90. E.Rabinowitch, "Photosynthesis" (Translated into Russian), Inostr.Lit., Moscow, 1953.
91. H.T.Witt, Naturwiss., 42, 72 (1955); Z.Elektrochem., 59, 981 (1955).
92. H.T.Witt and R.Moraw, Z.phys.Chem.(Frankfurt), 13, 119 (1957).
93. H.T.Witt, R.Moraw, and A.Müller, Z.phys.Chem.(Frankfurt), 14, 127 (1958).
94. R.S.Becker and M.Kasha, J.Amer.Chem.Soc., 77, 3669 (1955).
95. O.D.Dmitrievskii, V.L.Ermolaev, and A.N.Terenin, Dokl. Akad.Nauk SSSR, 114, 751 (1957).
96. I.Fernander and R.S.Becker, J.Chem.Phys., 31, 467 (1959).
97. R.S.Becker and I.S.Singh, J.Amer.Chem.Soc., 82, 2083 (1960).
98. A.V.Karyakin and A.V.Shablya, Optika i Spektrosk., 5, 665 (1957).
99. V.B.Evstigneev and V.A.Gavrilova, Dokl.Akad.Nauk SSSR, 95, 841 (1954); 96, 1201 (1954); 98, 1017 (1954); 100, 131 (1955); 103, 97 (1955); 108, 507 (1956); 114, 1066 (1957); 115, 530 (1957).
100. A.A.Krasnovskii and G.P.Brin, Dokl.Akad.Nauk SSSR, 67, 325 (1949).
101. A.A.Krasnovskii, G.P.Brin, and K.K.Voikovskaya, Dokl. Akad.Nauk SSSR, 69, 393 (1949).

Vernadskii Institute of Geochemistry
and Analytical Chemistry,
Academy of Sciences of the USSR

OVERLAP INTEGRALS AND APPROXIMATE ESTIMATES OF THE ENERGIES OF CHEMICAL BONDS

V. M. Volkov

CONTENTS

1. Introduction 730
2. Estimation of chemical bond strength by means of overlap integrals 731
3. Use of overlap integrals to explain the properties of compounds containing *d* electrons 733
4. Determination of the amount of ionic character in bonds by means of overlap integrals 734
5. Use of overlap integrals to determine the most advantageous hybridisation of atomic orbitals in a molecule 734

1. INTRODUCTION

Estimation of the strength of a chemical bond constitutes one of the most important problems of theoretical chemistry, since in several cases there are no reliable experimental data on bond energies.

However, quantum-mechanical calculations of these quantities are very complicated, and there is no great certainty that the results obtained are correct. Therefore approximate, semiquantitative calculations, which enable comparative assessments to be made[1], now play a great part in quantum chemistry.

A simple method for the quantum-mechanical estimation of the strength of a chemical bond is the use of overlap integrals. These integrals may also be used to solve several other chemical problems, and we therefore think it necessary to bring them to the attention of a wide circle of chemists.

Overlap integrals are the simplest of all molecular integrals. If the state of an electron in an atom A is described by the wave function χ_A, and that in an atom B by the function χ_B, the overlap integral of these two functions is

$$S_{AB} = \int \chi_A \chi_B \, d\tau. \qquad (1)$$

Integration is carried out with respect to the coordinates of one electron over the whole configurational space. Only non-orthogonal wave functions can overlap, their degree of non-orthogonality being a measure of their overlap; therefore overlap integrals are still termed also "non-orthogonality integrals".

The energy of a bond can be regarded as roughly proportional to the overlap integral[2], since it consists mainly of the exchange energy. If, however, the expression is written down for the exchange integral in the case of the formation of the simplest molecule H_2^+, it is evident that almost all its terms contain overlap integrals as cofactors:

$$H_{12} = H_{21} = \int \chi_A \left(E_0 + \frac{1}{R} - \frac{1}{r_B}\right) \chi_B dr =$$

$$= E_0 \int \chi_A \chi_B dr + \frac{1}{R} \int \chi_A \chi_B dr - \int \chi_A \frac{1}{r_B} \chi_B dr =$$

$$= E_0 S + \frac{1}{R} S - K, \qquad (2)$$

where E_0 is the energy of the hydrogen atom, R the internuclear distance, r_B the instantaneous distance between the electron and the nucleus B, and K the resonance integral.

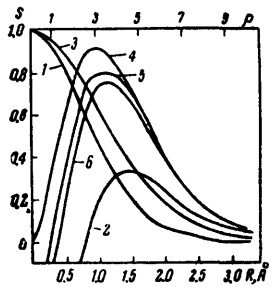
The following semiempirical formula has been suggested for the exchange integral $H_{ij} = \int \chi_a^2 \chi_b^2 (1/r_{12}) d\tau_1 d\tau_2$, which presupposes that the latter is proportional to the overlap integral S_{ij}:

$$H_{ij} = \frac{1}{2} F_x S_{ij} (H_{ii} + H_{jj}), \qquad (3)$$

where H_{ij} and H_{jj} are integrals representing the energy of the electron in the i-th or the j-th orbital in the field of the nuclear skeleton of the molecule and the remaining valence electrons, and F_x is an empirical correction, its value being 1.67 for a σ bond and 2.00 for a π bond[3]. The exchange energy calculated according to this formula agrees well with experimental data for several compounds[3,4].

Hence it can be seen that overlap integrals vary in the *same* sense as exchange integrals, *i.e.* in the *same* sense as the energies of chemical bonds.

However, overlap integrals cannot be "absolute" measures of the energy of a chemical bond or other characteristics of chemical interaction in a molecule. Whether it is more advantageous for the molecular orbital formed by the overlapping of atomic orbitals to be occupied by one or two electrons cannot be determined from an examination of the overlap integrals.



Variation in overlap integrals with change in internuclear distance for various bonds between two carbon atoms: 1) between 2s orbitals; 2) between $2p\sigma$ orbitals; 3) between $2p\pi$ orbitals; 4) on linear hybridisation; 5) on trigonal hybridisation; 6) on tetrahedral hybridisation.

Therefore all conclusions based on the change in value of the overlap integrals are usually valid only for sufficiently similar compounds. Here we can detect several interesting regularities and make some predictions. But caution must be exercised in transferring all this to other compounds.

In the calculation of overlap integrals, atomic orbitals are most often taken in the form of Slater functions. Exact expressions for atomic orbitals, obtained by the self-consistent field method, are employed only for rigorous calculations. The Slater orbitals have the following form

$$\chi_A = Y(\theta, \varphi) r^{n-1} e^{-\frac{Z'}{n'} r}, \qquad (4)$$

where $Y(\theta, \varphi)$ is the angular function, and Z' and n' are the effective charge and the effective quantum number calculated according to definite rules[5]. Calculation of overlap integrals presents no difficulty if χ_A and χ_B are taken to have the form (4), since detailed tables exist for computing the expressions resulting from the integration[5]. There are also special tables of overlap integrals, which are very convenient to use[6,7]. The integrals are tabulated in the form of functions of two parameters depending on the internuclear distance (R) and the difference in electronegativity between the interacting atoms. These parameters are denoted by ρ and t:

$$\rho = \frac{1}{2} \frac{R}{a_H} (\mu_A + \mu_B); \quad t = \frac{\mu_A - \mu_B}{\mu_A + \mu_B}; \quad \mu = Z'/n', \qquad (5)$$

where a_H is the Bohr radius.

An overlap integral is a function which depends on the form of the atomic orbitals, the internuclear distance, and the parameter t. Such integrals vary between 0 and +1 or -1†. With increase in R they fall off very rapidly to zero. Increase in the parameter t in the positive or the negative direction also markedly diminishes the value of the overlap integral, maximum overlap occurring when $t = 0$. The overlap of the orbitals depends also on the type of bond – σ, π, or δ – formed between them. The Figure illustrates the overlap integrals for various bonds.

† The overlap integral can be negative when the positive part of one atomic orbital overlaps the negative part of the other. This occurs, for example, in the formation of σ bonds from p or f orbitals, in which positive and negative lobes are oriented in opposite directions along the line of the bond.

When the overlap integral is used as a criterion of bond strength, it is usually assumed that a σ bond is sufficiently strong if its overlap integral is about 0.4. The overlap integrals for π and δ bonds have values of at least 0.2.

2. ESTIMATION OF CHEMICAL BOND STRENGTH BY MEANS OF OVERLAP INTEGRALS

Pauling's well-known criterion of bond strength starts from the postulate that the radial parts of the wave functions involved in bond formation are equivalent. It is formulated thus: "... for s-p hybridisation the bond energy is closely proportional to S^2, with S the magnitude of the angular part of the bond orbital in the bond direction"[2].

The overlap integral is a clearer criterion of chemical bond strength, since it takes into account the overlap in both angular and radial parts of the atomic orbitals, and is furthermore a function of the interatomic distance, which allows the variation in energy with change in distance to be assessed. Therefore the overlap integral is a more precise measure of the strength of a chemical bond.

A systematic comparison of overlap integrals with energies and other properties of chemical bonds was first undertaken by Mulliken and his collaborators[8] using data on simple compounds of elements in the short periods of Mendeleev's system.

Mulliken uses, in addition to overlap integrals, the concept of the reduced internuclear distances ξ, defined by the relation: $\xi = R/(r_A + r_B)$. On putting $r = n' a_H/\mu$, we obtain, when $n'_A = n'_B = n'$, $\xi = (1 - t^2)\rho/2n'$, where n', μ, ρ, and t have the same significance as in Eqns. (4) and (5), a_H being the Bohr radius. If the Slater orbitals represent correctly the actual motion of the electrons, $\xi = 1$ should correspond to the maximum bond strength at the equilibrium distance. Hence ξ also may be a characteristic of the chemical bond, but it is cruder than the overlap integral, since it takes account only of the radial overlap. The greater is ξ, the smaller is the overlap integral.

Table 1 compares values of R, ξ, and overlap integrals for several homopolar bonds between atoms of elements in the Short Periods I and II (according to Mulliken).

These data show that, in agreement with Pauling's criterion, the overlap integrals for the hybrid sp orbitals are larger than those for the purely s and p orbitals. On the other hand, the overlap integrals are larger for $s-s$ bonds than for $p-p\sigma$ bonds (apart from O_2 and F_2, in which ρ is very large); this contradicts Pauling's criterion, according to which a $p'-p\sigma$ bond is always more stable than an $s-s$ bond by a factor of $\sqrt{3}$. The overlap integrals for linear and trigonal hybridisation are larger than that for tetrahedral hybridisation (according to Pauling the converse should be true). This is confirmed by data on the C–H interatomic distances in ethane, ethylene, and acetylene, which are 1.11, 1.07, and 1.06 Å respectively[9]. With low values of ρ, the overlap integral is greater for $p\pi$ bonds than for $p\sigma$ bonds, because in this case the Slater $p\pi$ orbitals are more exact than the $p\sigma$-orbitals, and therefore the general variation of the overlap integrals for the $p\sigma$ bonds is somewhat distorted‡. The value of ξ increases monotonically with increase in atomic number, the greatest

‡ This provides an example of the inexactness of the Slater functions, showing clearly that they must be used with caution, as otherwise it might be wrongly concluded that in a multiple bond the π component is stronger than the σ component.

TABLE 1.

Bond	R, Å	ξ	Overlap integrals for various bonds (at $t = 0$)					
			$s-s$	$p\sigma-p\sigma$	$p\pi-p\pi$	hybridisation: linear sp	trigonal sp^2	tetrahedral sp^3
H—H	0.74	0.70	0.75					
Li—Li	2.67	0.82	0.59	0.05	0.55			
B—B	1.52	0.94	0.50	0.30	0.33		0.80	
B=B	1.76	1.08	0.40	0.33	0.24		0.74	
B≡B⁻	1.92	1.02	0.44	0.32	0.28			0.73
C≡C	1.21	0.93	0.54	0.29	0.33	0.88		
C=C	1.34	1.03	0.44	0.32	0.27		0.77	
C—C	1.54	1.18	0.34	0.33	0.19			0.65
N≡N	1.095	1.01	0.45	0.32	0.28			
N=N	1.24	1.15	0.36	0.33	0.22			
N—N	1.47	1.36	0.25	0.29	0.13			
O=O	1.21	1.30	0.28	0.31	0.15			
O—O	1.47	1.58	0.16	0.23	0.07			
F—F	1.435	1.77	0.11	0.17	0.05			
Na—Na	3.08	0.87	0.48	0.03	0.58			
Al—Al	2.50	1.08	0.32	0.33	0.35			
Si=Si	2.04	1.03	0.35	0.30	0.371			
Si—Si	2.32	1.17	0.26	0.37	0.28			
P≡P	1.89	1.10	0.31	0.36	0.31			
P—P	2.20	1.28	0.20	0.38	0.21			
S=S	1.89	1.24	0.23	0.38	0.22			
S—S	2.10	1.38	0.16	0.36	0.16			
Cl—Cl	1.99	1.281	0.21	0.291	0.101			

deviations in its value from unity being observed with O_2, F_2, Cl_2, and S_2.

Mulliken found similar relations for heteropolar bonds, with the difference that the overlap integral in this case depends on the parameter t, which is roughly proportional to the electronegativity difference $x_A - x_B$. We shall not give these results, since they do not differ fundamentally from the data in Table 1.

Overlap integrals make it possible to estimate the interaction between electrons in different orbitals. Table 2 gives values of the integrals for the P—O bond (R = 1.64 Å) for phosphorus and oxygen orbitals having different quantum numbers.

As can be seen from Table 2, the overlap integral between a valency orbital of one atom and an inner orbital of another may be as much as 10% of the overlap integral of the valency orbitals, which must be taken into account in the more exact quantum-chemical calculations. Nevertheless, the overlap between two inner orbitals of the interacting atoms is very slight. Thus the overlap integrals for 1s orbitals in the bonds Li—Li, C=C, and F—F and for 2s, $2s'-2p\sigma$, and $2p\pi-2p\pi$ orbitals in the Na—Na, Si=Si, and Cl—Cl bonds are almost zero. Finally, the overlap integrals show that the overlap in ionic bonds is negligible (in the NaF molecule the overlap integral for the $2s-2p\sigma$ orbitals is 0.019).

Overlap integrals allow an estimate to be made of the relative strength of bonds in molecules in which not all the bonds are equivalent. In the PCl_5 and PF_5 molecules, which have the structure of a trigonal bipyramid, for example, the P—X bonds in the direction of the principal axis of symmetry are found to be weaker than the equatorial bonds[10]. This result does not contradict experimental data on the interatomic distances and the frequencies of P—X stretching vibrations in these molecules. Use of Pauling's criterion to assess the relative strength of the bonds in these molecules led to the opposite result, which did not agree with the experimental data.

For the direct estimation of the energy of a chemical bond Mulliken suggested the so-called "magic formula"[11], which for a polyatomic molecule can be written in the form:

$$D_0 = \sum X_{ij} - \frac{1}{2}\sum Y_{kl} + \frac{1}{2}\sum K_{mn} - P + E_R, \qquad (6)$$

where ΣX_{ij} is the exchange energy over all bonding pairs of electrons, ΣY_{kl} and ΣK_{mn} represent the energy of non-bonding pairs of electrons (the term with the minus sign represents repulsion, and that with the plus sign attraction), P is the energy of promotion, *i.e.* the energy required to transfer the electrons of an atom to the valency state, E_R the energy of ionic interaction, and D_0 the dissociation energy of the molecule (disregarding zero-point vibrations).

This formula is a generalisation of formulae for simple molecules (such as H_2^+, H_2, He_2^+), which result from calculations by the molecular orbital or valence bond methods. As already state, exchange integrals are usually proportional to overlap integrals. Furthermore, the exchange energy is proportional to the ionisation potential of the valence electron. This makes it possible to write the following approximate expression for the term X_{ij}:

$$X_{ij} = A_j S_{ij} \bar{I}_{ij} / [1 + S_{ij}] \qquad (7)$$

where $\bar{I}_{ij}$ is the mean ionisation potential, S_{ij} the overlap integral, and A_j an empirical parameter whose value is 0.65 for $s-s$ bonds, 1.0 for most σ bonds, and 1.5 for π bonds.

The electron—electron repulsion energy Y_{kl} can also be expressed in terms of an overlap integral and an ionisation potential

$$Y_{kl} = \nu A_k S^2 \bar{I}_{kl}, \qquad (8)$$

where ν is an empirical parameter.

Eqns. (7) and (8) give quite good agreement for the simplest molecules. Thus the dissociation energy of H_2 calculated according to Eqn. (7) is 4.07 eV, which is less than the experimental value by only 0.69 eV. Table 3 shows the variation in the electron—electron repulsion energy for two

TABLE 2

Overlap of outer orbital of one atom with inner orbital of the other for the P—O bond				
Overlapping orbitals	$2s_P - 2s_O$	$2s_P - 2p\sigma_O$	$2p\sigma_P - 2p\sigma_O$	$2p\pi_P - p\pi_O$
Overlap integral	0.017	0.029	0.022	0.004
Overlap of outer orbitals for the P—O bond				
Overlapping orbitals	$3s_P - 2s_O$	$3s_P - 2p\sigma_O$	$3p\sigma_P - 2p\sigma_O$	$3p\pi_P - 2p\pi_O$
Overlap integral	0.24	0.20	0.23	0.14

TABLE 3.

R/a_H	2.01	2.51	3.01	4.01	5.01
Overlap integrals	0.275	0.161	0.091	0.049	0.0075
Y_{kl} from Eqn. (8)	2.61	0.85	0.77	0.01	0.0018
Y_{kl}, theoretical	2.31	0.81	0.26	0.025	0,0023

TABLE 4.

Molecule	Optimum effective Z	D, kcal	
		from Eqn. (9)	expt.
H_2	0.611	98.0	109.8
Li_2	1.30	26.2	26.0
Na_2	1.88	18.2	17.0
K_2	2.13	14.8	12.0

He atoms calculated by means of Eqn. (8). The agreement with more rigorous theoretical calculations is quite satisfactory [8].

In order to calculate for more complicated molecules, all the terms in the "magic formula" must be taken into account, and variable parameters must be introduced. Mulliken calculated from Eqn. (6) the dissociation energy of the molecules CH, O_2, N_2, F_2, Li_2, CH_4, C_2H_6, C_2H_4, and C_2H_2. By a suitable choice of coefficients, satisfactory results were obtained. It must be especially emphasised that, if calculations are being applied to a new type of compound, the "magic formula", like other similar formulae, cannot give *a priori* any certainty that the results obtained are correct. This formula has not, therefore, been widely used.

Still simpler formulae can be chosen. For example, we suggest the following:

$$D = \left(\frac{Z^2}{R} - \frac{2ZS}{(1+S)^2}\right) \times n^{-2}, \qquad (9)$$

where n is the principal quantum number, the term Z^2/R represents repulsion between atoms, and the second term represents exchange interaction. Eqn. (9) does not give sufficient weight to repulsion between inner electrons, and therefore it, too, is unsuitable for "absolute" calculations, but represents the variation in energy in a series of similar compounds quite correctly, especially if the effective charge Z is varied. Table 4 gives dissociation energies for molecules of the alkali metals which we have calculated from Eqn. (9).

It is evident from the above that calculations based on simplified formulae using only overlap integrals cannot give good quantitative results even for comparatively simple compounds, let alone complicated compounds. But they can be employed relatively successfully for the qualitative assessment of the properties of chemical compounds.

3. USE OF OVERLAP INTEGRALS TO EXPLAIN THE PROPERTIES OF COMPOUNDS CONTAINING *d* ELECTRONS

Compounds of the transition metals having valence *d* electrons are of considerable interest to chemists, and we shall therefore discuss the application of overlap integrals to these compounds separately.

A good example of how the overlap integral and the "magic formula" enable a qualitative explanation to be given of the properties of molecules is provided by the work of Jaffé and Doak on the stability of organometallic compounds [12]. They compared values of the overlap integrals and the mean ionisation potentials for the element–carbon (E–C) bonds, and also values of X_{ij}, which represents the exchange energy in the magic formula, calculated by means of Eqn. (7). On comparing these quantities and also values of the ionic interaction energy $E_{\overline{IR}}$, it is possible to divide metals into three groups according to their ability to form bonds with carbon, as can be seen from Table 5.

The following conclusions can be drawn from Table 5. The metals Na, Mg, and Al should give quite strong M–C bonds, since the corresponding overlap integrals are quite large, and the term X_{ij}, representing the exchange energy, is very considerable. However, this applies also to the non-metals of this period, Si, P, Cl, and S, with the difference that with them the E–C bonds should be still stronger.

Metals of a transition period should not form stable bonds with carbon, since S_{ij} and X_{ij}/A are considerably smaller with them. The ionic interaction energy is also low.

The metals Zn, Ga, and Ge and non-metals As, Se, and Br should give stable organometallic compounds, the bonds they form with C being almost completely covalent.

The metals K and Ca, it would seem, should not form M–C bonds, since their overlap integrals and X_{ij} are of the same order as with the transition metals. But the organometallic compounds of these metals are quite stable. This is because in this case the M–C bond is to a considerable extent ionic, since the term $E_{\overline{IR}}$, representing the ionic interaction energy, is quite large. All these conclusions are confirmed by experiment§.

Overlap integrals are of great help in ascertaining the role of *d* electrons in simple and multiple bonds. Pauling's criterion shows that *d* orbitals should give more stable bonds than do *s* or *p* orbitals, since they are more concentrated in definite directions. The overlap integrals, which take into account the radial components, give a more

TABLE 5.

Elements	Mean overlap integral	Mean ionisation potential, $\overline{I}$	Exchange energy, X_{ij}/A	Ionic interaction $E_{\overline{IR}}$
Na	0.397	5.11	2.67	4.0
Mg, Al, Si, P, S, Cl	~0.4—0.6	~6—10	~3.6—5.7	~2.6—0.0
K	0.145	4.32	1.14	4.41
Ca	0.244	6.09	1.94	3.42
Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu	~0.3—0.4	~6—7.5	~2.5—3.0	~0.5—0.6
Zn, Ga, Ge, As, Se, Br	~0.5—0.6	~8—11	~4	~0.5—1.0

§ We have been speaking throughout of an M–X bond; if, however, the bonding molecular orbitals are formed by *d* orbitals of a transition metal and π orbitals of the ligands, such organometallic compounds may be very stable, for example the various "metallocenes". The above considerations are not applicable to such compounds, for they contain no localised M–C bonds.

precise answer. This is especially important with multiple bonds, to which Pauling's criterion is not applicable.

By means of overlap integrals Jaffé [13] showed that d electrons can form not only σ and π but also δ bonds, with overlapping of all four lobes of each d orbital.

In complexes, π and δ bonds are found quite often, and their reality is demonstrated by the shortening of the interatomic distance and by calculation of the corresponding overlap integrals. In the $[OsNCl_5]^{2-}$ ion, for example, the Cl atom located *trans* to the nitrogen atom is linked with the osmium by a δ bond, which shortens the Os–Cl distance by 0.27 Å. [14,15] The overlap integral of this δ bond is about 0.20. The δ bond is formed from a d_{xy} orbital of the Os occupied by a pair of electrons and a free d_{xy} orbital of the *trans* Cl atom, belonging to the same point group.

The overlap integrals show that multiple bonds are more advantageous in an octahedron and a square than in a tetrahedron, since in this last case they are conjugated to a less extent. This results in a decrease in the total overlap in the tetrahedron of 20% compared with the square and the octahedron (for molecules having the same ligands [13]).

Overlap integrals can be used also in discussing compounds having f electrons. Coulson and Lester compared the overlap integrals of the p, d, and f orbitals of uranium with NO_3^- groups in the $[UO_2(NO_3)_6]^{4-}$ ion, and showed that participation of f electrons is necessary for the formation of molecules having D_{6h} symmetry [16].

Examination of the overlap integrals between various orbitals of uranium and oxygen in the uranyl ion UO_2^{2+} leads to the conclusion that the d orbitals of uranium may form σ and π bonds with the oxygen atoms, whereas such bonds involving f electrons should be far weaker [17].

In computing overlap integrals involving d orbitals it is important to determine correctly the effective charges for d electrons, since Slater's rules often do not give good results, especially with elements of Short Period III. Several modifications of these rules exist which give better results [18]. In comparing overlap integrals for different bonds, it is necessary that the effective charges should be computed according to the same rules, as otherwise the results will not be comparable.

4. DETERMINATION OF THE AMOUNT OF IONIC CHARACTER IN BONDS BY MEANS OF OVERLAP INTEGRALS

Overlap integrals can provide quite a convenient measure of the ionic character of a polar bond. Let us consider the ratio of such an integral in a real molecule to that in a hypothetical comparison molecule: *i.e.* let us compare the real molecule with a molecule consisting of the same atoms for which $t = 0$ (the bond is assumed to be ideally covalent), while the internuclear distance is the sum of the covalent radii of the atoms forming the bond. The "degree of ionisation" i of bonds involving s or p electrons is determined from the equation

$$i = 1 - \frac{\sum A_j S_j - \frac{1}{2}\sum A_{j'}(S_{j'})^2 + 0.82\sum S_k}{\sum A_j S'_j - \frac{1}{2}\sum A_{j'}(S'_{j'})^2 + 0.82\sum S'_k}, \qquad (10)$$

where A has the value 1 for S_{s-s}, 1.72 for $S_{s-p\sigma}$ and $S_{p\sigma-p\sigma}$, and 0.82 for $S_{p\pi-p\pi}$. The term $\frac{1}{2}\sum A_{j'}(S_{j'})^2$ represents the repulsion of non-binding electrons. The numerator relates to the real molecule, and the denominator to the comparison molecule.

By this method Batsanov and Durakov calculated the degrees of ionisation of the bonds in 32 hydrides and halides [19]. They obtained results which agreed quite well with those obtained from measurements of the dipole moments [20].

5. USE OF OVERLAP INTEGRALS TO DETERMINE THE MOST ADVANTAGEOUS HYBRIDISATION OF ATOMIC ORBITALS IN A MOLECULE

The most widespread method for determining hybrid orbitals as a linear combination of the original atomic orbitals consists in finding the angles θ and φ at which the value of the function is a maximum. The atomic orbitals are selected according to the symmetry of the molecule [21], the difference in the radial components of the orbitals being neglected.

Overlap integrals permit a more objective assessment of the most advantageous hybridisation in any actual compound, since they take into account not only differences in angular and radial components of the atomic orbitals but also the interatomic distances in the molecule.

How the radial components of the Slater s, p, and d orbitals can differ may be shown by two examples. With nickel ($3d^94p$) the maximum value of the radial component for the $3d$ orbital is at 1.25 atomic units, while for the $4s$ or $4p$ orbitals it is at 3.7 atomic units. With sexivalent sulphur ($3s3p^33d^2$) the maximum values of the radial components are 1.46 and 5.45 atomic units for the $3p$ ($3s$) and $3d$ orbitals respectively [22].

Overlap integrals give different relations for the relative stabilities of various configurations from those given by the Pauling criterion based on the maximum values of the angular components of hybrid functions. According to Pauling, the octahedral configuration d^2sp^3 should be more stable than the tetrahedral sp^3 by a factor of 1.5, and than the square sdp^2 by a factor of 1.2. The square configuration should be more stable than the tetrahedral by a factor of 1.35.

Calculation of the overlap integrals for nickel compounds with $\rho = 6.0$ and $t = 0$ shows the octahedral configuration to be more stable than the tetrahedral by only 15%, and than the square by 10%. The variation in the overlap integrals with different values of ρ and t shows that the overlapping of the hybrid orbitals of nickel with the orbitals of the ligands is in most cases the same in different molecular configurations [22]. This, however, occurs also with compounds of other elements.

In conclusion, let us consider the possibility of constructing hybrid orbitals taking into account their maximum overlap with the orbitals of the ligands [23]. This method, which can be termed the "maximum overlap method", gives a set of bonding and non-bonding hybrid orbitals in the form of a linear combination of atomic orbitals for the given molecular configuration.

Let us consider a molecule MX_k. Let us represent the valence orbitals of the central atom by Φ_1, Φ_2, ..., Φ_n, and those of the ligands by Θ_1, Θ_2, ..., Θ_n ($n \geqslant k$). We try to

find hybrid orbitals of M in the LCAO form¶: $\Psi_j = \sum_{i=1}^{n} a_{ij}\,\Phi_i$ such that the sum of the overlap integrals of all the resulting hybrid orbitals with the corresponding orbitals of the ligands

$$\sum_{i=1}^{k} \langle \Psi_i \Theta_i \rangle = \sum_{i=1}^{k} \sum_{j=1}^{k} a_{ij} \langle \Phi_i \Theta_i \rangle$$

should be a maximum.

First we consider the overlap of all the valence orbitals of the central atom with all those of the ligands which can form bonds with the central atom. Then the set of linear equations is solved to find the coefficients for bonding and non-bonding orbitals taking into account their normalisation and mutual orthogonality. The number of equations depends on the number of bonds in the molecule and on the number of valence orbitals of the central atom.

In the ClF_3 molecule, for example, the chlorine atom has nine valence orbitals, comprising one *s*, three *p*, and five *d* orbitals, occupied by seven electrons. The molecule has a T-shaped structure (symmetry C_{2v})[24]. Of these seven electrons, three take part in forming three σ bonds with three fluorine atoms, while the remaining four occupy in pairs two non-bonding σ orbitals which are orthogonal to all the bonding orbitals. The overlap matrix for this molecule is as follows (disregarding the difference in the radial components of the *sp* and *d* orbitals of the chlorine).

$R =$

	Θ_1	Θ_2	Θ_3
s	1	1	1
p_z	$\sqrt{3}$	0	0
p_x	0	$\sqrt{3}$	$-\sqrt{3}$
d_{z^2}	$\sqrt{5}$	$-1/2\sqrt{5}$	$-1/2\sqrt{5}$
$d_{x^2-y^2}$	0	$1/2\sqrt{15}$	$-1/2\sqrt{15}$
p_y	0	0	0
d_{xy}	0	0	0
d_{xz}	0	0	0
d_{yz}	0	0	0

Inspection of this matrix shows that the overlap of the p_y, d_{xy}, d_{xz}, and d_{yz} orbitals of the chlorine with all the ligands is zero; hence they are not involved in forming hybrid bonding orbitals. The p_z, p_x, d_{z^2}, and $d_{x^2-y^2}$ orbitals of the chlorine can take part in the formation of σ bonds.

Five linear combinations are formed from these five orbitals. Three of them will be bonding σ orbitals, and two non-bonding. The latter are found from the condition of minimum overlap with all the fluorine atoms. The three bonding σ orbitals are then constructed, orthogonal to the non-bonding orbitals. The last stage of the calculations by the maximum overlap method consists in finding those linear combinations of bonding orbitals which would have maximum overlap with all the ligands.

The calculation shows that these three best hybrid σ orbitals of Cl, corresponding to maximum overlap with all the *p* orbitals of the F atoms, are as follows[23]

$$\psi_1 = 0.385s + 0.588p_z + 0.708d_{z^2} + 0.089d_{x^2-y^2},$$

$$\psi_2 = 0.708p_x + 0.316s + 0.039p_z - 0.278d_{z^2} + 0.568d_{x^2-y^2},$$

$$\psi_3 = -0.708p_x + 0.316s + 0.039p_z - 0.278d_{z^2} + 0.568d_{x^2-y^2},$$

One electron from the Cl atom and one from each of the F atoms are placed in each of these three orbitals, which yields three σ bonds.

The value of the method consists in the fact that it enables us to find the orbitals which are most advantageous from the point of view of their maximum overlap, not for an abstract configuration but for an actual molecule, taking into account its structure, interatomic distances, and effective charges on the atoms.

Molecular orbitals found by the maximum overlap method are no less accurate than those calculated with self-consistency, provided that proportionality between overlap and exchange integrals is observed[25]. In general they can be successfully employed as starting orbitals for further calculations by the self-consistent field method.

Recently the maximum overlap method has been generalised by replacing the condition that the sum of the overlap integrals should be a maximum by the condition that the sum of their squares should be a maximum[25,26]. This general statement of the problem does not require proportionality to be postulated between the total energy of the molecule and the overlap. However, additional data are then required on the relation between energy and overlap, which considerably diminishes the practical value of the method.

On the assumption of proportionality between energy and overlap, both maximum conditions (of the sum or of the sum of the squares of the overlap integrals) yield identical results.

¶ LCAO = linear combination of atomic orbitals.

1. Ya. K. Syrkin and M. E. Dyatkina, Vestnik Akad. Nauk SSSR, No. 6 (1959).
2. L. Pauling and I. Sherman, J. Amer. Chem. Soc., 59, 1450 (1937).
3. M. Wolfsberg and L. Helmholz, J. Chem. Phys., 20, 837 (1952).
4. J. Kiga *et al.*, Bull. Chem. Soc. Japan, 31, 79 (1958).
5. M. Kotani *et al.*, "Tables of Molecular Integrals", Tokyo, 1955.
6. R. Mulliken, C. Rieke, D. Orloff, and H. Orloff, J. Chem. Phys., 17, 1248 (1949).
7. H. Jaffé, J. Chem. Phys., 21, 258 (1953).
8. R. Mulliken, J. Amer. Chem. Soc., 72, 4493 (1950).
9. L. E. Sutton, "Tables of Interatomic Distances and Configuration in Molecules and Ions", Chemical Society, London, 1958.
10. F. Cotton, J. Chem. Phys., 35, 228 (1961).
11. R. Mulliken and C. Rieke, J. Phys. Chem., 56, 295 (1952).
12. H. H. Jaffé and G. Doak, J. Chem. Phys., 21, 196 (1953).
13. H. H. Jaffé, Uspekhi Khim., 26, 1060 (1957).
14. G. B. Bokii, L. A. Atovmyan, and T. S. Khodasheva, Dokl. Akad. Nauk SSSR, 128, 78 (1959).
15. V. M. Volkov and M. E. Dyatkina, Dokl. Akad. Nauk SSSR, 134, 351 (1960).
16. C. Coulson and G. Lester, J. Chem. Soc., 3650 (1956).
17. R. Belford and G. Belford, J. Chem. Phys., 34, 1330 (1961).
18. Ya. K. Syrkin and V. I. Belov, Zhur. Fiz. Khim., 23, 664 (1949).

19. S.S.Batsanov and V.I.Durakov, Zhur.Strukt.Khim., 1, 353 (1960).
20. L.Pauling, J.Phys.Chem., 56, 361 (1952).
21. M.G.Shirmazan, Candidate's Thesis (Ph.D.Equivalent), Karpov Institute of Physical Chemistry, Moscow, 1950.
22. D.Craig, A.Maccoll, R.S.Nyholm, L.E.Orgel, and L.E. Sutton, J.Chem.Soc., 354 (1954).
23. J.Murrell, J.Chem.Phys., 32, 767 (1960).
24. T.Smith, J.Chem.Phys., 21, 609 (1953).
25. P.Lykos and H.Schmaising, J.Chem.Phys., 35, 288 (1961).
26. T.Gilbert and P.Lykos, J.Chem.Phys., 34, 2199 (1961).

Kurnakov Institute of General and
Inorganic Chemistry
Academy of Sciences of the USSR

