A revised set of values of single-bond radii derived from the observed interatomic distances in metals by correction for bond number and resonance energy

(statistical theory of resonance of covalent bonds)

LINUS PAULING* AND BARCLAY KAMB[†]

*Linus Pauling Institute of Science and Medicine, 440 Page Mill Road, Palo Alto, CA 94306; and †Department of Geological and Planetary Sciences, California Institute of Technology, 1201 East California Street, Pasadena, CA 91125

ABSTRACT   An earlier discussion [Pauling, L. (1947) J. Am. Chem. Soc. 69, 542] of observed bond lengths in elemental metals with correction for bond number and resonance energy led to a set of single-bond metallic radii with values usually somewhat less than the corresponding values obtained from molecules and complex ions. A theory of resonating covalent bonds has now been developed that permits calculation of the number of resonance structures per atom and of the effective resonance energy per bond. With this refined method of correcting the observed bond lengths for the effect of resonance energy, a new set of single-bond covalent radii, in better agreement with values from molecules and complex ions, has been constructed.

In 1947 a set of single-bond covalent radii of atoms derived from the observed interatomic distances in metals by correction for the fractional bond numbers and for the effect of resonance energy was published (1). Some small changes were made (2) in 1960. We have now found that the original method of correcting for resonance energy should be replaced by a more reliable method, which leads to the revised set of single-bond covalent radii given in Table 1, together with the corresponding values for ligancy 12.

The Original Set of Metallic Radii. The bond number n for a metal with valence v and ligancy L is equal to v/L. Eq. 1 represents satisfactorily the bond lengths, in Å, for single, double, and triple bonds in H_3C—CH_3, H_2C=CH_2, and HC≡CH, with $A = 0.700$ Å and $n = 1, 2$, and 3:

$$D(n) = D(1) - A \log n. \tag{1}$$

A similar equation might be expected to be valid, with n less than 1, for fractional bonds.

The effect of resonance energy in reducing the bond lengths was reported (3) in 1935: for graphite, with $n = 1.33$, and benzene, with $n = 1.5$, the bond lengths are 0.035 and 0.023 Å, respectively, shorter than the values given by Eq. 1. In 1947 it was assumed (1) that the resonance-energy correction for values of n less than 1 could be made by changing the coefficient A in Eq. 1 from 0.70 Å to 0.60 Å. Our recent analysis of the problem has shown that this assumption is invalid.

The Theory of Resonating Covalent Bonds in Metals. In the first long period of the periodic table, the physical properties of the metals from K to Cr correspond to a steady increase in the total strength of the bonds in proportion to the number of outer electrons, increasing from one to six, which suggests that these electrons are all involved in the formation of covalent bonds. From Cr to Ni the physical properties,

including the values of the saturation ferromagnetic moment (4), show that the covalence remains at the value 6 for these elements. The ligancy L is greater than the covalence, and hence the covalent bonds resonate among the available positions; nickel, for example, has $v = 6$, $L = 12$ (cubic closest packing, the A1 structure), and bond number $n = 1/2$.

A theory of the resonance of the covalent bonds, mentioned briefly (5) in 1949, has now been developed in detail (6, 7). The theory is developed separately for hypoelectronic metals (6) and hyperelectronic metals (7). Equations are given in these papers for the number of resonance structures, v_{hypo}, equation 4 of ref. 6, and v_{hyper}, equation 8 of ref. 7. It is also shown in ref. 7 that the metallic valence for hyperelectronic metals is close to the half-integral values 5.5 for Cu and its congeners, 4.5 for Zn, 3.5 for Ga, and 2.5 for Ge.

These equations apply to crystals in which the bonds all have the same length. In the A2 body-centered structure, each atom forms eight stronger bonds and six weaker ones, which are 15% longer. For a crystal in which each atom forms two kinds of bonds, L_1 bonds with bond number $n_1 = v_1/L_1$ and L_2 bonds with bond number $n_2 = v_2/L_2$, the number of resonating structures per atom is found by an extension of the statistical theory to be given by a somewhat more complicated expression, equation 9 of ref. 7. We have used this equation to evaluate v for some special cases.

In Table 2 and Table 3 we give values of v for some important structures and also the values of L', the effective ligancy for equivalent bonds corresponding, with the value of v, to the calculated value of v.

Correction of Bond Lengths for Resonance Energy and Bond Numbers. In the region near equilibrium the resonance energy increases in magnitude with decrease in the interatomic distance, so that the bond length becomes smaller. We assume that this shortening is the same for all the bonds formed by the atom and that it can be expressed as a reasonably good approximation by Eq. 1 with the bond number n replaced by the bond order $n [1 + B (v - 1)]$. Here the factor $v - 1$ is used because there is no resonance energy for $v = 1$. Eq. 1 is then revised to read

$$D(n) = D(1) - A \log \{n [1 + B(v - 1)]\} \tag{2}$$

We have selected the values $A = 0.700$ Å and $B = 0.064$ to obtain agreement with known single-bond, tetrahedral, octahedral, and enneacovalent radii, such as the value for Co of 1.230 Å in many organometallic compounds containing Co clusters. Although our treatment is partially empirical and somewhat arbitrary, we believe that it provides a useful set of single-bond radii and an increased understanding of the nature of metals and intermetallic compounds.

In Eq. 2 we make use of a bond number n, the number of shared electron pairs contributing to the bond, and a bond

Table 1.   Metallic single-bond radii and radii for ligancy 12 (in Å)

Element	v	R_1	$R (L = 12)$	Element	v	R_1	$R (L = 12)$
Li	1	1.196	1.547	Sn	4	1.405	1.487
Be	2	0.905	1.126	Cs	1	2.361	2.712
B	3	0.836	0.975	Ba	2	1.996	2.217
C	4	0.772	0.816	La	3	1.726	1.865
Na	1	1.550	1.901	Ce	3	1.713	1.852
Mg	2	1.381	1.602	Ce	4	1.555	1.637
Al	3	1.293	1.432	Pr	3	1.699	1.838
Si	4	1.176	1.258	Nd	3	1.683	1.822
K	1	2.001	2.352	Pm	3	1.670	1.809
Ca	2	1.755	1.976	Sm	3	1.663	1.802
Sc	3	1.515	1.654	Eu	2	1.823	2.044
Ti	4	1.384	1.466	Gd	3	1.660	1.799
V	5	1.310	1.354	Tb	3	1.641	1.780
Cr	6	1.260	1.282	Dy	3	1.632	1.771
Mn	6	1.250	1.272	Ho	3	1.624	1.763
Fe	6	1.250	1.272	Er	3	1.615	1.754
Co	6	1.230	1.252	Tm	3	1.604	1.743
Ni	6	1.224	1.246	Yb	2	1.718	1.939
Cu	5.5	1.245	1.276	Lu	3	1.593	1.732
Zn	4.5	1.307	1.368	Hf	4	1.503	1.585
Ga	3.5	1.258	1.366	Ta	5	1.418	1.462
Ge	4	1.225	1.307	W	6	1.378	1.400
Rb	1	2.167	2.518	Re	6	1.352	1.374
Sr	2	1.931	2.152	Os	6	1.328	1.350
Y	3	1.659	1.798	Ir	6	1.335	1.357
Zr	4	1.515	1.607	Pt	6	1.365	1.387
Nb	5	1.417	1.461	Au	5.5	1.410	1.441
Mo	6	1.371	1.393	Hg	4.5	1.466	1.527
Tc	6	1.338	1.360	Tl	2	1.508	1.729
Ru	6	1.315	1.337	Pb	2	1.513	1.734
Rh	6	1.323	1.345	Ra	2	2.050	2.271
Pd	6	1.353	1.375	Ac	3	1.800	1.939
Ag	5.5	1.412	1.443	Th	4	1.722	1.804
Cd	4.5	1.466	1.527	Pa	5	1.555	1.599
In	3.5	1.442	1.550	U	6	1.402	1.424
Sn	2.5	1.418	1.594				

order $1 + B (v - 1)$ (for a single bond, with bond number 1), which involves the correction for the resonance energy. The bond order, based on the consideration of the resonance energy, was introduced by Coulson (8).

Evaluation of the Single-Bond Metallic Radii. Most of the metals for which radii are given in Table 1 have closest packed structures, with $L = 12$, for which Eq. 2 can be easily applied (for $L = 12$, the values of v for $v = 1$ to 6 are 8.38, 10.39, 12.65, 14.11, 14.18, and 12.73). For the A2 structures and others with two or more different bond lengths, the values of n_i can be obtained from v and the correction 0.77 log n_i, by assuming that the bond-order correction is the same for all of the bonds. The value of v can then be determined from Tables 2 and 3 or the corresponding equations. All of the values in Table 1 are based on the observed bond lengths reported by Donohue (9).

Protactinium is the only element for which the atoms have ligancy 10. The body-centered tetragonal unit has $a = 3.925$, $c = 3.238$ Å, $c/a = 0.825$, each atom having eight neighbors at 3.213 Å and two at 3.238 Å, average 3.218 Å, which leads with Eq. 2 ($v = 5$, $v = 8.00$) to $R_1 = 1.555$ Å. The bonds are half-bonds.

Each atom in the stable form of Ga has seven neighbors, twice its valence, one at 2.465 Å ($n = 0.963$) and two each at 2.700, 2.735, and 2.792 Å ($n = 0.477, 0.430,$ and 0.362). As an approximation for v we use v_{hypo} for $L = 7$ and $v = 3.5$, which is 4.24, and obtain the value 1.258 Å for R_1.

As discussed in refs. 6 and 7, the outer s orbital for Sn is occupied by an unshared pair of electrons for Sn^0 and Sn^- but

is used for bonding for Sn^+. The $s - p$ energy difference in Pb is greater, requiring Pb^+ to form only one bond, retaining the unshared pair. Evidence that Pb metal has valence 2 is provided by the observed bond length, 3.469 Å, which is greater than expected for $v = 2.5$. For Tl, which is both univalent and trivalent in its compounds, we have assumed metallic valence 2, giving $R_1 = 1.508$ Å.

The value $R_1 = 1.378$ Å for W in Table 1 is from the observed bond lengths in α-W, with the A2 structure. In the β-W modification each W_I has 12 W_{II} neighbors at 2.822 Å, with each W_{II} having 14 neighbors with four different bond lengths. The value 2.822 Å with $L = 12$ and $v = 6$ leads to $R_1 = 1.389$ Å.

For several elements with complex structures or uncertain metallic valence (Mn, In, Ce), interpolated or otherwise estimated values are given in Table 1.

DISCUSSION

As one example of use of the values of R_1, we discuss the structure of four allotropic forms of cerium, all with the cubic closest packed arrangement. It has long been known (1) that for some of the forms the valence is neither 3 nor 4, but has intermediate values. A high-pressure form, stable from 44 to 80 kbar, has very low compressibility, indicating that v is constant. The bond length at 1 atmosphere (1.013×10^5 Pa), by extrapolation, 3.274 Å, leads to $R_1(v = 4) = 1.555$ Å. The value of $R_1(v = 3)$ is obtained as 1.713 Å by interpolation between neighboring elements. It corresponds to bond length

Chemistry: Pauling and Kamb

Proc. Natl. Acad. Sci. USA 83 (1986) 3571

Table 2. Values of ν, the number of resonating structures per atom, and of L', the equivalent ligancy with equation 4 of ref. 6, for hypoelectronic metals with the A2 structure, $L_1 = 8$, and $L_2 = 6$

Valence	ν_1	ν	L'
$\nu = 6$	6	2.151	8
	5.9	2.955	8.520
	5.5	6.260	10.063
	5.0	11.320	11.644
	4.5	16.626	12.870
	4.0	20.837	13.672
	3.75	22.122	13.896
	3.4286	22.737	14
$\nu = 5$	5	3.704	8
	4.75	7.116	9.649
	4.5	9.386	10.510
	4.25	12.295	11.455
	4.0	15.142	12.263
	3.75	17.743	12.928
	3.5	19.910	13.440
	3.25	21.475	13.790
	3.0	22.317	13.972
	2.8571	22.447	14
$\nu = 4$	4	5.188	8
	3.75	8.657	9.779
	3.5	11.708	11.084
	3.25	14.508	12.146
	3.00	16.895	12.976
	2.75	18.698	13.566
	2.5	19.762	13.908
	2.2857	20.080	14
$\nu = 3$	3	6.173	8
	2.75	9.744	10.311
	2.5	12.434	11.881
	2.25	14.492	13.014
	2.0	15.833	13.720
	1.9	16.144	13.882
	1.75	16.363	13.996
	1.7143	16.372	14.000
$\nu = 2$	2	6.453	8
	1.9	8.008	9.580
	1.8	9.124	10.715
	1.7	10.045	11.653
	1.6	10.804	12.425
	1.5	11.410	13.042
	1.4	11.866	13.506
	1.3	12.171	13.816
	1.2	12.327	13.976
	1.1429	12.351	14
$\nu = 1$	1	6.419	8
	0.9	7.795	10.728
	0.85	8.225	11.664
	0.8	8.566	12.434
	0.75	8.830	13.048
	0.7	9.023	13.508
	0.65	9.152	13.818
	0.6	9.217	13.976
	0.5714	9.227	14

Table 3. Values of ν, the number of resonating structures per atom, and of L', the equivalent ligancy, for some hyperelectronic metals

$L_1 = 4, L_2 = 2, \nu = 2.5$			$L_1 = L_2 = 6, \nu = 4.5$		
ν_1	ν	L'	ν_1	ν	L'
2.5	2.156	4	4.5	1.772	6
2.4	2.761	4.588	4.4	2.457	6.572
2.3	3.183	4.984	4.25	3.410	7.251
2.2	3.523	5.296	4.0	5.095	8.258
2.1	3.796	5.543	3.75	6.903	9.164
2.0	4.008	5.733	3.5	8.755	9.973
1.9	4.163	5.871	3.25	10.536	10.670
1.8	4.262	5.958	3.0	12.114	11.237
1.75	4.291	5.984	2.75	13.355	11.656
1.71	4.305	5.996	2.5	14.150	11.913

A collapsed form with the A1 structure is obtained at normal pressure by cooling to 90 K or at room temperature by compressing to 20 kbar (2 GPa). Its bond length at standard conditions is 3.408 Å, which corresponds to valence 3.68. Both this form and the room-temperature stable form have unusually high compressibility, indicating an increase in valence with increased compression. The normal form and the compressed form merge at a critical point, about 600 K and 20 kbar, where their values of ν and R_1 become equal.

A body-centered form becomes stable above 1000 K. With the assumption that its thermal expansion is the same as for the normal form, each atom forms eight bonds with length 3.534 Å and six bonds with length 4.081 Å. These values correspond to valence 3.30.

There are accordingly forms of Ce in which ν has values 3.12, 3.30, 3.68, and 4, corresponding to the increasing fraction of an electron transferred from a $4f$ atomic orbital to a bond orbital. This transfer does not occur for Pr and the following elements because of the stabilization of $4f^2$, $4f^3$ ... by the exchange integrals that stabilize the state with maximum spin. The transfer may be expected to occur first with

Ce^+, from $-Ce^+$ to $-Ce^+$, then for Ce^0, and then for Ce^-.

The proportions of Ce^+, Ce^0, and Ce^- are 31%, 38%, and 31%, respectively (7), and the corresponding values of the valence for successive complete transfer are 3, 3.31, 3.69, and 4. The value 3.12 for the normal form indicates a partial transfer for Ce^+, the value 3.30 for the high-temperature A2 form indicates complete transfer for Ce^+, the value 3.68 for the collapsed form indicates complete transfer also for Ce^0, and the value 4 for the supercollapsed form is that for complete transfer. The resonating-valence-bond theory thus provides a reasonable explanation of the existence of these several forms of Ce.

1. Pauling, L. (1947) *J. Am. Chem. Soc.* **69**, 542–553.
2. Pauling, L. (1960) *The Nature of the Chemical Bond* (Cornell Univ. Press, Ithaca, NY), 3rd Ed., pp. 394–404.
3. Pauling, L., Brockway, L. O. & Beach, J. Y. (1935) *J. Am. Chem. Soc.* **57**, 2705–2709.
4. Pauling, L. (1938) *Phys. Rev.* **54**, 899–904.
5. Pauling, L. (1949) *Proc. R. Soc. London Ser. A* **196**, 343–363.
6. Pauling, L. (1984) *J. Solid State Chem.* **54**, 297–307.
7. Kamb, B. & Pauling, L. (1985) *Proc. Natl. Acad. Sci. USA* **82**, 8284–8285.
8. Coulson, C. A. (1939) *Proc. R. Soc. London Ser. A* **165**, 413–423.
9. Donohue, J. (1974) *The Structure of the Elements* (Wiley, New York).

3.876 Å, which is larger than has been reported for any modification. We may use the observed bond lengths of other modifications to determine the corresponding values of ν.

The form stable at room temperature and 1 atmosphere pressure has bond length 3.649 Å. Nearly the same values, 3.662 and 3.677 Å, are observed for a double-hexagonal form that is also stable at room temperature. These bond lengths, with use of Eq. 2, correspond to valence 3.12 ± 0.01.