2.9	0
Mg	IIA	7.646	−0.15	3.8	3.8	3.66	2.6
Mn	VIIB	7.435	<0	3.7	4.4	4.1	6.8
Mo	VIB	7.099	1.0	4.1	4.7	4.6	2.1
Na	IA	5.139	0.546	2.9	2.8	2.75	0
Nb	VB	6.88	1.0	4.0	4.3	4.3	0
Ni	VIII	7.635	1.15	4.4	4.8	5.15	−8.3
Os	VIII	8.7	1.1	4.9	5.3	4.83	9.4
Pb	IVA	7.416	1.1	4.3	4.5	4.25	4.4
Pd	VIII	8.34	0.6	4.5	4.9	5.12	−4.1
Pt	VIII	9.0	2.128	5.6	6.0	5.65	5
Rb	IA	4.177	0.4860	2.4	2.3	2.16	4.4
Re	VIIB	7.88	0.15	4.0	4.7	4.96	−6.4
Rh	VIII	7.46	1.2	4.4	4.8	4.98	−4.2
Ru	VIII	7.37	1.1	4.3	4.7	4.71	0
Sb	VA	8.641	1.05	4.9	4.8	4.55	4.2
Sc	IIIB	6.54	<0	3.3	3.5	3.5	0
Se	VIA	9.752	2.02	5.9	5.6	5.9	−5.4
Si	IVA	8.151	1.385	4.8	5.0	4.85	2.0
Sn	IVA	7.344	1.25	4.3	4.5	4.42	2.2
Sr	IIA	5.695	<0	2.9	2.9	2.59	10.3
Ta	VB	7.89	0.6	4.3	4.6	4.25	6.5
Tc	VIIB	7.28	0.7	4.0	4.7	—	—
Te	VIA	9.009	1.97	5.5	5.2	4.95	3.9
Ti	IVB	6.82	0.2	3.5	4.1	4.33	−4.9
Tl	IIIA	6.108	0.3	3.2	4.2	3.84	9.5
V	VB	6.74	0.5	3.6	3.9	4.3	−10.3
W	VIB	7.98	0.6	4.3	4.9	4.55	6.1
Y	IIIB	6.38	≈0	3.2	3.4	3.1	8.8
Zn	IIB	9.394	−0.49	4.5	4.3	4.33	0
Zr	IVB	6.84	0.5	3.7	4.3	4.05	4.7

zation potential and electron affinity characteristic of the surface atoms. If this equality is true, then a plot of χ vs ϕ has a slope of precisely 1.0. Accordingly, for each of these families of points a straight line was plotted as a least-squares fit to define $\chi = f(\phi)$ for elements in that subgroup.

Table 4 Electronegativity values (eV) for additional elements.

Element	*First ionization potential I* [24]	*First electron affinity EA* [23]	*Mulliken relation* $\chi_M = (I + EA)/2$
At	9.5	2.8	6.2
B	8.298	0.28	4.3
C	11.26	1.26	6.3
P	10.486	0.743	5.6
Po	8.43	1.9	5.2
Rn	10.748	<0	5.4
S	10.360	2.0772	6.2
Lanthanide series:			
Ce	5.47	≲0.5	3.0
Pr	5.42	.	3.0
Nd	5.49	.	3.0
Sm	5.63	.	3.1
Eu	5.67	.	3.1
Gd	6.14	.	3.3
Tb	5.85	.	3.2
Ho	6.02	.	3.3
Er	6.10	.	3.3
Tm	6.18	.	3.3
Yb	6.254	.	3.4
Lu	5.426	≲0.5	3.0

The line for Group IIA elements intersects the coordinates (0, 0) in Fig. 3(a), and so its equation is $\phi_{calc} = 1.0\,\chi_M - P_{IIA}$, in which the parameter $P_{IIA} = 0$. Because all lines in Fig. 3 are of slope 1.0, the general equation is

$$\phi_{calc} = \chi_M - P, \tag{10}$$

where the parameter P is a measure of the shift to the right or to the left of line IIA, the displacement being in units of electron volts. The values of P for the various subgroups are actually a measure of how the amplitude of the curve $\phi_{calc} = f(Z)$ differs from the amplitude of the curve $\chi_M = f'(Z)$. The quantity P is thus a measure of the difference between atomic and solid-state periodicities, and defines that difference for the columns of the periodic table. For this reason the quantity P is called the "periodicity parameter" in Table 1.

The spread of points around each line in Fig. 3 would not indicate a statistical significance for P values when the normal variation of ±0.2 eV for ϕ_{exp} is included in the evaluation. There are two reasons, however, for making a subsequent test for Eq. (10) and its parameter P. The first is the intriguing regularity in sequences of P in Figs. 3(a) and 3(b) and in Table 1. The sequences observed are columns IA to IIIA, IVA to VIA, IB to IVB, and VB to VIIB.

The second reason for further consideration of Fig. 3 is a study of nearest neighbors of several elements having doubtful values of ϕ_{exp}. These are of definite interest because subsequent corrections support the listed values of P.

Interpolations between nearest neighbors of In, Sc, and Y were done in 1950 [30] and were closely confirmed by subsequent experiments [32–34]. Useful interpolations can be made along those portions of the ϕ_{exp} vs Z curve where a ϕ value is missing or is misaligned on an otherwise smooth curve.

Six such doubtful points were identified in Fig. 3, compared with interpolated values, and are listed in Table 2. In each case the nearest-neighbor interpolations give strong support to the P parameters in Table 1.

The first example of this is the unmeasured value of Tc. Its nearest neighbors are Mo ($\phi_{exp} = 4.6$ eV) and Ru ($\phi_{exp} = 4.71$ eV). Interpolation gives $\phi_{Tc} = 4.65$ eV, which falls on the VIIB line in Fig. 3(b), drawn previously for only two points, Mn and Re. But nearest-neighbor interpolations for Mn and Re give values of 4.5 and 4.7 eV, respectively, bringing those points closer to the VIIB line and giving still further support to the validity of the value $P_{VIIB} = -0.7$.

A second important example is the value of Tl, which has not been adequately investigated by experiment, and the published value of ϕ_{Tl} (3.84 eV) is open to question. Inspection of line IIIA in Fig. 3(a) shows that Tl is an outlier. Interpolation from nearest neighbors Hg and Pb gives an estimate of 4.37 eV, which falls directly on line IIIA and confirms $P_{IIIA} = -1.0$. In the same way, interpolations for La place it precisely on line IIIB, confirming $P_{IIIB} = -0.2$, and Sb supports $P_{VA} = 0.1$.

Because nearest-neighbor estimates are entirely unrelated to the method of establishing the P parameter in (10), these interpolated values give more confidence in the accuracy of the P values. For this reason, it seems worthwhile to proceed with an overall test of (10), including all its P values.

Work function values calculated from Eq. (10) are listed in Table 3. The data for ϕ_{exp} vs ϕ_{calc} are plotted in Fig. 4. For 30 elements the deviation of ϕ_{exp} from ϕ_{calc} is between zero and five percent, and for 21 elements, between five and ten percent. It should be noted that for the 20 transition elements [35], the deviations are about the same: for 16 elements, zero to five percent, and for ten elements, five to ten percent.

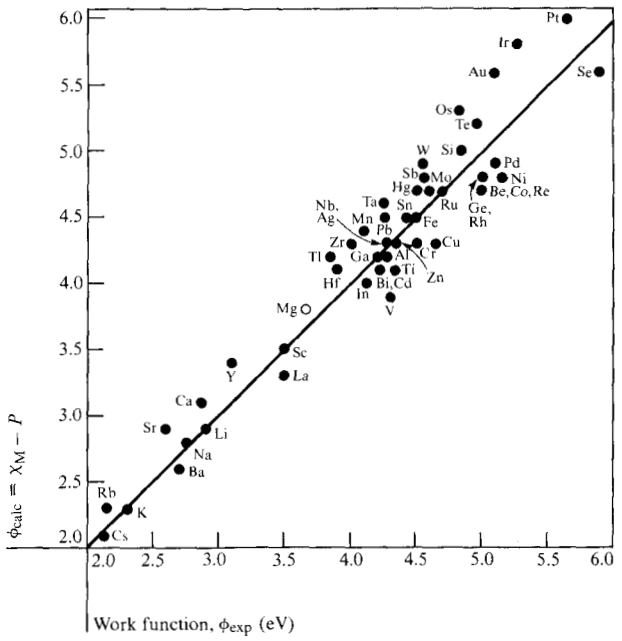

Figure 4 Work function calculations from Eq. (10) plotted against experimental values from Table 3.

Critique of the results

This paper offers two new results: 1) a computed scale of χ_M based on the Mulliken relation, for an extended number of chemical elements, and 2) an empirical relation between χ_M and recently compiled best values of ϕ_{exp}.

The first result provides a comparison of the Mulliken and Pauling scales, which is of particular interest in that they differ in the values for transition elements [36].

The second result, Eq. (10), can be useful in future studies of the work function and in the theory of metals. Another aspect of the empirical equation (10) is the effect of the differences between atomic and solid-state properties for a given chemical element, which seem to be incorporated in the periodicity parameter P. The quantity P appears to provide a unique method for predicting the work functions of transition metals as accurately as those of simple metals.

Although the method of determining parameter P is not rigorous, the final result in Fig. 4, using all computations of P, is a close fit to Eq. (10). That final analysis should be viewed in the context of comparing atomic quantities (χ_M) with solid-state quantities (ϕ_{exp}). The sum of the uncertainties that are due to small inaccuracies of published ϕ_{exp} data and to certain systematic atomic effects may amount to about ± 0.5 eV. The completed test of Eq. (10) in Table 3 and Fig. 4, however, shows that the deviations $\phi_{exp} - \phi_{calc}$ do not exceed ± 0.5 eV. This statement, of course, assumes the accuracy of the P values, some of which are supported by correlation with nearest-neighbor estimates.

It should be especially noted that those estimates for Tl, Sb, La, Tc, Mn, and Re are not included in the analysis of Table 3 and Fig. 4. If they were, the fit to Eq. (10) would be still closer than shown.

The remaining question is the physical meaning—if any—of parameter P. The answer is beyond the scope of this paper, but a brief observation by a referee seems pertinent:

> "The microscopic meaning of P is that it corrects for multiplet structure in the atom which is absent in the solid because of the quenching of orbital angular momentum. Such an effect, to lowest order, should be roughly constant for a given column (same number of valence electrons, similar multiplet parameters, which vary slowly with atomic size—more slowly than χ, anyway)."

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References and notes

1. B. E. Conway and J. O'M. Bockris, *J. Chem. Phys.* **26,** 532 (1957).
2. W. Gordy and W. J. Orville Thomas, *J. Chem. Phys.* **24,** 439 (1956).
3. D. Steiner and E. P. Gyftopoulos, *Proceedings of the 27th Annual Conference on Physical Electronics*, Massachusetts Institute of Technology, Cambridge, March 1967, p. 160.
4. A. R. Miedema, F. R. de Boer, and P. F. de Chatel, *J. Phys. F: Metal Phys.* **3,** 1558 (1973).
5. C. H. Hodges and M. J. Stott, *Phil. Mag.* **26,** 375 (1972).
6. A. H. Nethercot, Jr., *Phys. Rev. Lett.* **33,** 1088 (1974).
7. R. T. Poole, D. R. Williams, J. D. Riley, J. G. Jenkin, J. Liesegang, and R. C. G. Leckey, *Chem. Phys. Lett.* **36,** 401 (1975).
8. S. Trasatti, *J. Chem. Soc., Faraday Trans. I* **68,** 229 (1972).
9. L. Pauling, *J. Am. Chem. Soc.* **54,** 3570 (1932).
10. N. D. Lang and W. Kohn, *Phys. Rev. B* **3,** 1215 (1971).
11. R. S. Mulliken, *J. Chem. Phys.* **2,** 782 (1934).
12. R. S. Mulliken, *J. Chem. Phys.* **3,** 573 (1935).
13. A. L. Allred and E. G. Rochow, *J. Inorg. Nucl. Chem.* **5,** 264 (1958).
14. W. Gordy, *Phys. Rev.* **69,** 604 (1946).
15. W. Gordy, *J. Chem. Phys.* **19,** 792 (1951).
16. W. Gordy, *J. Chem. Phys.* **14,** 305 (1946).
17. L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, New York, 1960.
18. J. C. Phillips, *Phys. Rev. Lett.* **20,** 550 (1968).
19. R. T. Sanderson, *J. Chem. Phys.* **23,** 2467 (1955).
20. A. D. Walsh, *Proc. Roy. Soc. (London) A* **207,** 13 (1951).
21. H. O. Pritchard and H. A. Skinner, *Chem. Rev.* **55,** 745 (1955).

22. R. P. Iczkowski and J. L. Margrave, *J. Am. Chem. Soc.* **83,** 3547 (1961).
23. H. Hotop and W. C. Lineberger, *J. Phys. Chem. Ref. Data* **4,** 539 (1975). For more recent data on elements having small negative values for *EA*, the author was referred by W. C. Lineberger to a recent paper by P. D. Burrow, J. A. Michejda, and J. Comer, *J. Phys. B: Molec. Phys.* **9,** 3225 (1976). Data from that source on Mg, Zn, Cd, and Hg are included in Table 3.
24. C. E. Moore, *National Standard Reference Data Series 34*, National Bureau of Standards, U.S. Government Printing Office, Washington, DC, 1970.
25. J. J. Cuomo, R. J. Gambino, J. M. E. Harper, and J. D. Kuptsis, *IBM J. Res. Develop.* **21,** 580 (1977).
26. H. B. Michaelson, "Work Functions of the Elements," *Handbook of Chemistry and Physics*, R. C. Weast, ed., CRC Press, Cleveland, Ohio, 58th ed., 1977–1978, p. E-81.
27. V. S. Fomenko, *Emission Properties of Materials* (in Russian), Naukova Dumka, Kiev, 3rd ed., 1970.
28. J. C. Rivière, *Solid State Surface Science*, Vol. 1, M. Green, ed., Dekker, New York, 1969, Ch. 4.
29. S. Trasatti, *La Chimica e L'Industria (Milan)* **53,** No. 6, 559 (1971).
30. H. B. Michaelson, *J. Appl. Phys.* **21,** 536 (1950).
31. A. R. Miedema, *J. Less-Common Metals* **32,** 117 (1973).
32. D. E. Eastman, *Phys. Rev. B* **2,** 1 (1970).
33. L. J. Peisner, P. Roboz, and P. B. Barna, *Phys. Status Solidi A* **4,** K187 (1971).
34. H. B. Michaelson, *J. Appl. Phys.* **48,** 4729 (1977).
35. Although the noble metals are sometimes referred to as being in the transition element series, they are excluded from that category here.
36. A paper recently published by C. Mande, P. Deshmukh, and P. Deshmukh, "A New Scale of Electronegativity on the Basis of Calculations of Effective Nuclear Charges from X-ray Spectroscopic Data," *J. Phys. B* **10,** No. 12, 2293 (1977), gives a χ scale for elements up to $Z = 54$. Most values are close to Pauling's but, as in Fig. 1 on page 73, the χ values for transition metals in the palladium group are consistently lower than Pauling's.

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