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Atom Sizes and Bond Lengths in Molecules and Crystals

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Abstract: Atom size parameters are derived for 75 elements. In conjunction with an "electronegativity" parameter, these can be used to determine bond valence parameters and hence to derive bond lengths for a wide variety of homopolar, heteropolar, and metallic bonds. The size parameter of an atom is close to the distance from the nucleus at which the electrostatic potential is equal to the first ionization potential.

The chemist wishing to estimate an unknown bond length in a molecule or crystal is confronted with an intimidating array of covalent radii, tetrahedral radii, univalent radii, ionic radii, metallic radii etc. from which to choose.[1] The bond valence method[2,3] has recently had considerable success in predicting and interpreting bond lengths in "ionic" solids particularly with the development[4,5] of algorithms to determine expected valences. But despite its roots[1] in molecular and metallic chemistry, the method is not so widely applied in those contexts. In this paper we show that bond valence parameters (defined below) can be simply estimated for a large number of chemical bonds and then used to estimate bond lengths for a wide variety of bond types.

The Bond Valence Method

The valence v_{ij} of a bond between two atoms i and j is defined so that the sum of all the valences from a given atom i with valence V_i obeys

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

The most commonly adopted empirical expression for the variation of the length d_{ij} of a bond with valence is

$$v_{ij} = \exp[(R_{ij} - d_{ij})/b] \qquad (2)$$

Here b is commonly taken to be a "universal" constant equal to 0.37 Å;[6,7] we use this equation with this value of b throughout. In his pioneering discussion of C–C bonds, Pauling[1] used a value of $b = 0.31$. The parameter R we refer to as the *bond valence parameter*. In a formal sense, R is the length of a single bond, but it is usually determined to fit the bond lengths in compounds that are stable at normal temperatures and pressures. Thus for bonds between Na and F the parameter is determined for bonds in solid sodium fluorides rather than from the bond length in diatomic NaF.

We[7] recently determined bond valence parameters for bonds in a large number of solids and developed an interpolation scheme for absent data. We observed that the predicted bond valence parameters for atoms such as P, S, etc. considered as "cations" bonded to P, S, etc. considered as "anions" were very close to single bond lengths suggesting that data for "ionic" crystals and for "covalent" molecules formed a single set. In that work we presented almost 1000 empirically determined bond valence parameters. Here we show that to a good approximation the bond valence parameters can be obtained from two parameters characteristic of each atom.

Much early work on prediction of bond lengths as sums of radii ignored the fact that bond lengths depend on the bond valence and sets of radii such as the Bragg–Slater radii[8] are generally unsatisfactory. Ionic radii[9] were adapted for changes in coordination number (and hence changes in valence) but are of limited applicability.

It has long been recognized[1,10] that to express single bond lengths as sums of radii, corrections for differences of electronegativity of the atoms should be applied. Our work is in this spirit, but we wish to determine bond valence parameters for a wide range of bonds using an empirically determined "size" parameter and a second empirical parameter that may, or may not, be related to electronegativity.

Determination of Atomic Parameters

Let r_i be the "size" parameter and c_i be a second parameter for an atom. We want to express the bond valence parameter as $R_{ij} = r_i + r_j - f(c_i,c_j,r_i,r_j)$ with $f = 0$ for $i = j$.

We used 600 values of R determined from crystal and molecular structures for bonds to as many as 16 different "electronegative" elements and found the best values of c and r that minimized the squared deviation of the calculated and observed values of R for 75 elements. The "electronegative" elements are H, B, C, Si, N, P, As, Sb, O, S, Se, Te, F, Cl, Br, and I.

For the function f we considered the Schomaker–Stevenson[10] form $f = |c_1 - c_2|$ and several other empirical expressions of which the simplest was $f = (c_2r_1 + c_1r_2)/(c_1 + c_2)$, i.e. $R = (c_1r_1 + c_2r_2)/(c_1 + c_2)$. However, the best expression we found was one derived, in a somewhat different context, by Ray, Samuels, and Parr[11]

$$R_{ij} = r_i + r_j - \frac{r_ir_j(\sqrt{c_i} - \sqrt{c_j})^2}{c_ir_i + c_jr_j} \qquad (3)$$

We found that, not only did eq 3 result in the smallest deviation, but the c parameters for the more electronegative elements were roughly proportional to electronegativity as in the original derivation of eq 3. Of course one has a rich choice of electronegativity scales to choose from; we have chosen to use the Allred-Rochow[12] (AR) scale as our reference because of its completeness and wide acceptance. The value of c for some of the metallic elements was erratic owing to a paucity of the data for those elements. It should be noted that the c parameters appear only in f which is generally much smaller than $r_1 + r_2$ so that they are less well defined and less important than r. Specifically, the average value of f/R is 0.012 and the maximum value is 0.11 for Cs–F.

In subsequent analysis we decided to fix the c parameters of all but the 17 electronegative elements at the AR electronegativity values (the range is from 0.86 for Cs to 1.82 for Ga but close to 1.2 for most elements) but allowed the remaining values to vary. We thus had to fit 600 data points with 92 variables. Omitted were data for the following bonds: O–F, O–O, F–F, Cu–O, Cu–F,

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[1] Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell: Ithaca, New York, 1960.

[2] Brown, I. D. In *Structure and Bonding in Crystals*; O'Keeffe, M., Navrotsky, A., Eds.; Academic: New York, 1981; Vol. 2.

[3] O'Keeffe, M. *Struct. Bonding* **1989**, *71*, 162.

[4] Brown, I. D. *Acta Crystallogr.* **1977**, *B33*, 1305.

[5] O'Keeffe, M. *Acta Crystallogr.* **1990**, *A46*, 138.

[6] Brown, I. D.; Altermatt, D. *Acta Crystallogr.* **1985**, *B41*, 244.

[7] Brese, N. E.; O'Keeffe, M. *Acta Crystallogr.* In press.

[8] Slater, J. C. *Quantum Theory of Molecules and Solids*; McGraw-Hill: New York, 1965; Vol. 2.

[9] A commonly used tabulation suitable for oxides is that of: Shannon, R. D.; Prewitt, C. T. *Acta Crystallogr.* **1969**, *B25*, 925. See also the extensive discussion in ref 1.

[10] Schomaker, V.; Stevenson, D. P. *J. Am. Chem. Soc.* **1941**, *63*, 37.

[11] Ray, N. K.; Samuels, L.; Parr, N. G. *J. Chem. Phys.* **1979**, *70*, 3680.

[12] Allred, A. L.; Rochow, E. G. *J. Inorg. Nucl. Chem.* **1958**, *5*, 264. Little, E. J.; Jones, M. M. *J. Chem. Educ.* **1960**, *37*, 231. An electronegativity scale recently proposed by Allen (Allen, L. C. *J. Am. Chem. Soc.* **1989**, *111*, 9003) is very similar. It is noted that the dimensions of c do not enter into eq 3, so we consider this parameter to be dimensionless.

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Table I. Derived Parameters for Calculating *R* for Bonds[a]

Z		*c*	*r*	*Z*		*c*	*r*	*Z*		*c*	*r*	*Z*		*c*	*r*
1	H	0.89	0.38	23	V	*1.45*	1.21	44	Ru	*1.42*	1.21	65	Tb	*1.10*	1.56
3	Li	*0.97*	1.00	24	Cr	*1.56*	1.16	45	Rh	*1.54*	1.18	66	Dy	*1.10*	1.54
4	Be	*1.47*	0.81	25	Mn	*1.60*	1.17	46	Pd	*1.35*	1.11	67	Ho	*1.10*	1.53
5	B	1.60	0.79	26	Fe	*1.64*	1.16	47	Ag	*1.42*	1.12	68	Er	*1.11*	1.51
6	C	2.00	0.78	27	Co	*1.70*	1.09	48	Cd	*1.46*	1.28	69	Tm	*1.11*	1.50
7	N	2.61	0.72	28	Ni	*1.75*	1.04	49	In	*1.49*	1.34	70	Yb	*1.06*	1.49
8	O	3.15	0.63	29	Cu	*1.75*	0.87	50	Sn	*1.72*	1.37	71	Lu	*1.14*	1.47
9	F	3.98	0.58	30	Zn	*1.66*	1.07	51	Sb	1.72	1.41	72	Hf	*1.23*	1.42
11	Na	*1.01*	1.36	31	Ga	*1.82*	1.14	52	Te	2.72	1.40	73	Ta	*1.33*	1.39
12	Mg	*1.23*	1.21	32	Ge	1.51	1.21	53	I	2.38	1.33	74	W	*1.40*	1.38
13	Al	*1.47*	1.13	33	As	2.23	1.21	55	Cs	*0.86*	2.05	75	Re	*1.46*	1.37
14	Si	1.58	1.12	34	Se	2.51	1.18	56	Ba	*0.97*	1.88	77	Ir	*1.55*	1.37
15	P	1.96	1.09	35	Br	2.58	1.13	57	La	*1.08*	1.71	80	Hg	*1.44*	1.32
16	S	2.35	1.03	37	Rb	*0.89*	1.84	58	Ce	*1.08*	1.68	81	Tl	*1.44*	1.62
17	Cl	2.74	0.99	38	Sr	*0.99*	1.66	59	Pr	*1.07*	1.66	82	Pb	*1.55*	1.53
19	K	*0.91*	1.73	39	Y	*1.11*	1.52	60	Nd	*1.07*	1.64	83	Bi	*1.67*	1.54
20	Ca	*1.04*	1.50	40	Zr	*1.22*	1.43	62	Sm	*1.07*	1.61	90	Th	*1.11*	1.70
21	Sc	*1.20*	1.34	41	Nb	*1.23*	1.40	63	Eu	*1.01*	1.62	92	U	*1.22*	1.59
22	Ti	*1.32*	1.27	42	Mo	*1.30*	1.37	64	Gd	*1.11*	1.58				

[a] Values in italics are assumed equal to Allred–Rochow[12] electronegativities. *r* is in Å.

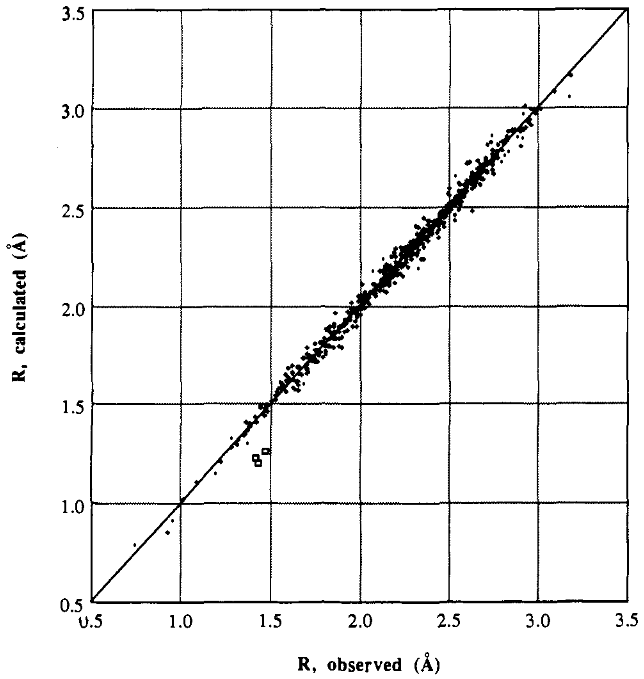

Figure 1. The bond valence parameter *R* calculated from eq 3 compared with values from observed bond lengths for 600 different atom pairs. Open squares are the values for O–O, O–F, and F–F bonds (not used in the fit).

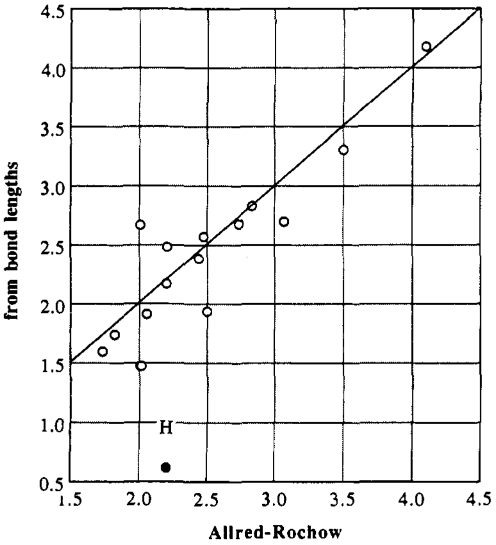

Figure 2. The parameter *c* of eq 3 from the fit to experimental data shown in Figure 1 compared to Allred–Rochow[12] electronegativities for the 16 electronegative atoms identified in the text. The filled circle is the point for H.

Ag–O, and Ag–F. *R* for the first three are much longer (by about 0.2 Å) than predicted; *R* for the last four are known[7] to depend strongly on the oxidation state of the metal and they are also significantly longer than predicted. The derived parameters fit the data with a root-mean-square deviation of 0.037 Å which is the same order of magnitude of the observed range of bond lengths for a given valence and atom pair.

Figure 1 shows the fit of the input data and Figure 2 shows the correlation of the parameters *c* with AR electronegativities. Except for H the agreement is close suggesting that eq 3 is soundly based. The anomalous value of *c* for H no doubt reflects the well-known fact[13] that bonds to hydrogen appear to be exceptional.

For bonds between atoms that are close to each other in electronegativity, the correction term *f* is generally less than the expected range of bond lengths and may be ignored. One might then consider the parameters *r* as "covalent single bond radii". However an important theme of this work is that one can subsume bonds of different kinds within one general scheme, and for bonds between atoms of very different electronegativities ("ionic" bonds), the correction term *f* is important and can amount to some tenths of angstroms. Thus although the root-mean-square deviation of the fit with $f = 0$ is only increased to 0.049 Å, the data for ionic bonds now form a significant set of outliers.

In determining the parameters reported, we supplemented the input data with 283 values of *R* previously obtained[7] from a rather elaborate interpolation scheme (for a total of 883 points to be fit). The values of *r* thus obtained changed by less than 0.01 Å from the original set obtained from the 600 experimental data and the *c* changed by less than 5% except for H ($c = 0.89$ as opposed to 0.62 previously). These latter values are reported in Table I.

Illustrative Applications

The reader unfamiliar with the bond valence method may find some simple examples of its use helpful. The method has been well documented in application to crystals,[2-7] so just one very simple example is adduced. In the high-pressure form of B_2O_3, B is bonded to one O(1) atom and to three O(2) atoms; O(1) is bonded to two B atoms and O(2) is bonded to three B atoms. Taking the valence of oxygen to be 2, one deduces that the bond valence of the B–O(1) bonds should be 1 and that of the B–O(2) bonds should be $^2/_3$. R_{BO} from Table I is 1.38 Å so that from eq 2 one predicts that the B–O bonds will be 1.38 and 1.53 (3X)

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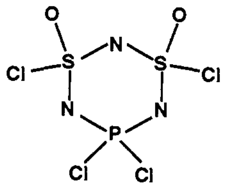
(13) For example: Calder, G. V.; Ruedenberg, K. *J. Chem. Phys.* **1968**, *49*, 485.

Table II. Bond Valences, *v*, and Observed (obs) and Calculated (calc) Bond Lengths (Å) in $NPCl_2(NSOCl)_2$

bond	*v*	*d*(obs)	*d*(calc)
S–O	2	1.42	1.40
S–N	$^3/_2$	1.68	1.60
P–N	$^3/_2$	1.59	1.64
S–Cl	1	2.03	2.01
P–Cl	1	1.96	2.07

Å; the observed values are 1.37 and 1.51 (3X) Å. Actually in this instance we would prefer to use R_{BO} = 1.37$_1$ Å derived[6,7] directly from the crystal structures of borates.

As an example of application to a molecule $NPCl_2(NSOCl)_2$ (**1**) has been chosen more or less at random as an example of a simple molecule with a variety of bonds of different valences. Table II lists observed[14] bond lengths and the bond valences and bond lengths calculated from the assumed atomic valences: $V_{Cl} = 1$, $V_O = 2$, $V_N = 3$, $V_P = 5$, $V_S = 6$. The agreement is generally satisfactory except for the P–Cl bond which is atypically much shorter (1.96 Å) than predicted (2.07 Å). We note however that the P–Cl bond lengths in PCl_3 (2.04 Å) and in PCl_5 (average 2.07 Å) are much longer; and it might be fruitful to enquire why the P–Cl bonds are so much shorter in **1**.



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One motivation for this work was an interest in bonding in transition-metal silicides and germanides. Data for such compounds were not included in our data base (largely on account of abiguities in assigning transition-metal valences). It is gratifying therefore that the predicted single bond lengths are generally in accord with those found in molecules. Some examples of single bond lengths in molecules are the following: for Ni–Si, observed[15] 2.16 and 2.18 Å, predicted 2.16 Å; for Fe–Ge, observed[16] 2.36–2.43 Å, predicted 2.37 Å; for Co–Ge, observed[16] 2.34 Å, predicted 2.30 Å.

Application to Metals

Although no data for metallic compounds have been used in deriving the values of *r*, it is interesting that they quite successfully predict interatomic distances in the metallic elements. Figure 3 shows a comparison of observed[17] (at 293 K) and predicted distances for metallic elements with either a close-packed or the body-centered cubic structure. We have included all such elements in groups I–VI except Cu, Ag, and Au (i.e. groups 1–6 and 12–14) for which we have *r* and used the group number as the valence.[1,18] For groups VII, VIII, and IB (7–11) it is not clear what valence is appropriate[15] and we do not wish to become embroiled in that controversy. For close-packed metals the calculated interatomic distance is $d = R - b \ln (V/12)$. For body-centered metals, the coordination number was taken to be 14, so that *d* is the solution of $V = 8 \exp[(R - d)/b] + 6 \exp[(R - 2d/\sqrt{3})/b]$. The worst predictions are within 10% of the observed values and the average deviation is 3%. Predicted values for the alkali metals are generally low, but it should be noted that at room temperature the root-mean-square amplitude of vibration is about 0.5 Å for these metals (in contrast to about 0.1 Å for transition metals). Any really precise evaluation of interatomic distances in metals will therefore have to include some allowance for the effect of thermal vibrations on interatomic distance. Possibly an accurate treatment would need also to distinguish sp bonds from d bonds.

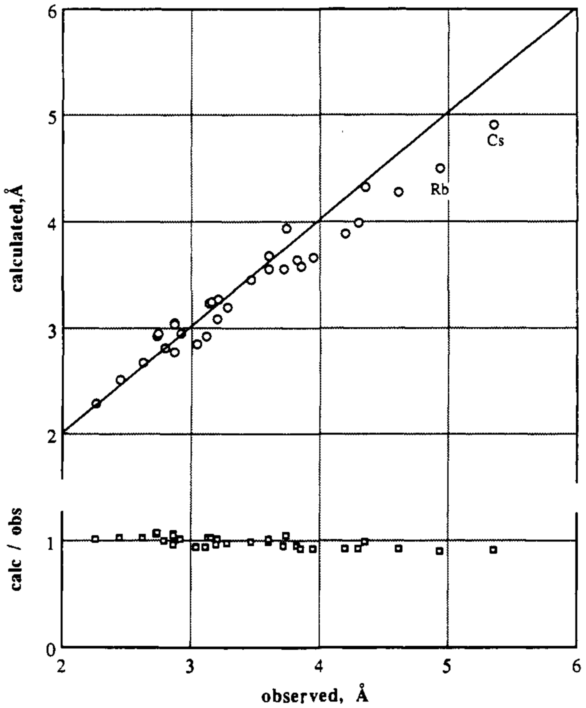

Figure 3. Top: Calculated and observed interatomic distances for metallic elements. Bottom: The corresponding ratio of calculated and observed distances.

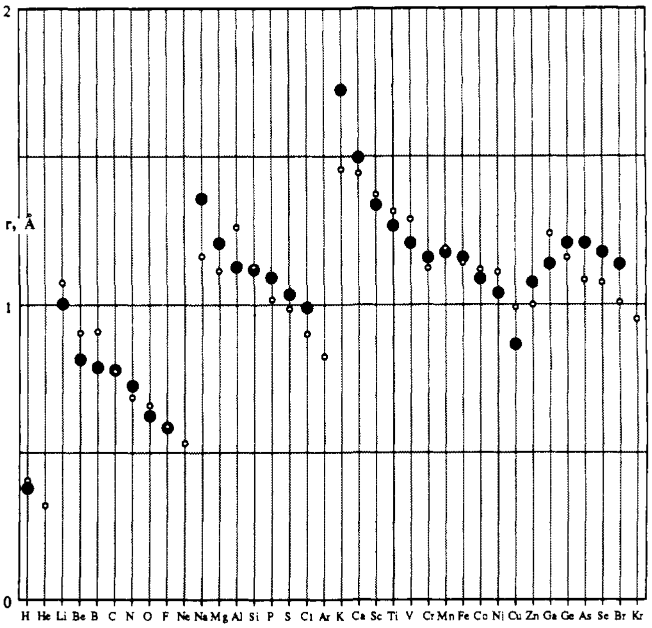

Figure 4. Filled circles are the atomic "size" parameter in eq 3 plotted as a function of atomic number. Smaller open circles are the values of r_I, the distance from the nucleus at which the atomic electrostatic potential is equal to the ionization potential.

The large interatomic distances in metals point up a difficulty with the bond valence method. This is that if one uses distances to calculate valences it is the absolute error in distance that determines the error in valence. To take an extreme example, our parameters predict an interatomic distance of 4.90 Å in *bcc* Cs. The value observed at 25 °C is 5.35 Å—an error of 8%.

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[14] van de Grampel, J. C.; Vos, A. *Acta Crystallogr.* **1969**, *B25*, 651.

[15] Brezinski, M. J. M.; Schneider, J.; Radonovich, L. J.; Klabunde, K. *J. Inorg. Chem.* **1989**, *28*, 2414.

[16] Bennett, M. J.; Brooks, W.; Elder, M.; Graham, W. A. G.; Hall, D.; Kummer, R. *J. Am. Chem. Soc.* **1970**, *92*, 208 and references therein.

[17] Donohue, J. *The Structures of the Elements*; Wiley: New York, 1974.

[18] The Engel–Brewer approach to the valence of transition metals is summarized by: Brewer, L. In *Phase Stability in Metals and Alloys*; Rudman, P. S., Stringer, J., Haffee, R. I., Eds.; McGraw-Hill: New York, 1967. For a discussion of valence in metals such as elemental Ni and Cu see also: Brewer, L. In *Structure and Bonding in Crystals*; O'Keeffe, M., Navrotsky, A., Eds.; Academic: New York, 1981; Vol. 1.

However an error of 0.45 Å in bond length results in the valence being incorrect by a factor $e^{0.45/b} = 3.4$. Thus it is probably not reasonable to expect that an analysis of bond lengths in the later transition metals will solve the vexed question of their valences.

A Connection to Atomic Properties

The r parameters we have derived appear to have wide applicability to a variety of bond types. It is therefore tempting to suppose that they reflect some simple atomic property. The electron density $\rho(r)$ (r is the size parameter) varies by more than an order of magnitude from atom to atom and the variation of $r^2\rho(r)$ is almost as large.

Politzer, Parr, and Murphy[19] have suggested that the distance from the nucleus at which the electrostatic potential, ϕ, is equal to the Mulliken electronegativity ($\chi = (I + A)/2$) should be a good measure of atomic size. Here I is the first ionization potential[20] and A the electron affinity.[21] We found in fact that $\phi(r)$ was closer to the ionization potential[22] and so calculated[23] r_I where $\phi(r_I) = I$.

Figure 4 shows r and r_I for the first 36 elements as a function of atomic number. Both follow the expected periodic trends except that r does not have the sharp change for the transition from s^2 to s^2p manifest for r_I (see especially Mg,Al and Zn,Ga). One expects therefore that an even better correlation might be found if some sort of average orbital ionization energy (cf. Allen[12]) were used instead of I. The discrepancy for copper possibly reflects the ds valence state used in bonding by that element. We do not pursue this topic other than to remark that it appears to offer an interesting challenge to the theoretician.

Concluding Remarks

We have shown that expected bond lengths for a wide range of bond types may be easily calculated from atomic parameters. However, it is well to recall that bond lengths are not determined solely by the atom pair forming the bond. For example it is well-known[24] that the A–X bond length in molecules AY_nX depends in part of the nature of Y. In solids, particularly oxides, with high coordination numbers the role of nonbonded repulsions in stretching and weakening bonds is well-established.[3,25] These, and other, effects must be considered before *accurate* predictions of bond lengths can be made.[26] In general it will be preferable to use experimentally determined[6,7] values of R when those are available and to use those derived from the data in Table I to fill in missing values.

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Registry No. H, 12385-13-6; Li, 7439-93-2; Be, 7440-41-7; B, 7440-42-8; C, 7440-44-0; N, 17778-88-0; O, 17778-80-2; F, 14762-94-8; Na, 7440-23-5; Mg, 7439-95-4; Al, 7429-90-5; Si, 7440-21-3; P, 7723-14-0; S, 7704-34-9; Cl, 22537-15-1; K, 7440-09-7; Ca, 7440-70-2; Sc, 7440-20-2; Ti, 7440-32-6; V, 7440-62-2; Cr, 7440-47-3; Mn, 7439-96-5; Fe, 7439-89-6; Co, 7440-48-4; Ni, 7440-02-0; Cu, 7440-50-8; Zn, 7440-66-6; Ga, 7440-55-3; Ge, 7440-56-4; As, 7440-38-2; Se, 7782-49-2; Br, 10097-32-2; Rb, 7440-17-7; Sr, 7440-24-6; Y, 7440-65-5; Zr, 7440-67-7; Nb, 7440-03-1; Mo, 7439-98-7; Ru, 7440-18-8; Rh, 7440-16-6; Pd, 7440-05-3; Ag, 7440-22-4; Cd, 7440-43-9; In, 7440-74-6; Sn, 7440-31-5; Sb, 7440-36-0; Te, 13494-80-9; I, 14362-44-8; Cs, 7440-46-2; Ba, 7440-39-3; La, 7439-91-0; Ce, 7440-45-1; Pr, 7440-10-0; Nd, 7440-00-8; Sm, 7440-19-9; Eu, 7440-53-1; Gd, 7440-54-2; Tb, 7440-27-9; Dy, 7429-91-6; Ho, 7440-60-0; Er, 7440-52-0; Tm, 7440-23-5; Yb, 7440-64-4; Lu, 7439-94-3; Hf, 7440-58-6; Ta, 7440-25-7; W, 7440-33-7; Re, 7440-15-5; Ir, 7439-88-5; Hg, 7439-97-6; Tl, 7440-28-0; Pb, 7439-92-1; Bi, 7440-69-9; Th, 7440-29-1; U, 7440-61-1.

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(19) Politzer, P.; Parr, R. G.; Murphy, D. R. *J. Chem. Phys.* **1983**, *79*, 3859. A related proposal is made by: Balbas, L. C.; Alonzo, J. A.; Vega, L. A. *Z. Phys. D* **1984**, *1*, 215.

(20) Moore, C. E. *Ionization Potentials and Ionization Limits Derived from the Analyses of Optical Spectra*; NSRDS-NBS 34; US Government Printing Office: Washington, 1970.

(21) Hotop, H.; Lineberger, W. C. *J. Phys. Chem. Ref. Data* **1985**, *14*, 731.

(22) The distances at which $\phi = I$ or $I + A$ or $I - A$ are not very different. We found however that r_I was closest on average to r. The point at which $\phi = (I + A)/2$ is significantly larger.

(23) The electrostatic potential at a point in a spherically averaged atom is readily expressed in terms of known integrals if the wave function is given in terms of Slater-type orbitals. Accordingly we used the tabulation in this form of Hartree–Fock wave functions by: Clementi, E.; Roetti, C. *Atomic Data and Nuclear Data Tables* **1974**, *14*, 177.

(24) Many examples can be found in the extensive tables presented by: Wells, A. F. *Structural Inorganic Chemistry*, 5th Ed.; Clarendon Press: Oxford, 1984.

(25) O'Keeffe, M.; Hyde, B. G. *Nature (London)* **1984**, *309*, 411.

(26) The meaning of "accuracy" depends on the context. In some oxides variations in bond length smaller than 0.01 Å are considered significant. See for example: O'Keeffe, M.; Domengès, B.; Gibbs, G. V. *J. Phys. Chem.* **1985**, *89*, 2304 and references therein. More generally ±0.03 Å might be a reasonable goal.