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F. D. Hardcastle
Arkansas Tech University, fhardcastle@atu.edu

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Valence-Length Correlations for Chemical Bonds from Atomic-Orbital Exponents

F.D. Hardcastle

Department of Physical Sciences, Arkansas Tech University, Russellville, AR 72801

Correspondence: fhardcastle@atu.edu

Running Title: Valence-Length Correlations for Chemical Bonds

Abstract

Pauling's empirical bond valence-length correlation has proven valuable because it offers a quick and convenient way of checking and evaluating molecular structures and determining oxidation states from measured bond lengths. In this study, a simplified quantum-mechanical approach was used to derive Pauling's empirical bond valence-length relationship by considering overlap of hydrogen-like orbitals. An expression for the *b* "empirical" fitting parameter was derived in terms of atomic-orbital exponents. A new set of orbital exponents is presented using published atomic/covalent radii and a continuous function for the effective principal quantum. The *b* parameters calculated from the orbital exponents are consistent with bond valence-length data from crystallographic data. In general, atomic-orbital exponents may be used to determine bond valence-length relationships for any chemical bond regardless of state, oxidation number, or environment.

Introduction

Pauling's second rule of chemical bonding (Pauling 1929) is the principle of local charge neutrality where the negative charge of each anion is neutralized by the positive charges of neighboring cations and, conversely, that the cationic charges are neutralized by neighboring anions. This rule, called the valence sum rule, states that the sum of the bond strengths (in valence units) around each bonding atom is compensated by the total valence of that atom

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

where s_{ij} is the bond valence for each bond to the atom, and V_i is the oxidation state of the atom and/or the number of electrons used 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, Zachariasen 1954, Brown and Altermatt 1985, Brown 2002, Brown 2009). Perhaps the two most commonly used relationships are

$$s = (R / R_o)^{-N} \qquad (2)$$

and

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

where *s* is the bond valence, sometimes referred to as the bond order or bond number; it is also the number of shared electron pairs involved in the bond. *R* is bond length, R_o is the bond length of a chemical bond having unit valence, and *N* and *b* are empirical fitting parameters and sometimes associated with the softness of the bond. Eq. (3) is the most widely used and was first proposed by Pauling in 1947 to describe metal-metal bonding (Pauling 1947).

In practice, *b* and R_0 are both adjustable parameters found by minimizing the difference between the bond valence sums and the atomic valence of the central bonding atom. Most values of *b* have been experimentally found to range between 0.25 and 0.55 Å, but because of limited results, *b* is often assumed to be a universal constant of 0.37 Å (average of tabulated values). This common assumption changes Eq. (3) to a one-parameter fit and makes it easier to use, but severely limits the applicability of the relationship, decreasing reliability for very short and very long bonds. In fact, there is a large variability in reported *b* parameters that is sensitive to the selection of R_o as well as crystallographic data. Adams (Adams 2001, Adams 2008) 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.

Bond valence–length relationships, Eq. (3),

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combined with the valence sum rule, Eq. (1), have obvious applications where molecular structures are of interest. The relationships are typically used to check crystal structures or to evaluate the reasonableness of a proposed molecular structure for crystalline and amorphous systems. They can also be used to determine oxidation states of cations or anions, or to determine coordination numbers for organo-metallic complexes.

In the present study, a simplified quantum-mechanical approach is used to derive Pauling's empirical bond valence – bond length relationship. An expression for the *b* parameter was derived in terms of atomic-orbital exponents. A new set of orbital exponents is presented using published atomic/covalent radii and a proposed continuous function for the effective principal quantum, *n**. The *b* parameters calculated from the orbital exponents were found to be consistent with bond valence-length data from crystallographic data.

Theory

Defining Bond Valence

Following the widely used method of linear combination of atomic orbitals (LCAO) to represent the bonding between two atoms

$$\psi = \chi_1 + \chi_2 \qquad (4)$$

where ψ is the bonding molecular-orbital wave function, and χ_1 and χ_2 are atomic-orbital wave functions for the bonding atoms. The probability density is given by the square of the wave function

$$\psi^2 = (\chi_1 + \chi_2)(\chi_1 + \chi_2) = \chi_1^2 + \chi_2^2 + 2\chi_1\chi_2 \qquad (5)$$

where integration over all space is normalized to unity. The integrated third term ($2\chi_1\chi_2$) is the Mulliken population density (Mulliken 1955), or the integrated sum of the overlap between the two atomic-orbital wave functions. This term represents the electronic interaction between the two atoms and is associated with bond strength or bond valence. We define the bond valence, s, as the cross-section or thickness of this overlap region (non-integrated form)

$$s \equiv 2\chi_1\chi_2 \qquad (6)$$

Hydrogen-Like Wave Functions and Orbital Exponents

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

$$\psi_{n,l,m} = R^{n-1} e^{-\frac{(Z-\sigma)}{a_0 n} R} Y_{l,m}(\theta, \phi) \qquad (7)$$

where Z is the nuclear charge of the atom, σ 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). The pre-exponential factor R^{n-1} scales the function by broadening and shifting as the principal quantum number *n* increases. Slater replaces the principal quantum number *n* with an effective principal quantum number *n**. The effective nuclear charge, $Z_{eff} = Z - \sigma$, with respect to the effective principle quantum number, *n**, is expressed as an orbital exponent, ξ,

$$\xi = \frac{Z_{eff}}{n*} \qquad (8)$$

Slater proposed values of *n** = 1, 2, 3, 3.7, 4.0 and 4.2 for principal quantum numbers *n* = 1, 2, 3, 4, 5 and 6, respectively. Slater's values are still used today, although investigators suggest that *n** is some function of *n*. The simplest method of calculating orbital exponents is to use Slater's rules to determine screening constants, outlined in most inorganic chemistry texts (Miessler and Tarr 2003). Self-consistent field methods yield more reliable numbers (Clementi and Raimondi 1963, Clementi et al. 1967). In a previous study, we attempted to reproduce Clementi and coworkers' exponents by incorporating a modified Pauling covalency factor (Hardcastle and Laffoon 2012). In the present study, new orbital exponents are reported using a best fit to published atomic radii and single-bond covalent radii. A few exponents were independently verified using empirical bond length – valence relationships derived from crystallographic data.

For our application, the wave function is "shifted" or "scaled" when the corresponding bond length is normalized to the bond length at unit valence; that is, $R = R_0$ when $s = 1$. We therefore eliminate the R^{n-1} pre-exponential scaling term from Slater's wave function, Eq. (7). Since only the overlap region between the two

bonding atoms is of interest, the spherical harmonic term, $Y(\theta,\phi)$, is also ignored (constant). The bond valence between bonding atoms 1 and 2 can now be written, using Eq. (6), as

$$s = 2\left(c_1 e^{-\xi_1 R_1 / a_0}\right)\left(c_2 e^{-\xi_2 R_2 / a_0}\right) \tag{9}$$

in terms of orbital exponents, Eq. (8).

The radial probability density function (RDF) for the Slater wave function is obtained by multiplying Eq. (7) by $4\pi R^2$. The derivative of the RDF with respect to R yields the atomic radius, which is the maximum of the RDF. The atomic radius for both the Slater function and the hydrogen-like orbital, Eq. (9) occurs at

$$R_{max} = \frac{a_0}{\xi} n* \tag{10}$$

where $n*$ is the effective principal quantum number and scales the atomic radius (actually scaled by $n*^2$). Because this is the maximum of the RDF, it is equivalent to finding R for the wave function when the electron density is 1/e times its initial value.

The same reasoning is used within the overlap region of the chemical bond. The average value for the electron density of the exponential functions expressed in Eq. (9) with respect to the chemical bond is defined as the bond length at which the electron density decays to 1/e (or 37%) of its maximum radial value for both bonding atoms: $R_1=R_2=R/e$. This is an assumption and should be equivalent to finding the minimum of the electron density between the two atoms.

Bond Valence-Length Relationship

Taking the natural logarithm of Eq. (9),

$$\ln s = \ln 2 + \ln c_1 + \ln c_2 - \frac{\xi_1 R_1}{a_0} - \frac{\xi_2 R_2}{a_0} \tag{11}$$

Substituting $R_1=R_2=R/e$ and collecting terms

$$\ln s = \ln 2 + \ln c_1 + \ln c_2 - \frac{(\xi_1 + \xi_2)}{a_0 e} R \tag{12}$$

For a chemical bond of unit valence, $s=1$ and $R=R_0$, Eq. (12) becomes

$$\ln(1) = \ln 2 + \ln c_1 + \ln c_2 - \frac{\xi_1 R_0}{a_0 e} - \frac{\xi_2 R_0}{a_0 e} \tag{13}$$

Subtracting Eq. (13) from Eq. (12), simplifying and collecting terms, yields

$$\ln s = \left[\frac{\xi_1}{a_0 e} + \frac{\xi_2}{a_0 e}\right](R_0 - R) \tag{14}$$

$$\ln s = \frac{(R_0 - R)}{b} \tag{15}$$

Eq. (15) is Pauling's *empirical* bond valence -length relationship, Eq. (3), where the b "empirical" fitting parameter is

$$b = \frac{a_0 e}{(\xi_1 + \xi_2)} \tag{16}$$

The b parameter may be calculated from appropriate atomic-orbital exponents ξ_1 and ξ_2 for the two bonding atoms, and verified from crystallographic bond-length data.

Results and Discussion

The b and R_0 fitting parameters from the bond length-valence relation, Eq. (15-16), may be optimized from published data from several sources. These data are not reproduced here, but are conveniently compiled into a few major references (Adams 2001, Brown 2002, Brown 2009), as well as on a web site (Adams 2008). A comprehensive list has been tabulated and referenced in a recent publication in this journal (Hardcastle and Laffoon 2012). It is important to recognize that b values are closely coupled to the choice of R_o, so that a different (or erroneous) choice of R_0 necessarily affects the value of b and also the value of the orbital exponents determined in this way. For this reason, published bond valence parameters were not utilized to determine atomic-orbital exponents, but are used only to corroborate values.

Atomic size or radius is generally regarded as a vague concept and not well defined. Published atomic radii and single-bond covalent radii for elements 1 through 103 were collected from several widely used sources (Slater 1964, Clementi and Raimondi 1963, Clementi et al. 1967, Pyykkö and Atsumi 2009, Cordero et al. 2008). Based on this data, a continuous function for the effective principal quantum number $n*$ was found from a best fit of the average atomic/covalent radii using the functional form

$$n* = A(C - e^{-kZ}) \tag{17}$$

where A = 4.286, C = 1.176, k = 0.0588, and Z is the atomic number of the element. The maximum possible value of $n*$ is AC = 5.04, whereas Slater (Slater 1930) set this value at 4.2.

Using published atomic/covalent radii, Eq. (17) for $n*$, and Eq. (10), atomic-orbital exponents for elements 1 through 103 were calculated and tabulated in Table 1. For comparison, orbital exponents from Clementi and coworkers (Clementi and Raimondi 1963, Clementi et al. 1967) and Ghosh's (Gosh and Biswas 2002) are included in italics. Most of the values calculated in the present study are similar to those published. Our value of 1.9369 for helium is consistent with a smaller shielding ($\sigma=0.0631$) caused by the paired electron in the 1s orbital, compared with the variation-method result of 1.6875 ($\sigma=0.3125$). Table 1 shows that our values for elements in the second shell (n=2) are slightly smaller than those published, but our orbital exponents are very similar to those published for the remainder of the main-group elements. The largest discrepancy is observed for first-and second-row transition elements, scandium through zinc and yttrium through cadmium, where our values are significantly higher. This discrepancy is attributed mainly to the use of different effective principal quantum numbers $n*$; we assumed a continuous function that depends on Z, Eq. (17), while other investigators use a constant-value step-function approach according to Slater ($n*=3$ (3d), $n*=3.7$ (4d), $n*=4.0$ (5d)). The third-row transition elements, lutetium through mercury, have orbital exponents only slightly higher than those of Clementi and coworkers (Clementi and Raimondi 1963, Clementi et al. 1967), but much smaller than those of Ghosh and Biswas (2002).

All oxide valence-length data tabulated in a previous study (Hardcastle and Laffoon 2012) were simultaneously fit to the oxygen orbital exponents, and the error was significantly reduced when the exponent was reduced from Clementi's value of $\xi=2.2266$ to our value of $\xi=1.9535$. Substituting this value (1.9535 from Table 1) into Eq. (16) results in $b= 0.3682$; the O-O unit valence bond length is $R_0 = 1.462$ Å. This results in the following bond valence for O-O bonds:

$$s_{O-O} = \exp\left(\frac{1.462 - R}{0.3682}\right) \qquad (18)$$

This relationship accurately predicts the double bond of O_2 at 1.207 Å (Huber and Herzberg 1979). For oxide molecules where the oxidation state of oxygen is always 2, Eq. (18) can also be used in conjunction with

the valence sum rule

$$2.000 = \sum_j s_{ij} \qquad (19)$$

where s_{ij} is the bond valence for each bond to the oxygen atom. The valence sum of all bonds to the oxygen atom will add to the total oxygen valence. This is similar to Kirchoff's law that states that the current at an electrical junction (in this case an atom) is additive - in units of electrons.

For titanium-oxygen bonds, the Ti-O bond length having unit valence was found to be $R_0 = 1.789$ Å. Table 1 shows the orbital exponents of Ti and O are 1.3710 and 1.9535, respectively, yielding a value of $b = 0.4327$ Å, Eq. (16). Substituting these values into Pauling's relationship, Eq. (15), yields

$$s_{Ti-O} = \exp\left[\frac{(1.789 - R)}{0.4327}\right] \qquad (20)$$

For silicon-oxygen bonds, the necessary parameters are $\xi=1.4814$ (Table 1) and $R_0=1.605$ Å, yielding

$$s_{Si-O} = \exp\left[\frac{(1.605 - R)}{0.4188}\right] \qquad (21)$$

Eqs. (20) and (21) describe quantitative relationships between Ti-O and Si-O bond valence and corresponding bond length in units of Angstroms. These two relationships have been verified using published crystallographic bond distances for silicates (Laffoon et al. to be submitted) and titanates (Dodd et al. 2013), by converting these values to bond valences and using the valence sum rule. These bond valence–length relationships hold regardless of environment, physical state, or oxidation state. In addition to verifying the validity of this approach for Si-O and Ti-O bonds, orbital exponents for carbon, nitrogen, phosphorus, chromium, molybdenum, tungsten and rhenium were also tested by combining data from metal-metal bonding, published bond lengths for diatomic gas phase molecules (Huber and Herzberg 1979), published b parameters, and best fits to crystallographic data (Hardcastle, *unpublished results*).

Conclusions

Pauling's bond valence–bond length empirical correlation has been used for many years along with the valence sum rule as a check on crystal structures

Valence-Length Correlations for Chemical Bonds

Table 1: Atomic-orbital exponents for elements 1-103.

Each cell lists the element symbol followed by three values: the first (bold) exponent, the second (italic, from Clementi), and the third (from Ghosh).

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H 0.9994 / 1.0000 / 1.0000																	**He** 1.9369 / 1.6875 / 1.7
Li 0.5319 / 0.64 / 0.65	**Be** 0.8504 / 0.9560 / 0.9750											**B** 1.1653 / 1.2107 / 1.3	**C** 1.4571 / 1.5679 / 1.625	**N** 1.6958 / 1.917 / 1.95	**O** 1.9535 / 2.2266 / 2.275	**F** 2.2499 / 2.55 / 2.6	**Ne** 2.4267 / 2.8792 / 2.925
Na 0.8568 / 0.8358 / 0.7333	**Mg** 1.0732 / 1.1025 / 0.95											**Al** 1.2872 / 1.3552 / 1.1667	**Si** 1.4814 / 1.4284 / 1.3833	**P** 1.6408 / 1.6288 / 1.6	**S** 1.7790 / 1.8273 / 1.8167	**Cl** 1.9023 / 2.0387 / 2.0333	**Ar** 2.0326 / 2.2547 / 2.25
K 0.8933 / 0.8738 / 0.5946	**Ca** 1.0811 / 0.9995 / 0.7703	**Sc** 1.2417 / 1.1581 / 0.8108	**Ti** 1.3710 / 1.2042 / 0.8514	**V** 1.4635 / 1.2453 / 0.8919	**Cr** 1.5413 / 1.2833 / 0.9324	**Mn** 1.5419 / 1.3208 / 0.973	**Fe** 1.6419 / 1.3585 / 1.0135	**Co** 1.7060 / 1.3941 / 1.0541	**Ni** 1.7514 / 1.4277 / 1.0946	**Cu** 1.7127 / 1.4606 / 1.1351	**Zn** 1.7416 / 1.2891 / 1.1757	**Ga** 1.7452 / 1.5554 / 1.3514	**Ge** 1.8524 / 1.6951 / 1.527	**As** 1.9843 / 1.8623 / 1.7027	**Se** 2.0642 / 2.0718 / 1.8784	**Br** 2.1260 / 2.257 / 2.0541	**Kr** 2.2219 / 2.4423 / 2.23
Rb 1.0394 / 0.9969 / 0.55	**Sr** 1.2062 / 1.2141 / 0.7125	**Y** 1.3434 / 1.2512 / 0.75	**Zr** 1.4738 / 1.2891 / 0.7875	**Nb** 1.5759 / 1.1842 / 0.825	**Mo** 1.6285 / 1.2212 / 0.8625	**Tc** 1.6875 / 1.4453 / 0.9	**Ru** 1.7854 / 1.2969 / 0.9375	**Rh** 1.7818 / 1.3279 / 0.975	**Pd** 1.8054 / 1.5675 / 1.0125	**Ag** 1.6922 / 1.3511 / 1.05	**Cd** 1.6958 / 1.6384 / 1.0875	**In** 1.6822 / 1.6940 / 1.2500	**Sn** 1.7608 / 1.8204 / 1.4125	**Sb** 1.7903 / 1.9989 / 1.5750	**Te** 1.8851 / 2.1617 / 1.7375	**I** 1.9420 / 2.3223 / 1.9	**Xe** 2.0216 / 2.4849 / 2.0625
Cs 1.0103 / 1.0605 / 0.5238	**Ba** 1.1912 / 1.2625 / 0.6786	**Lu** 1.4720 / 1.4674 / 3.0000	**Hf** 1.5606 / 1.5274 / 3.1500	**Ta** 1.6720 / 1.5875 / 3.3095	**W** 1.7317 / 1.6424 / 3.4643	**Re** 1.7578 / 1.686 / 3.619	**Os** 1.8622 / 1.7205 / 3.7739	**Ir** 1.8633 / 1.7611 / 3.9286	**Pt** 1.8932 / 1.7919 / 4.0833	**Au** 1.8521 / 1.8230 / 4.2381	**Hg** 1.7843 / 1.8589 / 4.3929	**Tl** 1.6653 / 2.0423 / 1.1905	**Pb** 1.6801 / 2.0655 / 1.3452	**Bi** 1.7097 / 2.2233 / 1.5	**Po** 1.7384 / 2.3701 / 1.6548	**At** 1.7858 / 2.5270 / 1.8095	**Rn** 1.9051 / 2.6793 / 1.9643
Fr 1.0988 / / 0.5116	**Ra** 1.2501 / / 0.6628	**Lr** 1.6534 / / 2.8140															

Lanthanides:

La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
1.3779	1.4108	1.3075	1.3731	1.3809	1.3402	1.3310	1.3660	1.3953	1.3983	1.4057	1.4147	1.4221	1.3873
0.34	0.419	1.2911	1.5511	1.5659	1.3353	1.3536	1.3691	1.3834	1.3906	1.4065	1.4127	1.4307	1.4233
0.8333	0.9881	1.1429	1.2976	1.4524	1.6071	1.7619	1.9167	2.0714	2.2262	2.3810	2.5357	2.6905	2.8452

Actinides:

Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No
1.3365	1.4336	1.4966	1.4966	1.5630	1.5726	1.6089	1.5876	1.5831	1.5834	1.6124	1.5933	1.5383	1.5123
0.6977	0.7326	1.0000	1.0000	1.1512	1.3023	1.7209	1.7558	1.7558	2.0233	2.1744	2.3256	2.4767	2.6279
0.7326			1.1512	1.3023	1.5698		1.7558		2.1744	2.3256	2.4767	2.6279	2.7791

Second number (italics) is from Clementi (1963, 1967) and the third from Ghosh (2002).

and to evaluate the reasonableness of proposed molecular structures for metallic, ionic and covalent systems. Unfortunately, two adjustable fitting parameters, b and R_0, are required, which severely limits the range of applicability if erroneous values are selected. The empirical relationship would be more useful if independent methods of determining b and R_o were found.

In this study, a simplified quantum-mechanical approach was used to derive Pauling's empirical bond valence–bond length relationship by considering overlap of hydrogen-like orbitals. An expression for the b parameter was derived in terms of atomic-orbital exponents. New values for atomic-orbital exponents were determined using published atomic/covalent radii and a continuous function for the effective principal quantum number n^*. The b parameters calculated from the orbital exponents are consistent with bond valence-length data from crystallographic data. In general, atomic-orbital exponents may be used to determine bond valence-length relationships for any chemical bond regardless of state, oxidation number, or environment.

Acknowledgments

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