A General Valence-Length Correlation for Determining Bond Orders: Application to Carbon-Carbon and Carbon-Hydrogen Chemical Bonds

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Abstract

A quantum-mechanical LCAO approach was used to derive Pauling's popular empirical bond valence-length relationship $s = exp((R_o-R)/b)$, where s is the bond order or bond valence associated with bond length R, and R_o and b are fitting parameters. An expression for the b "empirical" fitting parameter is derived in terms of atomic orbital exponents. The b parameters calculated from the atomic orbital exponents are consistent with optimized b parameters. In general, atomic orbital exponents may be used to determine bond valence-length relationships for any chemical bond regardless of valence state, oxidation number, physical or chemical environment.

In this study, almost two-thousand carbon-carbon and carbon-hydrogen bond lengths were evaluated from over 40 compounds to yield reliable bond valence – bond length relationships for C-C and C-H bonds. The atomic orbital exponent for carbon was found to be $\xi_C = 1.651$. Unit valence bond lengths (R_0 where $s = 1$) were found to be 1.493 Å for the carbon-carbon bond and 1.061 Å for the carbon-hydrogen bond.

Introduction

Linus Pauling's principle of electrostatic neutrality (Pauling 1929), or the law of conservation of valence, dictates that the negative charge of each anion in a molecule or crystal is neutralized by the positive charges of neighboring cations and, conversely, that the cationic charges are neutralized by neighboring anions. In application, this is recast as the valence sum rule which states that the sum of the bond strengths (in valence units) around each bonding atom is compensated by the total atomic valence V_i

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

where s_{ij} is the bond valence for each bond to the atom, and V_i is the number of electrons used for bonding (sometimes identical to the oxidation state). The sum of bond valences around any ion, i, is equal to its valence, V_i.

Bond valence – length empirical correlations have been used for many years (Brown and Altermatt 1985; Brown 2002; Brown 2009; Pauling 1947; Zachariasen 1954). In 1947, Linus Pauling presented his empirical bond valence-length expression for carbon-carbon bonds

$$s = \exp\left(\frac{R_o - R}{0.307}\right) = \exp\left(\frac{R_o - R}{b}\right) \qquad (2)$$

where s is the bond valence, sometimes referred to as the bond order or bond number – this is also the number of shared electron pairs involved in the bond. R is bond length, R_o sometimes defined as the average bond length and sometimes as the length of a chemical bond having unit valence ($s = 1$), and b is an empirical fitting parameter and sometimes associated with the chemical softness of the bond (Adams 2001). Pauling found that $b = 0.307$ for carbon-carbon bonds (see Eq. (2)), but also successfully used this same equation 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 0.65 Å, but because of limited results, b is often assumed to be a universal constant of 0.37 Å which is an average of all tabulated values (Brown and Altermatt 1985). This common assumption changes Eq. (2) 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 2004; Adams 2001) 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.

If the b and R_0 parameters have been properly chosen, the combined use of Eqs (1) and (2) have many applications in chemistry. For example, crystal structures may be checked, or the reasonableness of a proposed molecular structure may be evaluated. Another useful application is to determine the total atomic valence (i.e., the number of electrons used in bonding) which is sometimes identical to the oxidation state.

In the present study, the quantum-mechanical LCAO approach is used to derive Pauling's empirical bond valence – length relationship. An expression for the b parameter is derived in terms of atomic-orbital exponents. The b parameters calculated from the orbital exponents were found to be consistent with bond valence-length data from crystallographic data. This approach was applied to carbon-carbon and carbon-hydrogen bonds by curve-fitting almost two-thousand carbon-carbon and carbon-hydrogen bond lengths collected from crystallographic information files (cif files; Crystallographic Open Database) (Grazulis et al. 2009) from over 40 compounds to yield reliable bond valence – bond length relationships for C-C and C-H bonds.

Theory

Following the widely used method of linear combination of atomic orbitals (LCAO) to represent the bonding between two atoms labeled as 1 and 2,

$$\psi\psi^* = \psi^2 = (\chi_1 + \chi_2)(\chi_1 + \chi_2) = \chi_1^2 + \chi_2^2 + 2\chi_1\chi_2 \tag{3}$$

where ψ is the bonding molecular-orbital wave function, and χ_1 and χ_2 are atomic-orbital wave functions for the bonding atoms, ψ^2 is the probability density distribution function, χ_1 is the wave function for atom 1 and χ_1^2 is its probability density, χ_2 is the wave function for atom 2 and χ_2^2 is its probability density. Once integration over volume space is carried out, the third term ($2\chi_1\chi_2$) becomes 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. But prior to integration, the $2\chi_1\chi_2$ term represents the cross-section, or thickness, of the overlap region. For the present purpose, the thickness of the probability density in the overlap region is defined as the "bond order" or "bond valence" or "s." That is,

$$s \equiv 2\chi_1\chi_2 \qquad . \tag{4}$$

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 can be approximated as a single exponential node-less function

$$\chi_{n,l,m} = r^{n-1} e^{-\frac{(Z-\sigma)}{a_0 n^*}r} Y_{l,m}(\theta,\phi) \tag{5}$$

where Z is the nuclear charge of the atom, σ is a screening constant (the core electrons shield the valence electron(s) from the nuclear charge), n^* is the effective principal quantum number, a_0 is the Bohr radius (0.529 Å), and $Y(\theta,\phi)$ is the spherical harmonic term. The pre-exponential factor r^{n-1} scales the function by broadening and shifting as the effective principal quantum number n^* increases.

For the present application, the wave function is "shifted" or "scaled" when the corresponding bond length is normalized to the bond length at unit valence; that is, $2r = R_0$ when $s = 1$; this will be done at a later point in the paper. The pre-exponential scaling term r^{n-1} is therefore removed from Slater's wave function, Eq. (5). Since only the radial overlap region between the two bonding atoms is of interest, the spherical harmonic term, $Y(\theta,\phi)$, is also ignored as a constant. The bond order or bond valence (cross section or thickness) between bonding atoms 1 and 2 is now written, starting with Eq. (4), as

$$s = 2\left(c_1 e^{-\xi_1 r_1/a_0}\right)\left(c_2 e^{-\xi_2 r_2/a_0}\right) \tag{6}$$

in terms of orbital exponents where, in general, $\xi=(Z-\sigma)/n^*$. Taking the natural logarithm of Eq. (6) gives

$$\ln s = \ln 2 + \ln c_1 + \ln c_2 - \frac{\xi_1 r_1}{a_0} - \frac{\xi_2 r_2}{a_0} \tag{7}$$

The problem here is how to express the two different atomic radii r_1 and r_2 belonging to two unique

atoms (and two electrons!) in terms of only one variable, R, which is the bond length or interatomic distance between the two different atoms. Clearly, an approximation must be made. In a previous paper (Hardcastle 2013), it was noted that the derivative of the radial distribution function RDF in the overlap region of the chemical bond with respect to R yields the maximum which was identified as the atomic radius and the $1/e$ distance: $r_1=r_2=R/e$. This led to an erroneous (inconsistent with the data) result for the "b" parameter in Eq. (2). In this paper, this disparity will be corrected by using a much simpler approach.

The concept of electronic potential and absolute electronegativity as described by Parr and Pearson (Parr and Pearson 1983) is used in the present study. The absolute electronegativity of Mulliken (in eV) is defined as the average of the ionization potential (I) and the electron affinity (A) (Mulliken 1934). The instantaneous slope of the change in electronic energy with number of electrons, $(\partial E/\partial N)$, is equal rigorously to the chemical potential μ of the density functional theory, which is the negative of the absolute electronegativity (Parr and Pearson 1983). That is,

$$\chi = -\left(\frac{\partial E}{\partial N}\right)_z = \left(\frac{I+A}{2}\right) = -\mu \qquad (8)$$

After Parr, the absolute chemical hardness η is defined as

$$2\eta = -\left(\frac{\partial \mu}{\partial N}\right) \qquad (9)$$

which may be recast in a difference form, also using Eq. (8), as

$$\Delta N = \frac{(\chi_1 - \chi_2)}{2(\eta_1 + \eta_2)} \qquad (10)$$

Eq. (10) quantitatively describes the fractional electron transfer from one atom (or molecular species) to another. This relationship shows that electrons will flow from the atom of lower χ (higher potential) to that of higher χ (lower potential) until the electronegativities (or chemical potentials) become equalized. Once the bond is formed, at equilibrium, the $(\partial E/\partial N)$ curves for both atoms are identical, as indicated by Eq. (8). This means that once a chemical bond is formed, the new radius of either atom 1 or atom 2 is one-half the resulting interatomic distance, $R/2$ (at equilibrium, where both chemical potentials and electronegativities are equal). That is, once the

chemical bond is formed, $r_1=r_2=R/2$.

Continuing from Eq. (7), substituting $r_1=r_2=R/2$, and collecting terms, results in

$$\ln s = \ln 2 + \ln c_1 + \ln c_2 - \frac{\xi_1 R}{2a_0} - \frac{\xi_2 R}{2a_0} \qquad (11)$$

For a chemical bond of unit valence, $s=1$ and $R=R_0$ are substituted. Eq. (11) becomes

$$\ln(1) = \ln 2 + \ln c_1 + \ln c_2 - \frac{\xi_1 R_0}{2a_0} - \frac{\xi_2 R_0}{2a_0} \qquad (12)$$

Subtracting Eq. (12) from Eq. (11), simplifying and collecting terms, yields

$$\ln s = \left[\frac{\xi_1}{2a_0} + \frac{\xi_2}{2a_0}\right](R_0 - R) \qquad (13)$$

$$\ln s = \frac{(R_0 - R)}{b} \qquad (14)$$

where,

$$b = \frac{2a_0}{(\xi_1 + \xi_2)} \qquad (15)$$

Eq. (14) is precisely Pauling's empirical bond valence - length relationship, Eq. (2), where the b "empirical" fitting parameter is now defined in terms of atomic orbital exponents, Eq. (15). Eq. (15) shows that the b parameter may be calculated only from appropriate atomic-orbital exponents ξ_1 and ξ_2 for the two bonding atoms, provided that the atomic orbital exponents are precisely known. Conversely, this also provides a method of determining atomic orbital exponents from experimental bond length data.

Results and Discussion

The b and R_0 fitting parameters from the bond length-valence relation, Eq. (2) or Eq. (14), may be found from published crystallographic data, for example from crystallographic information files (cif files). Unreliable XRD data was discarded from the data set only when the results grossly deviated from the known valence of carbon. Using these bond length data, and the conservation of valence formula, Eq. (1), optimized parameters have been found and conveniently compiled into a few major references (Adams 2001; Brown 2002; Brown 2009), as well as

on a web site (Adams 2004). 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. Incorrect values of b and R_o are noted to result in a correlation that seems to work well for intermediate bond lengths, but not for very long and very short bonds; this observation is common among researchers (Brown 2002). Eq. (15) allows an independent determination of the b parameter, so that the only floating parameter is R_o, defined as the bond length of unit valence for that particular pair of atoms.

The simplest method of calculating an atomic orbital exponent can be traced back to Slater's original work (Slater 1930) where he introduced the node-less single exponential wave function, Eq. (5), and defined the atomic orbital exponent as

$$\xi = \frac{(Z - \sigma)}{n^*} \tag{16}$$

where Z is the nuclear charge of the atom, σ is a screening constant, and n^* is the effective principal quantum number and a function of n. Slater presented a list of rules (aka, Slater's Rules) for determining the shielding constant σ, the effective quantum number n*, and consequently the orbital exponent ξ, and these rules are routinely included in inorganic chemistry textbooks (Miessler, Fischer, Tarr 2014). More refined values require computation and have been published by many authors including Clementi and coworkers (Clementi and Raimondi 1963; Clementi, Raimondi, Reinhardt 1967), Ghosh and Biswas (Ghosh and Biswas 2002). In this study, it was founds that the atomic orbital exponents found by using the empirically adjusted exchange parameters of Herman (Herman 2004) were more consistent with our curve-fitted results using published diffraction data for elements in the second row of the periodic table (Dodd., Hardcastle, Laffoon 2013).

Carbon-carbon and carbon-hydrogen bond lengths from about 41 carbon compounds were collected as well as almost two-thousand bond lengths from the Crystallographic Open Database (COD). Mercury (version 3.6) free software was used to evaluate the bond lengths from the crystallographic information files (www.ccdc.cam.ac.uk/mercury/). All bond distances up to 4.5 Å were considered in all valence calculations (see Supplemental file). The bond valences were normalized using the valence sum rule,

Eq. (1), where carbon uses four electrons for bonding ($V_c = 4.000$) and hydrogen uses one electron for bonding ($V_H = 1.000$). This results in the following bond valence-length relationships for C-C and C-H bonds, respectively,

$$s_{C-C} = \exp\left[\frac{(1.493 - R)}{0.3205}\right] \tag{17}$$

$$s_{C-H} = \exp\left[\frac{(1.0610 - R)}{0.3992}\right] \tag{18}$$

It is a universal practice to assume that the orbital exponent of hydrogen is $\xi_H = 1.000$ since there is no electron screening and the principal quantum number is assumed to be 1; according to Eq. (16), $\xi_H = (Z-s)/n^* = (1-0)/1 = 1.000$. After a best-fit analysis of all C-C and C-H bond length data, the orbital exponent for carbon was determined to be $\xi_C = 1.651$. This compares favorably with reported values of 1.5679 (Clementi and Raimondi 1963), 1.625 (Ghosh and Biswas 2002), 1.7210 (2s) and 1.6105 (2p) (Herman 2004). Note that the "b" parameter for C-C bonds is 0.3305 in Eq. (17) which is approximately that of 0.307 determined by Pauling in 1947 (see Eq. (2)) in spite of the fact that there was little accurate C-C bond length data available at that time.

To present a few applications showing the usefulness of Eqs (17) and (18), consider the structure of diamond at ambient temperature and pressure (Hom, Kiszenik, Post 1975). The C-C bond lengths in units of Angstroms are 4x1.544, 12x2.52, 12x2.953, 8x4.368 which result in a total carbon valence of 4.02 electrons (or valence units) using Eq. (17). Note that a carbon atom is assumed to form a chemical bond not just to each of its nearest neighbors at 1.544 Å, but to all carbons in the lattice; of course this effect is negligible at distances greater than 4.5 Å. According to valence bond theory, the sp^3 hybridization predicted from the valence bond theory shows the preferred direction of bonding, but not the only direction of C-C bonding in the diamond structure. Another sp^3-hybridized carbon lattice is that of the hexagonal (synthetic) diamond lattice (Bundy and Kasper 1967) which has bond lengths of 3x1.543, 1.545, 6x2.52, 6x2.522, 6x2.956, 6x2.575, 8x3.603 resulting in a total carbon valence of 4.18 electrons.

Consider results from an early structure determination of graphite (Wyckoff 1963) with bond lengths of 3x1.418, 6x2.456, 3x2.836, 2x3.348,

12x3.636, 12x4.152 yielding a total carbon valence of 4.16 electrons. Naphthalene (Fabbiani et al. 2006) shows C-C bond lengths (in Angstroms) of on the C3-labeled carbon as 1.400, 1.423, 1.424, 2.424, 2x2.431, 2.438, 2.796, 2.816, 3.458, 3.520, 3.792, 3.987, 2x4.366, 2x4.671, 4.684, 4.692, 4.702, 4.757, 4.906, and 4.930; applying Eq. (17) yields a total valence of 4.07 electrons for this carbon.

It is also interesting to calculate the C-C and C-H bond valences or bond orders for diatomic species and functionalities. From Eq. (17), C-C bond orders are calculated as follows: C_2^-(doublet), R = 1.2233 Å, s = 2.32 electrons; C_2(singlet), R = 1.24253 Å, s = 2.18 electrons; C_2(triplet), R = 1.3119 Å, s = 1.76 electrons (Huber and Herzberg 1979). Using Eq. (18), the C-H bond order in the diatomic CH doublet can be calculated: R = 1.1019 Å, s = 0.903 electrons.

Conclusions

A quantum-mechanical LCAO approach was used to derive Pauling's empirical bond valence-length relationship. The *b* parameters calculated from the orbital exponents are consistent with optimized *b* parameters calculated from bond valence-length data determined from published crystallographic data.

In this study, almost two-thousand carbon-carbon and carbon-hydrogen bond lengths were evaluated from over 40 compounds to yield reliable bond valence – bond length relationships for C-C and C-H bonds. The atomic orbital exponent for carbon was found to be ξ_C = 1.651 which compares favorably with published values of 1.5679 ((Clementi and Raimondi 1963), 1.625 (Ghosh and Biswas 2002), 1.7210 (2s) and 1.6105 (2p) (Herman 2004). Unit valence bond lengths (R_0 where $s = 1$) were found to be 1.493 Å for the carbon-carbon bond and 1.061 Å for the carbon-hydrogen bond.

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