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# ORBITAL RADII, BOND LENGTH AND RESONANCE

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# ORBITAL RADII, BOND LENGTH AND RESONANCE[1]

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[1] Part I: G. R. Somayajulu, J. Chem. Phys. 31, 919 (1959).

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The radius of a s-p hybrid orbital has been found to be given by the expression: $r = A - B/(1 + \lambda^2)$ where A is the radius of the pure p orbital, B, a universal constant equal to 0.336 A and $\lambda$, the coefficient of mixing in the hybrid $s + \lambda p$. When radii appropriate for the orbitals that are paired together are used, bond length is additive of the orbital radii and no Schomaker-Stevenson correction is necessary. This shows that most bonds can be treated as covalent, single and localized.

## 1. INTRODUCTION

According to the current theories on bond length[2-4], covalent bond

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[2] L. Pauling, The Nature of the Chemical Bond, 3rd ed. (Cornell University Press, Ithaca, New York, 1960).

[3] V. Schomaker and D. P. Stevenson, J. Am. Chem. Soc. 63, 37 (1941).

[4] W. Gordy, W. V. Smith, and R. F. Trambarulo, Microwave Spectroscopy (John Wiley & Sons, Inc., New York, 1953), p. 313.

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length is additive of the radii of the orbitals that are paired together. Deviations from additivity occur when the bonds are either partially ionic or partially double. The suggestion that some bonds are partially ionic is usually taken to follow from the concept of ionic-covalent resonance; the suggestion that some bonds acquire partial double bond character follows from the concept of $\pi$-electron resonance. It has been found, however, that C-C bond length in various molecules with one ground state structure is a sum[1,5] of the orbital radii. Also the C-C bond energy has

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[5] M. G. Brown, Trans. Faraday Soc. 55, 694 (1959).

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been found[6] to be a sum of the orbital strengths. These results indicate

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[6] G. R. Somayajulu, submitted for publication.

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two things; first of all they show that π-electron resonance is either negligible or absent in such molecules; secondly, they indicate the inapplicability of the Schomaker-Stevenson correction.

In many cases when hybridization is taken into account, we may speak of the molecule as composed of localized electron-pair bonds. Such bonds should be covalent. Their lengths will be simply sums of the orbital radii and the Schomaker Stevenson term becomes redundant. Similarly, Pauling's term, $(\Delta x)^2$, which represents the square of the difference between the electronegativities of the bonded atoms, becomes redundant when we use appropriate orbital strengths for the estimation of the bond energy. However, Mulliken's electronegativity[7], which is conceptually

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[7] R. S. Mulliken, J. Chem. Phys. 2, 782 (1934); 3, 573 (1935).

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different from that of Pauling, retains its full significance even when we take hybridization into account. Mulliken's electronegativity increases with increase in the strength (with increase in the s-character) of the hybrid and may rightly be related to the strength of the orbital. If resonance due to other schemes of pairing were to be important, we should have to seek a new relationship between the resonance energy and the electronegativities of the paired orbitals. It would seem more reasonable to expect the value of $(\Delta x)^2$ to vary with hybridization than having a constant value.

In this paper, we have suggested values for the orbital radii of some atoms, obtained on the assumption that the radius of a s-p hybrid is

linearly related[8] to the percentage s-character in the hybrid. These

[8] M. J. S. Dewar and H. N. Schmeising, Tetrahedron 5, 166 (1959).

radii prove the additive nature of the bond length. In the following paper[6], we have estimated the energies of some bonds and showed them to be sums of the orbital strengths.

## 2. METHOD OF ESTIMATION OF ORBITAL RADII

The expression for the radius of a s + λp hybrid may be written as:

$$r = A - B/(1 + \lambda^2) \qquad (1)$$

where A and B are constants characteristic of each atom and λ is the coefficient of mixing. $100/(1 + \lambda^2)$ gives the percentage s-character in the hybrid. When λ = 0, r(= A-B) represents the radius of a pure s orbital. When λ = ∞, r(=A) represents the radius of the pure p orbital.

The tetrahedral and digonal radii of carbon are known to be[1,5] 0.772 A and 0.688 A respectively. With the help of these values, the values of A and B of Eq. (1) are 0.856 A and 0.336 A respectively. For $\lambda^2 = 2$, i.e., for the trigonal orbital, Eq. (1) leads to a value of 0.744 A, a value which may be deduced from the length[9,10] of such a bond in 1,3-butadiene (1.483 A) and

[9] A. Almenningen, O. Bastiansen and M. Traetteberg, Acta Chem. Scand. 12, 1221 (1958).

[10] A. Almenningen and O. Bastiansen, D.K.N.V.S. Skrifter, 1958, NR 4.

diphenyl (1.493 A). A slightly lower value will result for the trigonal radius if the radius of the hybrid orbital is linearly related[5] to $\lambda^2$; also it leads to a higher value for the radius of the pure s orbital. Expressions relating r and $\lambda$, suggested by Coulson[11] and Wilmhurst[12] lead

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[11] C. A. Coulson, Victor Henri Commemmoratif Volume (Desoer, Liege, 1948), p. 15.

[12] J. K. Wilmhurst, J. Chem. Phys. 33, 813 (1960).

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to radii which on addition necessitate a correction[13,14] for the effect of

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[13] See B. Bak and L. Hansen-Nygaard, J. Chem. Phys. 33, 418 (1960).

[14] See R. S. Mulliken, Tetrahedron 6, 68 (1959).

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resonance or for the ionic character of the bond. When appropriate radii for the orbitals are used such corrections are unnecessary.

Estimation of radii using Eq. (1) is, however, difficult because of our poor knowledge of the valence states of atoms in various molecules. Excepting in a few simple cases, the bond angles do not seem to provide sufficient clues to the nature of bonding. However, we may take advantage of the fact that the shortenings for the double and triple bond radii of various atoms in the Periodic Table are almost the same as for carbon; one may assume, therefore, that the shortening from one hybrid to another will be approximately equal to those for the hybrids of carbon. This is equivalent to the assumption that B of Eq. (1) is constant for all atoms.

Then knowing the radius for one orbital of an atom, we may deduce the radii for the other orbitals of that atom by using Eq. (1). This procedure has been followed for the derivation of the orbital radii. When atoms use orbitals other than s and p for the formation of the hybrid orbitals, the radii of such orbitals may be worked out through the method of additivity. Such radii have not been considered in this paper. The results for the s-p hybrids are now discussed. The bond lengths in the halides of the second group elements are those obtained by Akishin et al[15] and quoted by

[15] P. A. Akishin and V. P. Spiridonov, Kristallografiya 2, 475 (1957).

Bastiansen and Lund[16]. The interatomic distances in crystals with the

[16] O. Bastiansen and E. W. Lund, Ann. Rev. Phys. Chem. 10, 31 (1959).

sphalerite and wurtzite arrangements are from Wyckoff[17]. If not indicated

[17] R. W. G. Wyckoff, Crystal Structures, Vol. I. (Interscience Publishers, Inc., New York, 1960).

otherwise, all other bond lengths quoted in this paper are from the Tables of Interatomic Distances and Configuration of Molecules and Ions (The Chemical Society, London, 1958).

## 3. ORBITAL RADII OF NITROGEN

If we assume that nitrogen uses p orbital for bonding with another

nitrogen atom in hydrazine, the length (1.47 A) of the N-N bond of hydrazine leads to the radii, 0.735 A for p, 0.651 A for $sp^3$ and 0.623 A for $sp^2$ orbitals. The above values for the tetrahedral and trigonal radii of nitrogen may be supported as shown below:

The $\widehat{HNH}$ angle of ammonia is close to the tetrahedral indicating that nitrogen atom in this molecule is in the tetrahedral state of hybridization. Additivity of the tetrahedral radius of nitrogen and the normal covalent radius of hydrogen (0.371 A) gives 1.022 A for the length of the N-H bond: this value compares satisfactorily with the observed value, 1.016 ± 0.01 A.

There are sufficient grounds to believe that the nitrogen atom of formamide is hybridized in the trigonal state[18]. The C-N and N-H bonds

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[18] W. J. O. Thomas, Chem. Rev. 57, 1179 (1957).

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of formamide have[19] the lengths of 1.343 ± 0.007 A and 0.995 ± 0.007 A

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[19] R. J. Kurland and E. B. Wilson, Jr., J. Chem. Phys. 27, 585 (1957).

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respectively. Our values for the $C(sp^2)$-$N(sp^2)$ and $N(sp^2)$-H bonds are 1.367 A and 0.994 A respectively. These are in satisfactory agreement with the observed values. The length of the $>C$-$NH_2$ bond in p-nitraniline is 1.37 A; this is also in good agreement with our value, 1.367 A.

The molecule, $S_4N_4H_4$, is a puckered eight-membered ring of alternating sulphur and nitrogen atoms[20,21]. The sulphur bond angle and the dihedral

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[20] R. L. Saas and J. Donohue, Acta Cryst. 11, 497 (1957).

[21] E. W. Lund and S. R. Svensen, Acta Chem. Scand. 11, 940 (1957).

angle have values close to those of $S_8$. The $S\hat{N}S$ angle has been found to be close to 120°, which suggests the presence of trigonal planar S-NH-S groupings. The average S-N bond length is 1.674 A. Assuming the radius of sulphur atom to be 1.04 A as in $S_8$, and by using the trigonal radius of nitrogen, we obtain a value of 1.663 A for the length of this bond. This is in good agreement with the observed value.

In trisilylamine, $N(SiH_3)_3$, the $Si\hat{N}Si$ angle is close to 120° and the length of the Si-N bond is 1.738 A. Using our revised value for the tetrahedral radius (1.118 A) of silicon (see Section 5) and the trigonal radius of nitrogen, our value for the $Si(sp^3)$-$N(sp^2)$ bond is 1.741 A. This is in good agreement with the observed value. Thus these examples provide some support for our assumptions in deriving these radii. The results for the C-N and N-H bonds of formamide also show that one ground state structure involving a $C(sp^2)$-$N(sp^2)$ bond represents the structure of formamide. Slight discrepancies in the estimated lengths are probably due to the neglect of the correction for the non-equivalence of the orbitals in some of these compounds.

## 4. ORBITAL RADII OF HALOGENS

A good deal of information about the bonding orbitals may be obtained from a consideration of the interatomic distances in a diatomic hydride, HX, and its ion, $HX^+$. Two classes of hydrides may be recognized[22]; one in

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[22] H. A. Bent, J. Chem. Phys. 33, 1258 (1960).

which the length of the X-H bond increases when an electron is removed from X; examples for this class of hydrides are provided by CH, NH, OH, HCl, HBr, etc. In the second class of hydrides, the length of the X-H bond decreases when an electron is removed from X; examples for this class are provided by BeH, MgH, HgH, BH, AlH, etc. The reason for this may be attributed[22] to a change in the s-content of the bonding orbital of X; in the first class of hydrides there may be a decrease in the s-content of the bonding orbital of X resulting in an increase in the orbital radius of X; this makes the length of the X-H bond in $HX^+$ greater than in HX. Just the opposite of this probably takes place in the second class of hydrides. It follows from this that the bonding orbital of C in CH is not pure p as it is usually thought to be. Likewise, in hydrogen halides, the halogen atoms do not use their pure p orbitals but hybrids of s and p. Since there are no easy methods to predict the percentage s-character in these hybrids, we will assume the applicability of Eq. (1) to these hybrids and predict the percentage s-character in the hybrid from the observed radius.

As already stated in Section 2, Eq. (1) can be used only when the radius of at least one orbital is known. It is possible to obtain the radii of the atoms in various molecules, but it is not possible in most cases to say to which orbitals they actually correspond. For example, it is customary to assume that the bonding orbitals of chlorine atoms in $Cl_2$ are p; what is the proof for this? In fact, there are now a number of evidences, as shown below, which suggest that the single bond in $Cl_2$ is probably a tetrahedral-tetrahedral bond. Pauling showed that the tetrahedral radius of chlorine in the crystal of CuCl with the sphalerite arrangement

is close to the radius of the chlorine atom in $Cl_2$. Recently we have found[23]

[23] G. R. Somayajulu, J. Chem. Phys. 33, 1541 (1960).

the value of $k_e r_e/D_o$ (where $k_e$ is the force constant, $r_e$ the internuclear distance, and $D_o$, the dissociation energy) to be constant for similar diatomic molecules with constant bond type. Among the halogens, $F_2$ behaves anomalously indicating that the bond type in $F_2$ is different from that in $Cl_2$, $Br_2$ and $I_2$. However, the values of $k_e r_e/D_o$ for all the four hydrogen halides are approximately constant indicating that the bond type in the hydrogen halides is nearly the same. Further we have found the radius of the fluorine atom in $F_2$ is about 0.170 A greater than its radius in HF. On the basis of Eq. (1) the difference between the p and digonal radii is also 0.168 A. From this it may be inferred that the bonding orbital of F is p in $F_2$ and sp in HF. In the case of Cl, the difference between its radii in $Cl_2$ and HCl is 0.090 A. On the basis of Eq. (1), the difference between either p and tetrahedral or between tetrahedral and digonal is 0.084 A. Since the bond type in all the hydrogen halides is nearly the same (as indicated by the $k_e r_e/D_o$ values) we may infer from the above that the bonding orbital of Cl is tetrahedral in $Cl_2$ and digonal in HCl. As expected the results for Br and I are consistent with the results for Cl. On the basis of the considerations presented above, the orbital radii of the halogen atoms have been deduced and presented in Table I. We have shown in Table II that, with the help of these radii, it is possible to estimate the lengths of the carbon-halogen bonds in several molecules. The type of bonding may be inferred from the values of the orbital

Table I

Orbital radii of the halogen atoms

| Halogen | r(p) | r($sp^3$) | r($sp^2$) | r(sp) | Radius in $X_2$ | $HX^+$ | HX |
|---|---|---|---|---|---|---|---|
| F | 0.715 | 0.631 | 0.603 | 0.547 | 0.715 | | 0.547 |
| Cl | 1.078 | 0.994 | 0.966 | 0.910 | 0.994 | 0.944 | 0.904 |
| Br | 1.225 | 1.141 | 1.113 | 1.057 | 1.141 | 1.088 | 1.043 |
| I | 1.417 | 1.333 | 1.305 | 1.249 | 1.333 | | 1.237 |

Table II

Comparison of the estimated and observed interatomic distances of carbon-halogen bonds in various compounds[a]

| Molecule | Bond | r(C) | r(X) | r(C-X) | $r(C\text{-}X)_{Obs.}$ |
|---|---|---|---|---|---|
| $CF_4$ | C-F | 0.772(te) | 0.547(di) | 1.319 | 1.325 ± 0.005 |
| $C_2F_4$ | C-F | 0.744(tr) | 0.547 | 1.291 | 1.30 ± 0.01 |
| $C_6H_5F$ | C-F | 0.744 | 0.547 | 1.291 | 1.30 ± 0.01 |
| CHFO | C-F | 0.744 | 0.603(tr) | 1.343 | 1.351 ± 0.013 |
| $CH_3F$ | C-F | 0.772 | 0.631(te) | 1.403 | 1.391 ± 0.005 |
| $CCl_4$ | C-Cl | 0.772 | 0.994(te) | 1.766 | 1.766 ± 0.005 |
| $CH_2{=}CHCl$ | C-Cl | 0.744 | 0.994 | 1.738 | 1.736 ± 0.01 |
| $C_6H_5Cl$ | C-Cl | 0.744 | 0.944[b] | 1.688 | 1.69 ± 0.01 |
| $C_2Cl_2$ | C-Cl | 0.688(di) | 0.944 | 1.632 | 1.635 ± 0.004 |
| $CBr_4$ | C-Br | 0.772 | 1.141? | 1.913? | 1.942 ± 0.005 |
| $CH_2{=}CHBr$ | C-Br | 0.744 | 1.141(te) | 1.885 | 1.891 ± 0.01 |
| $C_2Br_2$ | C-Br | 0.688 | 1.141 | 1.829 | 1.80 ± 0.03 |
| $CI_4$ | C-I | 0.772 | 1.333(te) | 2.105 | 2.12 ± 0.02 |
| $CH_2{=}CHI$ | C-I | 0.744 | 1.333 | 2.077 | 2.089 ± 0.01 |
| $C_2I_2$ | C-I | 0.688 | 1.333 | 2.021 | 2.03 ± 0.01 |

(a) The orbitals to which the radii correspond are shown in parentheses, te = tetrahedral, tr = trigonal and di = digonal.
(b) Orbital radius of chlorine in $HCl^+$.

radii required to fit the bond lengths. Further examples in support of the orbital radii of the halogens will be given elsewhere in this paper.

## 5. TETRAHEDRAL AND OTHER RADII OF SOME ELEMENTS

Pauling derived the tetrahedral radii of several elements from the interatomic distances in crystals with the diamond, sphalerite and wurtzite arrangements. With slight revisions most of his values are acceptable to us. In the case of silicon, however, the value, 1.116 A that may be obtained from the interatomic distance in silicon carbide appears to be more appropriate than the value 1.17 A obtained by Pauling from the interatomic distance in Si (c). Similarly, the value, 1.22 A suggested by Pauling for the tetrahedral radius of Ge appears to be quite high. We suggest a value of 1.16 A. We also suggest the values: 1.405 A, 1.45 A, 1.26 A and 1.37 A for the tetrahedral radii of Sn, Pb, Ti and Zr, respectively. These radii may be supported as shown in Table III.

From the interatomic distances in the crystals of AlN, AlAs, AlSb, GaN, GaP, GaAs, GaSb, InN, InP, InAs, and InSb, the tetrahedral radii of Al, Ga, In, N, P, As and Sb have been found to be 1.30, 1.30, 1.49, 0.65, 1.05, 1.13 and 1.33 A respectively. From these, the p and trigonal radii of these elements have been obtained by using Eq. (1). These are presented in Table IV. We have also included in this table the orbital radii of bismuth obtained from the interatomic distances in the compounds of bismuth.

It is quite interesting to see that the trigonal radius (1.277 A) of gallium from the length (2.50 A) of the Ga-I bond in $GaI_3$ is quite close to 1.272 A estimated by us. From the interatomic distances in AlH and InH,

Table III

Comparison of the estimated and observed interatomic distances in $MX_4$ and other types of compounds of Si, Ge, Sn, Pb, Ti and Zr.

| Molecule | Bond | r(M) | r(X) | r(M-X) | $r(M-X)_{Obs.}$ |
|---|---|---|---|---|---|
| $SiH_4$ | Si-H | 1.118(te) | 0.371 | 1.489 | 1.480 ± 0.005 |
| $SiCl_4$ | Si-Cl | | 0.910(di) | 2.028 | 2.03 ± 0.01 |
| $SiBr_4$ | Si-Br | | 1.057(di) | 2.175 | 2.17 ± 0.01 |
| $SiI_4$ | Si-I | | 1.333(te) | 2.451 | 2.435 ± 0.01 |
| $Si(CH_3)_4$ | Si-C | | 0.772(te) | 1.890 | 1.888 ± 0.02 |
| $(C_6H_5)_2SiCl_2$ | Si-C | | 0.744(tr) | 1.862 | 1.84 ± 0.015 |
| $Si_2Cl_6$ | Si-Si | | 1.118 | 2.236 | 2.24 ± 0.06 |
| $GeH_4$ | Ge-H | 1.160(te) | 0.371 | 1.531 | 1.53 ± 0.01 |
| $GeClF_3$ | Ge-F | | 0.547(di) | 1.707 | 1.688 ± 0.017 |
| | Ge-Cl | | 0.910 | 2.070 | 2.067 ± 0.003 |
| $GeBr_4$ | Ge-Br | | 1.141(te) | 2.301 | 2.297 ± 0.005 |
| $GeI_4$ | Ge-I | | 1.333 | 2.493 | 2.50 ± 0.03 |
| $SnCl_4$ | Sn-Cl | 1.405(te) | 0.910 | 2.315 | 2.33 ± 0.02 |
| $SnBr_4$ | Sn-Br | | 1.057 | 2.462 | 2.46 ± 0.02 |
| $SnI_4$ | Sn-I | | 1.249(di) | 2.654 | 2.64 ± 0.04 |
| $Sn(CH_3)_4$ | Sn-C | | 0.772 | 2.177 | 2.18 ± 0.03 |
| $PbCl_4$ | Pb-Cl | 1.450(te) | 0.994(te) | 2.444 | 2.465 ± 0.02 |
| $Pb(CH_3)_4$ | Pb-C | | 0.772 | 2.222 | 2.203 ± 0.01 |
| $Pb_2(CH_3)_6$ | Pb-Pb | | 1.450 | 2.900 | 2.88 ± 0.03 |
| $TiCl_4$ | Ti-Cl | 1.260(te) | 0.910 | 2.170 | 2.18 ± 0.04 |
| $TiBr_4$ | Ti-Br | | 1.057 | 2.317 | 2.31 ± 0.02 |
| $ZrCl_4$ | Zr-Cl | 1.370(te) | 0.910 | 2.280 | 2.33 ± 0.05 |

Table IV

Orbital radii of Al, Ga, In, N, P, As, Sb and Bi

| Element | r(p) | Tetrahedral radius | Trigonal radius |
|---|---|---|---|
| Al | 1.384 | 1.30 | 1.272 |
| Ga | 1.384 | 1.30 | 1.272 |
| In | 1.574 | 1.49 | 1.462 |
| N | 0.734 | 0.65 | 0.622 |
| P | 1.134 | 1.05 | 1.022 |
| As | 1.214 | 1.13 | 1.102 |
| Sb | 1.414 | 1.33 | 1.302 |
| Bi | 1.514 | 1.43 | 1.402 |

the radii of Al and In are 1.276 A and 1.466 A respectively; these are quite close to the trigonal radii obtained by us.

The values 1.214 A and 1.414 A obtained by us for the radii of the p orbitals of As and Sb are quite close to the values assigned by Pauling for the single bond radii of these elements. Support of these values is shown in Table V.

Pauling's values for the tetrahedral radii of S, Se and Te are 1.04 A, 1.14 A and 1.32 A respectively; they are acceptable to us. Pauling's value for the tetrahedral radius of O is 0.66 A; we recommend the value 0.651 A, which leads to the values 0.735 A and 0.623 A for the p and trigonal radii of oxygen. The p orbital radii of Se and Te are 1.224 A and 1.404 A respectively. These radii may be supported as shown in Table VI.

The tetrahedral radii of Be, Mg, Zn, Cd and Hg have been found to be about 0.084 A greater than the radii of these elements in their monohydrides. According to Eq. (1), the expected difference between the tetrahedral and digonal radius is 0.084 A. Consequently, we may assume the bonding orbitals of these elements in their monohydrides to be digonal. We have, therefore, assigned the radii obtained from the interatomic distances in their monohydrides to their digonal orbitals and deduced their tetrahedral radii by using Eq.(1). The radii, thus obtained, have been compared with the tetrahedral radii obtained by Pauling in Table VII. There is a slight discrepancy in the case of Hg; we recommend the value 1.475 A for its tetrahedral radius.

According to Eq. (1), the difference between the tetrahedral and s orbital radius is 0.252 A. In $HHg^+$, the radius of Hg is 1.223 A; this is exactly 0.252 A less than its tetrahedral radius 1.475 A. On this basis,

Table V

Comparison of the estimated and observed interatomic distances in $MX_3$ type compounds of P, As, Sb and Bi

| Molecule | Bond | r(M) | r(X) | r(M-X) | $r(M\text{-}X)_{Obs}$ |
|---|---|---|---|---|---|
| $PH_3$ | P-H | 1.05(te) | 0.371 | 1.421 | 1.4206 ± 0.005 |
| $PCl_3$ | P-Cl | 1.05 | 0.994(te) | 2.044 | 2.043 ± 0.003 |
| $PBr_3$ | P-Br | 1.05 | 1.141(te) | 2.191 | 2.18 ± 0.03 |
| $PI_3$ | P-I | 1.134(p) | 1.333(te) | 2.467 | 2.46 ± 0.03 |
| $AsH_3$ | As-H | 1.13(te) | 0.371 | 1.501 | 1.519 ± 0.002 |
| $AsCl_3$ | As-Cl | 1.214(p) | 0.994 | 2.208 | 2.17 ± 0.02 |
| $AsBr_3$ | As-Br | 1.214 | 1.141 | 2.355 | 2.36 ± 0.04 |
| $AsI_3$ | As-I | 1.214 | 1.333 | 2.547 | 2.55 ± 0.03 |
| $SbH_3$ | Sb-H | 1.33(te) | 0.371 | 1.701 | 1.707 ± 0.0025 |
| $SbCl_3$ | Sb-Cl | 1.33 | 0.994 | 2.324 | 2.325 ± 0.005 |
| $SbBr_3$ | Sb-Br | 1.33 | 1.141 | 2.471 | 2.47 ± 0.04 |
| $SbI_3$ | Sb-I | 1.33 | 1.333 | 2.663 | 2.67 ± 0.03 |
| $BiCl_3$ | Bi-Cl | 1.514(p) | 0.994 | 2.508 | 2.48 ± 0.02 |
| $BiBr_3$ | Bi-Br | 1.514 | 1.141 | 2.655 | 2.63 ± 0.02 |
| $(CF_3)_3P$ | P-C | 1.134 | 0.772(te) | 1.906 | 1.937 ± 0.017 |
| $(CH_3)_3As$ | As-C | 1.214 | 0.772 | 1.986 | 1.98 ± 0.02 |
| $(CF_3)_3Sb$ | Sb-C | 1.414 | 0.772 | 2.186 | 2.20 ± 0.016 |
| $(C_6H_5)_3Bi$ | Bi-C | 1.514 | 0.744(tr) | 2.258 | 2.30 ? |

Table VI

Comparison of the estimated and observed lengths of some bonds containing O, S, Se and Te atoms

| Molecule | Bond | r(A) | r(B) | r(A-B) | $r(A-B)_{Obs.}$ |
|---|---|---|---|---|---|
| $CH_3OH$ | C-O | 0.772(te) | 0.651(te) | 1.423 | 1.427 ± 0.007 |
| HCOOH | C-O | 0.744(tr) | 0.623(tr) | 1.367 | 1.37 ± 0.01 |
| $CH_3SH$ | C-S | 0.772 | 1.04(te) | 1.812 | 1.818 ± 0.005 |
| $CH_3COSH$ | C-S | 0.744 | 1.012(tr) | 1.756 | 1.78 ± 0.02 |
| $(CH_3)_2Se$ | C-Se | 0.772 | 1.224(p) | 1.996 | 1.98 ± 0.02 |
| $(p\text{-}CH_3C_6H_4)Te$ | C-Te | 0.744 | 1.32(te) | 2.064 | 2.05 |

Table VII

Comparison of the tetrahedral radii of Be, Mg, Zn, Cd and Hg obtained from the interatomic distances in the crystals with the sphalerite and wurtzite arrangements and those obtained from the digonal radius in monohydride.

| Element | Digonal radius= r(X-H)-0.371 | Tetrahedral radius= digonal radius + 0.084 | Tetrahedral radius in crystals |
|---|---|---|---|
| Be | 0.972 | 1.056 | 1.05 |
| Mg | 1.360 | 1.444 | 1.44[a] |
| Zn | 1.224 | 1.308 | 1.31 |
| Cd | 1.391 | 1.475 | 1.48 |
| Hg | 1.369 | 1.453 | 1.48 |

(a) Pauling's value is 1.40 A, but subtraction of the tetrahedral radius of Te from the interatomic distance in MgTe crystal gives 1.44 A.

Hg in $HHg^+$ has a s bonding orbital. From the interatomic distances in $HMg^+$, $HZn^+$, and $HCd^+$, we obtain the values 1.278 A for Mg, 1.144 A for Zn and 1.296 A for Cd. These radii correspond to about 75 % s-character. From the length of the C-Hg bond in $CH_3$-HgCl, the radius of Hg is 1.285 A. This also corresponds to about 75% s-character. It is very strange that in dihalides (chlorides, bromides and iodides) of these elements, the radii which correspond to 75% s-character are found instead of the digonal radii. Calcium, strontium and barium, however, use their digonal radii obtained from the interatomic distances in CaH, SrH and BaH. The values for their digonal radii are 1.631 A for Ca, 1.775 A for Sr and 1.861 A for Ba. The digonal radius of Be is 0.972 A but it uses a radius of 0.85 A in its dihalides. It is quite interesting to find that the Schomaker-Stevenson rule also leads[16] to similar values for the radii of these elements. The results by using the above orbital radii are shown in Table VIII.

## 6. TRIGONAL RADIUS OF BORON

For the trigonal radius of boron, we propose a value of 0.795 A. This value may be obtained from the interatomic distance in $B_2$. There is, however, considerable doubt as to whether the bonding in $B_2$ is $\sigma$ or $\pi$. The results using this value have been shown in Table IX. In borazole and BBB-trichloroborazole, both boron and nitrogen are hybridized in the trigonal state. The calculated length of the $B(sp^2)$-$N(sp^2)$ bond is 1.418 A in good agreement with the observed value. Previously, several authors including the present[24] have thought that the structure of borazole is represented

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[24] G. R. Somayajulu, J. Chem. Phys. 26, 822 (1958).

Table VIII

Comparison of the estimated and observed interatomic distances in the halogenides of the Group II elements

| Molecule | r(M) | r(X) | r(M-X) | $r(M-X)_{obs.}$ |
|---|---|---|---|---|
| $BeF_2$ | 0.85(?) | 0.547(di) | 1.397 | 1.40 ± 0.03 |
| $BeCl_2$ | | 0.910(di) | 1.760 | 1.75 ± 0.02 |
| $BeBr_2$ | | 1.057(di) | 1.907 | 1.91 ± 0.02 |
| $BeI_2$ | | 1.249(di) | 2.089 | 2.10 ± 0.02 |
| $MgCl_2$ | 1.278(?) | 0.910 | 2.188 | 2.18 ± 0.02 |
| $MgBr_2$ | | 1.057 | 2.335 | 2.34 ± 0.03 |
| $MgI_2$ | | 1.249 | 2.527 | 2.52 ± 0.03 |
| $CaCl_2$ | 1.631(di) | 0.910 | 2.541 | 2.51 ± 0.03 |
| $CaBr_2$ | | 1.057 | 2.688 | 2.67 ± 0.03 |
| $CaI_2$ | | 1.249 | 2.88 | 2.88 ± 0.03 |
| $SrCl_2$ | 1.775(di) | 0.910 | 2.685 | 2.67 ± 0.03 |
| $SrBr_2$ | | 1.057 | 2.832 | 2.82 ± 0.03 |
| $SrI_2$ | | 1.249 | 3.024 | 3.03 ± 0.03 |
| $BaCl_2$ | 1.861(di) | 0.994(te) | 2.855 | 2.82 ± 0.03 |
| $BaBr_2$ | | 1.141(te) | 3.002 | 2.99 ± 0.03 |
| $BaI_2$ | | 1.333(te) | 3.194 | 3.20 ± 0.03 |
| $ZnCl_2$ | 1.144(?) | 0.910 | 2.054 | 2.05 ± 0.01 |
| $ZnBr_2$ | | 1.057 | 2.201 | 2.21 ± 0.01 |
| $ZnI_2$ | | 1.249 | 2.393 | 2.38 ± 0.02 |
| $CdCl_2$ | 1.296(?) | 0.910 | 2.206 | 2.21 ± 0.02 |
| $CdBr_2$ | | 1.057 | 2.353 | 2.37 ± 0.02 |
| $CdI_2$ | | 1.249 | 2.545 | 2.55 ± 0.02 |
| $HgCl_2$ | 1.285(?) | 0.994 | 2.279 | 2.28 ± 0.02 |
| $HgBr_2$ | | 1.141 | 2.426 | 2.41 ± 0.02 |
| $HgI_2$ | | 1.333 | 2.618 | 2.59 ± 0.05 |

Table IX

Comparison of the observed and estimated lengths of $B(sp^2)$ - X bonds. r(B) = 0.795 A

| Molecule | Bond | r(X) | r(B-X) | $r(B-X)_{Obs.}$ |
|---|---|---|---|---|
| $BCl_3$ | B-Cl | 0.910(di) | 1.705 | 1.73 ± 0.02 |
| $BBr_3$ | B-Br | 1.057(di) | 1.852 | 1.87 ± 0.02 |
| $B(CH_3)_3$ | B-C | 0.772(te) | 1.567 | 1.56 ± 0.02 |
| Borazole | B-N | 0.623(tr) | 1.418 | 1.44 ± 0.02 |
| BBB-Trichloro-borazole | B-N | 0.623 | 1.418 | 1.41 ± 0.02 |
| | B-Cl | 0.994(te) | 1.789 | 1.78 ± 0.03 |
| $C_6H_5BCl_2$ | B-C | 0.744(tr) | 1.539 | 1.52 ± 0.07 |

by a resonance hybrid of two Kekulé-like structures, each B-N bond possessing about 50% double bond character. From the present considerations, the B-N bond of borazole appears to be a single bond.

## 7. CONCLUSION

From the results presented in the previous sections, we can see that this theory of bond length gives us an insight into the structure of bonding in compounds. Several examples quoted in the Tables II, III, V, VI, VIII and IX illustrate this. Our analysis is, however, qualitative. If we have to get a further insight into the structure of bonding, we shall have to consider the bond energies also. For example, the C-F bond in $CF_4$ is much shorter than indicated by the radii of the tetrahedral carbon of diamond and that of the F atom in $F_2$. However, when the radius of the F atom in HF is used, the agreement is good. Consequently, we should also expect the F atom of $CF_4$ to have a much greater valence state energy than it has in $F_2$, and presumably equal to that in HF. On the other hand, the C-Cl bond length in $CCl_4$ is given by the tetrahedral radius of carbon and the radius of the Cl atom in $Cl_2$. It may be inferred from this that the valence state energy of Cl in this compound will presumably be equal to that in $Cl_2$. This may be seen to be partly true. The heat of formation of $CF_4$ is -218 kcal/mole. Four times the heat of formation of HF is -256 kcal. On the other hand, the heat of formation of $CCl_4$ is -25 kcal/mole, a value which is just 9 kcal more negative than that of methane.

However, based on this theory we have failed to account for the lengths of bonds in some molecules such as $CH_4$, $SiF_4$, $BF_3$, etc. Also

we were unable to obtain the lengths of the bonds in the halides of Be, Mg, Zn, Cd and Hg on the basis of the digonal radii of these metals. On the basis of the Pauli exclusion principle, these elements are expected to use digonal hybrids for bond formation. On the basis of Eq.(1) the radii used by them correspond to 75% s-character only. Taking these cases into consideration we think there are other factors besides hybridization which determine the bond lengths. Also Eq. (1) may not be applicable to all the elements. Probably cases which fall beyond the scope of this treatment necessitate considerations of resonance or corrections for the ionic character.

Also in some cases the bond lengths could not be estimated unambiguously. For example, we have estimated the length of the P-Br bond of $PBr_3$ on the basis of the tetrahedral radii of P and Br. Thus we obtain the value of 2.044 A. This value may be obtained also by the addition of the p orbital radius of P and the digonal radius of Br. It is in such cases the bond energies will prove extremely useful.

Thus this theory suffers from several curious defects but still has several advantages over the current theories. It needs to be refined.

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