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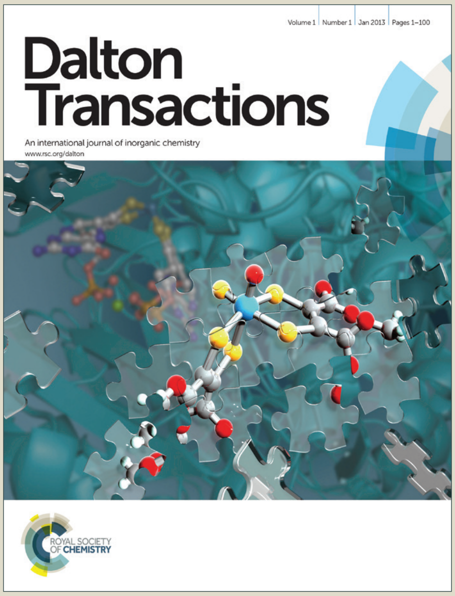

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Electronegativity effects and Single Covalent Bond Lengths of Molecules in the Gas Phase

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Summary

This paper discusses in detail the calculation of internuclear distances of heteronuclear single bond covalent molecules in the gaseous state. It reviews briefly the effect of electronegativity in covalent bond length. A set of single bond covalent radii and electronegativity values are proposed. Covalent bond lengths calculated by an adapted form of a simple expression (which calculated internuclear separation of different Group 1 and Group 2 crystalline salts to a remarkable degree of accuracy) show very good agreement with observed values. A small number of bond lengths with double bonds as well as bond lengths in the crystalline state are calculated using the same expression and when compared with observed values also give good agreement. This work shows that covalent radii are not additive and that radii in the crystalline state are different from those in the gaseous state. The results also show that electronegativity is a major influence on covalent bond lengths and the set of electronegativity scale and covalent radii proposed in this work can be used to calculate covalent bond lengths in different environments that have not yet been experimentally measured.

Introduction

At an elementary level, when two atoms (which can be parts of two molecules) share one or more pairs of electrons a covalent bond is formed. Although over three quarters of elements are metals there are many more compounds formed between non-metallic elements than between metallic elements. Since the bonds formed between non-metallic elements are mainly covalent bonds, reliable data on covalent radii, bond strengths and bond lengths are very helpful indeed. For example, bond lengths, in conjunction with other measurements can provide a guide to the stability of compounds.

Covalent Radii Data

There are a number different sets of published reference covalent radii data[1]. The available data vary from estimates to theoretical calculations to statistical fits of experimental measurements. Sometimes it is unclear if the radii refer to the gaseous state or solid state or both.   Herzberg[2] produced one of the earliest list of experimental data which gave covalent bond lengths of gaseous molecules. Other observed data can be found in, for example, *Molecular Spectra and Molecular Structure IV*[3] (which provided extensive data of spectral measurements and original references), *Structural Inorganic Chemistry*[4] (although provide data mainly on internuclear distances in the crystalline state it does provide some data in the gas phase which are used to compare bond lengths between the gaseous and crystalline states), *Molecular Structure of Gas Phase Polyatomic Molecules*[5] or in the *CRC Handbook of Chemistry and Physics*[6] (which provided extensive data on bond lengths in both the gaseous and crystalline state). The *Crystal Data Determination Tables*[7] and the Cambridge Structural Database[8] provide observed bond lengths in the solid state. The uncertainty in the measurements quoted are in many cases 0.1% or less. There is also the MOGADOC database (administered by the University of Ulm) which can be purchased as a CD-Rom but this database does not appear to be updated regularly. Whereas much of the experimental data refer to lengths of specific bonds between particular atoms (of elements) many published tables of covalent data tend to provide a single value for each element. It is sometimes not pointed out in the literature that the some of the published sets of reference covalent radii are in many respects some form statistical average. Recently, Cordero[9] et al. undertook a large scale statistical exercise and published a set of covalent radii (applicable for the solid state) deduced from crystallographic data. Cordero discussed in detail the need for covalent radii, the lack of experimental data of radii of some elements, uncertainties and limitations of some data and methodology used to derive the set. However, that the covalent radius of an element may vary (and how it changes) when in different chemical environments was not properly discussed. Pyykko and Atsumi[10] also carried out a straight forward statistical exercise and published a list of "additive" single bond covalent radii derived from both experimental and calculated data.

At first we were surprised to find that although both Cordero and Pyykko deduced their sets of covalent radii by completing statistical fitting exercises (see for example Table 1 which is a comparison of the two sets from element number 11 to 20)

Table 1. Observed covalent radii of hydrogen and Group 7 elements (in Å)

Element	Na	Mg	Al	Si	P	S	Cl	Ar	K	Ca
Cordero	1.66	1.41	1.21	1.11	1.07	1.05	1.02	1.06	2.03	1.76
Pyykko	1.55	1.39	1.26	1.16	1.11	1.03	0.99	0.96	1.96	1.71

We then went though the papers and some of the references quoted and found that the radii in Cordero's paper are derived from experiemental data in the crystalline state, whereas, Pyykko used data measured in the gas phase and solid state as well as calculated (or estimated) data to deduce the proposed set.

At normal temperature and pressure, many compounds exist in the gas phase. We have made comparisons between particular bond lengths/internuclear distances of molecules in the gaseous and solid state (using experimental data provided in references 2 to 7). We found in the majority of cases the quoted uncertainty in the measurements is less than ±0.002 Ǻ (or averaged about 0.1% or less) and the differences in internuclear distances between the gaseous and solid states are fairly small, for example the Cl-I distance in the gaseous state is 2.321 Ǻ and 2.303 Ǻ in the solid state. But in some cases such as the Groups 1 and 2 halides and hydrides, the differences can be significant. For example, the internuclear distance between Li-F and Li-H in the gaseous and solid states are 1.564 and 1.595 Ǻ versus 2.013 and 2.043 Ǻ respectively. We have to bear in mind that any reference covalent radius no matter how it is devised is only meaningful if it resembles some value close to the observed. Further more, it was recognised long ago by Pauling and others[11] that except for homonuclear diatomic molecules, similar to ionic radii, covalent radii are not additive even though it is claimed by some authors[10] to be so. In this work our primary aim is to devise covalent radii that can reproduce bond lengths of molecules in the gaseous state and to show that covalent bond lengths covalent bond lengths can be calculated from a simple equation.

Electronegativity and Covalent bond lengths

Schomaker and Stevenson[12] were among the first to recognise that there are large deviations from additivity of the covalent radii in the bond lengths between atoms of different elements. They suggested that these discrepancies originate from the partial ionic character of the bonds formed. It was proposed that the interatomic distance for a bond A-B be taken as the sum of the radii for the atoms A and B with a correction of C [abs($x_a - x_b$)] where C is a constant and abs($x_a - x_b$) is the absolute value of the difference in electronegativity of the two atoms. Electronegativity is the ability of an atom (in a molecule) to attract electrons to itself. Pauling[13] discussed in detail in his many writings the dependence of bond length on the differences in electronegativity between the different elements which created the partial ionic character in the bonds. He was also the first to produce a practical electronegativity scale of the main group and transition elements. Pauling's original set of electronegativities has since been revised and other sets which are calculated by slightly different methods have also been published[14]. Since different sets may be produced for different purposes and not every set is suitable for use in calculating covalent bond lengths.

In this work we have devised a set of electronegativity values to calculate covalent bond lengths. We first assumed that electronegativity of an element is a measure of both the ionisation energy and electron affinity. We produced many different sets calculated by the relationship where the electronegativity of an element is a simple function of [val(I_a) + (1-val)(E_a)] with val being a fraction less than 1 and I_a is the ionisation energy and E_a is the electron affinity. However, we found that none of these sets are very satisfactory but a set deduced from the ionisation energies adjusted for pairing and exchange interactions[15,16] when used to calculate bond lengths produced the best agreement with observed values.

The Soft-sphere model of bond lengths

In very simplistic terms we assume that atoms behave like soft spheres. As 2 atoms approach to form a conventional chemical bond 2 things can happen. Firstly, 1 atom can donate 1 or more electrons to the other atom and the result is an ionic bond. As the 2 ions (soft spheres) are attracted by the opposite charges and move very close to each other the soft spheres are deformed (slightly squashed) and their sizes become smaller than if they are on their own away from other ionic soft spheres. This accounts for the fact that ionic radii are not additive[17]. Secondly, if each atom may give up 1 or more electrons and both atoms share 1 or more pairs of electrons which bonds the 2 atoms together a covalent bond is formed. However, when the 2 atoms possess different electronegativities, the electron pair(s) between the two atoms tend(s) to move closer to the nucleus with a higher electronegativity. When this happens, the size of the atom/soft sphere (with a lower electronegativity) becomes smaller since it has lost some of the electron density to the other atom. If the electronegativity between the 2 atoms is very different, the bonding electron pair(s) binds sufficiently close to the atom with high electronegativity and produces ionic character in the bond and the size of the atom (soft sphere) with lower electronegativity becomes even smaller. Hence, the internuclear distance between 2 atoms forming a bond can be calculated by the following relationship:

$$D[AB] = [AB]^{1/k} - C[\mathrm{abs}(x_a - x_b)^r]\ ; \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \ [1]$$

$$\text{and}\ \ D[AB]^k = [A]^k + [B]^k\} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \ [2]$$

In the above relationship, D[AB] is the internuclear separation between A and B and [abs($x_a - x_b$)] is the absolute difference between the electronegativities x_a and x_b of the 2 atoms A and B. C and the exponents k and r are constants but may vary depending on whether the bond is a single, double or triple bond. [A] and [B] are the radii of 2 two atoms.

The exponents *k* and *r* and the constant C

We estimate that the size of an atom is of the order of 1 Å and found that in many cases the internuclear distance between 2 atoms forming a single bond is different from the sum of the individual covalent radii by between 5 to 30%. A value of 0.1 for the constant C then seems to be a reasonable average to use. As discussed in our previous work[17], the exponent *k* is a function of the deformation of the soft ionic spheres. It is bigger than 1 when the bond is more ionic than covalent otherwise it is equal to 1 and when there is much less deformation of the soft spheres. For an "ionic" bond, the term $C[\mathrm{abs}(x_a - x_b)^r]$ does not apply since the 2 atoms do not share an electron pair and are positive and negative ions instead. The internuclear separation between the 2 ions can be express simply as:

$$D[AB]^k = [A]^k + [B]^k \quad \ldots\ldots\ldots\ldots\ldots\ldots [2]$$

The above expression was used to produce internuclear distances of Group 1 and Group 2 salts showing excellent agreement with experimental values. The internuclear distance between two atoms forming a covalent bond with little or no ionic character is then expressed as:

$$D[AB] = [A]^1 + [B]^1 - C[\mathrm{abs}(x_a - x_b)^r] \quad \ldots\ldots\ldots\ldots\ldots\ldots [3]$$

However, if there is substantial ionic character in the bond but the amount of ionic character is not large enough for the bond to be truly "ionic" the following expression should be used to calculate the internuclear distance:

$$D[AB] = [AB]^{1/k} - C[\mathrm{abs}(x_a - x_b)^r] \text{ with } [AB]^k = [A]^k + [B]^k \ldots\ldots\ldots\ldots [4]$$

Since a difference in electronegativty between the atoms forming a covalent bond leads to the creation of a force (related to electric charge) that pulls the electron pair towards 1 of the atoms we expect (without theoretical justification) the force to obey the inverse square law similar to electrostatic forces. The force which is a function of $\mathrm{abs}(x_a - x_b)$ can be represented by the following expression where F is the force, R is some constant and d represents the change in bond length (distance between the 2 atoms):

$$F = [R\ \mathrm{abs}(x_a - x_b)]/d^2 \text{ then} \quad \ldots\ldots\ldots\ldots\ldots\ldots [5]$$

$$d^2 = (R/F)\mathrm{abs}(x_a - x_b) \text{ and} \quad \ldots\ldots\ldots\ldots\ldots\ldots [6]$$

$$d = C[\mathrm{abs}(x_a - x_b)^{0.5}] \quad \ldots\ldots\ldots\ldots\ldots\ldots [7]$$

Therefore, we take it for granted that the exponent *r* is 0.5 and the constant C may be different for single, double or triple bonds. In our previous work we have presumed that the exponent *k* is a rational number (such as 5/4 or 3/2) and there is no reason to change that supposition. There is no theoretical justification to suppose that *k* cannot be an irrational number, but since the simple fractions we used produced internuclear distances that gave good agreement with experimental values there is no necessity to try more complex values.

Assumptions

We assume that in the gaseous state, both the electronegativity and the size of the atom have influence on the probability of covalent bonds possessing ionic character. It is fairly obvious that a bond between a large atom and a much smaller atom is more likely to have ionic character than 2 atoms of similar size since it is easier for the smaller atom to draw the bonding electrons closer to itself. Since atoms of elements in Groups 1 and 2 are larger than atoms of other elements in the same period we consider that bonds between elements in Groups 1 or 2 with other elements will exhibit "ionic character" if the difference between their electronegativities is greater than 1. Bonds between Groups 1 or 2 elements with other elements will show "significant/substantial ionic character" if the difference between their electronegativities is greater than 2 (on a scale of 0 to 4) and there is "some/appreciable ionic character" if the difference between their electronegativities is between 1 and 2. For all other elements, the difference in size between the atoms forming the bond may not be as great in size will have less influence on ionic character. Covalent bonds formed between them will exhibit "sufficient/appreciable ionic character" if the difference between their electronegativities is greater than 2 and ionic character is insignificant if the difference in electronegativities is less than 2. For molecules that show "significant ionic character" we found that *k* has a value of between 1.25 (5/4) and 1.4 (7/5). For simplicity, we have only used 1.3 as the exponent to calculate the internuclear distances of these molecules. As for molecules that possess "sufficient/appreciable ionic character" *k* lies approximately between 1.083333 (13/12) and 1.0625 (17/16) and we have used 1.066667 (16/15) in this work. In all other cases *k* equals 1. We also assume that the covalent radius of an atom may be different (say by more than 5% in many cases) between that of a single bond and a double or triple bond.

Choice of radii

Unless otherwise stated, observed covalent radii/bond lengths are taken from (a) *Molecular Spectra and Molecular Structure IV*, (b) *Structural Inorganic Chemistry* and (c) the *CRC Handbook of Chemistry and Physics* to compare with soft sphere calculated results for molecules in the gaseous state. There is no reason to believe that data quoted in the above publications are not reliable. The observed homonuclear covalent radii of hydrogen and Group 7 elements in the gaseous state can be considered to be completely covalent without any ionic character and are shown in Table 2.

Table 2. Observed covalent radii of hydrogen and Group 7 elements (in Å)

Element	H	F	Cl	Br	I
	0.371	0.706	0.994	1.141	1.333

We have not used the internuclear distances of diatomic gaseous Group 1 elements to derive single bond covalent radii of other elements because we suspect these bonds may possess ionic character. All other single bond covalent radii (see Table 3 below) are derived from the averaged bond lengths of simple compounds between those elements with elements in Group 7 and/or with other elements whose radii have been already deduced. Those single bond covalent radii are then refined/fitted (manually) to give the best agreement with observed internuclear distances of covalent bonded compounds. Table 3 shows the atomic numbers, symbols, single bond covalent radii derived in this work and applicable electronegativities of the elements.

There are some elements such as technetium and polonium, where little observed data on bond lengths or covalent radii are available. In such cases, their radii and electronegativies are estimated by interpolation/extrapolation of radii/electronegativies of neighbouring elements. Since we are concerned with single bond covalent radii, even for elements with multiple valencies, we have derived only 1 proposed radius per element as shown in the Table below. Since experimental uncertainties are in most cases less than ±0.002 Å (or about 0.1% or less) all bond lengths and radii in this work are shown/rounded to three decimal places (of an Å). We also believe that it is reasonable to show differences between calculated and observed values to the nearest 0.1% as that is similar to or bigger than the experimental uncertainties.

Table 3. Electronegativities & Single Bond Covalent Radii.

Atomic Number	Symbol	Electronegativity	Covalent Radius (Å)
1	H	2.00	0.371
2	He	N/A	N/A
3	Li	1.24	1.292
4	Be	2.14	0.930
5	B	1.81	0.848
6	C	2.30	0.795*
7	N	2.82	0.759
8	O	3.39	0.732
9	F	4.00	0.706
10	Ne	N/A	N/A

11	Na	1.18	1.613
12	Mg	1.76	1.450
13	Al	1.31	1.200
14	Si	1.66	1.124
15	P	2.05	1.080
16	S	2.49	1.072
17	Cl	2.95	0.994
18	Ar	N/A	N/A
19	K	1.00	1.952
20	Ca	1.40	1.723
21	Sc	1.51	1.395
22	Ti	1.57	1.294
23	V	1.62	1.260
24	Cr	1.65	1.250
25	Mn	1.71	1.310
26	Fe	1.77	1.235
27	Co	1.84	1.225
28	Ni	1.92	1.187
29	Cu	2.02	1.140
30	Zn	2.16	1.199
31	Ga	1.31	1.233
32	Ge	1.62	1.234
33	As	1.95	1.230
34	Se	2.30	1.170
35	Br	2.67	1.141
36	Kr	N/A	N/A
37	Rb	0.96	2.077
38	Sr	1.31	1.880
39	Y	1.54	1.520
40	Zr	1.57	1.430

41	Nb	1.61	1.490
42	Mo	1.66	1.380
43	Tc	1.71	1.310
44	Ru	1.76	1.300
45	Rh	1.84	1.260
46	Pd	1.91	1.200
47	Ag	1.92	1.350
48	Cd	2.06	1.340
49	In	1.26	1.450
50	Sn	1.49	1.432
51	Sb	1.73	1.425
52	Te	2.01	1.340
53	I	2.32	1.333
54	Xe	N/A	N/A
55	Cs	0.89	2.200
56	Ba	1.20	2.000
57	La	1.28	1.720
58	Ce	1.27	1.640
59	Pr	1.25	1.640
60	Nd	1.27	1.630
61	Pm	1.28	1.620
62	Sm	1.30	1.620
63	Eu	1.30	1.610
64	Gd	1.41	1.600
65	Tb	1.35	1.600
66	Dy	1.36	1.590
67	Ho	1.38	1.580
68	Er	1.40	1.570
69	Tm	1.42	1.570
70	Yb	1.44	1.560

71	Lu	1.25	1.550
72	Hf	1.57	1.428
73	Ta	1.73	1.370
74	W	1.81	1.355
75	Re	1.80	1.345
76	Os	1.94	1.350
77	Ir	2.06	1.300
78	Pt	2.06	1.220
79	Au	2.12	1.200
80	Hg	2.40	1.316
81	Tl	1.34	1.580
82	Pb	1.51	1.565
83	Bi	1.68	1.535
84	Po	1.90	1.450
85	At	2.12	1.440

The covalent radius of carbon shown in the above table as 0.795 (*) is to be taken as the usual *sp*^{3} covalent radius. However, for say *sp*^{1} carbon, the radius is shorter and is assigned a value of 0.766. In bonds such as metal carbonyls where bonding electrons are not supplied by the central metal but by the π electrons of carbon monoxide we assume the radius is shorter and is equal to 0.750. We should bear in mind that in arenes the carbon to carbon bonds on the ring are delocalised but not the bond(s) between a carbon to any atom not on the ring itself.

In addition to the list of electronegativies given in Table 3, we have made the assumption that the electronegativity values of functional groups such as (OH) as in hydroxide, (SO_4) and (NO_3) are equivalent to a value of 4 and that of (COOH), (CN) and CO(NH_2) are equivalent to 2.8. These are included because they are fairly common parts of simple covalent molecules. The covalent "radius" of (SO_4) and (NO_3) are assigned 0.74 and 0.73 respectively.

Representative examples of calculated covalent bond lengths involving common elements and bonds involving carbon are shown in below. In order to evaluate the accuracy of the soft sphere model, bond lengths are calculated first by the soft sphere equation and then by the Schomaker and Stevenson equation. Differences with the observed values are shown next to the calculated results of each equation and a simple comparison can be made.

Bonding involving hydrogen

Examples of calculated internuclear separation of molecules involving bonding of hydrogen with elements of Group 1 and Group 7 as well as across Period 2 and some other common molecules are shown in Table 4. The molecules (with the specific bond in question in bold type) are shown in Column 1 of the table, Column 2 shows observed distances. Columns 3 and 4 show the calculated results and absolute % differences between observed and calculated. Columns 5 and 6 show the results and differences using the Schomaker and Stevenson equation.

Table 4. Examples of bonding involving hydrogen

Molecule (1)	Internuclear distances(Å) Observed (2)	Soft sphere (3)	Abs % difference (4)	Schomaker & Stevenson (5)	Abs % difference (6)
H-F	0.917	0.936	2.0	0.887	4.3
H-Cl	1.275	1.267	0.6	1.270	0.4
H-Br	1.414	1.430	1.1	1.445	2.2
H-I	1.609	1.648	2.4	1.672	3.9
Li-H	1.595	1.576	1.2	1.587	0.5
Na-H	1.887	1.893	0.3	1.902	0.8
K-H	2.244	2.223	0.9	2.223	0.9
Rb-H	2 .367	2.346	0.9	2.344	1.0
Cs-H	2.494	2.466	1.1	2.460	1.3
H-BeH	1.326	1.264	4.2	1.287	3.0
H-BH_2	1.190	1.176	1.2	1.200	0.9
H-CH_3	1.087	1.112	2.3	1.136	4.6
H-NH_2	1.012	1.039	2.7	1.048	3.6
H-(NO_3)	0.960	0.960	0.0	0.901	6.2
H-(SO_4H)	0.970	0.970	0.0	0.911	6.1
H-SH	1.336	1.373	2.8	1.394	4.4

For the bond between hydrogen and the rest of the molecule in nitric acid and sulphuric acid, the difference in electronegativity is taken to be the difference between hydrogen and the functional group (NO_3) and (SO_4). As shown in the above Table, agreement between calculated and observed internuclear separation is 97% or better in all cases except the H-Be bond (where the agreement is 95.8%) whereas for the results calculated by the Schomaker and Stevenson equation 6 of the figures have agreement of less than 97% and 4 of the figures show agreement was less than 95%.

Bonding involving oxygen

Oxygen forms double bonds more frequently than single bonds. Examples of single bonds involving oxygen with the Group 1 metals, copper, silver and in some organic molecules are shown in Table 5 below.

Table 5. Examples of bonding involving oxygen

Molecule	Internuclear distances(Å)		Abs % difference	Schomaker & Stevenson	Abs % difference
	Observed	Soft sphere			
(1)	(2)	(3)	(4)	(5)	(6)
Li-O Li	1.606	1.598	0.5	1.809	12.6
H-OH	0.958	0.985	2.9	0.964	0.7
Li-OH	1.578	1.579	0.1	1.748	10.8
K-OH	2.212	2.186	1.2	2.384	7.8
Rb-OH	2.301	2.303	0.1	2.505	8.9
Cs-OH	2.395	2.418	1.0	2.621	9.5
Mg-OH	1.770	1.740	1.7	1.958	10.6
Ca-OH	1.985	1.983	0.1	2.195	10.6
Sr-OH	2.111	2.127	0.8	2.343	11.0
Ba-OH	2.200	2.237	1.7	2.452	11.4
Cu-OH	1.769	1.731	2.1	1.674	5.4
Ag-OH	2.016	1.938	3.9	1.874	7.0
H_3**C-O**H	1.425	1.422	0.2	1.418	0.5
H_3**C-O**CH_3	1.416	1.422	0.5	1.418	0.1
H_5**C_6-OH**	1.364	1.393	2.2	1.389	1.8

To calculate the hydrogen to oxygen bond length in water we consider that the hydrogen atom is bonded to the hydroxyl functional group and hence the value of the difference in electronegativity is not that between hydrogen and oxygen but between hydrogen and the hydroxyl functional group. Again, as shown in the above table, agreement between calculated and observed is very good with only the Ag-O bond in AgOH agreement differing from the observed by more than 3% (actual difference 3.9%). As for the results calculated by the Schomaker and Stevenson equation, 11 out of 15 agree to less than 95% and what is more significant is that over a third of the results show a discrepancy of over 10% when compared to the observed.

Bonding involving carbon

Carbon forms an extended range of single bonds and the examples given below in Table 6 show bonding to phenyl, cyanide, methyl groups by halides, other *p* block elements and transition metals and include transition metal carbonyls.

Table 6. Examples of bonding involving carbon

Molecule	Internuclear distances(Å)		Abs % difference	Schomaker & Stevenson	Abs % difference
	Observed	Soft sphere			
(1)	(2)	(3)	(4)	(5)	(6)
F-CF$_3$	1.323	1.370	3.6	1.331	0.6
H$_5$**C$_6$-H**	1.101	1.083	1.7	1.107	0.6
H$_5$**C$_6$-C**ONH$_2$	1.511	1.490	1.4	1.511	0.0
H$_5$**C$_6$-Br**	1.850	1.846	0.2	1.870	1.1
H$_5$**C$_6$-C$_6$**H$_5$	1.490	1.532	2.8	1.532	2.8
H$_5$**C$_6$-C**H$_3$	1.524	1.561	2.4	1.561	2.4
(H$_5$**C$_6$)$_3$-N**	1.420	1.453	2.3	1.473	3.7
H$_5$**C$_6$-Cl**	1.737	1.679	3.3	1.694	2.5
H$_3$**C-C**O$_2$H	1.519	1.519	0.0	1.540	1.4
H-CO$_2$H	1.097	1.077	1.9	1.086	1.0
H$_3$**C-C**N	1.468	1.490	1.5	1.511	2.9
H-CN	1.066	1.048	1.7	1.057	0.8
Ni-CN	1.828	1.859	1.7	1.865	2.0

Zn-CN	1.955	1.894	3.1	1.915	2.1
H$_3$**Si-C**N	1.850	1.819	1.7	1.849	0.5
Cu-CN	1.832	1.818	0.8	1.828	0.2
Co-CN	1.883	1.893	0.5	1.895	0.6
H$_3$**C-Be**CH$_3$	1.698	1.686	0.7	1.710	0.7
H$_3$**C-Zn**CH$_3$	1.929	1.957	1.4	1.980	2.7
H$_3$**C-S**CH$_3$	1.802	1.823	1.1	1.847	2.5
H$_3$**C-Se**CH$_3$	1.943	1.965	1.1	1.965	1.1
H$_3$**C-Hg**CH$_3$	2.083	2.079	0.2	2.101	0.9
H$_3$**C-Cd**CH$_3$	2.112	2.064	2.3	2.085	1.3
H$_3$**C-P**(CH$_3$)$_2$	1.847	1.826	1.1	1.851	0.2
H$_3$**C-Al**(CH$_3$)$_2$	1.957	1.896	3.1	1.896	3.1
H$_3$**C-As**(CH$_3$)$_2$	1.979	1.966	0.7	1.990	0.6
H$_3$**C-Bi**(CH$_3$)$_2$	2.263	2.252	0.5	2.269	0.3
H$_3$**C-B**(CH$_3$)$_2$	1.578	1.574	0.3	1.595	1.1
H$_3$**C-N**(CH$_3$)$_2$	1.458	1.482	1.6	1.502	3.0
H$_3$**C-Ge**(CH$_3$)$_3$	1.945	1.947	0.1	1.961	0.8
H$_3$**C-Pb**(CH$_3$)$_3$	2.238	2.271	1.5	2.281	1.9
H$_3$**C-Si**(CH$_3$)$_3$	1.875	1.839	1.9	1.856	1.0
H$_3$**C-Sn**(CH$_3$)$_3$	2.144	2.137	0.3	2.146	0.1
(CO)-Cr(CO)$_5$	1.920	1.932	0.6	1.954	1.8
(CO)-Mo(CO)$_5$	2.063	2.050	0.6	2.066	0.2
(CO)-Fe(CO)$_4$	1.821	1.912	5.0	1.932	6.1
(CO)-Ni(CO)$_3$	1.837	1.876	2.0	1.899	3.3
(CO)-V(CO)$_5$	2.015	1.928	4.3	1.942	3.6
(CO)-W(CO)$_5$	2.059	2.035	1.2	2.056	0.1

The comparison provided in Table 6 shows that there is good agreement in the majority of cases of the calculated values in agreement to 97% or better with the observed ones with the Schomaker and Stevenson equation performing marginally better for a few molecules and worse for some others.

Bonding involving flourine

There is some ionic character in most fluorine bonds , since fluorine is the most electronegative, and there is significant ionic character in the bonds between fluorine and Group1 and Group 2 metals (differences in electronegativities being greater than 2).

Table 7. Fluorine bonds with 3s, 3p and 3d elements.

Molecule (1)	Internuclear distances(Å) Observed (2)	Soft sphere (3)	Abs % difference (4)	Schomaker & Stevenson (5)	Abs % difference (6)
Na-F	1.926	1.854	3.7	2.037	5.8
F-MgF	1.771	1.721	2.8	1.932	9.1
F-ScF_2	1.847	1.861	0.8	1.852	0.3
F-TiF_3	1.756	1.765	0.5	1.757	0.1
F-VF_2	1.751	1.733	1.0	1.728	1.3
F-VF_4	1.709	1.733	1.4	1.728	1.1
F-CrF_2	1.732	1.725	0.4	1.721	0.6
F-CrF_3	1.706	1.725	1.1	1.721	0.9
F-MnF	1.811	1.785	1.4	1.787	1.3
F-FeF	1.769	1.714	3.1	1.718	2.9
F-FeF_2	1.763	1.714	2.8	1.718	2.5
F-CoF	1.754	1.707	2.7	1.715	2.2
F-CoF_2	1.732	1.707	1.5	1.715	1.0
F-NiF	1.729	1.672	3.3	1.685	2.6
Cu-F	1.745	1.705	2.3	1.648	5.5
F-CuF	1.713	1.705	0.4	1.648	3.7
F-ZnF	1.742	1.769	1.6	1.721	1.2
F-AlF_2	1.633	1.665	2.0	1.637	0.2

F-SiF_3	1.553	1.603	3.2	1.596	2.8
F-PF_2	1.570	1.647	4.9	1.592	1.3
F-SF	1.592	1.655	4.0	1.627	2.2

There is in general good agreement between calculated (of both equations) and observed values of the fluorides given above. All the calculated results agree with the observed to at least 95%. However, agreement for 3 of the bond lengths calculated by the Schomaker and Stevenson equation was less than 95%. These results also indicates that the covalent radius of an element, which possesses more than one valency, may not necessarily change by very much when the valency changes such as in the cases of (a) CoF_2 and CoF_3 and (b) FeF_2 and FeF_3.

Bonds with chlorine, bromine and iodine

Some molecules containing bonds with chlorine, bromine and iodine are shown in Table 8, examples shown below include 1 group in the *s* block, 2 groups *d* block and 1 group in the *p* block elements where there are sufficient data.

Table 8. Examples of bonding with chlorine, bromine and iodine.

Molecule	Internuclear distances(Å)		Abs % difference	Schomaker & Stevenson	Abs % difference
	Observed	Soft sphere			
(1)	(2)	(3)	(4)	(5)	(6)
Li-Cl	2.021	2.059	1.9	2.115	4.7
Li-Br	2.170	2.211	1.9	2.290	5.5
Li-I	2.392	2.410	0.8	2.517	5.2
Na-Cl	2.361	2.368	0.3	2.430	2.9
Na-Br	2.502	2.518	0.6	2.605	4.1
Na-I	2.712	2.715	0.1	2.832	4.5
K-Cl	2.667	2.691	0.9	2.751	3.1
K-Br	2.821	2.839	0.7	2.926	3.7
K-I	3.048	3.035	0.3	3.153	3.5
Rb-Cl	2.787	2.812	0.9	2.872	3.1
Rb-Br	2.945	2.960	0.5	3.047	3.5

Rb-I	3.177	3.154	0.7	3.274	3.1
Cs-Cl	2.906	2.930	0.8	2.988	2.8
Cs-Br	3.072	3.077	0.2	3.164	3.0
Cs-I	3.315	3.271	1.3	3.391	2.3
Cl-Ti Cl$_3$	2.170	2.171	0.0	2.150	0.9
Br-Ti Br$_3$	2.339	2.330	0.4	2.326	0.6
I-TiI$_3$	2.546	2.541	0.2	2.553	0.3
Cl-Zr Cl$_3$	2.328	2.307	0.9	2.286	1.8
Br-Zr Br$_3$	2.465	2.466	0.1	2.462	0.1
I-ZrI$_3$	2.660	2.677	0.6	2.689	1.1
Cl-Hf Cl$_3$	2.316	2.304	0.5	2.284	1.4
Br-Hf Br$_3$	2.450	2.464	0.6	2.459	0.4
I-HfI$_3$	2.662	2.674	0.5	2.686	0.9
Cl-Zn Cl	2.072	2.104	1.5	2.114	2.0
Br-Zn Br	2.304	2.269	1.5	2.289	0.7
I-ZnI	2.401	2.492	3.8	2.516	4.8
Cl-Cd Cl	2.284	2.240	1.9	2.245	1.7
Br-Cd Br	2.394	2.403	0.4	2.421	1.1
I-CdI	2.582	2.623	1.6	2.648	2.5
Cl-Hg Cl	2.252	2.236	0.7	2.255	0.1
Br-Hg Br	2.384	2.405	0.9	2.430	1.9
I-HgI	2.568	2.621	2.1	2.641	2.8
Cl-C Cl$_3$	1.767	1.708	3.3	1.723	2.5
Br-C Br$_3$	1.935	1.875	3.1	1.899	1.9
I-CI$_3$	2.150	2.113	1.7	2.126	1.1
Cl-Si Cl$_3$	2.019	2.004	0.7	1.989	1.5
Br-SiF$_3$	2.156	2.165	0.4	2.164	0.4
I-SiH$_3$	2.437	2.376	2.5	2.391	1.9
Cl-Ge Cl$_3$	2.113	2.113	0.0	2.095	0.9

Br-Ge Br$_3$	2.272	2.273	0.0	2.270	0.1
I-GeI$_3$	2.515	2.483	1.3	2.497	0.7
Cl-Sn Cl	2.335	2.305	1.3	2.280	2.4
Br-Sn Br	2.501	2.464	1.5	2.455	1.8
I-SnI	2.688	2.674	0.5	2.682	0.2
Cl-Pb Cl	2.444	2.439	0.2	2.415	1.2
Br-Pb Br	2.598	2.598	0.0	2.590	0.3
I-PbI	2.807	2.808	0.0	2.817	0.4

As shown in the above table, the calculated values from both equation in general agree with the observed ones. But whereas the results calculated by equation [4] all agree to 95% of better, 2 of the values calculated by the Schomaker and Stevenson equation have agreement of less than 95% and a few agree to less than 96%.

Double bonds - some examples

The covalent radii of oxygen, sulphur, selenium and tellurium are known as well as the internuclear separation of a number of oxides, sulphides, selenides and tellurides. Table 9 shows the double bond covalent radii of the above 4 elements and 6 others which we have arbitrarily assigned radii to test calculations of double bonds.

Table 9. Covalent bond radii of some double bonds (observed radii marked*)

O*	0.604	S*	0.945	Se*	1.083	Te*	1.279	Be	0.890
Ca	1.440	Sr	1.550	Ba	1.610	Sn	1.338	Pt	1.190

Table 10 shows the calculated and observed internuclear separations of 17 molecules (mostly oxides and sulphides) with double bonds..

Table 10. Examples of double bonding

Molecule	Internuclear distances(Å) Observed	Soft sphere	Abs % difference	Schomaker & Stevenson	Abs % difference
(1)	(2)	(3)	(4)	(5)	(6)
O=SO	1.431	1.454	1.6	1.459	2.0
Be=O	1.331	1.321	0.8	1.369	2.9

Be=S	1.742	1.776	2.0	1.800	3.4
Ca=O	1.822	1.828	0.3	1.846	1.3
Ca=S	2.318	2.281	1.6	2.276	1.8
Sr=O	1.920	1.932	0.6	1.946	1.4
Sr=S	2.441	2.386	2.2	2.377	2.6
Ba=O	1.940	1.987	2.4	1.995	2.8
Ba=S	2.507	2.441	2.6	2.425	3.3
Se=O	1.639	1.582	3.5	1.578	3.8
Te=O	1.825	1.766	3.3	1.745	4.4
Sn=O	1.833	1.804	1.5	1.752	4.4
Sn=S	2.209	2.183	1.2	2.182	1.2
Sn=Se	2.326	2.331	0.2	2.340	0.6
Sn=Te	2.523	2.545	0.9	2.565	1.7
Pt=O	1.727	1.679	2.8	1.661	3.8
Pt=S	2.040	2.069	1.4	2.092	2.5

As shown above, agreement between observed and calculated, although not as positive as with single bond calculations, still show good agreement. Only 2 of the values calculated by equation [4] agree to less than 97% with the observed but 6 of those calculated by the Schomaker and Stevenson equation agree to less than 97%. As for the other results, those calculated by equation [4] perform marginally better. We have kept the exponent *r* and constant C unchanged, which in good evidence that the soft sphere model also works for double bonds.

Covalent bonding in the solid state

Table 11 shows the covalent radii of elements in the solid state taken from the CRC Handbook of Chemistry and Physics. In cases where there more than 1 value of the radius is given, we have quoted below (and used) the the figure we think is most appropriate. Covalent radii that are estimated are marked with an *.

Table 11. Covalent radii of elements in the solid state

Element (1)	Radii (Ǻ) (2)	Element Abs (3)	Radii (Ǻ) (4)

(sp^3) C	0.765	(sp^2) C	0.73
H	0.380*	(sp^2) C	0.658 (double bond)
F	0.690	Cl	1.114
Br	1.271	I	1.459
N	0.713	N	0.690 (double bond)
P	1.107	P	1.017 (double bond)
Se	1.170	Te	1.376
S	1.016	S	0.950* (double bond)
O	0.732	O	0.600* (double bond)
Sb	1.390*	Cr	1.420*

Examples of calculations of bond lengths involving single and double covalent bonds are shown below. In Table 12, the observed internuclear separations of SbX_3 and CrX_2 where X equals the halogens are quoted from Structural Inorganic Chemistry, all other observed values, which are quoted from the CRC Handbook, are bond lengths between 2 atoms which form parts of larger organic molecules.

Table 12. Examples of single and double bonds in the solid state.

Molecule (1)	Internuclear distances(Å) Observed (2)	Soft sphere (3)	Abs % difference (4)	Schomaker & Stevenson (5)	Abs % difference (6)
F-SbF_2	1.920	1.929	0.5	1.853	3.5
Cl-SbCl_2	2.360	2.393	1.4	2.381	0.9
Br-SbBr_2	2.500	2.564	2.6	2.567	2.7
I-SbI_2	2.870	2.772	3.4	2.789	2.8
F-CrF	2.000	1.957	2.2	1.875	6.5
Cl-Cr Cl	2.390	2.420	1.2	2.404	0.6
Br-Cr Br	2.540	2.590	2.0	2.590	2.0
I-CrI	2.740	2.797	2.1	2.812	2.6

sp^3 C-Br	1.910	1.975	3.4	1.999	4.7
sp^2 C-Br	1.883	1.940	3.0	1.964	4.3
sp^3 C-Cl	1.790	1.798	0.4	1.813	1.3
sp^2 C-Cl	1.734	1.763	1.6	1.778	2.5
sp^3 C-F	1.349	1.324	1.8	1.285	4.8
sp^2 C-F	1.340	1.289	3.8	1.250	4.8
sp^3 C-H	1.059	1.091	3.0	1.115	5.3
sp^2 C-H	1.077	1.056	2.0	1.080	0.3
sp^3 C-I	2.162	2.209	2.2	2.221	2.7
sp^3 C-N	1.468	1.405	4.3	1.425	2.9
sp^2 C-N	1.336	1.370	2.6	1.390	4.0
sp^2 C=N	1.279	1.276	0.3	1.296	1.3
sp^3 C-O	1.416	1.392	1.7	1.388	2.0
sp^2 C-O	1.354	1.357	0.3	1.353	0.1
sp^2 C=O	1.192	1.153	3.2	1.149	3.6
sp^3 C-P	1.813	1.823	0.5	1.848	1.9
sp^3 C-S	1.779	1.736	2.4	1.761	1.0
sp^2 C-S	1.751	1.701	2.8	1.726	1.4
sp^2 C=S	1.599	1.564	2.2	1.588	0.7
sp^3 C-Se	1.967	1.935	1.6	1.935	1.6
sp^2 C-Se	1.893	1.900	0.4	1.900	0.4
sp^3 C-Te	2.116	2.087	1.4	2.112	0.2
sp^2 C-Te	2.044	2.052	0.4	2.077	1.6
N-O	1.397	1.369	2.0	1.388	0.7
N=O	1.210	1.215	0.4	1.233	1.9
N-P	1.730	1.732	0.1	1.743	0.8
N=P	1.571	1.620	3.1	1.630	3.8
N-S	1.710	1.671	2.3	1.695	0.9
N=S	1.546	1.583	2.4	1.607	4.0
O-P	1.689	1.724	2.0	1.706	1.0

O=P	1.513	1.502	0.8	1.484	1.9

We have used the same expression to calculate a limited number internuclear separations in the solid state. The exponent *r* and the constant C are kept the same as in calculating bond lengths in the gaseous state. As shown in the above table the majority of the calculated results, by both equations, agree well with the observed, 2 values calculated by the Schomaker and Stevenson equation agree to less than 95%.

Discussion

It was obvious from the start that covalent radii are not additive except for homonuclear bonds and for some bonds between atoms in the same group and possess very similar electronegativities such as BrCl and BrI. In this work, we started by using the Schomaker and Stevenson equation and a set of electronegativity values proposed by Allred and Rochow[18]. We have used the electronegativity scales of Mulliken and Pauling as well and we have also analysed radii of the elements[19] and electron affinities[20] in detail as a way forward. We have used the Schomaker and Stevenson equation and the soft sphere equation (equation [4]) to calculate bond lengths which included bonds with and without carbon and between hydrogen or the halogens with both the main block and transition elements. We did not attempt to make comparisons between calculated and observed bond lengths of lanthanides because of insufficient experimental values. Although the Schomaker and Stevenson equation produced fairly reliable results in general, only 30% of those results show agreement of over 99% with the observed, but just over 40% of results produced by equation [4] show agreement with the observed of better than 99%. All the values produced by equation [4] show agreement to 95% or better with the observed, whereas with the Schomaker and Stevenson equation 10% of the results have agreement of less than 95% with the observed and 4% of those values show discrepancy of over 10% when compared with the observed. Initially, we did not intend to devise our own set of electronegativities but we found a new set may be needed. This set of electronegativity scales as shown in Table 3 improved the agreement between the calculated and the observed (where agreement with observed values are to 95% or better in all cases). We have used simple fractions as the exponents *k* and *r* (without theoretical justification) because there seems to be no necessity to use more complex exponents/coefficients .

We agree with Pauling that bonds of the alkali metals, and to a certain extent alkali earth metals, with all non-metals are more ionic than covalent. But, we also reckon that bonds of fluorine and oxygen with other elements probably also possess ionic character because these 2 elements are the most electronegative. We believe, as Pauling suggested, the electronegativity of an atom is a major factor[21] in influencing the character of a bond.

We also regard that ionic character of a bond is subject to other factors, such as size/steric constraints, but to a lesser extent in the gaseous state and much more so in the solid state. Hence, we have, in a very simplistic way, only taken into account of the size of atoms in Groups 1 and 2 elements in our equation without having to make the calculation over complicated.

It is evident from this work that the covalent radius of an atom is in many instances different between the gaseous and solid states. It is interesting to note that although equation [4] is developed to calculate covalent bond lengths in the gaseous state it may also be applied to calculate bond lengths in the solid state.

Conclusion

The above calculations show that covalent radii are definitely not additive for the majority of heteronuclear bonds and covalent radii of atoms in the gaseous state are different from that of the solid state in the majority of molecules. We have also shown that although Schomaker and Stevenson as well as Pauling correctly pointed out that electronegativity is a major factor on the variation of bond length may be other contributing factors such as atomic size or bond angle.

The Schomaker and Stevenson equation produced very good agreement with some observed values but other results calculated by their equation have discrepancy of over 10% when compared to the observed which makes the reliability of the equation in doubt in some cases. Internuclear distances calculated by equation [4] show agreement with observed values to 95% or better in all cases (and over 98% or better in over 80% of cases vs just half of those calculated by the Schomaker and Stevenson equation). This work also provides evidence that it is useful to take account of the electronegativities of functional groups when calculating bond lengths. The good agreement between calculated and observed bond lengths for molecules in both the gaseous and crystalline states and for single and double bonds is reliable evidence that the soft sphere equation is applicable for modelling both ionic and covalent radii/internuclear distances.

We accept that the coefficients used in our equation are deduced in a semi-empirical way without much theoretical justification. However, values from the set of electronegativities and covalent radii derived in this work produced internuclear distances (when substituted into the equation) that show very good agreement with observed values in the gaseous state. This is evidence that the electronegativities and covalent radii derived in this work are reliable.

Appendix 1

We regard a comparison between the set of covalent radii derived from this work with another set of radii fitted by a purely statistical exercise an interesting and instructive exercise since it can provide evidence of the reliability of our method. Calculations with early historical covalent radii may provide less good agreement with observed values so we use a recent set of covalent radii[10] for the comparison. Another important reason we selected this set of radii because the literature cited for many of the molecules (mainly homonuclear species and hydrides) used in their statistical fit refer to molecules in the gaseous state and we take this to mean that the set is relevant to radii in the gaseous state.

We have selected Group 1 fluroides, chlorides and hydroxides we have included fluorides and chlorides in the first transition series for this comparison. Table 13 lists the covalent radii published in reference 10 needed for the comparison.

Table 13. Single bond covalent radii proposed in reference 10 and used in the following calculations (Ǻ).

Li	1.330	Na	1.550	K	1.960	Rb	2.100	Cs	2.320
F	0.640	Cl	0.990	O	0.630	Mn	1.190	Fe	1.160
Cu	1.120	Co	1.110	Ni	1.100				

In the following, the internuclear separations/covalent bond lengths are calculated using 3 different methods. The first [a], as proposed by the authors in reference 10 is :

$$D[AB] = [A] + [B] \quad \text{..........}[8]$$

where D[AB] is the internuclear distance, [A] and [B] are the covalent radii of atoms A and B respectively.

The second method [b] is the Schomaker and Stevenson equation which is:

$$D[AB] = [A] + [B] - C[\text{abs}(x_a - x_b)] \quad \text{..........}[9]$$

where x_a and x_b are the electronegativities of A and B.

The electronegativities used with this equation is the set proposed by Allred and Rochow. The third method [c] is equation [4] proposed in this work. The results are shown in Table 14.

Table 14. Covalent bond lengths – alternative results.

Bond	Observed bond length in Ǻ	method [a]	abs. % difference	method [b]	abs. % difference	method [c]	abs. % difference
Li-F	1.564	1.970	26.0	1.657	6.0	1.804	15.4
Li-Cl	2.021	2.320	14.8	2.134	5.6	2.190	8.4
Na-F	1.926	2.190	13.7	1.881	2.3	2.024	5.1

Na-Cl	2.361	2.540	7.6	2.358	0.1	2.409	2.1
K-F	2.172	2.600	19.7	2.281	5.0	2.427	11.8
K-Cl	2.667	2.950	10.6	2.758	3.4	2.810	5.4
Rb-F	2.270	2.740	20.7	2.419	6.6	2.566	13.0
Rb-Cl	2.787	3.090	10.9	2.896	3.9	2.949	5.8
Cs-F	2.345	2.960	26.2	2.636	12.4	2.784	18.7
Cs-Cl	2.906	3.310	13.9	3.113	7.1	3.167	9.0
Li-OH	1.578	1.960	24.2	1.657	5.0	1.794	13.7
K-OH	2.212	2.590	17.1	2.281	3.1	2.417	9.3
Rb-OH	2.301	2.730	18.6	2.419	5.1	2.556	11.1
Cs-OH	2.395	2.950	23.2	2.636	10.1	2.774	15.8
F-MnF	1.811	1.830	1.1	1.580	12.8	1.679	7.3
F-FeF	1.769	1.800	1.8	1.554	12.2	1.651	6.7
F-CoF	1.754	1.750	0.2	1.51	13.9	1.603	8.6
F-NiF	1.729	1.740	0.6	1.505	13.0	1.596	7.7
Cu-F	1.745	1.760	0.9	1.525	12.4	1.619	7.2
Cl-Mn Cl	2.202	2.180	1.0	2.057	6.6	2.068	6.1
Cl-Fe Cl	2.132	2.150	0.8	2.031	4.7	2.041	4.3
Cl-Co Cl	2.113	2.100	0.6	1.987	6.0	1.994	5.6
Cl-Ni Cl	2.076	2.090	0.7	1.982	4.5	1.988	4.2
Cu-Cl	2.051	2.110	2.9	2.002	2.4	2.014	1.8

The above table shows that in most cases using the Schomaker and Stevenson equation or equation [4] proposed in this work improve agreement with observed values, although in a few cases the agreement got much worse. However, it is quite evident that using this particular set of covalent radii to calculate covalent bond lengths give agreement that is very poor in comparison to the values calculated in this work with the proposed covalent radii as shown in Table 3. This comparison is evidence that both the equation proposed and the covalent radii devised in reference 10 are not suitable for calculating covalent bond lengths of heteronuclear molecules.

References

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