

## Spectroscopically determined electronegativity values for heavy elements

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**Abstract.** A new scale of electronegativity based on X-ray spectroscopic data was earlier presented by Mande and others for the elements  ${}_{3}\text{Li}$  to  ${}_{54}\text{Xe}$ . The present paper reports an extension of this scale carried out for most of the heavier elements lying between  ${}_{55}\text{Cs}$  and  ${}_{92}\text{U}$ . The present approach is based on the physical interpretation of electronegativity of an atom as the attractive electrostatic force it exerts at a distance equal to its covalent radius. To estimate this force, experimental spectroscopic data have been employed. The merits of such an approach have been pointed out recently by Mullay and may be of interest in the context of the intimate relation found between electronegativity and superconducting transition temperature.

**Keywords.** Electronegativity; atomic spectroscopy.

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### 1. Introduction

As has been pointed out by Mullay (1987), there has been a sustained interest in the estimation of atomic electronegativities. Of the several scales of electronegativity in use, those due to Mulliken (1934, 1935), Gordy (1946), and Allred and Rochow (1958) attempt to offer (Mullay 1987) a physical interpretation of electronegativity. The Allred-Rochow scale (Allred and Rochow 1958; Little and Jones 1960) is widely used, apart from Pauling's scale (1960). In the Allred-Rochow scale, it has been assumed that atomic electronegativity is given by the attractive force an atom exerts at a distance equal to its covalent radius. In order to calculate this force, correction for the screening of the nuclear charge by the other atomic electrons was made using the "thumb rules" given by Slater (1951). This approach was maintained in the work of Mande *et al* (1977) in which they employed a semi-empirical method to estimate nuclear screening. The latter approach based on a calculation of the effective nuclear charge ( $Z_{\text{eff}}$ ) using X-ray spectroscopic data is less arbitrary and more reliable (Mullay 1987) compared to that employed in Allred-Rochow's scale. The electronegativity scale due to Mande *et al* (1977) was given for atoms with  $Z \leq 54$ . In the present paper we extend the scale to heavier atoms.

## 2. The electronegativity scale

The effective nuclear charge,  $Z_{\text{eff}}$ , can be obtained from the term value  $T$  of a given state through the following relation (Mande and Damle 1965, 1966; Mande *et al* 1977):

$$Z_{\text{eff}} = Z - \sigma_{n,l,j} = \{1/2[X + (X^2 - 4Y)^{1/2}]\}^{1/2}, \quad (1)$$

where

$$X = 1/2A\beta - 1/4(A - k^2)\alpha^2\beta^2; \quad Y = 1/16[A^2 - 4k^2(A - k^2)]\beta^2,$$

$$\beta = 4x - \alpha^2x^2; \quad x = T/R,$$

and

$$A = (n - |k|)^2 + k^2.$$

In the above equations,  $T$  referred to as the term value is the free atom binding energy,  $R$  is the Rydberg constant,  $\alpha = e^2/\hbar c$  is the Sommerfeld fine structure constant,  $Z$ , the atomic number,  $\sigma_{n,l,j}$ , the screening parameter,  $n$  the principal quantum number,  $k = -(l + 1)$  for  $j = l + 1/2$  and  $k = l$ , for  $j = l - 1/2$ ,  $l$  being the orbital angular momentum quantum number.

In the calculation of atomic electronegativity based on  $Z_{\text{eff}}$  values of lighter elements, Mande *et al* (1977) had used for term values the data on outer energy levels obtained from X-ray spectroscopic work. For the outer levels of heavier elements, we have in the present work made use of the binding energies of valence levels obtained from photoelectron spectroscopy (Carlson 1975). Since one is generally interested in employing the electronegativity concept for analyzing bulk solid state properties (e.g. Luo and Wang 1987; Ichikawa 1989; Asokamani and Manjula 1989; Balasubramanian and Rao 1989), we have subtracted the values of the workfunction (WF) (Landolt-Bornstein 1955; Lotz 1970) from the photoelectron spectroscopic data (Carlson 1975) on binding energies for each atom. The WF values for some rare earth elements are not available. For these elements ( $Z = 61$ , and  $Z = 63$  to  $71$ ) we have estimated the effective nuclear charge by using a stipulated value of WF to be 3 eV, which is roughly equal to the WF of the neighbouring lanthanide elements. Likewise, we have assumed that the value of WF for  ${}_{84}\text{Po}$  and  ${}_{85}\text{At}$  as 4 eV since no data on WF are available for these two atoms.

The free atom term values are obtained from the solid state binding energies by incorporating the correction for the work function as discussed above (Lotz 1970) given by

$$T = \text{BE} - \text{WF} \quad (2)$$

where the values of the solid state binding energy BE are from Carlson (1975) and of WF from Landolt-Bornstein (1955). Using these term values, the effective nuclear charge  $Z_{\text{eff}}$  is calculated for each atom using (1) which are listed in table 1.

As was done previously (Mande *et al* 1977) we have normalized the resultant force values to the Pauling's scale of electronegativity to obtain for the present scale of electronegativity values using the following relation:

$$\text{electronegativity} = 0.778 \{Z_{\text{eff}}/r_c^2\} + 0.5. \quad (3)$$

In the above equation  $r_c$  denotes the atomic covalent radii of the atoms, values for which have been taken from Sanderson (1967). The resulting atomic electronegativities,

**Table 1.** Comparison of the authors' spectroscopically determined electronegativity values with those of Pauling and of Allred and Rochow for the atoms with  $Z = 55$  to 92.

Element	Level	Electronegativity values				
		$Z_{eff}$	Authors		Pauling	Allred & Rochow
			Orbital	Average		
55Cs	$P_1$	2.27	0.82	0.82	0.7	0.86
56Ba	$P_1$	2.67	1.03	1.03	0.9	0.97
57La	$O_{4,5}$	2.12	1.08	1.14	1.1-1.2	1.08
	$P_1$	2.46	1.17			
58Ce	$N_{6,7}$	2.39	1.18	1.23	1.1-1.2	1.06
	$P_1$	2.71	1.27			
59Pr	$N_{6,7}$	1.97	1.07	1.15	1.1-1.2	1.07
	$P_1$	2.68	1.28			
60Nd	$N_{6,7}$	1.78	1.02	1.08	1.1-1.2	1.07
	$P_1$	2.41	1.20			
61Pm	$N_{6,7}$	1.80	1.03	1.08	1.1-1.2	1.07
	$P_1$	2.47	1.22			
62Sm	$N_{6,7}$	1.81	1.04	1.09	1.1-1.2	1.07
	$P_1$	2.54	1.25			
63Eu	$N_{6,7}$	1.88	0.93	0.97	1.1-1.2	1.01
	$P_1$	2.66	1.11			
64Gd	$N_{6,7}$	1.88	1.06	1.13	1.1-1.2	1.11
	$O_{4,5}$	2.35	1.20			
	$P_1$	2.89	1.36			
65Tb	$N_{6,7}$	1.88	1.06	1.11	1.1-1.2	1.10
	$O_{4,5}$	2.35	1.20			
	$P_1$	2.75	1.32			
66Dy	$N_{6,7}$	1.88	1.07	1.12	1.1-1.2	1.10
	$P_1$	2.78	1.35			
67Ho	$N_{6,7}$	1.88	1.09	1.13	1.1-1.2	1.10
	$P_1$	2.83	1.38			
68Er	$N_{6,7}$	1.88	1.09	1.13	1.1-1.2	1.11
	$P_1$	2.86	1.13			
69Tm	$N_{6,7}$	2.17	1.18	1.21	1.1-1.2	1.11
	$P_1$	2.90	1.40			
70Yb	$N_{6,7}$	2.30	1.12	1.14	1.1-1.2	1.06
	$P_1$	2.93	1.29			
71Lu	$O_{4,5}$	2.57	1.32	1.47	1.1-1.2	1.14
	$P_1$	3.25	1.54			
72Hf	$O_{4,5}$	2.52	1.45	1.58	1.3	1.23
	$P_1$	3.24	1.72			
73Ta	$O_{4,5}$	2.77	1.67	1.77	1.5	1.33
	$P_1$	3.16	1.87			
74W	$O_{6,7}$	2.87	1.82	1.84	1.7	1.40
	$P_1$	3.03	1.89			

(Continued)

Table 1. (Continued)

Element	Level	$Z_{\text{eff}}$	Electronegativity values			
			Authors			Allred & Rochow
			Orbital	Average	Pauling	
$_{75}\text{Re}$	$O_{6,7}$	2.92	1.89	1.87	1.9	1.46
	$P_1$	2.78	1.82			
$_{76}\text{Os}$	$O_{6,7}$	3.05	1.99	2.02	2.2	1.52
	$P_1$	3.23	2.08			
$_{77}\text{Ir}$	$O_{6,7}$	3.04	1.97	2.01	2.2	1.55
	$P_1$	3.46	2.17			
$_{78}\text{Pt}$	$O_{6,7}$	2.79	1.78	1.80	2.2	1.44
	$P_1$	3.10	1.93			
$_{79}\text{Au}$	$O_4$	3.78	2.14	2.04	2.4	1.42
	$O_5$	3.43	1.98			
	$P_1$	3.46	2.00			
$_{80}\text{Hg}$	$O_4$	4.17	1.96	1.87	1.9	1.44
	$O_5$	3.70	1.80			
	$P_1$	3.94	1.88			
$_{81}\text{Tl}$	$P_1$	3.23	1.65	1.54	1.8	1.44
	$P_{2,3}$	2.33	1.33			
$_{82}\text{Pb}$	$P_1$	3.97	1.93	1.67	1.8	1.55
	$P_{2,3}$	2.51	1.40			
$_{83}\text{Bi}$	$P_1$	4.50	2.14	1.77	1.9	1.67
	$P_{2,3}$	2.79	1.52			
$_{84}\text{Po}$	$P_1$	5.39	2.47	1.99	2.0	1.76
	$P_{2,3}$	3.42	1.75			
$_{85}\text{At}$	$P_1$	6.30	2.83	2.33	2.2	1.96
	$P_{2,3}$	4.03	1.99			
$_{90}\text{Th}$	$P_{4,5}$	2.59	1.24	1.30	1.3	1.11
	$Q_1$	3.02	1.36			
$_{92}\text{U}$	$O_{6,7}$	2.16	1.34	1.48	1.7	1.22
	$P_{4,5}$	2.65	1.52			
	$Q_1$	3.03	1.67			

also given in table 1, would then give a reliable measure (Mullay 1987) of the extent to which an atom in a molecule "would attract electrons towards itself". In the case of atoms for which the bonding electrons come from different subshells (e.g.  $_{58}\text{Ce}$ ), we have given the electronegativities for all such valence states. Also given in this table are average electronegativity values for these multiple valence states, wherein the average has been obtained by taking a weighted average of the individual subshell electronegativity, the weight factor being the occupancy of that subshell. In table 1 are also presented the electronegativity values on the Pauling (1931, 1932, 1960) and on the Allred and Rochow (1958) scales for comparison. These three scales are plotted in figure 1 to demonstrate the correspondence between them. The covalent radii for the elements  $_{86}\text{Rn}$  to  $_{89}\text{Ac}$ ,  $_{91}\text{Pa}$  and  $_{93}\text{Np}$  to  $_{105}\text{Ha}$  are not available, and hence the present method cannot be used for them.

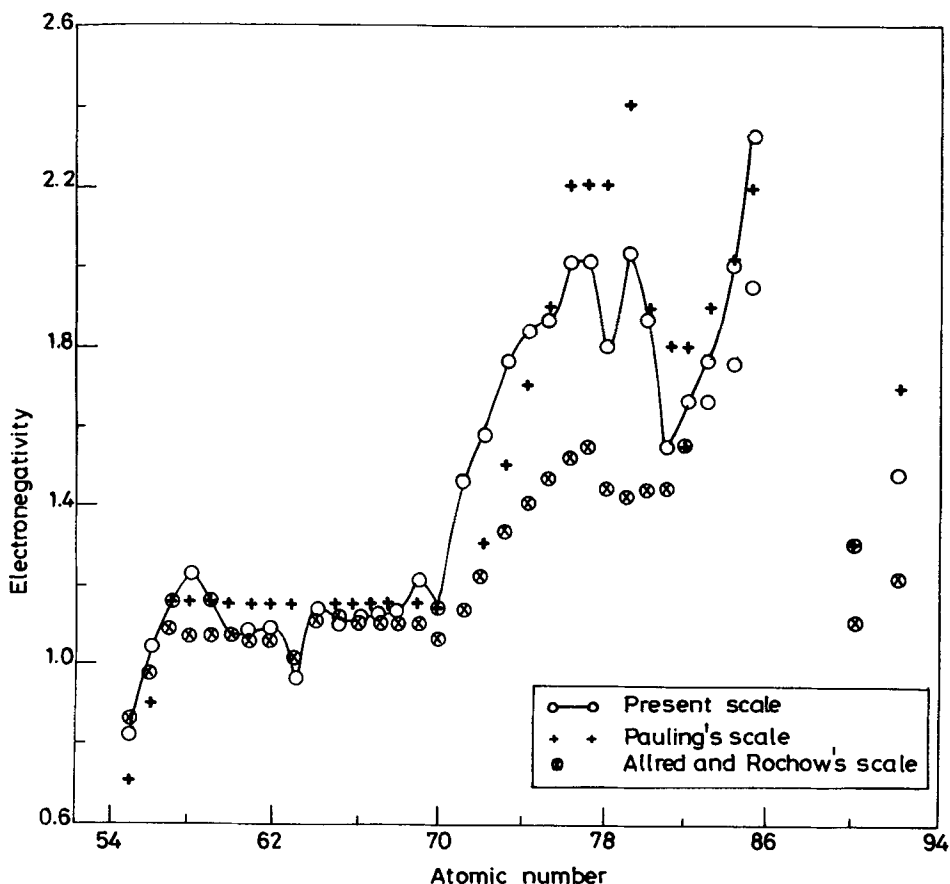


Figure 1. The electronegativity scale.

The electronegativity values of the noble gas elements fall in a class by themselves and hence it is possible to estimate the electronegativity of  $_{86}\text{Rn}$  by extrapolating the electronegativity values for the lighter noble gas elements (Mande *et al* 1977) as shown in figure 2. The resulting value of 2.35 for radon is in fair agreement with the value of 2.0 given by Rundle (1963).

As seen in figure 1, the present scale is in fair agreement with the Pauling scale and the Allred-Rochow scale. The drop in the electronegativity value for  $_{63}\text{Eu}$ ,  $_{70}\text{Yb}$ ,  $_{78}\text{Pt}$  and  $_{81}\text{Tl}$  mimics the trend shown by ionization potentials (Cotton and Wilkinson 1966) in conformity with Mulliken's interpretation of electronegativity as the arithmetic average of the ionization potential and the electron affinity (Mulliken 1934, 1935), the ionization potential being the dominant term.

### 3. Conclusions

The present work may be of some interest in the context of the intimate relationship observed between electronegativity and superconductivity (Luo and Wang 1987; Ichikawa 1989) in the case of elemental superconductors and also in the case of oxide superconductors (Asokamani and Manjula 1989; Balasubramanian and Rao

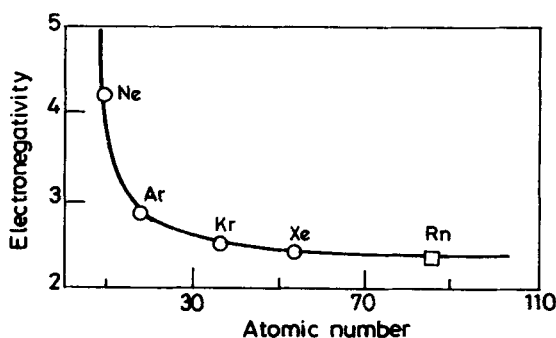


Figure 2. Extrapolation of the electronegativity value for  $_{86}\text{Rn}$ .

1989). These observations are reminiscent of those by Matthias (1953, 1955) who gave empirical rules connecting superconductivity and the number of valence electrons per atom. The construction of the electronegativity scale using the force concept is closely related to the physical considerations employed by Matthias and has the advantage of explicitly incorporating a major structural parameter,  $r_c$ . The pressure dependence of  $r_c$  can then be used to estimate the pressure dependence of superconductivity. Asokamani and Manjula (1989) found, using Gordy's electronegativity scale (1946) and the method of electronegativity equalization (Sanderson 1961) that several oxide superconductors have their mean electronegativity in a significantly narrow range, between 2.5 and 2.65. On the present scale we find that the mean electronegativity for the same compounds falls in a similar narrow range, 2.55 to 2.76. We trust that the present scale which incorporates valence state properties as well as the structural parameter  $r_c$  will thus be of help to physicists, chemists, and material scientists in obtaining preliminary pointers toward some important macroscopic properties based on the electronegativity concept.

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