

# Configuration Energies of the Main Group Elements

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**Abstract:** Configuration energies (CEs), formerly called spectroscopic electronegativities, are an attempt to quantum mechanically define, and extend, the important chemical concept of electronegativity. In a previous paper (*J. Am. Chem. Soc.* **1989**, *111*, 9003) we reported high-resolution experimental values obtained from the National Institutes of Science and Technology spectroscopic energy level tables using the formula  $CE = (n\epsilon_s + m\epsilon_p)/(n + m)$ , where  $n$  and  $m$  are the number of s and p electrons and  $\epsilon_s$  and  $\epsilon_p$  are their multiplet averaged one-electron energies, for the 34 s and p-block atoms H→Xe. This CE definition is a direct extension of N. Bohr's introduction of electron configurations to quantum mechanically rationalize the periodic table (hence its designation as configuration energy). Here we give experimental numbers for the remaining 8 sixth row representative atoms plus Zn, Cd, and Hg. In addition, we have carried out high accuracy numerical Dirac–Hartree–Fock solutions for all 45 atoms. Results from these calculations closely parallel the experimental values and enable us to estimate some of the atomic multiplet levels for which no experimental data exist. CE leads to numbers which are interpretable as an “electron attracting power” in the same manner as the traditional scales of Pauling and Allred & Rochow. They are also strongly correlated with atomic energy level spacings, therefore providing an additional interpretability compatible with energy level data and the molecular orbital diagrams that dominate much of contemporary chemistry. Likewise, CEs are able to rationalize the origin of the metalloid band (diagonal line separating metals from nonmetals) in the periodic table and the new determination of sixth row CEs permit designation of bismuth and polonium as *metalloids*, clarifying their previous uncertain classification between metal and metalloid.

## Introduction

Configuration energies (CEs) for the elements are defined as the average ionization energies for ground-state free atoms:

$$CE = \frac{n\epsilon_s + m\epsilon_p}{n + m} \quad (1)$$

where  $n$  and  $m$  are the number of s and p electrons, and  $\epsilon_s$  and  $\epsilon_p$  are the experimentally determined, multiplet averaged, one-electron energies obtained from the National Institute of Science and Technology (NIST) energy level tables.<sup>1</sup> The units are electronvolts per electron. The values for the first 34 representative elements were reported previously.<sup>2</sup> They have been tabulated, discussed, compared with traditional electronegativity scales, and used in the analysis of organic and inorganic systems in recent textbooks.<sup>3</sup>

CEs have a simpler conceptual basis than the traditional electronegativity scales and therefore significantly different properties. (1) They assume that molecules are constructed from neutral free atoms.<sup>4</sup> (2) CEs are independent of oxidation state and coordination numbers. (3) The ionization energies of all valence electrons are included.<sup>5</sup> (4) In addition to the traditional

descriptive meaning of electronegativity, the ability of an atom to attract and hold electrons,<sup>6</sup> CE is also strongly correlated with the spacing of its occupied and unoccupied energy levels.<sup>2</sup> (5) CE has an intimate relationship with fundamental properties of the periodic table: (a) The topography of CEs shows the

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(4) An in situ definition of electronegativity, termed bond polarity index, has been given in the following: Allen, L. C.; Egolf, D. A.; Knight, E. T.; Liang, C. *J. Phys. Chem.* **1990**, *94*, 5602. This scheme requires ab initio quantum calculations. We believe that the success achieved by eq 1 is due to the well-known very small binding energies of atoms relative to molecular total energies, therefore describable by unperturbed free atoms in first order perturbation theory,  $E_1 = \int \psi^0 H^1 \psi^0 d\tau$ .

(5) The maximum oxidation state assumption is in keeping with the neutral free atom assumption, (1). Chemical bonds almost always involve some participation by all valence electrons. Specific local bonding effects give rise to observed lower oxidation states.

(6) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, New York, 1960; p 88. Allen, L. C.; Huheey, J. E. *Inorg. Nucl. Chem.* **1980**, *42*, 1523.

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(1) Moore, C. E. *Ionization Potentials and Ionization Limits Derived From the Analyses of Optical Spectra*; NSRDS-NBS-34; Washington, D.C., 1971. Moore, C. E. *Atomic Energy Levels*; NSRDS-35; Washington, D.C., 1971; Vol. III.

(2) Allen, L. C. *J. Am. Chem. Soc.* **1989**, *111*, 9003.

origin of the diagonal line (metalloid band) separating metals from nonmetals.<sup>2</sup> (b) Metallization down groups are quantified by CE.<sup>2</sup> (c) Because of their correlation with energy level spacings, CEs themselves rationalize the structural trends of representative element molecules and solids.<sup>7</sup> (6) The CE formula, eq 1, is equally valid for all elements in the periodic table. For the transition metals,  $\epsilon_p \rightarrow \epsilon_d$ , and for the lanthanides,  $\epsilon_p \rightarrow \epsilon_f$ . (CEs for the transition elements and lanthanides will be given in future publications.) (7) G. D. Sproul<sup>8</sup> has constructed Van Arkel–Ketelaar triangles (AB bond type characterization diagrams with ionic (I), covalent (C), and metallic (M) species at the vertices) using the electronegativities of atoms A and B as the coordinates of the triangle. He found that 400 compounds known to be ionic, covalent, or metallic best fit their predicted I, C, or M domains when CE values were used compared to traditional electronegativity scales. (8) J. J. Berzelius introduced the concept of electronegativity, and in 1836 he was able to order the first 31 representative elements.<sup>9</sup> His order has a 0.95 correlation coefficient with the Pauling scale, 0.96 with Allred & Rochow, 0.97 with CEs, but considerably less with other scales.

## Methods

Beyond the direct use<sup>2</sup> of the experimental data from NIST, we employed high accuracy relativistic atomic structure calculation to interpolate some of the  $\epsilon_s$  and  $\epsilon_p$  values for which insufficient experimental data were available. In accord with our goal of constructing a universal set of neutral free atom CEs, it is obviously necessary that the atoms should be spherically symmetric. This is accomplished by the multiplet averaging of the experimental data and by using the average-of-configuration formulation in calculating atomic wave functions. Background for atomic structure theory is given in the treatise by Cowan,<sup>10</sup> and the Dirac–Hartree–Fock method that we used is described in three papers by one of us (J.B.M.).<sup>11</sup> This procedure obtains the lowest  $j$  subconfiguration ground state. A slightly different scheme (termed Dirac–Fock) by Desclaux<sup>12</sup> uses an average over all  $j$  subconfigurations arising from the single LS configuration and leads to separate solutions for  $j = l + 1/2$  and  $j = l - 1/2$ . When weighted according to their degeneracy ( $2j + 1$ ), Desclaux's one-electron orbital eigenvalues are very close to Mann's values (an average of less than 1% difference) and thus provide a valuable check on our computations (Table 1.) It is interesting to note that comparison with nonrelativistic calculations<sup>13</sup> shows very little relativistic effect on the  $\epsilon_{6p}$  values, but a very large (19% for Po) lowering of the  $\epsilon_{6s}$ .

## Results

Table 2 gives experimental and calculated  $\epsilon_s$  and  $\epsilon_p$  values, and experimental CE values, for 45 atoms (all of the main groups plus Zn, Cd, and Hg) in Rydbergs (the operating units for experimental spectroscopy), electronvolts (the most appropriate units; Rydberg to eV conversion factor = 13.6058),

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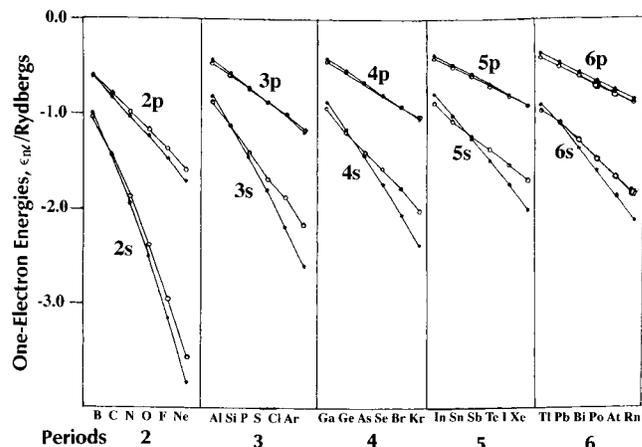
(12) Desclaux, J. P. *Atomic Data and Nuclear Data Tables* **1973**, *12*, 311.

(13) Froese-Fischer, C. *Atomic Data and Nuclear Data Tables* **1973**, *12*, 87.

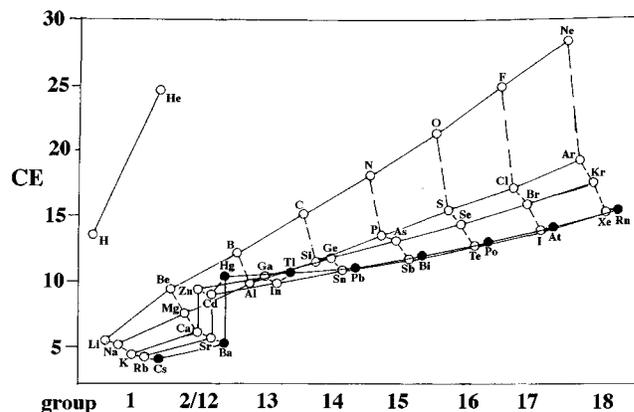
**Table 1.** Comparison of Calculated Orbital Energies (Energies in Rydberg) for the Heaviest p-Block Elements

atom	$\epsilon_{6s}$		$\epsilon_{6p}$	
	Desclaux <sup>a</sup>	this work	Desclaux <sup>a</sup>	this work
Tl	0.8984	0.8928	0.3763	0.3729
Pb	1.1330	1.1268	0.4766	0.4715
Bi	1.3724	1.3654	0.5739	0.5667
Po	1.6197	1.6118	0.6715	0.6619
At	1.8763	1.8675	0.7707	0.7583
Rn	2.1429	2.1332	0.8723	0.8567

<sup>a</sup> Derived from ref 12, see text.



**Figure 1.** Variation of one-electron energies ( $\epsilon_{nl}$ ) across periods: experimental values (open circles) and calculated values (closed circles).



**Figure 2.** Periodic variation of experimentally derived configuration energies: variation across periods (solid lines) and variation down groups (dashed lines). Closed circles represent sixth period elements.

and Pauling units (Rydberg to PU conversion factor = 2.30016, see ref 2). Comparisons between our computed Dirac–Hartree–Fock ground-state orbital energies and the experimental one-electron excitation energies are tabulated along with the Pauling<sup>14</sup> and Allred & Rochow<sup>15</sup> electronegativities. Figure 1 shows the remarkable parallelism between the experimental one-electron excitation energies and the atomic orbital energy eigenfunctions of the Dirac–Hartree–Fock solutions which approximate  $\epsilon_{nl}$ . Careful analysis of the trends for  $n = 2$  to 3 to 4 to 5 (particularly for the s electrons) enabled us to obtain very satisfactory sixth row values despite incomplete experimental data.

The main group CE graph of Figure 2 clearly displays the relatively small differences and intricacy of variation in groups

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(15) Allred, A. L.; Rochow, E. G. *J. Inorg. Nucl. Chem.* **1958**, *5*, 264.

**Table 2.** Orbital Energies and Configuration Energies: Main Group Elements (All Orbital Energies in Rydberg)

atom	calculated		experimental		configuration energy			$\chi^p{}^a$	$\chi^{AR}{}^b$
	$\epsilon_s$	$\epsilon_p$	$\epsilon_s$	$\epsilon_p$	Rydberg	eV	PU		
H	1.0000		1.0000		1.0000	13.61	2.300	2.20	2.20
He	1.8360		1.8074		1.8074	24.59	4.160		3.84 <sup>c</sup>
Li	0.3926		0.3963		0.3963	5.392	0.912	0.98	0.97
Be	0.6186		0.6852		0.6852	9.323	1.576	1.57	1.47
B	0.98899	0.6194	1.0323	0.6098	0.8915	12.13	2.051	2.04	2.01
C	1.4252	0.8134	1.4282	0.7838	1.1060	15.05	2.544	2.55	2.50
N	1.9297	1.0168	1.8784	0.9687	1.3326	18.13	3.066	3.04	3.07
O	2.5050	1.2317	2.3796	1.1646	1.5696	21.36	3.610	3.44	3.50
F	3.1522	1.4592	2.9526	1.3709	1.8228	24.80	4.193	3.98	4.10
Ne	3.8721	1.6997	3.5628	1.5870	2.0810	28.31	4.787		4.77 <sup>c</sup>
Na	0.3647		0.3778		0.3778	5.140	0.869	0.93	1.01
Mg	0.5069		0.5620		0.5620	7.646	1.293	1.31	1.23
Al	0.7889	0.4191	0.8320	0.4393	0.7011	9.539	1.613	1.61	1.47
Si	1.0910	0.5565	1.0942	0.5716	0.8329	11.33	1.916	1.90	1.74
P	1.4188	0.7000	1.3848	0.7095	0.9796	13.33	2.253	2.19	2.06
S	1.7746	0.8514	1.6689	0.8537	1.1254	15.31	2.589	2.58	2.44
Cl	2.1591	1.0114	1.8542	1.0046	1.2473	16.97	2.869	3.16	2.83
Ar	2.5731	1.1806	2.1491	1.1627	1.4093	19.17	3.242		3.29 <sup>c</sup>
K	0.2960		0.3190		0.3190	4.340	0.734	0.82	0.91
Ca	0.3926		0.4493		0.4493	6.113	1.034	1.00	1.04
Zn	0.5971		0.6905		0.6905	9.395	1.588	1.66	1.65
Ga	0.8684	0.4143	0.9270	0.4359	0.7633	10.39	1.756	1.81	1.82
Ge	1.1407	0.5362	1.1796	0.5544	0.8670	11.80	1.994	2.01	2.02
As	1.4235	0.6580	1.3921	0.6738	0.9611	13.08	2.211	2.18	2.20
Se	1.7251	0.7828	1.5710	0.7951	1.0537	14.34	2.424	2.55	2.48
Br	2.0414	0.9121	1.7914	0.9177	1.1673	15.88	2.685	2.96	2.74
Kr	2.3747	1.0465	2.0222	1.0453	1.2895	17.54	2.966	3.34 <sup>c</sup>	3.00 <sup>c</sup>
Rb	0.2800		0.3070		0.3070	4.177	0.706	0.82	0.89
Sr	0.3260		0.4186		0.4186	5.695	0.963	0.95	0.99
Cd	0.5622		0.6611		0.6611	8.995	1.521	1.69	1.46
In	0.7922	0.3896	0.8738	0.4118	0.7198	9.793	1.656	1.78	1.49
Sn	1.0193	0.4933	1.0702	0.5155	0.7928	10.79	1.824	1.96	1.72
Sb	1.2533	0.5953	1.2301	0.6178	0.8627	11.74	1.984	2.05	1.82
Te	1.4970	0.6986	1.3750	0.7196	0.9381	12.76	2.158	2.10	2.10
I	1.7516	0.8040	1.5352	0.8215	1.0254	13.95	2.359	2.66	2.21
Xe	2.0179	0.9133	1.7196	0.9235	1.1226	15.27	2.582	2.95 <sup>c</sup>	2.45 <sup>c</sup>
Cs	0.2561		0.2865		0.2865	3.898	0.659	0.79	0.86
Ba	0.3260		0.3830		0.3830	5.211	0.881	0.89	0.97
Hg	0.6506		0.7672		0.7672	10.44	1.765	2.00	1.44 <sup>d</sup>
Tl	0.8928	0.3729	0.9656	0.4019	0.7777	10.58	1.789	2.04	1.44 <sup>d</sup>
Pb	1.1268	0.4715	1.1111	0.5008	0.8060	10.97	1.854	2.33	1.55 <sup>d</sup>
Bi	1.3654	0.5667	(1.288)	0.5990	(0.874)	(11.9)	(2.01)	2.02	1.67 <sup>d</sup>
Po	1.6118	0.6619	(1.474)	(0.692)	(0.953)	(13.0)	(2.19)	2.0	1.76 <sup>d</sup>
At	1.8675	0.7583	(1.668)	(0.787)	(1.039)	(14.1)	(2.39)	2.2	1.90 <sup>d</sup>
Rn	2.1332	0.8567	(1.872)	0.8845	(1.131)	(15.4)	(2.60)		2.05 <sup>c</sup>

<sup>a</sup> Reference 14 unless otherwise noted. <sup>b</sup> Reference 15 unless otherwise noted. <sup>c</sup> Reference 22. <sup>d</sup> Reference 23.

12–15, which necessitated the spectroscopic accuracy we have obtained. Figure 3A for  $\epsilon_{ns}$  and Figure 3B for  $\epsilon_{np}$  show that this intricacy principally resides in the s electron energies. It results from three separate effects: (1) the poor screening by the d-subshell (due to the  $P(r) = r^3$  dependence near the nucleus) in going from group 2 to group 12, (2) the “lanthanide contraction” (poor screening by the f-subshell due to its  $P(r) = r^4$  dependence near the nucleus), which partly accounts for the close similarity between the fifth and sixth rows, and (3) relativity, which makes sixth row CEs slightly greater than fifth row values and appears to dominate over the lanthanide contraction. The effect of poor screening by d- and/or f-subshells decreases in the group order  $13 > 14 > 15$ , while relativistic effects<sup>16</sup> increase with  $Z$  as evident by the increasing separation of CEs at the end of the sixth row. (Forthcoming results for the d-block elements are consistent with relativistic stabilization of

the 6s orbitals dominating over the lanthanide contraction as cause for higher Tl–Rn CEs compared to those for In–Xe.)

One can gain some insight into the consequences of the complexity apparent in Figure 2 by imagining atoms whose d and f electrons had the same screening power as the p electrons of the second and third rows. Leaving relativity as is, Figure 2 would be approximated by five nearly straight lines with successively lower slopes. This hypothetical pattern was postulated by the eminent Russian chemical physicists V. P. Spiridonov and V. M. Tatevskii in 1963.<sup>21</sup> If this pattern were

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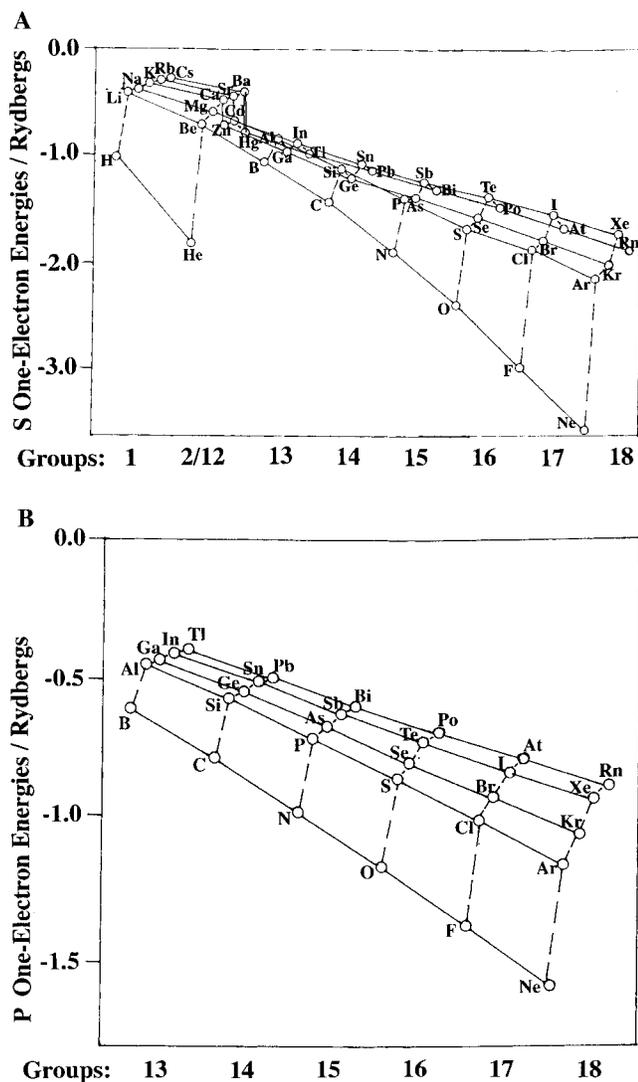
(18) Rochow, E. G. *The Metalloids*; D. C. Heath, 1966.

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(21) Spiridonov, V. P.; Tatevskii, V. M. *Russ. J. Phys. Chem.* **1963**, *37*, 1177 (Engl. Trans.).

(16) (a) Pitzer, K. S. *Acc. Chem. Res.* **1979**, *12*, 271. (b) Pyykko, P.; Desclaux, J.-P. *Acc. Chem. Res.* **1979**, *12*, 276.



**Figure 3.** (A) Periodic variation of experimental s-electron energies: variation across periods (solid lines) and variation down group (dashed lines). (B) Periodic variation of experimental p-electron energies: variation across periods (solid lines) and variation down group (dashed lines).

true, the atomic energies given by electronegativity scales would be a simple function of the nuclear charge  $Z$ .

**Bismuth and Polonium Are Metalloids.** CEs for bismuth and polonium fall within the narrow range of values (1.916–2.211 PU) established by the recognized metalloids: Si, Sb, Ge, B, Te, and As (in ascending CE order). The metalloids have a range of chemical and physical properties intermediate between metallic and nonmetallic and Bi and Po fit this categorization, although numerous authors (e.g. ref 17) have classified them as metals, presumably because of their moderate conductivity and the (unique) primitive cubic structure of Po.

However, Rochow's classic monograph on the metalloids<sup>18</sup> notes that Bi can be grouped with the metalloids because of its relatively low conductance and its amphoteric nature. Burdett et al.<sup>19</sup> have recently carried out calculations on solids and their relation to metallic and insulating behavior. In their analysis, Bi is a metalloid, distorted from a metallic structure and possessing localized bonds, but just short of opening any energy band gaps. This is manifested in the lattice structure<sup>17</sup> of its most stable allotrope in which each atom has three neighbors at 3.072 Å and three at 3.526 Å.

The electrical resistivity of Bi is 107  $\mu$  ohm cm and that of Po is 140  $\mu$  ohm cm (compared to 1.5  $\mu$  ohm cm for Cu and 8.5  $\mu$  ohm cm for Fe).<sup>20</sup> The values for the two metalloids, Sb and As, are 39 and 26  $\mu$  ohm cm, respectively, and these are never considered to be metals. Chemically, Bi forms a basic oxide and some cationic species in solution (e.g.  $[\text{Bi}_6(\text{OH})_{12}]^{6+}$ ) and in solid salts such as the hydrated  $\text{Bi}(\text{SO}_4)_3$ ,  $\text{Bi}(\text{NO}_3)_3$ , and  $\text{Bi}(\text{ClO}_4)_3$ , and in salts containing  $\text{BiO}^+$ , but its halides are molecular except for the (polymeric) fluorides. What little is known about Po chemistry is consistent with nonmetallic character: the oxides are acidic, and no cationic compounds have been observed. Thus both elements display some metallic and some nonmetallic properties, i.e., they are metalloids, and it is satisfying that CE can quantitatively resolve this long-standing ambiguity.

### Summary

1. Configuration energies (CEs) are experimentally derived quantum mechanical electronegativities which are defined as the average ionization energies of the valence electrons for free atoms in their ground states. Values for the 45 atoms of groups 1, 2, and 12–18 are given to four significant figure accuracy because of the small differences between some of the atoms. The units are electronvolts per electron.

2. Average-of-configuration Dirac–Hartree–Fock one-electron atomic orbital eigenvalues for the atomic ground states have been numerically calculated and a close parallelism with the multiplet averaged experimental excitation energies is obtained. This has permitted accurate extrapolation to some sixth row  $\epsilon_{nl}$  values for which experimental data were not available.

3. Each of the group 12–18 elements in the sixth period has a higher CE than those of the fifth period element in the same group. This is largely a consequence of the relativistic stabilization of the 6 s orbitals.

4. On the basis of their CEs, bismuth and polonium can be classified as metalloids, and this is consistent with their chemical and physical properties.

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