2. The formulas FeR, FeR_2 and FeR_3 for the blue, purple and red complexes, respectively, of iron and Tiron have been determined by these methods. These findings have been verified by the method of continuous variations.

3. The new slope ratio method shows the formula $FeCNS^{++}$ for the ferric thiocyanate complex, which agrees with results reported by others.

4. The applicability to these complexes of other spectrophotometric methods for determining formulas has been investigated.. Certain limitations of these methods are discussed.

5. The dissociation constants for the complexes have been determined by spectrophotometric methods.

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[CONTRIBUTION FROM THE PHYSICS DEPARTMENT, UNIVERSITY OF CHICAGO]

Overlap Integrals and Chemical Binding[1]

BY ROBERT S. MULLIKEN

I. Introduction

In their classical papers on the theory of valence, Slater and Pauling proposed the "criterion of maximum overlapping" of the bonding AO's (atomic orbitals) of two atoms for deciding what kinds of AO's should give the strongest bonds.[1a] Pauling[2] concluded that "the energy of a bond is about proportional to the product of the [strengths] of the bond orbitals of the two atoms," with "strength" defined as "the magnitude of the bond orbital in its angular dependence," that is, a number proportional to the value of the angular part of the bond orbital in the direction of the bond.[3,4] This index of bond-forming power has the value 1 for *s–s* bonds, $\sqrt{3}$ for $p\sigma$–$p\sigma$ bonds, and between 1 and 2 for $hy\sigma$–$hy\sigma$ bonds, where *hy* denotes any $s,p\sigma$ hybrid AO, with a maximum value 2 for *te–te* bonds (te = tetrahedral hybrid AO). The index is not defined for π–π bonds.

However, the *overlap integral S*, computed *at the experimental bond distance R* for the two AO's which overlap when a bond is formed, might reasonably be expected to form the basis of an even more satisfactory index of bond energy. This integral takes account of *both the radial and the angular properties* of the two AO's concerned, and *is a direct measure* of the extent of overlap of these AO's. It is defined by

$$S = \int \chi_a \chi_b \, dv \qquad (1)$$

where χ_a and χ_b stand for suitable normalized AO's of the two atoms *a* and *b* concerned. The integral is computed in terms of the coördinates of a single electron, and extends over all space. Its value is a function of the interatomic distance *R* as well as of the nature of the two AO's.

All overlap integrals have values between −1 and +1. The value of any overlap integral is zero for $R = \infty$, but increases as *R* decreases, provided the signs of χ_a and χ_b are suitably chosen. If χ_a and χ_b are *s* valence orbitals of two like atoms, then *S* steadily increases toward a limiting value +1 at $R = 0$ (*cf.* Fig. 1). For the hydrogen molecule at its actual bond distance, $S = 0.75$.

For $p\sigma$–$p\sigma$ bonds, if we choose the signs of χ_a and χ_b to be the same for the overlapping lobes of the two $p\sigma$ orbitals, then as *R* decreases, *S* first rises to a maximum, then falls again as the positive lobe of each orbital more and more overlaps the negative as well as the positive lobe of the other. For two identical atoms, $S = -1$ at $R = 0$, since χ_b then becomes identical with $-\chi_a$.

For the overlap of two like σ orbitals of *s,p hybrid* type, *S* behaves in a manner intermediate between that for *s* and that for $p\sigma$ overlap (*cf.* Fig. 1). For the overlap of π orbitals, *S* is always between 0 and +1, just as for *s* orbitals.

Partly because *S* might prove to be a useful index of bond energy, partly because *S* values are needed in quantum-mechanical computations on molecular electronic structures and spectra, Mrs. C. A. Rieke and the writer some time ago computed *S* values for several cases involving *s* and *p* AO's, supplementing previously existing calculations.[5] Later it was noted that the value of *S* for $p\pi$–$p\pi$ boron–boron bonds is remarkably large, and it was suggested that this might help in explaining the stability of certain boron hydrides.[6] It also seemed possible that a comparative study of overlap integrals in the first and higher rows of the periodic system might throw light on the relative weakness of multiple bonds in the latter.

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[1] This work was assisted by the ONR under Task Order IX of Contract N6ori-20 with the University of Chicago.

[1a] All AO's which have cylindrical symmetry about the bond axis are called σ AO's. This includes $s\sigma$ AO's (*i. e.*, *s* AO's), $p\sigma$AO's (often called *p* orbitals), and the various *s*, *p* hybrid AO's. Single bonds involve a pair of electrons in σ AO's. Double or triple bonds involve the use in addition to a σ pair of, respectively, one or two pairs of electrons in π AO's.

[2] *Cf.* L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939. For Pauling's index of bond strength see p. 78 and L. Pauling and J. Sherman, THIS JOURNAL, **54**, 1450 (1937).

[3] Pauling's index of bond strength involves the explicit assumption that Slater orbitals (including Slater's use of equal *Z* values for *ns* and *np* AO's) are adequate approximations for the AO's.[4]

[4] The effects of using more accurate AO's are discussed in Section III and in ref. 7.

[5] The results for C–C bonds in Table I were presented at a symposium some time ago, but only a descriptive abstract has hither to been published: R. S. Mulliken and C. A. Rieke, *Rev. Mod. Phys.*, **14**, 259 (1942).

[6] R. S. Mulliken, *Chem. Revs.*, **41**, 207 (1947).

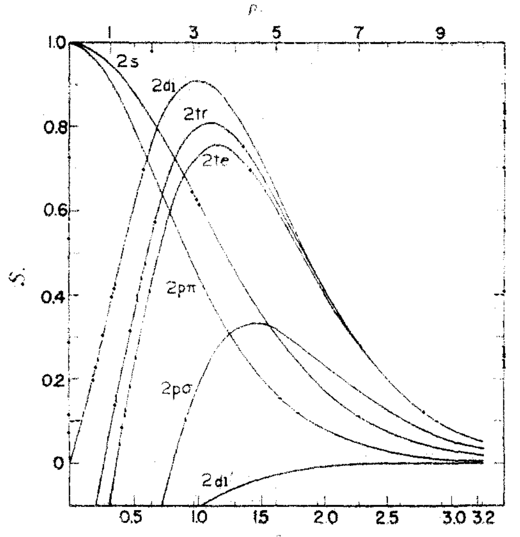

Fig. 1.—Overlap integral S as function of interatomic distance R for two-quantum homopolar bonds (*di*, *tr*, *te* refer to inward-facing digonal, trigonal and tetrahedral orbitals, respectively; *di′* to outward-facing digonal orbital). Lower scale (R_{CC}) is in Å. for C–C bonds. Upper scale is in ρ units (*cf.* Eq. (2)).

Comprehensive computations applicable to both homopolar and heteropolar bonds were undertaken. Resulting master formulas, numerical master tables, and methods of use, for bonds involving ns, $np\sigma$ and $np\pi$ AO's are given in a separate paper.[7] In the present paper, S values obtained for various bonds at their actual bond lengths, by use of the tables of ref. 7, will be discussed in relation to the theory of chemical binding.[8]

For all the computations, simplified AO's of the convenient Zener–Slater type $r^{n^*-1}e^{-Zr/a_Hn^*}Y(\theta,\phi)$ were used.[9,4] S may then be expressed as a function of two parameters ρ and t defined as[7]

$$\left.\begin{array}{l}\rho = {}^1/_2\,(\mu_a + \mu_b)(R/a_H) \\ t = (\mu_a - \mu_b)/(\mu_a + \mu_b) \\ \text{where } \mu \equiv Z/n^*\end{array}\right\} \qquad (2)$$

Here Z and n^* represent *effective* nuclear charges and effective principal quantum numbers for the Slater AO's, and R/a_H denotes internuclear distance in units of the Bohr hydrogen atom radius a_H. As will be seen later, t is a polarity index. The sign of t in Eq. (2) obviously depends on which atom is called a; to decide this, certain specific conventions adopted in ref. 7 will be followed here. For identical AO's, $t = 0$.

For bonds between atoms in the same row of the periodic system, ρ has the following significance (see Eq. (6) for the result). It is easily shown that the radial probability distribution corresponding to any Slater AO reaches its maximum at the radial distance r equal to n^*a_H/μ, *i. e.*, $n^{*2}a_H/Z$. For the valence AO's, this r may be taken as a reasonable theoretical value of the atomic radius for bonding, as was proposed by Slater.[9,10]

Now[11] we may define the *reduced interatomic distance*, ξ, for a bond between any two atoms a and b by

$$\xi = R/(r_a + r_b) \qquad (3)$$

Putting $r = n^*a_H/\mu$, we have in general

$$\xi = (R/a_H)[\mu_a\mu_b/(n^*_a\mu_b + n^*_b\mu_a)] \qquad (4)$$

If $n^*_a = n^*_b = n^*$, this can be reduced to

$$\xi = (1 - t^2)\rho/2n^* \qquad (5)$$

which in the homopolar case becomes

$$\xi = \rho/2n^* \text{ or } \rho = 2n^*\xi \qquad (6)$$

If Slater is right that $r = n^*a_H/Z$ is a good theoretical value for the bonding radius, then, by Eq. (3), ξ values near 1 would be expected for stable bonds at their equilibrium lengths. Variations in ξ should then reflect special features of the bonding (see Table I for some actual values). By Eq. (6), ρ is closely related to ξ, and its significance follows from this relation.

The computations of S values in the preceding paper[7] were made over a wide range of ρ values, for $t = 0$ and usually for several other t values. The primary tables are on overlaps involving pure s, $p\sigma$, or $p\pi$ AO's, but S values involving hybrid AO's are readily obtained from these.[7] In the following, if χ is a hybrid σ AO of the form

$$\chi = \alpha\chi_{ns} + (1 - \alpha^2)^{1/2}\chi_{np\sigma} \qquad (7)$$

the abbreviations *te*, *tr* and *di* (for tetrahedral, trigonal and digonal s,p hybrid AO's) will be used for hybrids with $\alpha^2 = {}^1/_4$, ${}^1/_3$ and ${}^1/_2$, respectively.[12]

Some results from a projected later paper on the use of overlap integrals in interpreting and in estimating bond energies will now be summarized. In that paper, it will be shown using molecular orbital methods[13] that the quantity

$$B = ASI/(1 + S) \qquad (8)$$

may be used as a rough expression for the bond energy, relative to the appropriate atomic "valence states,[14] of

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(7) R. S. Mullliken, C. A. Rieke, D. Orloff and H. Orloff, *J. Chem. Phys.*, **17**, 510 (L); 1248 (1949). The symbol p was used in the latter paper for what is here called ρ.

(8) For a valuable review on "The Interpretation of Bond Properties," see T. L. Cottrell and L. E. Sutton, *Quart. Rev. Chem. Soc.*, **2**, 260 (1947).

(9) J. C. Slater, *Phys. Rev.*, **36**, 57 (1930). Slater's n^* equals n for n = 1, 2 and 3; for n = 4, n^* = 3.7; for n = 5, n^* = 4. Slater's Z for outer-shell electrons is given by $0.65(N - 1)$ for n = 2, by $2.2 + 0.65(N - 11)$ for n = 3, where N is the atomic number.

(10) Atomic radii, together with improved AO's, will be discussed further in a later paper by H. Shull and the writer.

(11) *Cf.* R. S. Mulliken, *Rev. Mod. Phys.*, **4**, 1 (1932), especially pp. 39, 43 and Figs. 43, 44.

(12) For contour-portraits of some hybrid AO's, see W. E. Moffitt and C. A. Coulson, *Phil. Mag.*, **38**, 634 (1947).

(13) The theory of the valence-bond method suggests a relation of the form $B = AS^2I$, but in most cases Eq. (8) gives a better fit.

(14) The importance of properly defined valence states (J. H. Van Vleck, *J. Chem. Phys.*, **2**, 20, 397 (1934); R. S. Mulliken, *ibid.*, **2**, 782 (1934); H. H. Voge, *ibid.*, **4**, 581 (1936); **16**, 984 (1948); etc.) for the theory of bond energies has long been overlooked by many authors. (For example, the tetravalent valence state of carbon is *not* ^5S, but corresponds to a hybrid of this and several other sp^3 atomic states.) For a recent application in the determination of bond energies, see L. Pauling, *Proc. Nat. Acad. Sci.*, **35**, 229 (1949).

any not too polar single bond. "Bond energy" here means the contribution of any bond to the total energy of dissociation of the molecule into atoms in appropriate valence states. In the case of multiple bonds, there is one term of the form (8) for each bonding electron-pair. I is the average ionization energy for the valence AO's. A is assumed to be roughly a constant for any given type of bond; it is found empirically that $A \approx 0.65$ for s–s bonds, $A \approx 1$ for most σ bonds, 1.5 for π bonds.

In case two like atoms forming a bond contain lone-pair electrons in their valence shells, there are additional, negative, contributions to the total bond energy. The effect of the interaction of any two such pairs (*e. g.*, the two $2s^2$ pairs in fluorine) is equivalent to a positive contribution as given by Eq. (8), plus a negative contribution $-ASI/(1 - S)$, or a net contribution for each such pair of like lone pairs, of

$$B_{\text{l.p.}} = -2AS^2I/(1 - S^2) \qquad (9)$$

As will be shown in a later paper, the approximate validity of Eq. (9) can be established also by the atomic orbital (Heitler–London) method, including the case of lone pairs on unlike atoms (here I may be replaced by $\sqrt{I_aI_b}$). This indicates that Eq. (9) should hold for both small and large R values. In addition to the repulsions between lone pairs given by Eq. (9), further non-bonded repulsions exist; these are discussed in Section V.[14a]

Important in the application of Eqs. (8) and (9) is the fact that small amounts of hybridization (mixing of s into pure $p\sigma$, or of $p\sigma$ into pure s) often have large effects on S values. Larger amounts of hybridization then produce relatively small further effects. A separate paper on hybridization effects is in course of preparation.

II. Homopolar Bonds

First-row Atoms.—The behavior of the overlap integral S as a function of interatomic distance R is shown in Fig. 1 for homopolar bonds between first-row atoms. A corresponding figure for second-row overlap integrals would be similar except that the $p\sigma$ overlap would have a higher maximum.

Numerical values of S for various homopolar bonds at their actual equilibrium distances are given in Tables I and II. Pure-AO S values are given, with appropriate hybrid-AO values only in a few cases. Bold-face type is used in Table I to indicate S values for what are usually believed to be the actual bonding orbitals. The matter is

TABLE I

SLATER-AO OVERLAP INTEGRALS FOR HOMOPOLAR BONDS

Bond	R(Å)[a]	ξ[b]	Overlap integrals[c] $s\sigma$	$p\sigma$	$p\pi$	$di\sigma$	$tr\sigma$	$te\sigma$
H—H	0.74B	0.70	**0.75**					
Li—Li	2.67B	0.82	**.59**	0.05[d]	0.55[d]			
B=B	1.52P	0.94	.50	.30	**.33**		**0.80**	
B—B	1.76P	1.08	.40	.33	.24		**.74**	
B⁻—B⁻	1.92M	1.02	.44	.32	.28			**0.73**
C≡C	1.21B	0.93	.51	.29	**.33**	**0.88**		
C=C	1.34E	1.03	.44	.32	**.27**		**.77**	
C—C	1.54E	1.18	.34	.33	.19			**.65**
N≡N	1.095B	1.01	.45	**.32**	**.28**			
N=N	1.24E	1.15	.36	**.33**	**.22**			
N—N	1.47E	1.36	.25	**.29**	.13			
O=O	1.21B	1.30	.28	**.31**	**.15**			
O—O	1.47E	1.58	.16	**.23**	.07			
F—F	1.435E	1.77	.11	**.17**	.05			
Cl—Cl	1.99B	1.28	.21	**.29**	.10			
I—I	2.67B	1.20	.19	**.31**	.10			

[a] The R values are approximate equilibrium distances, obtained as follows. B, band spectra; E, electron diffraction; M, estimate by author; P, from Pauling's bond radii. [b] The ξ values are given by $\rho/2n$ (*cf.* Eq. (6)), where $\rho = (Z/n)(R/a_{\text{H}})$—see Eq. (2)—using Slater's Z values and equilibrium R values.[9] [c] Under the various types of orbitals are listed the corresponding S values, obtained from the tables of ref. 7, for $t = 0$. In cases where hybridization is believed to be especially strong, the S values for the appropriate hybrids are given in the last columns. The values for what are usually believed to be the actual valence orbitals are given in bold-face type. [d] The values for the Li $2p$ AO's are based on an improved Z value (1.04).[4]

TABLE II

SLATER-AO OVERLAP INTEGRALS FOR SECOND-ROW HOMOPOLAR BONDS USING REVISED Z VALUES

Bond	R(Å)[a]	Parameters[b] ξ_s	ξ_p	Overlap integrals[c] $s\sigma$	$p\sigma$	$p\pi$
Na–Na	3.08B	0.87	0.59	0.48	0.03	0.58
Al–Al	2.50M	1.08	.82	.32	.33	.35
Si≡Si	2.04M	1.03	.80	.35	.30	.37
Si=Si	2.14P	1.08	.84	.32	.35	.33
Si—Si	2.32E	1.17	.91	.26	.37	.28
P≡P	1.89B	1.10	.88	.31	.36	.31
P=P	2.00P	1.16	.93	.27	.38	.27
P—P	2.20E	1.28	1.02	.20	.38	.21
S=S	1.89B	1.24	1.00	.23	.38	.22
S—S	2.10E	1.38	1.12	.16	.36	.16
Cl—Cl	1.99B	1.45	1.19	.13	.34	.13

[a] See Table I, note *a*. [b] See Table I, note *b*, except that here improved Z values are used[10]; these are given by: $Z_{3s} = 2.7 + 0.71(N - 11)$, $Z_{3p} = 1.8 + 0.65(N - 11)$, where N is the atomic number. [c] See Table I, note *c*. Using Slater Z values,[9] the following hybrid S values are also obtained: for Al–Al $tr\sigma$, 0.82; for Si≡Si $di\sigma$, 0.88; Si=Si $tr\sigma$, 0.81; Si–Si $te\sigma$, 0.73. With the improved Z's, these values would become somewhat smaller.

(14a) Added April 20, 1950.—Essentially the following *tentative* general formula for the total energy of dissociation D of any molecule (containing not too strongly polar bonds) into its atoms in their ground states, was given by the writer, in a paper on the present work, at the Detroit meeting of the American Chemical Society on April 18

$$D = \sum_{\text{i}} [A_{\text{i}}S_{\text{i}}I_{\text{i}}/(1 + S_{\text{i}})] - \sum_{\text{j}} [A_{\text{i}}S_{\text{i}}^2I_{\text{i}}/(1 - S_{\text{i}}^2)] + RE - \sum_{\text{k}} P_{\text{k}}$$

with $A_s = 0.65$, $A_{p\sigma} = 1$, $A_{p\pi} = 1.5$. The first summation is over all electron-pair bonds. The second is over all non-bonded interactions involving non-bonding electron pairs (lone pairs), with one term for the interaction of each such pair with each other electron (bonding or non-bonding) in the molecule. The last summation is over the "promotion energies" P required to raise the various atoms to their appropriate valence states.[14] The I values are in general geometrical mean values for the appropriate orbitals of the two atoms involved, in their appropriate valence states. The term RE denotes "resonance energy" as computed in the ordinary empirical way on the basis of deviations of empirical dissociation energies from the usual approximate additivity relations for bond energies. Intentionally, terms for non-bonded interactions between bonding electrons have been omitted from the above formula because the writer has reached the tentative conclusion that these are approximately cancelled in polyatomic molecules by certain omnipresent concealed resonance-energy terms; for only in this way does it seem to be possible to understand the additivity of ordinary bond energies. According to this view, the usual "resonance energies" are really not true total resonance energies, but are *excess* resonance energies over and above the omnipresent concealed resonance energies just mentioned.

really somewhat more complicated (see last paragraph of Introduction).

In agreement with Pauling's index of bond strength, S for homopolar bonds has strikingly larger values for all the s,p hybrid bonds than for the pure s or pure $p\sigma$ bonds at equal bond lengths. In sharp contrast to Pauling's index, however, S is larger for s bonds than for $p\sigma$ bonds, except for large ρ values as in O_2 and F_2.[15,16] Again differing from Pauling's index, S is somewhat larger for trigonal and digonal than for tetrahedral homopolar bonds. Notably, $p\pi$ bonds give larger S values than $p\sigma$ bonds at small ρ values such as those for triple bonds; this effect is enhanced when more accurate AO's are used.[4]

The equilibrium-R ξ values in Tables I and II are of considerable interest. As expected, they are close to 1. For bonds of given n and given multiplicity, ξ increases regularly and markedly with increasing Z in both tables. Following is a qualitative explanation. First of all, s bonds are unusually short, as was noted some time ago by Slater.[9] This is evidently because strong overlap for s AO's requires relatively close approach (see Fig. 1). Since s bonds occur at the beginning of a row in the periodic table, ξ for equilibrium is relatively small there. For hybrid σ and still more for $p\sigma$ bonds, favorable overlap occurs at less close approach, hence ξ is larger for boron, carbon and following atoms. It decreases for multiple bonds as expected, since (1) the π components of these give rapidly increasing overlap for decreasing R; (2) non-bonded repulsions present with single bonds are reduced or removed. Beyond the middle of each row, $p\sigma$ bonds become increasingly important and favor large equilibrium ξ values, since S for $p\sigma$ has a maximum for ξ values near 1 (1.1 for $n = 2$, 1.0 for $n = 3$), and decreases if R is too small (see Fig. 1). Another factor favors large ξ, namely, lone-pair electrons (ns^2 in nitrogen and phosphorus and following atoms, plus $np\pi^2$ in oxygen and sulfur, or plus $np\pi^4$ in fluorine and chlorine) cause interatomic repulsions of the type that exists between two helium or two neon atoms. Pitzer[17] has called attention to the existence of these lone-pair repulsions, which he calls "valence-shell repulsions." These repulsions are diminished by an increase of ξ, and equilibrium with the attractions exerted by the bonding electrons is reached at relatively larger ξ, increasing from N–N to O–O to F–F, or from P–P to S–S to Cl–Cl. The general trend of the observed ξ values seems to be accounted for, and the relatively large R values and small dissociation energies[18] for the N–N, O–O and F–F bonds become intelligible.

Second-row Atoms.—There are certain marked differences between the first and second row bonds. The equilibrium values of the reduced interatomic distances ξ for p bonds are nearly all much smaller, and the S values for the p bonding electrons larger, in the second than in the first row. This effect becomes more pronounced toward the right in the row. This is seen to be true not only for single but also (though to a lesser degree) for multiple bonds.

This behavior of the equilibrium ξ values indicates that the preference of second and higher row atoms for single bonds is not the result of *loosening* of multiple bonds for these atoms as compared with the first row atoms, but of a *lesser tightening* for multiple than for single bonds.[19] When bond energies instead of bond lengths are examined, it is noted that these are actually *larger* for the single bonds P–P, S–S and Cl–Cl than for N–N, O–O and F–F.[18] For multiple bonds (S=S, P≡P) the data are unfortunately not very reliable; the available data when roughly corrected to valence state bond energies[14] indicate, relative to I in Eq. (8), about equal bond energies in the two rows.

Can these results on equilibrium ξ values and bond energies be explained in terms of a difference in overlap properties between first-row and higher-row s and p AO's? Tables I and II show that the S values are all much larger for chlorine than fluorine. But this is mainly a result of the much smaller ξ for chlorine, and precisely this is a fact which requires explanation. More suitable for our purpose is a comparison of S values for $n = 2$ and 3 at equal ξ, for ξ values near 1, assuming that S values may then be taken as measures of bond strength (*cf.* Eqs. (8), (9)). This comparison, made in Table III, indicates that s and $p\pi$ bonds (aside from the factor I in Eq. (8)) are *weaker* at any given ξ value for second row than for first row atoms, but that $p\sigma$ bonds are *stronger* for second row atoms for ξ values up to 1.2. (For $\xi > 1.2$, $p\sigma$ bonds like s and $p\pi$ bonds become weaker for second row than for first row atoms.) These effects are in

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(15) A. McColl of University College, London, England (private communication, 1948) has independently noted this same point in computations on S values for $p\pi$, s, $p\sigma$ and hybrid bonds.

(16) The smaller A required for s–s bonds than for σ bonds in Eq. (8) does indicate some tendency toward validity of Pauling's index for s bonds.

(17) K. S. Pitzer, THIS JOURNAL, **70**, 2140 (1948). Pitzer refers specifically only to $np\pi$ lone-pair repulsions, although the S values in Tables I and II now indicate (but see Section III, in particular Table V), that s lone-pair repulsions may often be more important. Repulsions of this type have long been recognized in terms of the assignment of valence electrons in molecules like N_2, O_2, F_2, etc., to anti-bonding as well as to bonding molecular orbitals with the former having a somewhat predominant effect. Equation (9) above is a qualitative formulation of this result.

(18) The recent downward revision of the dissociation energy of fluorine, to about 32 kcal. (H. Schmitz and H. J. Schumacher, *Z. Naturforschung*, **2a**, 359 (1947)) brings this quantity into harmony with the very large ξ of this molecule.

(19) Pitzer,[17] on the basis of qualitative considerations on "inner-shell repulsions," concluded that relative interatomic distances (*i. e.*, essentially ξ values) are larger, hence, bonding overlaps for π electrons smaller, for second-row than for first-row atoms, and in this way sought to explain the apparent weakness of multiple bonds for second-row atoms. The quantitative ξ and S values here obtained for second row atoms appear to be in disagreement with Pitzer's conclusions. Pitzer's suggestion that inner-shell repulsions are important is nevertheless of interest, and will be discussed further in Section IV.

the right direction to explain the observed phenomena, since they imply relatively increased strength of $p\sigma$ bonds for second row atoms (note that $\xi_p \lesssim 1.2$ for all atoms in Table II), aided by decreased strength of lone-pair repulsions (*cf.* Eq. (9)) for atoms beyond silicon.

However, they seem hardly adequate, especially for chlorine where $\xi_p = 1.2$, to explain fully the large bond energies and correspondingly small ξ values of second-row single bonds. It seems fairly certain that another important factor must be present to strengthen the σ bonds for $n = 3$. The most obvious and reasonable interpretation is one making use of $3d$ orbitals; specifically, that the $3p\sigma$ bonds are considerably strengthened by hybridization in which some $3d\sigma$ is admixed into the $3p\sigma$ orbitals.

TABLE III

COMPARISON OF S VALUES FOR FIRST AND SECOND ROW BONDS AT EQUAL ξ

Bond	Values of S at indicated ξ values ξ 0.8	1.0	1.2	1.5
2s–2s	0.60	0.46	0.33	0.19
3s–3s	.53	.38	.25	.11
2pσ–2pσ	.21	.32	.33	.25
3pσ–3pσ	.31	.39	.33	.20
2pπ–2pπ	.43	.29	.18	.09
3pπ–3pπ	.37	.22	.12	.05

Metals.—The magnitudes of overlap integrals are further relevant to an understanding of chemical binding in metals and other solids; for example, to the estimation of band-widths of s and p bands in metals as a function of R. Some S values for a simple example, lithium metal, may be interestingly suggestive. Values are given in Table IV for two interatomic distances, those of nearest neighbors (3.02 Å.), and of next-nearest neighbors (3.51 Å.).[2] For comparison, values for diatomic lithium (2.67 Å.) are also given. It will be seen that s, p and hybrid overlaps are very favorable at all the interatomic distances considered.[19a]

TABLE IV

SLATER-AO OVERLAP INTEGRALS FOR Li–Li OVERLAPS[a]

Distance, Å.	2s–2s	2s–2pσ	2pσ–2pσ	2teσ–2teσ	2pπ–2pπ
2.67	0.59	0.57	0.05	0.68	0.55
3.02	.51	.56	.15	.72	.47
3.51	.40	.51	.26	.80	.38

[a] See Table I, notes *b* and *d*, for Z values used.

III. Limitations of Slater-AO Overlap Integrals

A few words of caution are advisable. Slater AO's, although very useful because of their simplicity, often differ considerably from the most accurate AO's, obtained by the self-consistent field method of Hartree and Fock (SCF AO's).

SCF $2p$ AO's give considerably different values of S than Slater $2p$ AO's, as can be seen from Table V, which is based on a previous paper.[7] On the other hand, H. Shull has found[10] that SCF and Slater $2s$ AO's give overlap integrals which differ only slightly.

TABLE V

SCF (SELF CONSISTENT FIELD) AND SLATER $2p$ OVERLAP INTEGRALS FOR CARBON–CARBON BONDS

Slater ξ	2pσ SCF	 Slater	2pπ SCF	 Slater
0.92	0.14	0.29	0.43	0.34
1.18	.24	.33	.29	.19
1.54	.25	.24	.16	.08
2.14	.16	.08	.06	.016
3.1	.05	.01	.01	.001

It should be kept in mind that for ***normal bond lengths in actual molecules*** (*cf.* Table I), $2p\sigma$–$2p\sigma$ S values are important only in the ξ range 1.1–1.8, $2p\pi$–$2p\pi$ S values only in the ξ range 0.9–1.3. In these ranges, the SCF and Slater S values in Table V do not differ radically, although for $2p\pi$–$2p\pi$ bonds, SCF S values do consistently indicate stronger bonds than do Slater S values. However, if Slater S values are used as a measure of bond energies through Eq. (8), this difference can largely be taken care of by suitable adjustment of the empirical factor A. For σ bonds involving hybrid orbitals, or for mixed σ bonds (*e. g.*, $2s$–$2p\sigma$), SCF and Slater S values differ less than for $2p\sigma$–$2p\sigma$ bonds.

Slater AO's are characterized, (a) by their general form; (b) by the particular values of the parameters Z and n^*. Considerable improvements are sometimes possible by merely revising Slater's Z values; in particular, by using suitable different Z values for ns and np AO's. (Slater uses equal Z values for ns and np in all cases for simplicity.[9]) The possible improvements are mostly not large for first-row atoms,[10] and Slater's Z values have been used in Table I, except for $2p$ of lithium. For second-row atoms a considerable improvement is possible, and improved Z values have therefore been used in obtaining the Slater-type S values in Table II. The resulting S values are compared in the following table with those obtained using Slater's Z values.

COMPARISON OF S VALUES FOR SLATER AND IMPROVED Z VALUES[a]

		sσ	pσ	pπ
Na-Na	Slater	0.61	0.23[b]	0.45
	Improved	.48	.03[b]	.58
Si-Si	Slater	.37	.39	.22
	Improved	.26	.37	.28
S-S	Slater	.24	.33	.12
	Improved	.16	.36	.16

[a] For equilibrium bond lengths. [b] The large difference here is instructive but not really important, since p bonds are not important for Na.

If desired, SCF S values could be worked out and tabulated for all bonds where the forms of the SCF AO's are known.[7,10] However, this may not be worthwhile. SCF AO's are the most accurate AO's for electrons in free atoms, but the best AO's for bonding electrons in stable molecules are known to be very appreciably altered in size (governed by Z) and shape (this latter is partly taken care of by hybridization).

Hence, if due caution is exercised, and not too much importance is attached to the exact value of the second digit, it may be sensible for the present, for ξ values near 1, to use S values based on Slater AO's, or (for $n > 2$) on Slater

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(19a) Recently P.-O. Löwdin (*cf. J. Chem. Phys.*, **18**, 365 (1950)) has made important and extensive computations on interaction energies between closed shells in ionic crystals, showing the essential dependence of these energies on overlap integrals. He has also discussed molecular structure, and is extending this work to the structure of metals.

AO's with improved Z values. It may be well to add that *other indices of bond strength should also be used with similar caution.*[3]

Caution is especially required in cases where there may be a small amount of hybridization, since S values are very sensitive to this (see last paragraph of Introduction). However, for *te–te*, *tr–tr*, *di–di* and similar strong hybrid bonds at or near their normal bond lengths, S does not depend sensitively on degree of hybridization or on whether Slater or SCF AO's are used.

In the estimation of interactions between closed shells at large ξ values as in Section V, S values based on SCF AO's *must* be used, at least for outer electron shells. The difference between Slater and SCF AO's becomes very important for outer electron np AO's at large ξ values (*cf.* Table V), but fortunately can probably be neglected[10] for ns AO's.

IV. Heteropolar Bonds

In heteropolar bonds of moderate polarity, one expects to find relations similar to those in homopolar bonds. This expectation is confirmed by Tables VI–VIII.

TABLE VI

SLATER-AO OVERLAP INTEGRALS FOR FIRST ROW HETEROPOLAR BONDS

Bond	R, Å.[a]	Parameters[b] ρ	t	ξ	Overlap integrals[c] $s\sigma$	$p\sigma$	$p\pi$	di–$p\sigma$	tr–$p\sigma$	te–$p\sigma$	$p\sigma$–$s\sigma$
B—N	1.58P	4.86	0.20	1.17	0.33	0.29	0.17		0.39		0.42
B—F	1.30E	4.80	.33	1.07	.33	.23	.17		.31		.45
$C^-{\equiv}N^+$	1.17E	3.96	.19	0.95	.45	.28	.28	0.43			.53
C≡N	1.16E	3.92	.09	0.97	.47	.31	.30	.50			.50
C=N	1.28P	4.33	.09	1.07	.40	.32	.24		.47		.45
C—N	1.47E	4.96	.09	1.23	.31	.31	.17			.43	.36
C=O	1.22B	4.50	.17	1.10	.37	.30	.23		.43		.46
C—O	1.43E	5.27	.17	1.28	.27	.28	.14			.37	.36
C^+—O^-	1.40M	5.16	.08	1.28	.28	.30	.15		.42		.34
C—F	1.36E	5.41	.23	1.28	.26	.26	.13			.33	.36
$N{\equiv}O^+$	1.01M	4.20	.11	1.04	.42	.31	.25				
N=O	1.18P	4.70	.08	1.17	.35	.32	.19				
N—O	1.43E	5.69	.08	1.41	.22	.27	.11				
N—F	1.37E	5.90	.14	1.45	.20	.25	.10				
O—F	1.41E	6.50	.07	1.61	.15	.21	.06				

[a] See Table I, note *a*. [b] See Eqs. (2), (5); see text following Eq. (2) regarding the sign of t. Slater Z values[9] are used here. [c] *Cf.* Table I, note *c*. In the last columns, a designation such as, for example, *tr–pσ* refers to the S value for a *trσ* AO of the first-named atom (*e. g.*, B in B–N) overlapping a $p\sigma$ AO of the second. (Note that in using the tables of ref. 7, the order of the symbols must in some cases be reversed; *e. g.*, the $p\sigma$–$s\sigma$ figures above are obtained from the $2s$–$2p\sigma$ section of Table IX of ref. 7.)

TABLE VII

SLATER-AO OVERLAP INTEGRALS FOR MIXED FIRST-SECOND ROW BONDS

Bond	R, Å.[a,b]	Parameters[b,c] ρ_s	t_s	ρ_p	t_p	ξ_s	ξ_p	Overlap integrals[b,d] $s\sigma$	$p\sigma$	$p\pi$	$p\sigma$–$s\sigma$	$s\sigma$–$p\sigma$
Si—C	1.89E	5.77	0.01	5.14	0.13	1.16	0.99	0.30	0.28	0.21	0.49	0.28
Si=O	1.51B	5.55	.17	5.04	.29	1.04	0.87	.32	.17	.18	.50	.23
Si—O	1.64E	6.02	.17	5.46	.29	1.16	0.95	.27	.18	.16	.46	.20
Si—F	1.54E	6.13	.24	5.61	.35	1.10	0.92	.26	.15	.14	.44	.16
C—P	1.87E	6.13	−.06	5.47	.05	1.24	1.08	.26	.32	.18	.29	.43
P≡N	1.49B	5.34	.03	4.82	.14	1.06	0.91	.35	.26	.24	.55	.30
P—N	(1.80P)	(6.45)	.03	(5.81)	.14	(1.28)	(1.10)	(.23)	(.27)	(.15)	(.41)	(.23)
P—O	1.64E	6.38	.11	5.81	.22	1.23	1.06	.24	.23	.14	.42	.20
P—F	1.54B	6.48	.17	5.93	.28	1.22	1.04	.23	.20	.13	.41	.17
C=S	1.53B	5.37	−.12	4.80	−.02	1.09	0.96	.36	.33	.26	.38	.49
C—S	1.82E	6.38	−.12	5.70	−.02	1.29	1.14	.24	.33	.17	.29	.39
S=O	1.49B	6.13	.05	5.58	.15	1.21	1.06	.26	.27	.17		
S—O	(1.70P)	(6.99)	.05	(6.36)	.15	(1.38)	(1.21)	(.18)	(.25)	(.11)		
S—F	(1.68P)	(7.45)	.11	(6.82)	.21	(1.44)	(1.25)	(.15)	(.22)	(.09)		
Cl—O	1.68E	7.28	−.01	6.63	.09	1.46	1.29	.16	.26	.10		
Cl—F	1.64E	7.61	.06	6.98	.16	1.50	1.32	.14	.22	.08		

[a] See Table I, Note *a*. [b] Quantities based on Pauling–Huggins bond radii are given in parentheses, since they fall out of line with those based on experimental bond lengths. [c] See Eqs. (2), (4); see text following Eq. (5) regarding the sign of t. Slater Z values are used here for the first-row atoms, improved Z values (*cf.* Table II, note *b*) for the second-row atoms. Because $Z(3s)$ is different from $Z(3p)$, the resulting values of ρ, t and ξ also differ for $3s$ and $3p$ AO's of the second-row atom. [d] See Table VI, note *c*. The following additional S values are of interest: *teσ* for Si–C, 0.62; *te–pσ* for Si–F, 0.21; *te–pσ* for C–P, 0.49.

TABLE VIII

REDUCED INTERATOMIC DISTANCES ξ AND POLARITY[a]

Bond b—a	ξ	$-\Delta\xi$	t	$x_a - x_b$	Bond b—a	$\bar{\xi}$	$-\Delta\xi$	t	$x_a - x_b$
C≡N	0.97	0.00	0.09		Si=O	(1.09)	0.19	0.27	
C=N	1.09	.02	.09		Si—O	1.27	.27	.26	1.7
C—N	1.27	.04	.09	0.5	P—O	1.30	.23	.22	1.4
					S=O	1.15	.09	.15	1.0
C=O	1.17	.07	.17						(S—O)
C—O	1.38	.10	.17	1.0	Cl—O	1.38	.09	.09	0.5
					Si—F	1.37	.41	.32	2.2
C—F	1.48	.20	.23	1.5	P—F	1.40	.36	.28	1.9
N—F	1.57	.12	.14	1.0	Cl—F	1.48	.17	.16	1.0
N=O	1.22	.05	.08						
N—O	1.47	.06	.08	0.5	Li—H	0.76	.02	+ .21	+1.1
O—F	1.67	.06	.07	.5	C—H	0.94	.03	− .24	−0.4
					N—H	1.03	.09	− .32	−0.9
Si—C	1.08	.05	.10	.7	O—H	1.14	.18	− .39	−1.4
P—C	1.10	.02	.05	.4	F—H	1.23	.25	− .44	−1.9
S=C	1.01	.05	− .02		Na—H	0.79	− .03	+ .05	+1.2
S—C	1.15	.01	− .02	.0	S—H	0.91	− .01	− .26	−0.4
P≡N	0.95	.04	.14	.9	Cl—H	0.95	.02	− .31	−0.9
				(P—N)					

[a] For a bond b–a, $\bar{\xi}$ is the average of ξ(a–a) and ξ(b–b) from Tables I and II; $\Delta\xi$ is ξ(b–a) − $\bar{\xi}$, with ξ(b–a) from Tables VI, VII, IX. For $x_a - x_b$ (electronegativity differences) and R values, see ref. 21 (also ref. 17 for P–O). For the labeling of the atoms as a or b, and the signs of the t values, see text following Eq. (2). Only cases where $R(b\text{–}a)$ values are known experimentally are included above.

Heteropolar bonds are characterized not only by a parameter ρ or ξ, but also by a polarity index t (*cf.* Eq. (2)). By a direct comparison (*cf.* Table VIII), it is found that t values for bonds involving first and second row atoms are very closely proportional to electronegativity differences on the Pauling scale.[20] For hydrides the agreements are only qualitative.

First and Second Row Atoms.—A comparison between Tables I and VI shows that, when t is not too large, S values for mixed bonds involving only first row atoms are approximately the means of those of related homopolar bonds. Typical comparisons which the reader may find instructive are: C≡C, C≡N, N≡N; C=C, C=N, N=N; C—C, C—N, N—N. Others are C=C, C=O, O=O; C—C, C—O, O—O.

For mixed bonds involving both first and second row atoms (Table VII), the S values in most cases where t is small show a similar behavior, except that $S(2p\sigma, 3p\sigma)$ falls below the average of $S(2p\sigma, 2p\sigma)$ and $S(3p\sigma, 3p\sigma)$. Examples are: C=C, C=S, S=S; O=O, S=O, S=S; O=O, Si=O, Si=Si; N≡N, P≡N, P≡P.

From Table VI, it will be seen that the presence or absence of formal charges has *per se* only a small effect on the S values.

Any theory of bond energies for heteropolar bonds is necessarily more complicated than that for homopolar ones. If the polarity is not too great, S may still be taken as a rough index of the strength of the *covalent part* of the bonding. In certain highly polar bonds (notably, B-F, C-F, Si-F) the S values are still high in spite of strong polarity, considerably *larger* than the averages of the corresponding homopolar values. This, however, is because the R, hence ξ, values, are considerably smaller than the averages of the corresponding homopolar-bond values. If the ξ values had been equal to the averages mentioned, the S values would have been considerably *smaller* than the averages of the corresponding homopolar S values, though still large.

Bonds such as Si-O, P-O and P-F also are abnormally short. The small R values for heteropolar bonds formed by nitrogen, oxygen and especially fluorine atoms have been variously explained by different authors; a recent explanation proposed by Pitzer[17] will be considered in Section IV. Partial double-bond formation, of course, is partly responsible,[2] especially in B-F (many or most bonds formed by boron, except normal B-H bonds, are considerably shortened by conjugation or hyperconjugation[2,6]), but seems inadequate to explain the entire effect. That the effect is closely correlated with polarity as indicated by electronegativity differences has been shown by Schomaker and Stevenson.[21,22] Exactly the same correlation is found with t values (see Table VIII, omitting the hydrides). Table VIII shows that polarity shortenings are smaller for multiple than for single bonds with equal t values.[22,23]

Hydrides.—Bonds of the type A–H (see Table IX and Fig. 2) form an important special

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[20] For bonds formed by second row atoms, there are different t and ξ values according as s or p or hybrid valence is assumed. The above statement is based on assuming the usual types of valence.

[21] V. Schomaker and D. P. Stevenson, THIS JOURNAL, **63**, 37 (1941). The use of ξ values here rather than R values as by Schomaker and Stevenson makes no great difference, but perhaps represents a slight improvement.

[22] For critical discussion and further references, see ref. 8, pp. 270–274.

[23] See also W. Gordy, *J. Chem. Phys.*, **15**, 81 (1947).

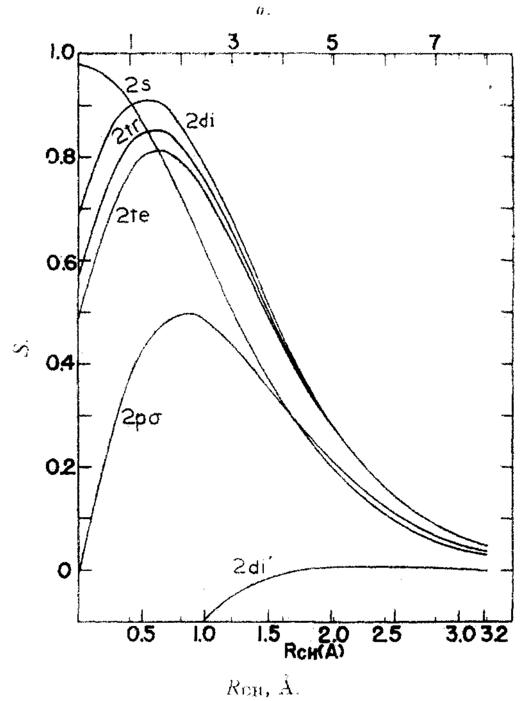

Fig. 2.—Overlap integral S as function of interatomic distance R for A–H bonds formed by first row atoms (*di*, *tr*, *te* refer to inward-facing digonal, trigonal and tetrahedral A atom orbitals, respectively; *di'* to outward-facing A atom digonal orbital). Lower scale (R_{CH}) is in Å. for C–H bonds. Upper scale is in ρ units, where $\rho = {}^1/_2(1 + {}^1/_2Z)\ (R/a_H)$, Z = Slater Z value of A atom. The figure is drawn for the case $l = -0.24$ as in CH.

class. As for other heteropolar bonds, S probably is a good index of the covalent bond strength, but polarity adds considerably to the strength in many cases. No doubt because of the strong overlapping ability of the 1*s* AO (*cf.* H_2 in Table I), all hydride bonds, whether formed by *s* or $p\sigma$ A atom AO's, show fairly large S values. Hybrid σ overlaps are stronger than either pure *s* or pure $p\sigma$ overlaps, but their advantage is much smaller than when both atoms have $n > 1$.

As Penney, Pauling and others have pointed out, the C–H bond is probably different depending on whether the other bonds to the carbon atom are single, double or triple.[24] Presumably the carbon atom uses a tetrahedral, trigonal or digonal orbital, respectively, in these three cases. As judged by the S values, this should lead to increasingly strong C–H bonds (but only moderately so) in the order named (see Fig. 2 and Table IX). Increasing negative character of the carbon atom is also predicted in the same order, because, as the author has pointed out,[14] electronegativity should increase with increasing *s* character in the carbon orbital. This prediction seems to be supported experimentally by the acidity of acetylene (see also ref. 24).

The last three columns of Table IX show S values for the overlap of a hydrogen atom $2p\pi$ AO with A atom $np\pi$ AO's ($n \geqslant 2$). The large S values suggest that π–π bonding of the type indicated may make an appreciable contribution to the wave function in favorable cases.[25] The effect might be classed as a kind of hyperconjugation in which idle lone pairs of π electrons on an A atom (*e. g.*, the chlorine $p\pi$ electrons in hydrogen chloride or the lone p_z pair in hydrogen sulfide or water) are partially shared by hydrogen atoms to give weak π bonding.

In terms of valence bond structures, this would mean resonance with certain excited structures. Consider hydrogen chloride as an example. For the chlorine atom the usual valence state for covalent binding is of configuration . . . $3p\sigma 3p\pi^4$, the bond being formed by the $3p\sigma$ AO with the 1*s* hydrogen atom AO. The principal resonance structure in the suggested π bonding is probably that with chlorine in the configuration . . . $3p\sigma^2 3p\pi^3$ and the hydrogen atom in its excited $2p\pi$ state, with a single π bond between one $3p\pi$ AO and the $2p\pi$ AO.[26]

There is supporting evidence from molecular spectra. Namely, when a π electron is removed from CH, OH, HCl or HBr, increases of R of 0.011, 0.058, 0.040 and 0.045 Å., respectively, are observed. In general, internuclear distances in molecular spectra are found to increase on excitation or removal of bonding electrons. Hence the above data tend to indicate that the π electrons in these molecules are weakly A–H bonding.[27] The type of weak hyperconjugation just discussed should occur in many hydrogen-containing molecules; for example, in acetylene and hydrogen cyanide, where no π hyperconjugation of the usual sort is possible, and in ethylene.

V. Interactions Between Closed Shells[19a]

Van der Waals Repulsions.—Overlap integrals in connection with Eq. (9) should be useful in estimating van der Waals repulsions between closed shells of like atoms, assuming that these repulsions are essentially due to valence (exchange) forces.[28,29] Here Slater-AO S values may be used if only *s* shells interact, but SCF-AO values are needed if *p* shells are involved (*cf.* last paragraph of Section III). For the case of two helium atoms, values of the repulsion energy computed from Eq. (9) using Slater-AO S values, and assuming A = 0.65, are found to agree rather well (*cf.*

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(24) *Cf.* C. A. Coulson, *Quart. Rev. Chem. Soc.*, **1**, 144 (1947), and p. 15 of Victor Henri commemorative volume "Contribution à l'Étude de la Structure Moléculaire," Desoer, Liège, 1948. See also, Discussions of the Faraday Soc., No. 2, 1947, The Labile Molecule: A. D. Walsh, p. 18, and discussions pp. 63–66. Further, ref. 8, pp. 261–263, and 275.

(25) Note that I in Eq. (8), which should here be taken as some sort of a mean for $2p\pi$ of hydrogen and $np\pi$ of the other atom, is smaller than for normal bonds. This would make the π–π bonds weaker than the large S values alone would indicate.

(26) Another resonance structure $H^-(1s2p\pi)$ $Cl^+(\ldots 3p\sigma 3p\pi^4)$ with a double bond between the H^- and Cl^+ may also be important.

(27) R. S. Mulliken, *Phys. Rev.*, **61**, 281 (1942); see Eq. (5).

(28) From theoretical work of Slater using SCF AO's, plus a second-order correction by Margenau using Slater AO's, the exchange repulsion energy between two helium atoms (here re-expressed in ev.) is $E = 484e^{-2.43R/a_H} - 352e^{-2.82R/a_H}$. This probably represents a rather good approximation in the range R/a_H = 2 to 4. The computed energy for R/a_H = 2 agrees well with that obtained empirically, but at smaller distances the agreement is considerably improved by adding another negative term (see I. Amdur, *J. Chem. Phys.*, **17**, 844 (1949)). At large R values, small van der Waals attraction terms must be added, but the theoretical formulas for these are invalid at smaller R values, where they give impossibly large attractive energies.

(29) For a valuable discussion of van der Waals potential energy curves, see T. L. Hill, *ibid.*, **16**, 399 (1948).

TABLE IX

SLATER-AO OVERLAP INTEGRALS FOR H–A BONDS[a]

		1s–nxσ Bonds						2pπ–npπ Bonds		
						S values				
Bond	R, Å[b].	ρ	t	ξ	1s–ns	1s–npσ	1s–nteσ	ρ	t	S
Li–H	1.60B	$2.49s$ $2.30p$	$+0.21s$ $+ .32p$	$0.74s$ $.62p$	0.48	0.50	0.64 (diσ)	1.54	+0.02	0.80
B–H	1.18P	2.56	− .13	.88	.59	.53	.76	2.01	− .44	.42
≡C–H	1.06B	2.62	− .24	.90	.59	.47	.75 (diσ)	2.31	− .53	.33
=C–H	1.07B	2.65	− .24	.91	.58	.47	.72 (trσ)	2.15	− .53	.33
—C–H	1.09B	2.70	− .24	.92	.57	.47	.69	2.19	− .53	.32
N–H	1.01B	2.82	− .32	.94	.54	.41	.62	2.35	− .59	.26
O–H	0.96B	2.98	− .39	.96	.51	.35	.55	2.52	− .64	.19
F–H	0.92B	3.13	− .44	.98	.47	.30	.49	2.70	− .68	.15
Na–H	1.89B	$3.38s$ $2.88p$	$+ .05s$ $+ .25p$	$.82s$ $.60p$	.42	.44	.59	1.97	− .09	.77
S–H	1.35B	$3.93s$ $3.43p$	$- .35s$ $- .26p$	$1.04s$ $0.92p$	.45	.52	.68	2.79	− .54	.41
Cl–H	1.27B	$3.98s$ $3.48p$	$- .40s$ $- .31p$	$1.05s$ $0.93p$	.45	.49	.65	2.89	− .58	.35
I–H	1.60B	4.39	− .31	0.97	.47	.50	.66	3.64	− .58	

[a] *Cf.* Table VII, note *c*, and Table I, noted *d*. For iodine in HI, Slater's Z was used. [b] See Table I, note *a*.

Table X) with values obtained from a theoretical equation of Slater and Margenau.[28] Thus it seems likely that Eq. (9) may be suitable in general for estimating van der Waals repulsions of rare gas atom pairs. For the heavier rare gases, *ns*, *npσ* and *npπ* AO's are all involved, so that SCF S values should be used.

TABLE X

VAN DER WAALS REPULSION ENERGY BETWEEN TWO HELIUM ATOMS[a]

R/a_H	2	2.5	3	3.5	4	5
S	0.275	0.161	0.091	0.049	0.026	0.0075
$2AS^2I/(1 - S^2)$ with A = 0.65	2.61	.85	.27	.077	.021	.0018
Slater–Margenau E	2.38	.81	.26	.080	.025	.0023

[a] Energies are in ev. For E formulas see Eq. (9) and ref. 28. I = 24.58 for the helium atom.

Overlap integrals may also prove useful in estimating van der Waals repulsions between non-bonded atoms in molecules,[29,30] for example, between hydrogen atoms in H_2O, NH_3, CH_4, C_2H_4, C_2H_6, etc. It is therefore of interest that the overlaps between such non-bonded hydrogen atoms have surprisingly large values (see Table XI).

The interaction between two like lone pairs one on each of two like atoms involves four individual electron–electron interactions, the energy for each of which is then one-fourth that given by Eq. (9). The non-bonded repulsion between two electron-pair bonds is quantum-mechanically similar to that of two lone pairs. It is reasonable to expect the non-bonded repulsion between two hydrogen atom electrons, each of which forms half of an electron-pair bond, to be given by Eq. (9), times a factor 0.25. To test this idea, values of $^1/_2AS^2I/(1 - S^2)$ with A set equal to 0.65 have been computed for the H–H non-bonded pairs in Table XI and are given there in the last column.[30] The values obtained are of a reasonable magnitude. (There are also electrostatic H–H repulsions, because of the polarity of AH bonds; these probably are usually smaller than the non-bonded repulsions.) For non-bonded atoms other than hydrogen, similar considerations apply, except that SCF AO's should be used.

TABLE XI

OVERLAP OF NON-BONDED HYDROGEN ATOMS

Compound	R_{HH}, Å.	$S_{1s,1s}$	$^1/_2AS^2I/(1 - S^2)$[a] with A = 0.65
H_2O	1.51	0.38	0.75 ev.
CH_4, C_2H_6	1.78	.28	.36
C_2H_6 (opposed)	2.31	.15	.12
C_2H_4	1.84	.26	.32
	2.42	.13	.07
C_6H_6	2.46	.12	.07

[a] Energies in ev.; I = 13.60 ev.

From infrared spectra, there is evidence[30a] that H–H non-bonded repulsions actually are practically nil at least in molecules AH_n, but that H–X and X–X non-bonded repulsions (X = halogen) are of expected magnitude. To explain this, one may postulate that the H–H repulsions are approximately cancelled by (unexpectedly strong) resonance between normal valence structures and H–H bonded structures.

Inner Shell–Inner Shell Interactions.—The possibility that repulsions between inner shells may play a part in determining bond energies and lengths was tested by obtaining the following overlap integrals: 1s–1s for Li–Li, C≡C and F–F; 2s–2s, 2s–2pσ and 2pπ–2pπ for Na–Na, Si=Si and Cl–Cl. S was found to be negligibly small (0.000) in all.

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(30) In this connection, see Pauling's book,[3] Section 24. Of especial interest are his remarks on the distortion of AO's by binding (which should lead to decreased S values and energies in Table XI), and his statement that non-bonded atomic radii are about 0.5 Å. shorter than ordinary van der Waals radii. On the latter see also A. L. G. Rees, *J. Chem. Phys.*, **16**, 995 (1948).

(30a) T. Simanouti, *J. Chem. Phys.*, **17**, 245, 734, 848 (1949); D. F. Heath and J. W. Linnett, *ibid.*, **18**, 147 (1950).

It is pertinent to determine the interatomic distance required for a specified value, say 0.01, for S. For the $1s$–$1s$ overlap in Li_2, this is R = 1.57 Å., whereas the equilibrium bond length is 2.67 Å. For Na_2, with bond length 3.08 Å., using Slater AO's, it is R = 1.66, 1.75 and 1.42 Å. for $2s$–$2s$, $2s$–$2p\sigma$ and $2p\pi$–$2p\pi$ overlaps, respectively. For Si=Si (bond length 2.14 Å.) it is R = 1.15, 1.22 and 0.98 Å. for $2s$–$2s$, $2s$–$2p\sigma$ and $2p\pi$–$2p\pi$, respectively.

Referring to Eq. (9), it seems clear that inner shell–inner shell repulsions at actual bond lengths in homopolar molecules must be completely negligible. The same conclusion holds also for inner shells in metals.

Inner Shell–Outer Shell Interactions.—As was mentioned in Section II, Pitzer[17] has postulated that non-bonded repulsions ("inner shell repulsions") between valence electrons of one atom and inner shells of its partner play an important part in the equilibrium and stability of bonds formed by second and higher row atoms. Quantum-mechanically, such interatomic outer shell–inner shell exchange forces must exist, and it seems probable that they are repulsive with energies proportional to S^2, as in Eq. (9).

For this reason, values of S using Slater AO's have been obtained for some sample cases, and are recorded in Table XII. While Slater forms may be fairly adequate for inner shell AO's, SCF forms should probably be used for outer shell p AO's in any careful computation of inner shell–outer shell or outer shell–outer shell overlaps, and would probably give larger S values. Hence the S values in the present subsection may be of qualitative significance only.

It is seen that between the last inner shell of one atom and the valence shell of another, the overlaps, though small, are not always negligible. It is of interest to see what repulsive energies are predicted by Eq. (9) with A = 1, taking I as the geometric mean between the I's of the two AO's involved. Then for C≡C, we have to consider interactions of the type $1s^2$–$2di\sigma$ between $1s^2$ of either atom and the $2di\sigma$ electron on the other—a total of four individual $1s$–$2di\sigma$ interactions, equivalent to a single pair–pair interaction of the type given by Eq. (9). (The $1s^2$–$2di'\sigma$ and $1s^2$–$2p\pi$ interactions—see Note b of Table XII—may be dismissed because of the respectively small and zero values of S^2.)[30b] Taking $I(1s)$ as 440 and $I(2di\sigma)$ as 16 ev., the geometric mean I is 84 ev., and the repulsion energy using Eq. (9) with A = 1 is 2.4 ev. In a similar way for Si≡Si, with a mean I of about 60 ev., and summing over the two sets of relevant interaction terms, of the types $2s$–$3di\sigma$($S \cong$ 0.1) and $2p\sigma$–$3di\sigma$($S \cong$ 0.04), Eq. (9) gives a total of 1.3 ev. These results suggest (a) that the repulsions postulated by Pitzer may be of considerable importance, but (b) that contrary to Pitzer's assumptions they are not larger for second row than for first row atoms. More thorough study is required.

If interatomic inner shell–outer shell non-bonded interactions are important, we should also consider *all* outer shell–outer shell non-bonded interactions, of which only inter-lone-pair interactions have been examined. The additional non-zero interactions of this type not yet considered are those between s^2 lone pairs and $p\sigma$ (or sometimes hybrid σ) bonding electrons. Some of the relevant s–$p\sigma$ overlaps are given for several heteropolar examples in Tables VI and VII, and are seen to be large. However, the I values are smaller than for inner shell–outer shell interactions, so that the corresponding repulsion energies computed using Eq. (9) are again in the range 1–4 ev. Similar relations exist also in the homopolar cases and also for $2s_A$–$1s_H$ interactions in the hydrides A–H (*cf.* Table IX for the $1s$–$2s$ hydride overlaps).

TABLE XII

SLATER-AO INNER SHELL–OUTER SHELL OVERLAP INTEGRALS

Bond[a]	ρ	t	Overlap integrals[b] $1s$–$2s$	$1s$–$2p\sigma$	$1s$–$2di\sigma$	$1s$–$2di'\sigma$
Li—Li	8.45	0.61	0.067			
C≡C	8.40	.56	.064	0.105	0.119	−0.029
F—F	15.38	.54	.006	.010	.011	− .003

Bond[a]	ρ	t	$2s$–$3s$	$2s$–$3p\sigma$	$2p\sigma$–$3s$	$2p\sigma$–$3p\sigma$	$2p\pi$–$3p\pi$
Na—Na	12.11	0.65	0.08		0.02		
Si≡Si	12.78	.56	.04	(0.1)	(.01)	(0.04)	(0.01)
Cl—Cl	15.9	.52	(.01)	(.02)	(.00)	(.01)	.00

[a] The overlap integrals are for each bond at its normal length. [b] Each integral is computed for the overlap of the first named AO on one atom with the second named AO on the other atom. The AO $2di'\sigma$ is exactly like $2di\sigma$ except that it faces outwards instead of inwards. Certain overlap integrals not listed, namely, those between (s or p)σ and $p\pi$ AO's, are zero by symmetry. AO's with unimproved Slater Z values were used above. The S values in parentheses are very rough.

It is believed that the foregoing considerations are relevant to Pitzer's discussion[17] of bond lengths in abnormally short bonds like P–O. By pictorial considerations, Pitzer makes it plausible that both inner shell–outer shell and outer shell–outer shell non-bonded repulsions should be smaller for P–O at comparable bond lengths (that is, perhaps, at a ξ value half-way between those for P–P and O–O) than for P–P or O–O bonds because of the relative sizes and shapes of the AO's, thus explaining the abnormal shortness of the actual P–O bond. Relevant overlaps are given in Table XIII. This should be compared with data for O–O, P–P and N–O in Tables I, II, VI, XII, noting that P–P should fall near Cl–Cl in Table XII. The comparison indicates that, for P–O at its actual bond length (ξ_p = 1.06), the overlaps are almost equal to the averages of corresponding values for O–O and P–P at their actual bond lengths (ξ = 1.58 and ξ_p = 1.02, respectively). This seems to be in general agreement with Pitzer's suggestions, except that there is no indication that

TABLE XIII

SOME OVERLAP INTEGRALS FOR P–O[a]

Inner–Outer				
$2s_P$–$2s_O$	$2s_P$–$2p\sigma_O$	$2p\sigma_P$–$2s_O$	$2p\sigma_P$–$2p\sigma_O$	$2p\pi_P$–$2p\pi_O$
0.017	0.029	0.013	0.022	0.004
Outer–Outer				
$3s_P$–$2s_O$	$3s_P$–$2p\sigma_O$	$2p\sigma_P$–$2s_O$	$3p\sigma_P$–$2p\sigma_O$	$3p\pi_P$–$2p\pi_O$
0.24	0.20	0.42	0.23	0.14

[a] Computed for the actual bond length 1.64 Å. found in P_4O_6,[17] using improved Z values for $3s$ and $3p$ of the phosphorus atom, otherwise Slater Z values.

(30b) However, in such cases, small *attractive* exchange interactions, not related to S, are predicted by quantum theory.

outer shell–outer shell non-bonding overlaps are unimportant.

Ionic Binding.—In extreme heteropolar cases, distinctly different situations arise than for homopolar bonds. As an example, consider the diatomic sodium fluoride molecule. For the ionic structure Na^+F^-, the only important overlap is between the outer, two-quantum, shells of Na^+ and of F^-. The main interactions of these should be the $1/R$ Coulomb attraction, a van der Waals exchange repulsion, a polarization attraction, and a presumably small penetration attraction or repulsion. Although the interatomic distance is not known experimentally, it may perhaps be estimated from a formula of Schomaker and Stevenson[21] as 1.98 Å. The Slater AO overlap integrals are then found to be

AO's	2*s*–2*s*	2*s*–2*p*σ (Na^+)(F^-)	2*p*σ–2*s* (Na^+)(F^-)	2*p*σ–2*p*σ	2*p*π–2*p*π
S	0.012	0.019	0.014	0.021	0.004

These overlaps are not large enough to account for much repulsion (about 0.03 ev. if Eq. (9) with a suitable mean *I* should hold). However, with SCF AO's the overlaps are much larger, and might give as much as 0.2–0.3 ev. repulsion energy. Since even these values are probably too small to correspond to sufficient exchange repulsion to set up equilibrium with the attractive forces, the overlap calculations indicate that the true interatomic distance in Na^+F^- may be less than 1.98 Å.[31,32]

Computations for the covalent structure Na–F, even though this does not represent the actual molecule, are instructive. The Slater AO overlaps, again computed for 1.98 Å., using improved *Z* values (see Table II, note *b*) for the sodium 3*s* and 3*p* AO's are

AO's	3*s*–2*p*σ	3*di*-2*p*σ	3*p*π–2*p*π	3*s*–2*s*	3*p*σ–2*p*σ
S	0.054	0.042	0.064	0.21	.005

According to usual ideas, the bond in covalent Na–F would be formed by a 2*p*σ fluorine AO with a sodium 3*s* AO. It is seen that the overlaps either for this or for other possible bond types are small, indicating that a pure covalent bond if it existed would be weak.

In this connection, the ultraviolet absorption spectra of the diatomic alkali halides are of some interest.[33] These spectra show for all these molecules the existence of a series of weakly bound or weakly repulsive excited states. Among the lowest of such excited states for sodium fluoride should be those corresponding to weak 3*s*–2*p*σ and to weak 3*p*π–2*p*π covalent bonding.

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Summary

1. Computed values of Slater-orbital overlap integrals for single and multiple bonds of first and second row atoms with one another and with hydrogen are tabulated. The use of overlap integrals as indicators of bond strength is discussed. Notable are the relatively large overlaps for *s* bonds (in disagreement with Pauling's index of bond strength) and for π bonds (not covered by Pauling's index) at moderate and small bond lengths. Hybrid *s*–*p*σ bonds give large overlaps in agreement with Pauling's index.

2. The existence of a striking increase in *reduced bond lengths* ξ (actual bond lengths divided by sums of theoretical atomic radii) on going to the right for homopolar bonds in the first and second rows is pointed out, and is explained in terms of the overlap properties of the orbitals involved, including those involved in lone-pair repulsions, here in part agreeing with a recent discussion by Pitzer. The differences between first and second row atoms, with respect to readiness of formation of multiple bonds, and to strengths of single bonds in the last columns of each row, are shown to be attributable to increased strengths of σ bonds in the second row. Metallic binding is briefly discussed.

3. Using a new polarity index, the familiar relative shortening of bond lengths in polar bonds is found (except for hydrides) to be well correlated with the value of this index in harmony with Schomaker and Stevenson.

4. The possibility of appreciable resonance structure contributions involving π bonding (a sort of hyperconjugation) in hydrides is indicated.

5. It is shown that overlap integrals may prove useful in estimating van der Waals and non-bonded repulsion energies. Exchange repulsions between inner shells of bonded atoms are shown to be wholly negligible at actual bond lengths. Ionic binding, and the interaction of inner-shell electrons of one atom with outer-shell electrons of another are discussed in relation to overlap integrals, in part in connection with recent proposals of Pitzer.

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[31] For CsF, a recent determination from radiofrequency spectra (J. W. Trischka, *Phys. Rev.*, **76**, 1365 (1949)) gives the value 2.34 ± 0.05 Å., as compared wth 2.67 Å. by Schomaker and Stevenson's formula. There are no electron diffraction values for the alkali fluorides.

[32] Prof. J. E. Mayer pointed out to the writer that distortion of the F^- ion by polarization should further increase the overlap at any given interatomic distance; but the resulting increase in exchange energy is presumably less than the polarization energy.

[33] *Cf.* R. S. Mulliken, *Phys. Rev.*, **51**, 310 (1937), in particular Fig. 3 and p. 327.