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# Theoretical Justification for Bond Valence – Bond Length Empirical Correlations

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## Abstract

Bond valence – bond length empirical correlations are of great interest in chemistry, biology, geology and materials science because they offer a quick and convenient way of checking and evaluating molecular structures. Linus Pauling's relationship is the most commonly used, but is a two-parameter fit where  $R_0$  and  $b$  must be optimized. In this study, a simplified quantum-mechanical approach was used to derive Pauling's empirical bond valence – bond length relationship. A covalency factor was also introduced to account for the difference in "softness" between cation and anion (resulting in increased orbital overlap). An expression for the  $b$  parameter was determined that yields values that are in agreement with experimental data. The derived relationship for the  $b$  parameter allows an independent determination of  $b$  using orbital exponents and electronegativity values for the cation and anion.

## Introduction

In 1929, Linus Pauling developed five basic rules of chemical bonding (Pauling 1929). Pauling's second rule is perhaps the most important and states the principle of local charge neutrality, where the negative charge of each anion is neutralized by the positive charges of neighboring cations and, conversely, the cationic charges are neutralized by neighboring anions. A restatement of this rule is that the sum of the bond strengths (in valence units) around each cation is compensated by the valence of the anions. This has since been generalized as the valence sum rule

$$V_i = \sum_j s_{ij} \quad (1)$$

where  $s_{ij}$  is the bond valence (equal to the bond flux) for each bond to the cation, and  $V_i$  is the oxidation state of the cation and/or the number of electrons available for bonding. The sum of bond valences around any ion,  $i$ , is equal to its valence,  $V_i$ .

Bond valence – bond length empirical correlations have been used for many years (Pauling 1947,

Zachariassen 1954). Perhaps the two most commonly used relationships are

$$s = (R/R_0)^{-N} \quad (2)$$

and

$$s = \exp\left(\frac{R_0 - R}{b}\right) \quad (3)$$

where  $s$  is the bond valence (bond order) or number of shared electron pairs involved in the bond,  $R$  is bond length,  $R_0$  is the bond length of a chemical bond having unit valence, and  $N$  and  $b$  are empirical fitting parameters that are sometimes associated with the softness of the bond. Equation (3) is the most widely used and was the one first proposed by Pauling in 1947 (Pauling 1947). In practice, the  $b$  and  $R_0$  parameters are found by minimizing the difference between the bond valence sums and the atomic valence of the central cation. Values of  $b$  have been found to range between 0.3 and 0.6 Å, but because of limited experimental results,  $b$  is often assumed to be a universal constant of 0.37 Å (average of tabulated values), although this limits the applicability of the relationship, decreasing the reliability of the relationship for very short and very long bonds.

Bond valence – bond length relationships, combined with the valence sum rule have obvious applications, and have found recent use in checking crystal structures and evaluating the reasonableness of proposed molecular structures. They can also be used to determine oxidation states of cations or anions and to determine coordination numbers for organo-metallic complexes. Furthermore, although first developed to model ionic crystals, these relationships have proven effective for both ionic and covalent systems.

Although a universal  $b$  parameter of 0.37 Å is used by many workers in order to change Equation (3) to a one-parameter fit, it is also conceded to be an approximation (Brown 1985). For a number of systems, especially for cations with lone electron pairs, the  $b$  parameter should be significantly larger than 0.37 Å (Krivovichev and Brown 2001). Adams demonstrated that the value of  $b$  for a given bond type depends on the arbitrarily chosen maximum bond

length and that the bond valence parameters determined using both the first and second coordination spheres were significantly different from those determined using the first coordination sphere alone (Adams 2001, 2008). Adams also found that, as the cutoff distance increases, the value of  $b$  increases, usually to values much greater than 0.37 Å. Furthermore, since  $b$  represents the apparent softness of the interaction between the cation and anion, there is a relationship between  $b$  and the atomic softness parameter,  $\sigma = 2/(IE-EA)$ , for alkali metals and chalcogenides (Parr and Pearson 1983), where IE is the ionization energy and EA is the electron affinity of the ion. It was found that the value of  $b$  depends on the difference between the anion and cation softness, and has a value close to 0.37 Å when anion and cation have the same softness, but increases to 0.7 Å when the difference in softness is great.

It has been noted (Brown 2009) that although the bond valence model works well for polar bonds, it does not work for homopolar bonds like the well-known C-C bonds for which bond lengths are routinely assigned bond orders. In fact, it has been remarked as “mathematically impossible” for bond valences to obey the valence sum rule for homopolar bonds (Brown 2009).

In the present study, a simplified quantum-mechanical approach is used to derive Pauling’s empirical bond valence – bond length relationship. A covalency factor is introduced to account for the difference in “softness” between cation and anion (resulting in increased orbital overlap). By using this approach, an expression for the  $b$  parameter is determined that yields values comparable to those that have been experimentally determined.

## Theory

### Defining Bond Valence

We use the method of linear combination of atomic orbitals (LCAO) to represent the bonding between two atoms

$$\psi = c_1\chi_1 + c_2\chi_2 \quad (4)$$

where  $\psi$  is the bonding molecular orbital wave function, and  $\chi_1$  and  $\chi_2$  are the atomic orbital wave functions with respective weighting coefficients of  $c_1$  and  $c_2$ . The probability density is given by the product of the wave function:

$$\begin{aligned} \psi^2 &= (c_1\chi_1 + c_2\chi_2)(c_1\chi_1 + c_2\chi_2) \\ &= c_1^2\chi_1^2 + c_2^2\chi_2^2 + 2c_1c_2\chi_1\chi_2 \end{aligned} \quad (5)$$

It is well known that integration over all space must have a probability equal to 1. The integrated third term,  $2c_1c_2\chi_1\chi_2$ , called the Mulliken population density (Mulliken 1955), or the integrated sum of the overlap between the two atomic orbital wave functions, represents the electronic interaction between the two atoms and is associated with bond strength. We define the bond valence as the cross-section (thickness) of this overlap region. That is, we define the bond valence,  $s$ , simply as

$$s \equiv 2c_1c_2\chi_1\chi_2 \quad (6)$$

### Using Hydrogen-Like Wave Functions

It is common to use hydrogen-like wave functions to represent a valence electron in a chemical bond. In 1930, Slater found that, when the radial function is approximated, the wave functions can be written as

$$\psi_{n,l,m} = r^{n^*-1} e^{-\frac{(Z-s)r}{a_0n^*}} Y_{l,m}(\theta, \phi) \quad (7)$$

where  $r^{n^*-1}$  serves to broaden and shift the function with increasing principal quantum number  $n$ . For our application, the function will be “shifted” when normalized to unit valence. Since we are interested only in the overlap region (region of chemical interest), far from the nucleus, we ignore the “ $r^{n^*-1}$ ” term as well as the spherical harmonics,  $Y(\theta, \phi)$ . The bond valence, Equation (6), becomes

$$s \equiv 2c_1c_2 \left( e^{-\frac{(Z-s)r_1}{a_0n_1}} \right) \left( e^{-\frac{(Z-s)r_2}{a_0n_2}} \right) \quad (8)$$

where  $Z$  is the nuclear charge of the atom,  $s$  is the screening constant (the core electrons shield the valence electron(s) from the nuclear charge), and  $a_0$  is the Bohr radius (0.529 Å). Typically, the effective nuclear charge ( $Z_{\text{eff}} = Z - s$ ) with respect to the effective principle quantum number,  $n$ , is expressed as orbital exponents,  $\xi$ ,

$$\xi = \frac{Z_{\text{eff}}}{n} \quad (9)$$

Orbital exponents may be calculated using Slater’s rules, which are outlined in most inorganic chemistry texts (Huheey 1978), or self-consistent field methods

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(Clementi et al. 1963, 1967), but are sometimes considered as adjustable parameters that are optimized based on the molecule or the basis set of interest. Substituting into Equation (8), designating atoms  $R_1$  and  $R_2$  as the cation and anion radii, respectively, then taking the natural logarithm,

$$\ln s = \ln 2 + \ln c_1 + \ln c_2 - \frac{\xi_1 R_1}{a_0} - \frac{\xi_2 R_2}{a_0} \quad (10)$$

For a chemical bond having unit valence ( $s=1$ ) and a corresponding bond length of  $R_0$  (by definition),

$$\ln 1 = \ln 2 + \ln c_1 + \ln c_2 - \frac{\xi_1 R_{1,0}}{a_0} - \frac{\xi_2 R_{2,0}}{a_0} \quad (11)$$

Subtracting Equation (11) from Equation (10) results in

$$\ln s = \frac{\xi_1 (R_{1,0} - R_1)}{a_0} + \frac{\xi_2 (R_{2,0} - R_2)}{a_0} \quad (12)$$

### Atomic Radius and the Covalency Factor

Textbooks of physical chemistry show that the atomic radius,  $R$ , can be expressed as its expectation value; for the hydrogen atom, this value is  $3a_0/2$  which provides a point of reference for defining  $R_1$  and  $R_2$ . We set  $R_1=R_2=R/3$ , where  $R$  is now the experimental bond length. The overlap region is also equal to  $R/3$ . Incorporating these new values for  $R_1$  and  $R_2$ ,

$$\ln s = \frac{\xi_1 (R_0 - R)}{3a_0} + \frac{\xi_2 (R_0 - R)}{3a_0} \quad (13)$$

This simplification works well for ionic bonds, but not bonds for which the electronegativity difference

$$\Delta\chi = |\chi_{cation} - \chi_{anion}| \quad (14)$$

is significant. Using a Gaussian function similar to that of Pauling's to define percent covalency, we define a "covalency factor" given simply by

$$e^{-\Delta\chi^2} \quad (15)$$

As bond covalency increases, the overlap region increases. Our covalency factor, which depends on electronegativity differences, can be compared to the difference in "softness" used by Parr and Pearson (1983), where  $b$  is close to  $0.37 \text{ \AA}$  when anion and

cation have the same softness, but increases to  $0.7 \text{ \AA}$  when the difference is great.

### The "b" Parameter

Incorporating the covalency factor into Equation (13), and re-labeling "1" as cation and "2" as anion, leads to

$$\ln s = \frac{(R_0 - R)}{(3 - e^{-\Delta\chi^2})a_0} (\xi_{cation} + \xi_{anion}) \quad (16)$$

Rearranging and substituting,

$$\ln s = \frac{(R_0 - R)}{b} \quad (17)$$

which is identical to Pauling's empirical bond valence – bond length relationship, where we have determined the  $b$  parameter to be

$$b = \frac{(3 - e^{-\Delta\chi^2})a_0}{(\xi_{cation} + \xi_{anion})} \quad (18)$$

## Results and Discussion

Equation (18) is used to compute  $b$  parameter values from cation and anion electronegativities (Pauling scale), orbital exponents, and the Bohr radius. Clementi's orbital exponents were used for the most part (Clementi and Raimondi 1963, Clementi et al. 1967), although Slater's rules were used for selenium, bromine, tellurium and iodine; another source was used for the lanthanides and actinides (Ghosh and Biswas 2002). The computed values are compared to experimentally-determined published values, and the results are presented in Tables 1-8.

Table 1 shows cations of periods 1 and 2, ranging from hydrogen to oxygen.  $R_0$  are cation-anion bond lengths of unit valency ( $s=1$ ). Orbital exponents (Equation (9)) of the respective cations and anions are listed in the next two columns (labeled  $Z_{eff/n}$ ). The covalency factor, Equation (15), determined from electronegativity differences, Equation (14), are shown in the next column. Calculated  $b$  values, computed using Equation (18), are shown in the next to last column.

Table 1: Hydrogen to Oxygen

		Ro	Zeff/n Cat	Zeff/n An	Cov Fact	Calc "b"	Lit "b"
H	O	0.914	1	2.227	0.215	0.457	0.404
H	N	0.885	1	1.917	0.494	0.455	0.37
H	C	1.08	1	1.568	0.494	0.516	0.26
H	P	1.08	1	1.629	1.000	0.403	0.403*
Li	O	1.172	0.6396	2.227	0.002	0.553	0.515
Li	N	1.15	0.6396	1.917	0.014	0.618	0.631
Li	F	1.101	0.6396	2.550	0.000	0.498	0.501
Li	S	1.507	0.6396	1.827	0.077	0.627	0.632
Li	Cl	1.342	0.6396	2.039	0.009	0.591	0.661
Li	Br	1.534	0.6396	1.900	0.020	0.621	0.665
Li	Se	1.53	0.6396	1.738	0.085	0.649	0.515
Li	Te	1.734	0.6396	1.390	0.285	0.708	0.717
Be	O	1.381	0.956	2.227	0.030	0.494	0.37
Be	F	1.281	0.956	2.550	0.003	0.452	0.37
B	O	1.371	1.2107	2.227	0.141	0.440	0.37
B	F	1.289	1.2107	2.550	0.023	0.419	0.37
B	S	1.815	1.2107	1.827	0.747	0.392	0.37
B	N	1.482	1.2107	1.917	0.368	0.445	0.37
B	P	1.92	1.2107	1.629	0.978	0.377	0.37
C	O	1.43	1.5679	2.227	0.453	0.355	0.38
C	N	1.471	1.5679	1.917	0.787	0.336	0.31
C	C	1.54	1.5679	1.568	1.000	0.338	0.37
N	O	1.4	1.917	2.227	0.852	0.274	0.274*
N	N	1.471	1.917	1.917	1.000	0.276	0.34*
O	O	1.455	2.2266	2.227	1.000	0.238	0.3931

Table 2: Sodium to Chlorine

		Ro	Zeff/n Cat	Zeff/n An	Cov Fact	Calc "b"	Lit "b"
Na	O	1.56	0.8358	2.227	0.002	0.518	0.483
Na	F	1.677	0.8358	2.550	0.000	0.469	0.475
Na	S	1.831	0.8358	1.827	0.066	0.583	0.621
Na	Cl	1.694	0.8358	2.039	0.007	0.551	0.603
Na	Se	1.879	0.8358	1.738	0.072	0.602	0.66
Na	Te	2.052	0.8358	1.390	0.254	0.653	0.684
Na	I	1.969	0.8358	1.520	0.050	0.663	0.688
Mg	O	1.693	1.1025	2.227	0.011	0.475	0.512
Mg	F	1.578	1.1025	2.550	0.001	0.435	0.504
Al	O	1.651	1.3552	2.227	0.035	0.438	0.424
Al	Cl	2.032	1.3552	2.039	0.090	0.454	0.646
Al	F	1.545	1.3552	2.550	0.004	0.406	0.519
Si	O	1.624	1.4284	2.227	0.093	0.421	0.432
Si	C	1.883	1.4284	1.568	0.655	0.414	0.37
Si	N	1.724	1.4284	1.917	0.273	0.431	0.37
Si	S	2.126	1.4284	1.827	0.630	0.385	0.37
P	O	1.617	1.62867	2.227	0.210	0.383	0.291*
P	N	1.704	1.62867	1.917	0.486	0.375	0.37
P	S	2.145	1.62867	1.827	0.859	0.328	0.37
P	P	2.21	1.62867	1.629	1.000	0.325	0.303*
S	O	1.624	1.82733	2.227	0.477	0.329	0.37
S	N	1.762	1.82733	1.917	0.809	0.310	0.37
Cl	O	1.632	2.03867	2.227	0.925	0.257	0.37

\*Experimental  $b$  parameters for P-H, C-N, N-O, N-N, O-O, P-O and P-P bonds determined by the authors (unpublished work).

Table 3: Potassium to Selenium

		Ro	Zeff/n Cation	Zeff/n Anion	Cov Factor	Calc "b"	Lit "b"
K	O	1.973	0.8738	2.227	0.001	0.512	0.422
K	F	1.992	0.8738	2.550	0.000	0.464	0.422
K	S	2.171	0.8738	1.827	0.045	0.579	0.571
K	Cl	2.087	0.8738	2.039	0.004	0.544	0.552
K	Se	2.257	0.8738	1.738	0.050	0.598	0.624
K	Br	2.1	0.8738	1.900	0.010	0.570	0.625
K	I	2.32	0.8738	1.520	0.034	0.656	0.641
Ca	O	1.967	1.0995	2.227	0.003	0.477	0.476
Ca	F	1.842	1.0995	2.550	0.000	0.435	0.467
Ga	O	1.73	1.5554	2.227	0.070	0.410	0.373
Ga	S	2.163	1.5554	1.827	0.553	0.383	0.483
Ge	O	1.748	1.6951	2.227	0.129	0.387	0.396
Ge	S	2.217	1.6951	1.827	0.723	0.342	0.514
As	O	1.767	1.575	2.227	0.204	0.389	0.411
As	S	2.272	1.575	1.827	0.852	0.334	0.534
As	F	1.62	1.575	2.550	0.039	0.380	0.503
Se	O	1.788	1.7375	2.227	0.453	0.340	0.416

Table 4: Rubidium to Iodine

		Ro	Zeff/n Cation	Zeff/n Anion	Cov Factor	Calc "b"	Lit "b"
Rb	O	2.057	0.9969	2.227	0.001	0.492	0.425
Rb	S	2.301	0.9969	1.827	0.045	0.554	0.552
Rb	Se	2.402	0.9969	1.738	0.050	0.571	0.581
Rb	Te	2.46	0.9969	1.390	0.194	0.622	0.616
Rb	F	2.957	0.9969	2.550	0.000	0.448	0.418
Rb	Cl	2.244	0.9969	2.039	0.004	0.522	0.54
Rb	Br	2.327	0.9969	1.900	0.010	0.546	0.579
Rb	I	2.467	0.9969	1.520	0.034	0.624	0.631
Sr	O	2.118	1.2141	2.227	0.002	0.461	0.455
In	O	1.902	1.694	2.227	0.064	0.396	0.353
In	F	1.792	1.694	2.550	0.008	0.373	0.421
In	S	2.37	1.694	1.827	0.527	0.372	0.456
Sn	O	1.905	1.8204	2.227	0.112	0.378	0.379
Sn	F	1.843	1.8204	2.550	0.017	0.361	0.37
Sn	S	2.399	1.8204	1.827	0.681	0.336	0.37
Sn	Cl	2.276	1.8204	2.039	0.237	0.379	0.37
Sb	O	1.908	1.26	2.227	0.145	0.433	0.409
Sb	F	1.797	1.26	2.550	0.024	0.413	0.489
Sb	S	2.474	1.26	1.827	0.755	0.385	0.37
Te	O	1.917	1.39	2.227	0.166	0.415	0.412
I	O	2.003	1.52	2.227	0.544	0.347	0.37

The last column in Tables 1-8 lists experimentally determined  $b$  values. These values are from many reference sources, but have been conveniently compiled into a few major references (Brown 2002, 2009), as well as a web site (Adams 2008). Where experimental  $b$  values were not determined, the general practice is to use  $b = 0.37 \text{ \AA}$ ; these are also listed in the tables, but are italicized. It is important to recognize that  $b$  values are coupled to the choice of  $R_o$ , so that a different choice of bond distance having unit valence

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would certainly affect the value of  $b$ . Experimentally determined  $b$  values for P-H, C-N, N-O, N-N, and O-O bonds were determined using published bond lengths for diatomics (Huber and Herzberg 1979).

Table 5: Cesium to Bismuth

Cat	An	Ro	Zeff/n	Zeff/n	Cov	Calc	Lit
			Cation	Anion		"b"	"b"
Cs	O	2.298	1.0605	2.227	0.001	0.483	0.419
Cs	S	2.515	1.0605	1.827	0.041	0.542	0.519
Cs	Se	2.657	1.0605	1.738	0.045	0.559	0.546
Cs	Te	2.736	1.0605	1.390	0.180	0.609	0.617
Cs	F	2.196	1.0605	2.550	0.000	0.440	0.428
Cs	Cl	2.505	1.0605	2.039	0.004	0.512	0.5
Cs	Br	2.515	1.0605	1.900	0.009	0.535	0.538
Cs	I	2.695	1.0605	1.520	0.030	0.609	0.608
Ba	O	2.285	1.2625	2.227	0.001	0.455	0.437
Ba	F	2.188	1.2625	2.550	0.000	0.416	0.428
Ba	S	2.769	1.2625	1.827	0.057	0.504	0.573
Tl	I	2.822	2.0423	1.520	0.339	0.395	0.37
Tl	S	2.545	2.0423	1.827	0.398	0.356	0.37
Pb	O	1.963	1.3452	2.227	0.292	0.401	0.354
Pb	S	2.541	1.3452	1.827	0.939	0.344	0.37
Pb	F	2.036	1.3452	2.550	0.066	0.399	0.424
Pb	Cl	2.447	1.3452	2.039	0.502	0.391	0.4
Pb	Br	2.598	1.3452	1.900	0.672	0.380	0.4
Pb	I	2.804	1.3452	1.520	0.897	0.388	0.386
Bi	O	2.094	1.5	2.227	0.133	0.407	0.371
Bi	Br	2.567	1.5	1.900	0.133	0.446	0.421
Bi	S	2.57	1.5	1.827	0.731	0.361	0.37

Tables 2, 3, 4 and 5 list calculated values of the  $b$  parameter for main group cation elements sodium to chlorine (period 3), Table 2, potassium to selenium (period 4), Table 3, rubidium to iodine (period 5), Table 4, and cesium to bismuth (period 6), Table 5. With few exceptions, agreement with experiment (calculated and literature columns) is excellent.

Application of these parameters is straightforward. For example, if a bond valence – bond length correlation were desired for silicon-oxygen bonds, Table 2 shows values of  $R_0 = 1.624 \text{ \AA}$  and  $b = 0.421 \text{ \AA}$  (calculated using Equation (18)). Substituting these values into Pauling's relationship, Equation (3) or (17), yields

$$s_{Si-O} = \exp\left[\frac{(1.624 - R)}{0.421}\right] \quad (19)$$

Equation (19) describes the quantitative relationship between Si-O bond strength (or valence) in valence units, and the Si-O bond length in Angstroms. The bond valence – bond length relationships hold

regardless of environment, physical state, or oxidation state.

Table 6: 1st-Row Transition Elements

Cat	An	Ro	Zeff/n	Zeff/n	Cov	Calc	Lit
			Cation	Anion		Factor	"b"
Sc	O	1.849	1.1581	2.227	0.013	0.467	0.494
Sc	S	2.321	1.1581	1.827	0.226	0.492	0.631
Ti	O	1.815	1.2042	2.227	0.027	0.459	0.463*
V	O	1.788	1.2453	2.227	0.038	0.451	0.51
Cr	O	1.794	1.2833	2.227	0.042	0.446	0.516
Cr	F	1.657	1.2833	2.550	0.005	0.414	0.37
Mn	O	1.753	1.3208	2.227	0.028	0.443	0.52
Mn	Cl	2.133	1.3208	2.039	0.075	0.461	0.37
Mn	F	1.666	1.3208	2.550	0.003	0.410	0.36
Fe	O	1.795	1.3585	2.227	0.075	0.432	0.42
Fe	C	1.689	1.3585	1.568	0.595	0.435	0.37
Fe	F	1.679	1.3585	2.550	0.010	0.405	0.411
Fe	S	2.149	1.3585	1.827	0.570	0.404	0.37
Co	O	1.692	1.3941	2.227	0.088	0.426	0.434
Co	Cl	2.033	1.3941	2.039	0.194	0.433	0.37
Co	C	1.634	1.3941	1.568	0.638	0.422	0.37
Ni	O	1.654	1.4277	2.227	0.096	0.420	0.443
Ni	F	1.596	1.4277	2.550	0.014	0.397	0.452
Cu	O	1.679	1.4606	2.227	0.093	0.417	0.449
Cu	C	1.716	1.4606	1.568	0.655	0.410	0.37
Cu	N	1.713	1.4606	1.917	0.273	0.427	0.37
Cu	I	2.108	1.4606	1.520	0.561	0.433	0.37
Cu	S	1.898	1.4606	1.827	0.630	0.381	0.37
Cu	F	1.594	1.4606	2.550	0.013	0.394	0.457
Zn	O	1.704	1.2891	2.227	0.041	0.445	0.403
Zn	S	2.09	1.2891	1.827	0.421	0.438	0.54
Zn	Cl	2.027	1.2891	1.827	0.102	0.492	0.521
Zn	Te	2.45	1.2891	1.390	0.817	0.431	0.616

\*Experimentally determined  $b$  parameter for Ti-O bonds was determined by the authors (unpublished work).

Table 6 lists the calculated  $b$  parameters for the first-row transition elements, and Table 7 for selected second- and third-row transition elements. Again, almost without exception, the calculated and literature  $b$  parameters are in reasonable agreement.

Table 8 lists the calculated  $b$  parameters for selected lanthanides and actinides. Although most of the orbital exponents ( $Z_{\text{eff}}/n$ ) used in the calculation of the  $b$  parameters were taken from Clementi (Clementi and Raimondi 1963, Clementi et al. 1967), we used the more recent values from Ghosh and Biswas (2002) for the lanthanides and actinides. As the list of experimentally determined  $b$  parameters from Table 8 indicates, the lanthanides and actinides have not been investigated to the same level as the transition elements; when data are not available, the  $b$  parameter is assumed to be 0.37.

Table 7: 2nd,3rd-Row Transition Elements

Cat	An	Ro	Zeff/n	Zeff/n	Cov	Calc	Lit
			Cation	Anion		"b"	"b"
Y	O	2.019	1.2512	2.227	0.007	0.455	0.478
Zr	O	1.928	1.2891	2.227	0.012	0.450	0.49
Zr	F	1.846	1.2891	2.550	0.001	0.413	0.388
Nb	O	1.911	1.1842	2.227	0.034	0.460	0.498
Mo	O	1.912	1.3952	2.227	0.194	0.410	0.405
Mo	S	2.067	1.3952	1.827	0.194	0.461	0.4705
Mo	F	1.738	1.3952	2.550	0.194	0.376	0.427
Mo	Cl	2.090	1.3952	2.039	0.194	0.432	0.5
Mo	Br	2.191	1.3952	1.900	0.194	0.451	0.541
Tc	O	1.909	1.4453	2.227	0.093	0.419	0.514
Ru	O	1.9	1.4905	2.227	0.215	0.396	0.425
Ag	O	1.842	1.3511	2.227	0.102	0.429	0.394
Ag	S	2.119	1.3511	1.827	0.655	0.390	0.365
Ag	I	2.38	1.3511	1.520	0.587	0.445	0.53
Cd	O	1.904	1.6384	2.227	0.047	0.404	0.407
Cd	N	1.951	1.6384	1.917	0.162	0.422	0.37
Cd	S	2.279	1.6384	1.827	0.453	0.389	0.37
Cd	Cl	2.216	1.6384	2.039	0.115	0.415	0.512
Cd	Br	2.334	1.6384	1.900	0.199	0.419	0.553
Cd	I	2.525	1.6384	1.520	0.390	0.437	0.613
Ta	O	1.92	1.5875	2.227	0.023	0.413	0.486
W	O	1.896	3.4643	2.227	0.311	0.250	0.28
Pt	O	1.879	1.7919	2.227	0.260	0.361	0.37
Pt	C	1.76	1.7919	1.568	0.930	0.326	0.37
Hg	O	1.972	1.8589	2.227	0.126	0.372	0.37
Hg	S	2.308	1.8589	1.827	0.714	0.328	0.37
Hg	Hg	2.5	1.8589	1.859	1.000	0.285	0.37

## Conclusions

Bond valence – bond length empirical correlations have been used for many years along with the valence sum rule as checks on crystal structures and evaluating the reasonableness of proposed molecular structures. Furthermore, these relationships have proven effective for ionic as well as covalent systems. Pauling's relationship, proposed in 1947, has become the most widely used, but requires two fitting parameters:  $b$  and  $R_0$  (bond length of unit valence) that are typically found by minimizing the difference between the bond valence sums and the atomic valence of the central cation. The empirical relationship would be more useful if an independent method of determining  $b$  and/or  $R_0$  was found.

In the present study, a simplified quantum-mechanical approach was used to derive Pauling's empirical bond valence – bond length relationship. A covalency factor was introduced to account for the difference in "softness" between cation and anion (resulting in increased orbital overlap). By using this approach, an expression for the  $b$  parameter was

determined which yields values comparable to those that have been experimentally determined. The derived relationship for the  $b$  parameter allows its independent determination using orbital exponents and electronegativity values for the cation and anion.

Table 8: Lanthanides/Actinides

Cat	An	Ro	Zeff/n	Zeff/n	Cov	Calc	Lit
			Cation	Anion		"b"	"b"
La	O	2.148	0.8333	2.227	0.004	0.518	0.451
La	N	2.26	0.8333	1.917	0.023	0.573	0.37
La	Cl	2.545	0.8333	2.039	0.014	0.550	0.451
La	S	2.632	0.8333	1.827	0.112	0.574	0.588
La	C	2.231	0.8333	1.568	0.122	0.634	0.37
Ce	O	2.116	0.9881	2.227	0.005	0.493	0.443
Ce	C	2.209	0.9881	1.568	0.129	0.594	0.37
Ce	S	2.593	0.9881	1.827	0.119	0.542	0.37
Ce	Cl	2.538	0.9881	2.039	0.016	0.522	0.37
Ce	N	2.179	0.9881	1.917	0.025	0.542	0.37
Pr	O	2.098	1.1429	2.227	0.005	0.470	0.439
Pr	C	2.172	1.1429	1.568	0.133	0.560	0.37
Pr	S	2.569	1.1429	1.827	0.122	0.513	0.499
Pr	Cl	2.521	1.1429	2.039	0.016	0.496	0.387
Pr	N	2.215	1.1429	1.917	0.026	0.514	0.37
Nd	O	2.086	1.2976	2.227	0.005	0.450	0.428
Nd	C	2.161	1.2976	1.568	0.137	0.529	0.37
Nd	S	2.559	1.2976	1.827	0.126	0.487	0.51
Nd	Cl	2.512	1.2976	2.039	0.017	0.473	0.37
Nd	N	2.201	1.2976	1.917	0.027	0.489	0.37
Sm	O	2.063	1.6071	2.227	0.006	0.413	0.433
Sm	S	2.538	1.6071	1.827	0.137	0.441	0.505
Sm	Cl	2.481	1.6071	2.039	0.019	0.433	0.37
Sm	N	2.176	1.6071	1.917	0.030	0.446	0.37
Eu	O	2.038	1.7619	2.227	0.007	0.397	0.434
Eu	S	2.509	1.7619	1.827	0.149	0.420	0.503
Eu	Cl	2.468	1.7619	2.039	0.021	0.415	0.485
Eu	N	2.161	1.7619	1.917	0.034	0.427	0.37
Eu	C	2.135	1.7619	1.568	0.162	0.451	0.37
Gd	O	2.031	1.9167	2.227	0.007	0.382	0.415
Gd	S	2.507	1.9167	1.827	0.149	0.403	0.552
Gd	Cl	2.457	1.9167	2.039	0.021	0.398	0.533
Gd	N	2.146	1.9167	1.917	0.034	0.409	0.37
Gd	C	2.118	1.9167	1.568	0.162	0.431	0.37
Lu	O	1.947	1.4674	2.227	0.009	0.428	0.37
Lu	Cl	2.361	1.4674	2.039	0.028	0.449	0.37
Lu	S	2.414	1.4674	1.827	0.180	0.453	0.37
Lu	C	1.999	1.4674	1.568	0.194	0.489	0.37
U	O	2.075	1.1512	2.227	0.014	0.468	0.37
U	F	2.038	1.1512	2.550	0.001	0.429	0.37

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**Theoretical Justification for Bond Valence – Bond Length Empirical Correlations****Literature Cited**

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