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A Re-Evaluation of the Covalent Radii of Some of the Elements

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The Schomaker-Stevenson correction for ionic character, $-\beta|x_A - x_B|$, of the covalent radii additivity rule, $d_{AB} = r_A + r_B$, is extended to double bonds. The value of the parameter β found for these is 0.06. Several revisions in the table of covalent radii are proposed. The double-bond covalent radii of oxygen and nitrogen are chosen as 0.604Å and 0.62Å, respectively, or one-half the bond lengths of O₂ and of the $\text{N}=\text{N}$ length in azomethane. The single- and double-bond covalent radii of carbon are revised upward to 0.79Å and 0.675Å to make them in accord with the lengths predicted by Mulliken, Rieke, and Brown for ideal single and double CC bonds. The newly assigned values are shown to be consistent with double bonds formed between unlike atoms when the shortening caused by ionic character is taken into account. Some other covalent radii are determined by extrapolation of curves determined by the known radii and by application of the revised additivity rule.

SCHOMAKER and Stevenson¹ have shown that the values of the single-bond covalent radii for N, O, and F in the Pauling-Huggins table² of covalent radii are significantly shorter than recent accurate measurements of the interatomic distances in H₄N₂, H₂O₂, and F₂ would indicate. They point out that the Pauling-Huggins values for nitrogen (0.70Å) and oxygen (0.66Å) were obtained from a curve drawn through the point for carbon (0.77Å) and the point for fluorine (0.64Å), and that the value used for fluorine was that obtained from the interatomic distance of F₂ in a state which is now known not to be the ground state. They accordingly proposed for the single-bond covalent radii of N, O, and F values of 0.74Å, 0.74Å, and 0.72Å, respectively, or one-half the interatomic

distances in hydrazine, hydrogen peroxide, and fluorine.¹

In the same contribution Schomaker and Stevenson demonstrated the effects of ionic character on the interatomic distances between atoms of unlike electronegativity; they showed that the equation,

$$d_{AB} = r_A + r_B - \beta|x_A - x_B|, \quad (1)$$

with $\beta = 0.09$, can be used to predict approximately the length of single bonds, d_{AB} , between atoms of widely different electronegativities. Here r_A and r_B are the normal single-bond covalent radii, and x_A and x_B are the electronegativities of the atoms *A* and *B*. Thus, when x_A equals x_B and the bond has no ionic character, the equation reduces to the additivity rule. For bonds between atoms differing greatly in electronegativity the bond lengths are significantly shorter than the added sum of the covalent radii.

¹ V. Schomaker and D. P. Stevenson, J. Am. Chem. Soc. **63**, 37 (1941).

² L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1940), p. 164.

TABLE I. Calculated and observed interatomic distances of some double bonds.

Link	Interatomic distance		Sum of radii ^b (Pauling)
	Observed	Calculated ^a	
Be=O	1.331 ^c	1.34	
\diagup C=C \diagdown	1.35 ^d 1.330 ^e	(1.35)	(1.330)
\diagup C=O	1.21 ^f 1.22 ^g 1.24 ^h	1.225	(1.215)
\diagup C=N \diagdown	1.26 ⁱ	1.27	1.265
\diagup C=S		1.61	1.605
\diagdown N=N \diagup	1.24 ^j	(1.24)	1.20
\diagdown N=O	1.22 ^k	1.20	1.15
O=O	1.208 ^c	(1.208)	1.10
S=O	1.494 ^c	1.49	1.49
S=S	1.89 ^c	(1.88)	(1.88)
Se=O		1.62	1.63
Se=Se	2.16 ^c	(2.16)	(2.16)

^a $d_{AB} = r_A + r_B - 0.06 |x_A - x_B|$, with r_A and r_B the revised double-bond covalent radii of Table II.

^b $d' = r_A' + r_B'$, with r_A' and r_B' the Pauling double-bond covalent radii values. Reference 2.

^c Reference 4.

^d For ideal or pure C=C double bond, see reference 10.

^e For CC bond in ethylene which has 12 percent triple-bond character, E. H. Eyster, *J. Chem. Phys.* **6**, 580 (1939).

^f For \diagup C=O bond in formaldehyde, D. P. Stevenson, J. E. LuValle, and V. Schomaker, *J. Am. Chem. Soc.* **61**, 2508 (1939).

^g For \diagup C=O bond in acetaldehyde, D. P. Stevenson, H. D. Burnham, and V. Schomaker, *J. Am. Chem. Soc.* **61**, 2922 (1939).

^h For \diagup C=O bond in thio-acetic acid, W. Gordy, *J. Chem. Phys.* **14**, 560 (1946); also for C=O of the formic acid monomer, J. Karle and L. O. Brockway, *J. Am. Chem. Soc.* **66**, 574 (1944).

ⁱ This value for the C=N double bond length has been indirectly deduced from x-ray diffraction data on dicyandiamide by E. W. Hughes, *J. Am. Chem. Soc.* **62**, 1258 (1940).

^j See reference 9.

^k For \diagdown N=O of methyl nitrite, G. W. Wheland, *The Theory of Resonance* (John Wiley and Sons, Inc., New York, 1944), p. 287. This bond is probably slightly longer than a pure N=O bond would be because of possible resonance of the normal structure, $\text{CH}_3\text{-O}^+=\text{N-O}^-$.

For example, the sum of the single-bond covalent radii of C and F in methyl fluoride is 1.51A, whereas the Schomaker-Stevenson rule gives 1.38A, close to the measured value,³ 1.396A.

EXTENSION OF THE SCHOMAKER-STEVENSON RULE TO DOUBLE BONDS

Schomaker and Stevenson did not treat cases involving double bonds. However, from the

³ D. M. Dennison, *Rev. Mod. Phys.* **12**, 175 (1940).

marked effects of ionic character on the single-bond lengths one might expect significant, though somewhat less pronounced, shortening of a double bond caused by ionic character. This is especially true of the first period elements where double bonds can be formed between atoms differing greatly in electronegativity.

With some degree of success I have extended the Schomaker-Stevenson rule to double bonds by determining empirically the value of the constant β which best applies to them. The value found for β , 0.06, is slightly more than one-half that, 0.09, which applies to single bonds. The equation

$$d_{AB} = r_A + r_B - 0.06 |x_A - x_B| \quad (2)$$

was found to apply satisfactorily to the few cases for which sufficient data were available for comparison. The results are shown in Table I. The values of r_A and r_B , double-bond covalent radii for the first period elements, are the revised values discussed below and listed in Table II. The double-bond radius used for sulfur is 0.94A, or one-half the bond length⁴ in S_2 ; that used for selenium is 1.08A, one-half the bond length⁴ in Se_2 . The electronegativity values are listed in the third column of Table I. That for sulfur is 2.53, and that for selenium is 2.4. Electronegativity values for these and many other elements are compiled elsewhere.⁵

SOME PROPOSED REVISIONS IN THE TABLE² OF COVALENT RADII

Since the values for the double-bond covalent radii as given by Pauling² were in some instances

TABLE II. Covalent radii and electronegativities of first period elements.^a

	Be	B	C	N	O	F
Single-bond radius		— (0.88)	0.79 (0.771)	0.74 ^b (0.70)	0.73 (0.66)	0.72 ^b (0.64)
Double-bond radius	0.86	— (0.76)	0.675 (0.665)	0.62 (0.60)	0.604 (0.55)	0.60 (0.54)
Triple-bond radius		— (0.68)	— (0.602)	— (0.547)	0.53 (0.50)	
Electronegativity	1.45	1.9	2.55	2.98	3.45	3.95

^a The values given in parentheses are those compiled by Pauling, reference 2. A dash is placed where no change from these values seemed justified.

^b A Schomaker-Stevenson value, reference 1.

⁴ G. Herzberg, *Molecular Spectra and Molecular Structure* (Prentice Hall, Inc., New York, 1939), p. 483.

⁵ W. Gordy, *Phys. Rev.* **69**, 604 (1946); also reference 2, p. 64.

determined by the application of the straight additivity rule to double bonds having considerable ionic character, it was necessary to revise some of his values before the Schomaker-Stevenson rule could be satisfactorily adapted to double bonds. New values for the first period elements, including some by Schomaker and Stevenson, are given in Table II, with the Pauling values for comparison.

Oxygen

For the double-bond covalent radius of oxygen I have chosen 0.604Å, or one-half the accurately measured bond distance⁴ in O_2 . This is not a new proposal as Sidgwick⁶ several years ago assigned 0.60Å as the double-bond radius of oxygen. However, the value more recently determined by

Pauling² from >C=O bonds, 0.55Å, is 9 percent lower. The ground state of O_2 is known to be a $^3\Sigma_g^-$ state.⁴ Pauling⁷ describes its bond as composed of a single electron-pair plus two three-electron bonds. This combination, he points out, is about equivalent in energy to the double-bond state. According to the molecular orbital theory there would be four more bonding than antibonding electrons in O_2 , and its bond may be regarded as a double one. The ground state⁴ of S_2 is also a $^3\Sigma_g^-$; and Pauling² has assigned for the double-bond covalent radius of S a value which is essentially one-half the interatomic distance in this molecule. That the oxygen radius determined from O_2 cannot be added to the double-bond carbon radius to give the >C=O length in acetaldehyde, for example, appears to be caused by the large difference in the electronegativity of C and O rather than by $^3\Sigma_g^-$ ground state* of O_2 .

To obtain the triple-bond radius listed for oxygen, I have merely extended the lower curve of Fig. 1. Since oxygen does not form a pure triple bond, the value obtained has no physical counterpart. Nevertheless, it may be useful in

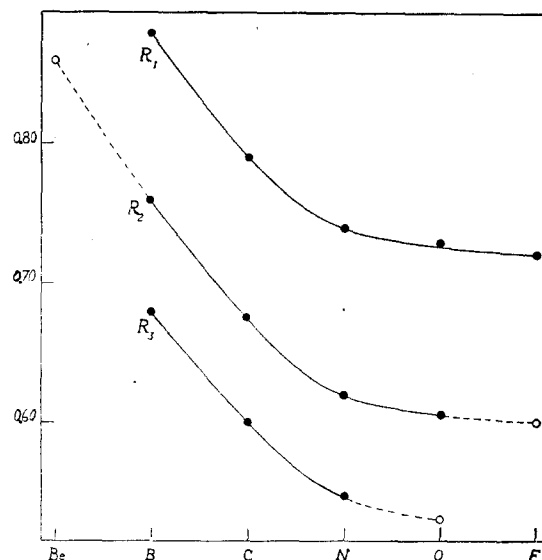
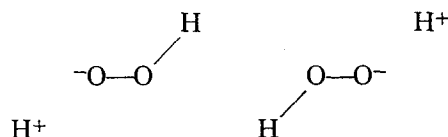


FIG. 1. A plot of covalent radii of first period elements. Top curve, R_1 , for single-bond covalent radii; middle curve, R_2 , for double-bond covalent radii; bottom curve, R_3 , for triple-bond covalent radii.

discussing bonds having some triple-bond character, as, for example, that of carbon monoxide.

Because the value of the single-bond covalent radius given by Schomaker and Stevenson¹ for oxygen, 0.74Å, does not lie on the smooth curve (top curve of Fig. 1) determined by the other first period elements, I have listed the value determined by this curve, 0.73Å, for the oxygen single-bond radius. This value is still within the possible experimental error of one-half the measured O—O distance in H_2O_2 and is exactly one-half that measured by x-ray diffraction of O—O in urea-hydrogen peroxide.⁸ Resonance of the types



may increase slightly the O—O distance in hydrogen peroxide over that expected for an ideal O—O single covalent bond. Similar resonance would occur in hydrazine, but it would be less than that in H_2O_2 because of the lower electronegativity of N as compared to O.

⁶ N. V. Sidgwick, *The Covalent Link in Chemistry* (Cornell University Press, Ithaca, New York, 1933), p. 85.

⁷ L. Pauling, reference 2, p. 273.

* The interatomic distance for the singlet state, $^1\Sigma_u^+$, is 1.223Å (W. Jevons, "Band spectra of diatomic molecules," Phys. Soc. London, p. 290, 1932), which leads to a value for the double-bond radius of oxygen 0.611, close to that determined by the $^3\Sigma_g^-$ state.

⁸ C. Lu, E. W. Hughes, and P. A. Giguère, *J. Am. Chem. Soc.* **63**, 1507 (1941).

Nitrogen

The double-bond covalent radius chosen for N is one-half the $\text{N}=\text{N}$ bond distance in azomethane,⁹ 1.24Å. This value, however, has not been measured accurately; and in the choice of the value as 0.62Å, first consideration was given to its being the value obtained by drawing a smooth curve through the points determined by carbon (0.675Å) and oxygen (0.604Å), and to the symmetry of this curve with the corresponding ones for the single and triple radii of the first period elements. These curves are shown in Fig. 1.

Carbon

Though Pauling's values for both single and double-bond carbon covalent radii were selected from CC bonds and hence are not subject to error caused by ionic character, the CC single and double bonds used to determine these radii have since been shown by Mulliken, Rieke, and Brown¹⁰ to have 11 percent double-bond character and 12 percent triple-bond character, respectively. I have accordingly listed for the carbon radii one-half the lengths predicted by Mulliken, Rieke, and Brown for an ideal single (1.58Å) and an ideal double (1.35Å) CC bond.

⁹ L. R. Maxwell, J. Opt. Soc. Am. **30**, 374 (1940). This is also the length of the $\text{N}=\text{N}=\text{N}$ bond in methyl azide, L. Pauling and L. O. Brockway, J. Am. Chem. Soc. **59**, 13 (1937).

¹⁰ R. S. Mulliken, C. A. Rieke, and W. G. Brown, J. Am. Chem. Soc. **63**, 41 (1941).

Beryllium

The beryllium double-bond radius, 0.86Å, was obtained by extrapolation of the smooth curve for double-bond covalent radii of the first period elements shown in Fig. 1. The value obtained in this way gives satisfactory agreement when used in relation (2) to predict the interatomic distance in BeO. See Table I.

Fluorine

The revised value, 0.60Å, for double-bond r_F was obtained by extrapolation of the middle curve of Fig. 1.

Calcium, Strontium, and Barium

Very approximate predictions of the double-bond covalent radii of these elements can be made with Eq. (2) from the measured interatomic distances⁴ in CaO, SrO, and BaO, assuming of course that double bonds exist in these molecules. The results obtained in this way are 1.29Å for Ca, 1.36Å for Sr, and 1.35Å for Ba.

EFFECTS OF IONIC CHARACTER ON TRIPLE-BOND LENGTHS

From a comparison with the value of the constant β in Eq. (1) for single and for double bonds, one may expect the Schomaker-Stevenson rule to hold for triple bonds with a value for β about 0.03 or 0.04. However, there are not enough sufficiently accurate data available on pure triple bonds to test the relation.