Extending electronegativities to superheavy Main Group atoms

by Paul J. Karol

IUPAC recently published recommendations on rules for oxidation states within which was an endorsement of the electronegativity scale, called configuration energies, conceived by Allen and constructed from available calculated results. In conjunction with the International Year of the Periodic Table and the recognized extension of the Periodic Table through the end of its seventh period, it seemed timely to broaden those simple electronegativity calculations to include Main Group superheavy elements.

Introduction

Electronegativity, although not experimentally measureable, nevertheless is one of the most useful and central concepts to chemistry, starting primarily in introductory courses at college and pre-college levels, our target audience here. Its use in predicting and/or understanding chemical reactive behavior is well-appreciated. With the Periodic Table now covering the complete collection of elements within the range of atomic numbers Z from 1 to 118 [1,2], it seems heuristically reasonable to explore the newest regime. Theoretical orbital energy calculations already available [3,4] facilitate this venture that can actually be extended with a good degree of confidence to $Z = 120$.

Pauling Electronegativities

The Gold Book [5], IUPAC's Compendium of Chemical Terminology, refers to electronegativity as a concept introduced by L. Pauling [6] measuring the qualitative property that a chemist calls electronegativity as "the power of an atom to attract electrons to itself." With the above empirical definition, electronegativity is an atom-in-molecule property, not an invariant property of the atom but a property dependent on the atom's environment in the molecule, on the number and types of atoms attached to it, on the atom's oxidation state. Recently, Rahm *et al.* have proposed extending the concept to include the external influence of compression [7]. Pauling's electronegativity values for the *Main Group* elements are illustrated in Figure 1. The periodic trends going across rows and down groups (columns) are evident and underly the usual discussion about electronegativity behavior.

Other Electronegativity Schemes

Other approaches espousing the view that electronegativity is a property of atoms in molecules also give multiple values for an atom, taking into account the oxidation state and molecular environment including the influence of solvation. Since the Gold Book also has entries on group electronegativities or substituent electronegativities, it seems reasonable to refer to atomic electronegativities (or perhaps to intrinsic electronegativities) when focusing on a property characteristic of a free atom. In that regard, as emphasized by the recent endorsement by IUPAC in their codification of oxidation states [8,9], the electronegativity hypothesis introduced by Allen and collaborators is advantageous and produces very reasonable values in qualitative agreement with other assignment venues although the transition elements are problematic and the inner transition elements were not addressed. Up-to-date comprehensive reviews of electronegativity have been published recently by Politzer and Murray [10] and by Rahm *et al.* [7,11,12], each of which acknowledge both the simplicity and accuracy of the Allen electronegativities for *Main Group* elements but definitely not for the transition and inner transition elements. Cao *et al.* [13] review the role of electronegativity as one of the main determinants of chemical behavior. Our particular argument here is not to sponsor nor review any particular scheme but rather to employ the one that seems both successful and uniquely applicable to extending the Periodic Table at this time and one that has been embraced by IUPAC [8,9].

Pauling Electronegativity Scale							
H 2.20							He
Li 0.98	Be 1.57	B 2.04	C 2.55	N 3.04	O 3.44	F 3.98	Ne
Na 0.93	Mg 1.31	Al 1.61	Si 1.90	P 2.19	S 2.58	Cl 3.16	Ar
K 0.82	Ca 1.00	Ga 1.81	Ge 2.01	As 2.18	Se 2.55	Br 2.96	Kr
Rb 0.82	Sr 0.95	In 1.78	Sn 1.96	Sb 2.05	Te 2.1	I 2.66	Xe
Cs 0.79	Ba 0.89	Tl 1.62	Pb 1.87	Bi 2.02	Po 2.0	At 2.2	Rn
Fr 0.7	Ra 0.9	Nh	Fl	Mc	Lv	Ts	Og
eka-Fr	eka-Ra						

Fig. 1: Pauling electronegativity values for Main Group elements. Colors are to guide the eye towards increasing electronegativity.

Allen Electronegativities

Attraction of an atom to its electrons is arguably quantified by the electron energies, negative relative to the binding threshold. Allen *et al.* [3,4] have logically identified an electronegativity scheme measuring the difficulty with which an atom yields its valence electron. The Allen scheme is not as fundamentally grounded as are many of the alternatives. It is quantitatively embodied in what they call the configuration energy (CE, symbol E_c): the average orbital energy of valence electrons in ground-state isolated atoms according to

$$E_c = \frac{n_s \varepsilon_s + n_p \varepsilon_p}{n_s + n_p} \quad (1)$$

in which n_s and n_p , respectively, are the numbers of s- and p-valence electrons in the ground state configuration for the *Main Group* elements we are restricting our considerations to here. Orbital energies for these electrons are indicated by ε_s and ε_p , respectively, and the latter are *j*-multiplet-averaged: $(2j+1)$. They approximate ionization energies.

In their publication, Allen *et al.* use experimentally determined spectroscopic electronic energies, ε , when available, as through the NIST Atomic Spectra Database (www.nist.gov/pml) tabulations. Alternatively, and in the cases of experimentally unknown energies, theoretical values for orbital eigenvalues determined by Dirac-Fock calculations can be employed. Allen *et al.* actually use Dirac-Hartree-Fock calculations acknowledging these compare very favorably with available Dirac-Fock results. Experimental (spectroscopic) and theoretical (Dirac-Fock) final orbital energy values differ only slightly, 1% or less in most cases as noted by Allen *et al.* [3,4] (*q.v.*). Theoretical Dirac-Fock values through $Z = 120$ have been published by Desclaux [14] and nowhere else to date. Table 1 has the calculated valence energies for *Main Group* elements from rows 6 and 7 of the Periodic Table, extending to the yet undiscovered s-block elements with $Z = 119$ and 120 beginning the eighth row. Unit of the energy is E_h (hartree) with ($1 E_h$ approximately 27.21 eV). The configuration energies are calculated according to eq. 1 from the ground state valence orbital configurations indicated in the first column. These are proportionately

Atom A.. $s^n p^m$	ε_s (calc) $/E_h$	ε_p (calc) $/E_h$	ε_s (spec) $/E_h$	ε_p (spec) $/E_h$	E_c	χ_A (theory)	χ_A (spec)
Cs.. s^1	0.2561	--	0.2865		0.2561	0.59	0.66
Ba.. s^2	0.3260	--	0.3830		0.3260	0.75	0.88
Tl.. $s^2 p^1$	0.8984	0.3763	0.9656	0.4019	0.7206	1.67	1.79
Pb.. $s^2 p^2$	1.1330	0.4766	1.1111	0.5008	0.8017	1.85	1.85
Bi.. $s^2 p^3$	1.3724	0.5739	1.288 ^a	0.5990	0.8905	2.06	2.01 ^a
Po.. $s^2 p^4$	1.6197	0.6715	1.474 ^a	0.692 ^a	0.9849	2.27	2.19 ^a
At.. $s^2 p^5$	1.8763	0.7707	1.685 ^a	0.787 ^a	1.1126	2.50	2.39 ^a
Rn.. $s^2 p^6$	2.1429	0.8723	1.872 ^a	0.8845	1.1875	2.74	2.60 ^a
Fr.. s^1	0.2654	--			0.2654	0.61	
Ra.. s^2	0.3325	--			0.3325	0.76	
Nh.. $s^2 p^1$	1.1762	0.3780			0.9101	2.09	
Fl.. $s^2 p^2$	1.4429	0.4827			0.9628	2.21	
Mc.. $s^2 p^3$	1.7150	0.5847			1.0368	2.38	
Lv.. $s^2 p^4$	1.9961	0.6874			1.1236	2.58	
Ts.. $s^2 p^5$	2.2878	0.7924			1.2204	2.81	
Og.. $s^2 p^6$	2.5913	0.9005			1.3232	3.04	
eka-Fr.. s^1	0.3177	--			0.3177	0.73	
eka-Ra.. s^2	0.3835	--			0.3835	0.88	

^a Values are approximations employed by the authors of Reference [4].

Table 1: Calculated (Dirac-Fock) and experimental (spectroscopic) s, p orbital energies, the resulting configuration energies (E_c , eq. 1), all in hartree. Electronegativities (EN, symbol χ_A) from calculations (theory) and spectroscopic measurements (spec) are scaled according to $\chi_A = 2.30016 E_c$.

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Na 0.87	Mg 1.29	Al 1.61	Si 1.92	P 2.25	S 2.59	Cl 2.87	Ar 3.24
K 0.73	Ca 1.03	Ga 1.76	Ge 1.99	As 2.21	Se 2.42	Br 2.69	Kr 2.97
Rb 0.71	Sr 0.96	In 1.66	Sn 1.82	Sb 1.98	Te 2.16	I 2.36	Xe 2.58
Cs 0.66	Ba 0.88	Tl 1.79	Pb 1.85	Bi 2.06	Po 2.27	At 2.50	Rn 2.74
Fr 0.61	Ra 0.76	Nh 2.09	Fl 2.21	Mc 2.38	Lv 2.58	Ts 2.81	Og 3.04
eka-Fr 0.73	eka-Ra 0.88						

Fig. 2: Periodic Table of all Main Group element Allen electronegativities. Values through Pb are from reference [4]. The superheavy ($Z > 103$) Main Group element electronegativities are from this work.

rescaled, as by Allen *et al.*, to electronegativities (EN) closely matching those of Pauling using the multiplicative factor 2.300 16. The preferred choice is to use the spectroscopically-determined values when available (through Pb) and the theoretical values for the rest. Complete results for *Main Group* elements are illustrated in Figure 2.

As with the previous scales, electronegativity increases from left to right across each row from alkali metal to noble element as is illuminated in Figure 3, monotonically in most cases. However, the monotonic drop in electronegativities proceeding down any group column reverses as the heavy elements are approached. This is most likely a reflection of relativistic effects in which the valence electrons are drawn in

Fig. 3: Three-dimensional display of *Main Group* element Allen electronegativities in a Periodic Table format starting on the left, row 1, with hydrogen.

Fig. 4: Demonstrating how the Allen electronegativities concur with those of the commonly advocated Pauling electronegativities and with the Rahm, Zeng, Hoffmann (RZH) electronegativities established for *Main Group* elements obtained from Reference 12.

closer to the nucleus and are more difficult to “move”.

Figure 4 shows the relative value of each Allen electronegativity from Figure 2 compared to its Pauling electronegativity counterpart from Figure 1 for the *Main Group* elements exclusive the noble gases. Also displayed are the values from the very recent stratum advocated by Rahm *et al.* [11]. The concurrence lends credibility to the extension of calculated *Main Group* heavy element electronegativities advocated in this work and, pending future more sophisticated theoretical calculations, will not be expected to be significantly modified. Their likely use in anticipating the chemistry of new elements [15,16] is reasonable as we enjoy speculating on where the International Year of the Periodic Table leads us. 🌐

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Paul J. Karol, <https://orcid.org/0000-0002-3555-6899>

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Bonnie Lawlor was Chair of IUPAC Committee on Publications and Cheminformatics Data Standards from 2014-2019 and is Secretary of *Chemistry International* Editorial Board.