THE PROBLEM OF BOND TYPE

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ABSTRACT

The difficulties of assessing ionic and covalent contributions to bonds are discussed. It is suggested that one of the best indications of such contributions can be obtained from a consideration of atomic orbital overlap in the linkages. The structures of the bonds in some compounds are discussed from a consideration of the overlap integrals.

INTRODUCTION

Numerous writers (Ahrens (1), Ramberg (2), Gruner (3)) have recently discussed the problems of bond type and its implications in geochemical problems. In a previous paper (4) the writer used the Pauling electronegativity scale to obtain information on bond type. At the present time some doubt must rest on the validity of some of these arguments and the present discussion is directed at focusing attention on what is now becoming accepted as one of the best indications of bond type, namely, the overlapping of atomic orbitals in a bond.

It is generally agreed that the bonds in a crystal or molecule formed between unlike atoms cannot be adequately described by considering only pure ionic or covalent structures, but that the actual structure is some combination of the limiting forms. The emphasis placed on the limiting forms differs considerably between workers. Ahrens (1), for example, prefers to use the ionic approach in most arguments while Pauling (5) considers most bonds as more nearly covalent. The wave function which will describe the state of affairs in a bond will in general have the form:

$$\psi \text{ mol} = \psi \text{ covalent} + k\, \psi \text{ ionic.}$$

The essential problem is to find some suitable means of evaluating the constant in this relation. The importance of the evaluation is obvious for upon it rest the steric properties, energies and lengths, etc., of the bond.

The various electronegativity scales have been directed at providing the necessary information on bond transition and all such scales (Pauling (6), Mulliken (7), Walsh (8)) agree in large part in the direction of such transitions. Thus, all would make cesium fluoride more ionic than lithium iodide. (It may be noted that some quite large differences do occur between the scales of Pauling and Walsh.) Although the data that can be derived from considerations of electronegativity differences between atoms can be invaluable in discussing some problems, there is considerable doubt in relating such differences to the actual *amount* of each contribution. The most important attempt to relate electronegativity to the quantitative evaluation of bond contributions was made by Pauling (6), who used the dipole moments of the hydrogen halides to fix limits to ionic contributions. At the present time considerable doubt must rest on this interpretation due to the complexity of the factors which lead to a molecule possessing a permanent dipole.

To elaborate on this latter difficulty we may consider bonding in the water molecule. At first sight we might expect oxygen with a structure $1s^2 \cdot 2s^2 \cdot 2p^2 \cdot 2p^1 \cdot 2p^1$ to use its two singly occupied "p" orbitals to form bonds with the $1s$ orbitals of the two hydrogen atoms. If this represented the true picture, then the lone pairs of electrons of the oxygen atom would remain in orbitals symmetrical about the oxygen nucleus and these would make no contribution to the dipole of the molecule. The bond angle in the water molecule (105°) is not that expected from "p" bonding (90°) and is close to the tetrahedral bond angle. This suggests that the oxygen atom may use an sp^3 hybrid state similar to the normal quadrivalent carbon atom. If such hybridization occurs, the lone pairs of the oxygen atom are no longer left with a symmetrical distribution and will make a contribution to the dipole moment. The large bond angle in the water molecule is often explained by considering that the normal "p" angle is opened slightly by repulsions between the adjacent hydrogens. If this occurred, the covalent bond would be weakened, an effect which is easily overcome by rehybridization of the oxygen orbitals. Confirmation of this hybridization in water has come from considerations of the structure of water and the calculations of hydrogen bond energies by Pople and Lennard-Jones (9) and Fyfe (10). The small moments of the carbon monoxide and nitrogen trifluoride molecules find ready explanation when lone pairs are considered but would not be explicable on the Pauling theory of ionic-covalent resonance. Coulson (11) from calculations of the various contributions to the water dipole has concluded that only a small proportion comes from ionic structures. It is thus clear, that if there is any hybridization of the halogen orbitals in the hydrogen halides, then the dipole moment cannot be a measure of the amount of ionic-covalent resonance. That such hybridization is likely to occur has been shown by Robinson (12). [Cf. Kastler (13)] For a full discussion of the dipole problem see Coulson (14).

From the above discussion it becomes clear that the Pauling relation of electronegativity difference to percentage ionic character of bonds (as used by writer (4)) is not entirely satisfactory. The Pauling relation must tend to place too much weight on ionic contributions. We may summarize by saying that although present electronegativity scales give us an order of bond transition, they can give us no quantitative data.

It should be noted that essentially there is little difference between the approach to bond transition from consideration of electronegativities to the approach via polarizability of Fajans and others which Ahrens uses (1). Consideration of charge and radius effects give an order of bond transition similar to that derived from electronegativities. The chief advantages in using electronegativities in the past has been that these functions are more likely to provide quantitative data.

Recently attention has been focussed on the overlap integral as a quantity capable of giving precise information on bond type and structure. The overlap integral S for overlap between any pair of atomic orbitals is defined by the relation

$$S(\psi_A\psi_B;\ R) = \int \psi_A\psi_B dv.$$

This integral gives a measure of the regions in space where the two atomic orbitals overlap. ψ_A, ψ_B represent suitable normalized atomic orbitals of atoms A and B and R is the internuclear distance. This quantity gives us a measure of the amount of classical covalent bonding and for purely ionic bonds should have a value of zero. The value of S depends upon the type of atomic orbital and the internuclear distance. Recently Mulliken (15), McColl (16) and Walsh (17) have made extensive use of overlap integrals in discussing bond properties.

Where possible it is desirable to use full self-consistent field wave functions to represent the atomic orbitals. However, because these are not always available and are rather unwieldy, the simple Slater functions (18) are almost always used. These functions express the outer part of atomic orbitals with considerable accuracy and are adquate for most problems at normal bonding distances. Numerous solutions exist for the necessary integrals; Mulliken (19), Couslon (20), Barnnet and Coulson (21). Recently Mulliken (22) has proposed relations between overlap integrals and bond energies greatly extending the usefulness of such calculations. The values of the overlap integrals for various orbital types also provide leading information on the state of an atom in an actual bond. These may be used along with the guiding principle enunciated by Pauling (6) that "of two orbitals in an atom the one which can overlap more with an orbital of another atom will form the stronger bond with that atom, and, moreover, the bond formed by a given orbital will tend to lie in the direction in which the orbital is concentrated."

Recently Pauling (5) has developed the "neutrality principle" which appears to be a most useful generalization. The principle essentially states that the formal charges on atoms in molecules or crystals probably rarely exceed $\pm\frac{1}{2}e$, and that charges as large as this are only found in bonds between atoms at the extreme ends of the electronegativity scale. Pauling has applied the following type of argument. The electronegativity difference between a cesium and a fluorine atom indicate that the bond in the diatomic molecule has about 9% covalent character. In the CsF crystal as each atom is surrounded by six others, the bond in the crystal may be described as a single bond with as much as 54% covalent character resonating among the six positions. Thus the charge in this extreme ionic case may not exceed $\frac{1}{2}e$. Again, if we consider the hexahydrated ferric ion in aqueous solution, the O-Fe bonds have about 50% covalent character. By the formation of six such bonds the charge on the ferric ion is essentially neutralized, the charge being relayed to the hydrogen atoms of the solvating water molecules. Pauling considers that the oxidation states of aqueous ions are controlled by such factors and not by the ionization potentials alone. The usefulness of the principle in the field of ion solvation has been developed by the writer (23). The principle greatly increases the weight to be given to covalent structures. It is of interest that similar trends are indicated in other work. Pitzer (24) and Mulliken (15) have both attributed repulsion effects to overlap of nonbonding electrons rather than to polarity. Walsh (17) has also demonstrated very clearly that polarity does not increase bond strength, a conclusion which might have been drawn from the original arguments of Pauling (6).

The remainder of this discussion will be concerned with overlap integrals for some typical types of bond and the calculation of bond lengths, etc.

OVERLAP INTEGRALS AND ELECTRONEGATIVITY DIFFERENCES

Primarily it must be emphasized that a general correlation exists between the amount of covalent bonding determined either from overlap integrals or electronegativity differences. In Table 1 some results for

TABLE 1. OVERLAP INTEGRALS AND ELECTRONEGATIVITY DIFFERENCES FOR Li-X BONDS

X	$S(ss)$	$S(sp)$	$S(ps)$	$S(pp)$	x_a-x_b
F	0.17	0.05	0.27	0.08	3.0
Cl	0.23	0.15	0.40	0.19	2.0
O	0.20	0.07	0.31	0.10	2.5
S	0.29	0.18	0.44	0.22	1.5
N	0.24	0.10	0.37	0.14	2.0
P	0.33	0.23	0.46	0.26	1.1
C	0.28	0.14	0.43	0.18	1.5
Si	0.37	0.28	0.50	0.29	0.8

Li-X bonds are summarized. (Note: See Appendix for meaning of terms $S(ss)$, etc. The orbitals always refer to the valence shell electrons.)

In almost all cases the order of increasing overlap of the orbitals concerned is that predicted from electronegativity differences $(x_a - x_b)$. Thus for the (ss) series the order is:

$$\mathrm{Si} > \mathrm{P} > \mathrm{S} > \mathrm{C} > \mathrm{N} > \mathrm{Cl} > \mathrm{O} > \mathrm{F}$$

while from the electronegativity differences we would expect

$$\mathrm{Si} > \mathrm{P} > \mathrm{C} \geqq \mathrm{S} > \mathrm{N} \geqq \mathrm{Cl} > \mathrm{O} > \mathrm{F}.$$

The differences in the S values are rather smaller than might be expected but small differences in S can lead to relatively large differences in covalent bond energy. Some of the values for lithium fluoride are sufficiently large to suggest that covalent terms in this bond are too large to be neglected. The order of overlapping of the electronegative atoms appears to be almost independent of the metal chosen and similar series have been found for beryllium, magnesium and hydrogen. (Note: The S values have been calculated using Slater functions at a distance corresponding to the covalent radius sum in all cases.)

If the Pauling neutrality principle is to be considered reasonable for classical ionic crystals such as the alkali halides, then, there should be substantial amounts of overlap between atoms in such crystals. To test this, the overlap integrals for some of these bonds have been evaluated and are summarized in Table 2. (Note: In calculating these overlap integrals the screening constants have been evaluated for the neutral atoms, not the ions. Thus for NaCl the overlap is considered between Na $(3s)$ and Cl $(3s \cdot 3p)$, etc. R refers to the internuclear distance in angstroms.)

It will be noticed that in all cases there is substantial overlap, even for RbF. However, in this case the contribution to the bonding energy would be small but could account for the 10% covalent character deduced from

TABLE 2. OVERLAP INTEGRALS FOR ALKALI HALIDES

Compound	R	$S(ss)$	$S(ps)$	$S(pp)$	$S(ps)$
LiF	2.01	0.20	0.32	0.09	0.06
LiCl	2.57	0.27	0.40	0.20	0.15
LiI	3.02	0.28			
NaF	2.31	0.16	0.27	0.05	0.03
NaCl	2.81	0.31			
NaI	3.23	0.28			
RbF	2.82	0.08			
RbCl	3.29	0.14			
RbI	3.66	0.26			

Pauling's electronegativity differences. It will be noted that the values for sodium chloride are larger than for the iodide, while for lithium chloride and iodide the values are approximately equal. This effect would not be expected either from consideration of electronegativities or polarizabilities. This effect is probably to be attributed to the very different size of the orbitals concerned. If two overlapping orbitals have different quantum numbers such as Li (2) and I (5), the space distributions of the electron clouds about such atoms are very different. Thus, for the "*s*" electrons, although in both sodium and iodine these have spherical distributions the radius of the cloud for iodine is much larger. In such a case it is not possible to obtain large amounts of overlap of the regions in space where these electrons are concentrated. The effect does not occur in the case of rubidium iodide where both metal and non-metal have the same quantum numbers.

In Table 3 values are given for the integrals for M-O and M-S bonds.

TABLE 3. OVERLAP INTEGRALS FOR M-S AND M-O BONDS

Bond	$S(ss)$	$S(sp)$	$S(pp)$	$S(ps)$	$S(\pi\pi)$
C-O	0.27	0.38	0.28	0.24	0.14
C-S	0.24	0.39	0.33	0.29	0.17
Si-O	0.27	0.20	0.18	0.46	0.16
Li-O	0.20	0.31	0.10	0.07	0.10
Li-S	0.29	0.18	0.22	0.44	0.14
Mg-O	0.23	0.38	0.12	0.09	0.10
Al-O	0.25	0.13	0.18	0.38	0.11
Na-O	0.20	0.33	0.08	0.05	0.08

From these figures it is apparent that even in linkages such as Na-O and Mg-O covalent contributions to the bond energy may be considerable. For Si-O and Al-O bonds all terms indicate fairly strong overlap. One feature of interest is the fairly large magnitude of the π overlap terms in some cases which suggest that double bonding may be important. The bond shortening in Si-O has been attributed to this effect. (Note: For definition of π bonds see appendix.)

BOND ENERGIES AND OVERLAP INTEGRALS

If covalent contributions to a bond are to be considerable it is necessary that the energy from such overlap be reasonably large compared with the total bond energy. From the values of the integrals alone little data of real value can be obtained except of a qualitative nature.

Recently Mulliken (22) has proposed semi-empirical relations between bond energies and overlap integrals. The general form of the relation is as follows:

$$D_0=\Sigma X_{ab}-1/2\Sigma Y_{ab}+1/2\Sigma K_{ab}-P+RE.$$

D_0 = dissociation energy of the molecule.
$X_{ab}=AS_{ab}I_{ab}/(1+S_{ab})$ (S for bonding electrons.)
$Y_{ab}=A'S_{ab}^2I_{ab}$ (S for non bonding electrons.)
P = Promotion energies to the valence state.
RE = Resonance energy of all types (as in benzene).
I = Mean ionization potentials of the electrons.

A and A' are constants determined by fitting the equation to the known bond energies of two molecules. The Y terms which cover repulsions due to overlap of filled shells are of two types, one due to inner shell electrons of A reacting with valence shell electrons of B and overlap of non-bonded electrons such as the two hydrogen atoms in a water molecule. The K terms cover exchange energy between full shells which is small, but not negligible. Mulliken has found that the above relation fitted to two molecules gave dissociation energies within 1–2% of the experimental values for eight others. The relation is extremely useful in obtaining some indication of the energy contributions from particular sets of orbitals. Thus in diatomic RbF the (*ss*) overlap corresponds to an energy of 16 k.cals/mol. while for LiF the (*ss*) overlap gives a bonding energy of about 43 k.cals/mol. The relation can also be applied to obtaining bond lengths. In this case it is necessary to evaluate the energy over a range of atomic distances to obtain maximum bond energy.

BONDING IN THE Si-O AND C-O GROUPS

It is well known that the bonds in the $Si\text{-}O_4$ and similar groupings are often abnormally short. Pauling (25) has discussed this and similar problems and attributes this shortening largely to the effect of π bonding between silicon and oxygen. Pitzer (24) considers that inner shell-outer shell repulsions are probably more important. Another feature of the chemistry of these groups is to explain why there is no SiO_3^{--} group corresponding to a CO_3^{--} group and conversely no CO_4^{----} group corresponding to SiO_4^{----}. Generally these effects are vaguely attributed to the influence of size and charge. However, if we are to take the neutrality principle seriously, the effect of polarity must take a less important place. To attempt to find factors influencing these problems some calculations have been made of the principal overlap energies in such bonds. It may be noted that size factors are not controlling, for molecules such as CI_4 are quite stable with the iodine atom much larger than oxygen. In Table 4 some of the important overlap integrals and the corresponding energies are recorded. As the CO_3^{--} ion is planar, the bonds are most

TABLE 4. OVERLAP INTEGRALS AND ENERGIES FOR C-O BONDS. (R=1.3 Å)

	S	E(e.v)	Notes
$(2s2s)$	0.33		
$(2s2p)$	0.42		
$(2p2s)$	0.28		
$(2p2p)$	0.30		
$(C_{sp^2}O_{sp})$	0.664	8.24	Carbon trigonal oxygen digonal hybrids
$(C_{sp^3}O_{sp})$	0.663	8.20	Carbon tetrahedral oxygen digonal hybrids
$(\pi\pi)$	0.18	4.15	
(pp)	0.12	0.124	Repulsion adjacent oxygens *S.C.F.* functions
$(C_{sp^3}O_{1s})$	0.072	0.61	Carbon valence shell oxygen inner shell repulsion
$(C_{1s}O_{sp})$	0.055	0.20	Oxygen valence shell carbon inner shell repulsion

probably formed from a carbon sp^2 trigonal hybrid. We have considered that oxygen may use an sp linear hybrid which will give maximum overlapping. The inclusion of a large amount of "s" character in this bond may not be justified, but certainly in the SiO_2 crystal this is justified by the Si-O-Si bond angle. One feature of interest is the very large values of the hybrid overlaps compared with the simple orbital overlaps. As Mulliken (26) says "a little hybridization goes a long way." It is also well established that the amount of overlap increases with "s" character of the bond. The remaining carbon "p" orbital will lie above and below the plane of the group and can thus form a strong π bond with the oxygen "p" orbitals. We may thus sum the energies of the two possible structures.

$$\begin{aligned} E(CO_3) &= 3E\sigma + E\pi - 3E(O\text{-}O) - 3E(C_{1s}O) - 3E(O_{1s}C) \\ &= 26.07 \text{ e.v.} \\ E(CO_4) &= 4E\sigma - 6E(O\text{-}O) - 4E(C_{1s}O) - 4E(O_{1s}C) \\ &= 28.60 \text{ e.v.} \end{aligned}$$

Thus neglecting any polarity we calculate that the bond energy of the CO_4 group is larger. This fact is not as alarming as might be first thought and will be discussed later. (Note. Allowance has been made for the smaller O-O distance in the tetrahedral grouping.)

By applying an exactly similar treatment to the Si-O groupings we arrive at energies of 22.62 e.v. for SiO_3 and 25.50 e.v. for SiO_4. Once more the four co-ordinated structure is favoured on these arguments.

We may now consider some of the factors indicated from these calculations. Firstly, the internuclear distances appear to be controlled more by inner shell, outer shell repulsions, which are much larger than the O-O repulsions. These latter values should be fairly accurate as *S.C.F.* functions have been used (26). Secondly, the inner shell repulsions are much less for silicon than for carbon. Thus the energy for the overlap of silicon (2*s*) orbitals with oxygen valence is almost negligible while for carbon this is not the case. This effect will favour higher co-ordination with silicon. The O-O repulsions in the silicon structures with larger bond lengths than in the case of carbon are only 25% as great, once more favouring higher co-ordination. Another feature of interest is that the π energy terms for C-O are 51% as strong as the σ bonds while for silicon this is reduced to 45%.

To obtain some indication of bond lengths, calculations have been made of the variation of energy with internuclear distance. The results are summarized in Table 5.

TABLE 5. VARIATION OF BOND ENERGY WITH BOND LENGTH

CO_3 $R=1.4, E=25.36$; $R=1.3, E=26.07$; $R=1.2, E=24.4$
CO_4 $R=1.5, E=27.92$; $R=1.4, E=28.83$; $R=1.3, E=28.6$
SiO_4 $R=1.7, E=23.87$; $R=1.6, E=25.50$; $R=1.5, E=24.83$

For all groups the calculated distance is close to the observed. It will be noticed that for a CO_4 group the calculated length is somewhat longer than for CO_3. This effect, with a similar order of magnitude to that indicated is observed with the borates where both co-ordination numbers are observed. (Wells 27.)

The calculations discussed above support the ideas of Pitzer (24) and show that extensive π bonding using "*d*" orbitals is not necessary to explain the short Si-O distance. It appears that the state of hydridization and its effect on repulsion energies may play a very important part in determining bond lengths. Thus if the oxygen orbitals in the SiO_4 group were not hybridized, the repulsion energies would be at least doubled.

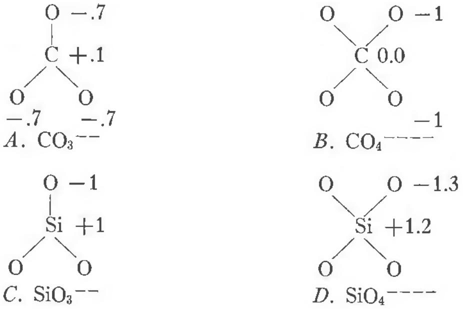
It should be emphasized that only limited conclusions can be drawn from considerations of the grouping alone. For example, the formation of the SiF_6^{--} group is controlled to large extent by the cations associated with it in the structure.

THE EFFECT OF POLARITY ON THE Si-O AND C-O GROUPS

To this stage we have assumed that the formal charges on the anionic groupings are small, i.e., the bonds between the oxygen atoms and metal atoms are sufficiently covalent to drain away the negative charge on the anion. The bond length calculations to some extent justify this conclusion. However, it is well to consider the conditions if these bonds carry charges as if the metal oxygen bonds were fully ionic. To calculate charge distributions in the groupings the electronegativities and relation to the polarity given by the writer (4) may be used. The charge distributions in the anions are summarized in the diagrams below. It is obvious at a glance that structure *B* is much less stable than structure *A* for the

FIG. 1.

CHARGE DISTRIBUTIONS IN C-O
Si-O GROUPINGS.



A. CO_3^{--} *B.* CO_4^{----}

C. SiO_3^{--} *D.* SiO_4^{----}

C-O groupings. However, the SiO_3 grouping is also electrostatically more stable. It will be noticed however, that the four co-ordinated structure is relatively more stable for silicon than carbon. It can be concluded that the inclusion of much smaller amounts of polarity than above could well adjust the additive effect of the covalent and ionic attractions in the correct direction. Covalently, both four co-ordinated members are more stable and conversely if a large amount of polarity is introduced. However, polarity has a larger effect on the C-O groupings than on the Si-O groupings.

VALENCE STATE PROMOTION ENERGIES

If an atom such as aluminum is to enter into six co-ordination and form strong covalent bonds, "*d*" orbitals will have to be used. The use of such orbitals requires considerable energy to promote electrons into the higher states, and such promotion energies must control the ease with which an atom may reach a higher state. Promotion energies can be obtained from spectroscopic data and some typical values are given below from Moore (28). It will be noticed that the relative ease of excitation increases greatly from carbon to silicon to aluminum. These spectroscopic excitation energies are possibly too large as has been emphasized by Gillespie (29) particularly when the atom is bound to an extremely

TABLE 6. EXCITATION ENERGIES OF CARBON, SILICON AND ALUMINUM

Carbon ground state to carbon sp^3 = 9 *e.v.*
Silicon ground state to silicon sp^3 = 6 *e.v.*
Aluminum ground state to aluminum sp^3 = 3.6 *e.v.*
Carbon ground state to carbon "*d*" = 18.6 *e.v.*
Silicon ground state to silicon "*d*" = 11.8 *e.v.*
Aluminum ground state to aluminum "*d*" = 7.5 *e.v.*

electronegative atom such as fluorine. They must, however, provide some indication of the relative ease of promotion. There is some correlation with the observation that carbon is not found in six-co-ordination, silicon only with the most electronegative atoms such as fluorine and aluminum very frequently in six.

EFFECT OF CATIONS ON OXYGEN HYBRIDIZATION

The state of oxygen hybridization might be expected to change with changes in the environment caused by cation distribution. Thus in the forsterite structure, each oxygen as well as being linked to silicon is linked by partially covalent bonds to three magnesium atoms. Thus it is in an almost tetrahedral environment. In such a situation we would expect some change from the *sp* hybrid which has been considered most closely approached in silica. It must be emphasized that all possible hybrids of *s* and *p* electrons are possible between the end members hybrids sp, sp^2 and sp^3. (See Coulson 14.) If in a structure such as forsterite the oxygen hybrids are more nearly sp^3, then the Si-O bonds will be considerably weakened. It would also be expected that as Si-O-Si bonds become important in determining the structure, that is, from isolated groups through chains, bands, sheets to three dimensional frameworks, that the Si-O bonds should increase in strength. The amount of *s* character should increase as Si-O bonding becomes more important. Within any single structural type we would expect that as the cation overlaps more with oxygen, the tendency for rehybridization will increase thus weakening the Si-O bonds. Thus in a series such as Ca_2SiO_4, Mg_2SiO_4, $(MgFe)_2SiO_4$ we would expect to find the strongest Si-O bonds in the calcium member. Similarly in feldspars, we would expect the Si-O bonds in albite to be weaker, although very slightly, than in orthoclase.

Some qualitative agreement with these ideas comes from the infra red studies of Launer (30 See Fig. 13). Here the principal absorbtion bands shift to the short wave length region as Si-O bonding becomes complex and in the orthosilicate series mentioned above the shift to the short wave length region is as expected.

THE ADDITIVITY OF RADII

It appears to the writer that rather too much weight is placed on values of radii in problems concerned with bond distances. The radius of an atom is by no means a constant quantity. Additivity of radii is only to be expected when the atoms are in very similar environments. The simple fact that we must postulate ionic, covalent, metallic and van der Waals radii, and that there is always some doubt as to which to use is sufficient evidence to demonstrate that radii are not constant. It would be expected that in many cases they should be approximately additive, but recent work, particularly from micro wave spectra, has shown that almost always small deviations occur, even in very similar compounds. These anomalous effects are often explained by postulating double bonding, etc., but surely small differences are to be expected, for a slight change in structure may alter repulsion effects very considerably. The striking effects of hybridization which Coulson and others have emphasized may have more influence on radius than change in bond type. Radii, although always a useful guide to the order of bond length can never possibly give us accurate lengths for a wide variety of compounds even although we may evolve more than one set of radii.

APPENDIX

(*a*) Slater atomic orbitals have forms of the type

$$\psi(1s) = N_{1s}e^{-cr}, \qquad \psi(2s) = N_{2s}e^{-cr/2} \text{ etc.}$$
$$\psi(2p) = N_{2p}Xe^{-cr/2}, \qquad \psi(3p) = N_{3p}Xe^{-cr/3} \text{ etc.}$$

The constants N are normalizing factors such that

$$\int \psi^2 dv = 1.$$

The constant c refers to the effective nuclear charge (Z-s) which refers to the atomic number minus the screening constants of the outer electrons which can be evaluated from the recipes of Slater (18). The overlap integral thus is simply the integral of the products of two such Slater functions. Thus $S(ss)$ is the overlap integral for two s orbitals, etc.

Self-consistent-field functions which are considerably more accurate can be expressed as a series of Slater functions and treated by the solutions mentioned earlier (19, 20, 21).

The x terms in the above relations refer to the angular dependence of the functions. The s orbitals being spherically symmetrical possess no such constant. It is of considerable value to have some picture of the electron distribution corresponding to these functions and illustrations of these are supplied by Coulson (14).

(*b*) The normal covalent bond such as occurs in a hydrogen molecule is referred to as a σ bond. The double bond in say ethylene is made of two parts, a normal σ bond and a π bond. The π bond is formed when two adjacent "*p*" orbitals with the same angular dependence (x) overlap. (See Coulson for illustrations.)

A hybrid atomic orbital can always be formed by suitable mixing of the simple types. For example a hybrid *sp* functions can have the form

$$\psi_{hyb.} = a\psi_s + (1 - a^2)^{1/2}\psi_p$$

where the constant "a" determines the contribution of each end member. For tetrahedral, trigonal and digonal hybrids $a^2 = \frac{1}{4}, \frac{1}{3}, \frac{1}{2}$, respectively. A tetrahedral hybrid has four equivalent orbitals directed towards the corners of a regular tetrahedron, a trigonal hybrid has three equivalent orbitals with trigonal symmetry in the one plane and a digonal hybrid has two equivalent orbitals 180° apart. In methane, for example, carbon uses a tetrahedral hybrid, in C_2H_4 ethylene, carbon uses a trigonal hybrid (the remaining unhybridized p orbitals forming the π bonds) and in acetylene carbon uses a digonal hybrid (the two remaining unhybridized p orbitals form two π bonds).

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