955. d-*Orbital Contraction in Chemical Bonding.*

By D. P. CRAIG and E. A. MAGNUSSON.

In molecules such as phosphorus pentachloride and sulphur hexafluoride the bonds can be described as covalent *dsp* hybrids, but a study of overlap integrals shows that the *d* orbitals of phosphorus and sulphur in the free atoms are too weakly bound and diffuse to contribute to the bond energy. A type of polarization is proposed in which such diffuse orbitals are contracted, bringing the electrons closer to the atoms or groups to which bonds are to be formed and so adapting them better to bonding. Charge transfer from the central atom into orbitals of the outer atoms is not considered, but the tendency for charge to accumulate there is manifest in the contraction of the central atom's orbitals. Some features of the contraction are examined in a model in which the potential field of outer atoms is replaced by a Coulomb field and the energy of the electron minimized with respect to the exponent in a Slater orbital. Applied to real molecules the results from the model suggest that contraction is enough to allow substantial participation by *d* orbitals in covalent bonding of this type.

IN an analysis of the conditions under which bonds might be formed using d and f atomic orbitals, a problem which has to be solved if the covalent-bond model is to be retained at all is that in a number of theoretically important cases the orbitals are apparently much too weakly bound and diffuse to participate appreciably in bonding. We shall find, for example, that without some hypothesis of modification of the orbital sizes, the suggestion that sulphur hexafluoride SF_6 is held by d^2sp^3 covalent bonds using sulphur $3d$ orbitals is untenable. It has been suggested that the difficulty arises from the use of free-atom parameters for the d orbitals, and that modifications occur in molecule formation by polarisation due to the attached groups. Craig, Maccoll, Nyholm, Orgel, and Sutton [1] noted that d orbitals which were as weakly bound as the free-atom data required (according, *e.g.*, to Slater's rules which, even if not really precise in such cases, are certainly correct in the qualitative sense of giving very low ionization potentials) would be strongly polarized by electronegative ligands through the partial withdrawal of charge from the weakly bound orbitals of the central atom and a tightening of the remaining charge to a size compatible with binding. In a general way this certainly describes what happens, but in detail it is not easily combined with a discussion of covalent-bond strengths in terms of overlap integrals; this is easily seen, for, if the withdrawal of charge proceeds to the point where $S^{2+}(F_6)^{2-}$ describes the electronic situation only four of the bonds are covalent and they are based on the $3s3p^3$ configuration of S^{2+}. The d overlap integral then has no bearing on the case, and its importance is reduced progressively as this limit is approached. For this reason we prefer to retain a description of the polarization which allows the bonding to be described without charge transfer. This does not imply the unrealistic limitation that the bonds divide their charge equally between the bound centres : on the contrary, the region of overlapping charge is much nearer to the more electronegative centre, as commonsense requires. It is only that, as detailed more fully elsewhere,[1] we regard the asymmetry of the electron charge as homopolar rather than heteropolar in origin. The bonds may thus be polar but not ionic. In a complex system it is almost meaningless to discuss which of the homopolar and heteropolar descriptions is " right; " they have to be looked upon as different approximations to the same electron distribution, both having

[1] Craig, Maccoll, Nyholm, Orgel, and Sutton, *J.*, 1954, 332.

useful features. In this paper we shall develop a description of the polarization of weakly bound orbitals by electronegative ligands which is compatible with the covalent-bond model. Our discussion, which follows an outline given earlier,[2,3] will be found to agree in most important consequences with that given by Craig *et al.*[1] in qualitative terms, but its underlying mechanism is somewhat different. The discussion begins with a description of the overlap criterion for bond strength, continues with a treatment of polarization in terms of the contraction of the loosely bound orbitals, and the detailed application of this to a series of highly idealized model situations, and ends by noting briefly the relevance of the idea of orbital contraction to the understanding of conditions in molecules.

The covalent-bond model is a *model* in the sense that it idealizes a complex situation to something very simple in the expectation that calculations based upon it will enable some of the properties of the actual system to be interpreted. In particular, each bond between the central atom A and a ligand atom B is idealized by the supposition that it is formed from appropriately directed and simply constituted atomic orbitals ϕ_A and ϕ_B. Our purpose is to examine within this framework the conditions under which the orbital ϕ_A, which is in general a linear combination of natural atomic orbitals, is strengthened by the hybridization of d orbitals with s and p. As an index of bond strength we use the *overlap criterion, i.e.*, we assume that a value of the overlap integral (1) of about 0·1 or greater is necessary for significantly strong covalent binding.[1]

$$S = \int \phi_A(\nu) \, \phi_B(\nu) \, \mathrm{d}\tau_\nu \qquad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

For equivalent octahedral bonds the orbital ϕ_A is determined by symmetry in its composition from s, p, and d orbitals, and the overlap integral S_o may be written as the sum (2) of contributions by the overlap integrals S_d, S_s, and S_p of the d, s, and p orbitals at the centre atom A with the orbital at B :

$$S_o = (1/\sqrt{3})S_d + (1/\sqrt{6})S_s + (1/\sqrt{2})S_p \quad . \quad . \quad . \quad . \quad (2)$$

Large values of S_o are associated with strong bonds, and this requires large values for the primitive overlaps S_d, etc., in (2). Moreover, whether d orbitals are to be used or not depends, amongst other factors, on whether their inclusion in the hybrid bond orbital ϕ_A strengthens the bond appreciably; that is, in terms of the overlap approximation, upon whether S_d in (2) is comparable to S_s and S_p. In the specific case of sulphur hexafluoride the sulphur atom is taken to be in the valence-state configuration $3s3p^33d^2$. S_s and S_p are in the range 0·2—0·3. The two $3d$ electrons are well screened from the nucleus by the inner electrons, and S_d on account of this efficient screening and consequent diffuseness of the $3d$ orbitals is nearly zero.[1] Under these conditions we should not expect d hybridization to occur for the following reason. In the covalent-bond model promotion of two electrons into $3d$ orbitals occurs if the bond energy of six bonds minus the promotion energy gives a favourable energy balance compared with mechanisms of bonding not requiring promotion. If the d orbitals contribute nothing to the bond energy all that happens is that the bond-forming ability of the available s and p orbitals is spread over a larger number of bonds, and the potential gain in *total* bond energy will be small. It therefore seems essential to the idea of d-hybridization that the d character in the orbitals is appreciably bond-strengthening, a condition which is not satisfied by the diffuse orbitals of the free atom. It becomes necessary to allow for polarization of the d orbitals, and this allows their participation to be understood, as will be shown.

Orbital Contraction.—We construct a simple model to represent d electrons in an octahedral molecule and postpone the consideration of actual examples. A single d electron will be supposed to move in the field of a nucleus of charge Z_a; and upon this hydrogen-like atomic system a perturbation will be superposed consisting of six positive *

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* The reason for choosing positive charges is that the field of an atom capable of forming a covalent bond is electron-attracting. The familiar theory of the effect of crystalline fields on $3d$ electrons in transition metals normally involves negative charges, because the field sources are either negative ions or electron pairs in formed bonds.

[2] Craig, *Rev. Pure Appl. Chem.*, 1954, **4**, 4.
[3] Craig and Magnusson, *J. Chem. Phys.*, 1956, **25**, 383.

charges of magnitude Z_s in a regular octahedral array of radius σ atomic units. Because the model is to be used to simulate conditions in covalent bonds no provision is made for migration of the electron into orbitals at the perturbing centres. This would be another plausible method of allowing for the movement of the electron towards the positive charges; but in the present model the electron concentrates near the perturbing charge only as the changing size of the central orbit allows : the electron is, in other words, confined to an orbital based at the central nucleus. For $Z_s = 0$ the eigenfunctions and energy levels are, of course, those of the hydrogen-like atom of charge Z_a, otherwise the charges distort the orbital, expanding it if the orbital is small compared with the radius σ and contracting if it is large. Roughly we may expect that contraction will occur if the radial maximum of the orbital is greater than σ. As will be shown this conditions holds for the d orbitals whose usefulness for covalent bonding is at issue. The potential of the outlying charges may be expanded as a sum in the usual $1/r$ series,[4] which reduces to the following expressions for a regular octahedral field :

$$V_{r < \sigma} = -6Z_s/\sigma - (7/2)(Z_s/\sigma)(r^4/\sigma^4)\left\{\sqrt{(2/9)}\Theta_4{}^0 + (5/8)\sin^4\theta\cos 4\varphi\right\}\ldots$$

$$V_{r > \sigma} = -6Z_s/r - (7/2)(Z_s/r)(\sigma^4/r^4)\left\{\sqrt{(2/9)}\Theta_4{}^0 + (5/8)\sin^4\theta\cos 4\varphi\right\}\ldots \quad . \quad (3)$$

where $\Theta_4{}^0$ is the normalized Legendre polynomial.

The first terms in each expression have a particularly simple interpretation. They measure the potential of a charge $-6Z_s$ spread uniformly over a spherical shell of radius σ. Inside the sphere the potential is uniform and equal to $-6Z_s/\sigma$, and outside it is that of a charge $-6Z_s$ placed at the centre of the sphere. An orbital of the unperturbed atom which lies largely inside the sphere is unaffected in form by the perturbation, but its binding energy is increased by $6Z_s/\sigma$ atomic units, corresponding to the extra energy required to ionize the electron through the charged surface. Alternatively, if the energy zero is moved down by $-6Z_s/\sigma$ in the presence of the perturbation, orbitals of this type are entirely unaffected by the first term in the potential (3). On the other hand an orbital of the unperturbed system which projects significantly beyond the radius σ is specifically perturbed by the additional attractive potential $-6Z_s/r$ acting outside the sphere. This tends to draw charge inside, until a balance is reached between the increased kinetic energy of the contracted orbital and its reduced potential energy. The effect is thus a movement of charge into the sphere, giving a more compact orbital and therefore enhanced bonding power. An orbital of this projecting type also has its binding energy increased by the perturbation, but by an amount which is less than that for an orbital wholly within the sphere. This effect, which we shall study separately before dealing with following terms in the expansion (3), might be described theoretically in several different ways. The perturbed wave function could be expanded in a series of unperturbed hydrogen-like atomic wave functions for a central nuclear charge Z_a; this expansion would converge slowly except for very small perturbing charges Z_s. A quicker convergence would be obtained with a set of atomic functions for an increased charge $Z_a + \delta$, and it would be possible to choose δ, for a given Z_s, to give optimum convergence behaviour. Elaborate calculations however are not justified; we shall show, for example, that interconfiguration mixing is small (*i.e.*, participation by orbitals of principal quantum number greater than the original), and it is adequate to take a single Slater atomic wave function of radial factor (4) and to minimize its energy with respect to the exponent α. Z_a, Z_s, and σ appear as parameters.

$$\phi_n = (2\alpha)^{n+\frac{1}{2}}\, r^{n-1}\, e^{-\alpha r/n}\Big/\left\{(2n)!\ n^{2n+1}\right\}^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad (4)$$

For diffuse orbitals in the presence of the perturbation $\alpha > Z_a$, and since Slater radial functions have their maxima at $r_m = n^2/\alpha$, the increase in α over Z_a corresponds to a contraction of the orbital.

[4] Eyring, Walter, and Kimball, " Quantum Chemistry," Wiley, New York, 1944, p. 369.

The perturbation energy due to the first term in (3) is given by the expression (5) :

$$(\phi_n|V^0|\phi_n) = -(6Z_s/\sigma)\int_0^\sigma \phi_n^2 \, r^2 \, \mathrm{d}r - 6Z_s \int_\sigma^\infty \phi_n^2 r \, \mathrm{d}r \quad \ldots \ldots \quad (5)$$

This may be evaluated from tables.[5] We have, for $n = 3$

$$(\phi_3|V^0|\phi_3) = -(6Z_s/\sigma)(2\alpha\sigma/3)^7 (1/6\,!)\left\{6\,!\ 3^7/(2\alpha\sigma)^7 - A_6(2\alpha\sigma/3) + A_5(2\alpha\sigma/3)\right\} . \quad (6)$$

where
$$A_n(\omega) = \int_1^\infty r^n \, \mathrm{e}^{-\omega r} \, \mathrm{d}r$$

More generally, expression (6) involves a special case of an integral which recurs in several sections of our work. It is :

$$R_{nn}^p = \int_0^\sigma \phi_n(r^p/\sigma^{p+1})\phi_n r^2 \mathrm{d}r + \int_0^\infty \phi_n(\sigma^p/r^{p+1})\phi_n \, r^2 \, \mathrm{d}r = \sigma^{-1}(2\alpha\sigma/n)^{2n+1}\left\{1/(2n)\,!\right\}\times$$

$$\left[(2n+p)\,!\,\Big/\left\{2\alpha\sigma/n)^{2n+p+1} - A_{2n+p}(2\alpha\sigma/n) + A_{2n-p-1}(2\alpha\sigma/n\right\}\right] . \quad (7)$$

Tables of the auxiliary functions σR_{nn}^p for selected values of p and n are given in an Appendix.

The total energy is the sum of the perturbation term (5) and the unperturbed energy given by (8) for hydrogen-like orbitals. The latter have radial factors identical with the Slater functions (4) for 1s, 2p, 3d, 4f . . . *i.e.*, when the azimuthal quantum number l has its maximum value of $(n - 1)$.

$$W_n = (\alpha/n^2)(\alpha/2 - Z_a) \quad \ldots \ldots \ldots \quad (8)$$

The procedure is to find the value of α for which the total energy given by (5) plus (8) is a minimum for selected value of the parameters σ, Z_a, and Z_s. The results are shown in Fig. 1. They allow a number of trends to be discerned. It has been noted that an orbital largely contained within the radius σ is little altered by the perturbing field, so that in the limits either of large σ or large Z_a we expect the effective charge increment $(\alpha - Z_a)$ to vanish. In harmony with this $(\alpha - Z_a)$ in Fig. 1 is less for $\sigma = 4$ than $\sigma = 3$ for given Z_a and Z_s values and it decreases in the order $Z_a = 0$, 1, and 2. The dependence upon the bond distance σ is sensitive in the model, and in real systems we expect that ligands joined by short bonds (*i.e.*, first-row elements) will cause larger perturbations than others. The values $\sigma = 3$ and 4 are roughly those for bonds between a first- and second-row element and two second-row elements respectively. Table 1 gives additional results illustrating the rapid decrease in $(\alpha - Z_a)$ with increasing Z_a : in general for $Z_a > 2n^2/\sigma$ contraction is negligible. The quantities P_a and P_α in Table 1 are the fractions of the electronic charge lying outside a sphere of radius $\sigma = 4$ in 3d orbitals of effective nuclear charges Z_a and α respectively. Contractions are large only when a significant amount of the unperturbed orbital lies outside the sphere.

TABLE 1. *Variation of the charge increment* $(\alpha - Z_a)$ *with* Z_a.

$\sigma = 4$, $Z_s = 0.167$.

Z_a	P_a	α	P_α	$\alpha - Z_a$	Z_a	P_a	α	P_α	$\alpha - Z_a$
1	0.98	1.7	0.82	0.7	4	0.085	4.05	0.075	0.05
2	0.72	2.38	0.55	0.38	5	—	5.01	—	0.01
3	0.31	3.15	0.27	0.15	6	—	6.00	—	0

Small orbital contractions in our sense have long been known in simple systems for which detailed energy calculations have been made. For example, in H_2, Wang found that an effective nuclear charge of 1.166 units minimized the ground state energy in an

[5] Kotani, Amemiye, Ishiguro, and Kimura, " Tables of Molecular Integrals," Maruzen, Tokyo, 1955.

HLSP approximation. This result involves a consideration of all the energy terms and so depends strongly on the particular molecular state; for excited states of H_2 the effective nuclear charge may be less than unity. The relationship in detail between such changes in effective nuclear charge and those in our own work is thus slight.

The results in Fig. 1 show that the contraction of loosely bound orbitals may be large.

FIG. 1.   *Values of the increment* $(\alpha - Z_a)$ *to the effective nuclear charge plotted as a function of the total perturbing charge* ΣZ_s. *The curves refer to different values of* Z_a, *the actual nuclear charge, and* σ, *the distance in a.u. of the perturbing charges from the nucleus.*

(a) $Z_a = 0$, $\sigma = 3$.   (b) $Z_a = 1$, $\sigma = 3$.
(c) $Z_a = 2$, $\sigma = 3$.   (d) $Z_a = 0$, $\sigma = 4$.
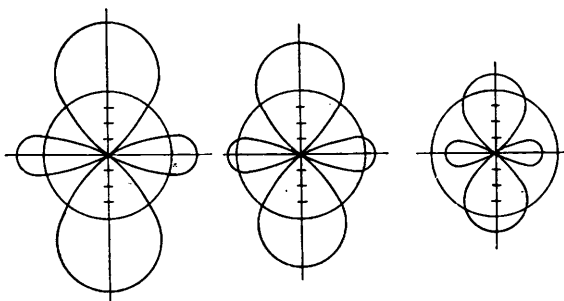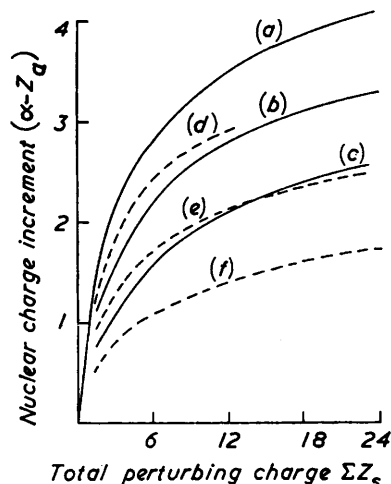(e) $Z_a = 1$, $\sigma = 4$.   (f) $Z_a = 2$, $\sigma = 4$.

FIG. 2.   *The contraction in an octahedral field of a* d_{z^2} *orbital of nuclear charge* $Z_a = 1.5$. *The orbital is shown by the contour on which* $|\psi| = 0.02$, *and the circle has a radius* $\sigma = 4$ a.u., *equal to the bond distance.*

Left-hand diagram :   Field charges $Z_s = 0$.
Centre diagram : $Z_s = 0.2$, $\alpha = 2$.
Right-hand diagram : $Z_s = 1.5$, $\alpha = 3$.

FIG. 3.   *Increase in the energy of promotion from a non-projecting orbital to a 3d orbital of nuclear charge* Z_a *in the field of octahedral unit charges.*

Upper curve : bond length $\sigma = 3$ a.u.
Lower curve : $\sigma = 4$ a.u.
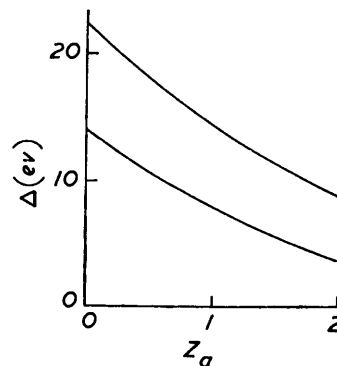
A 3d orbital with $Z_a = 1$ (as in the $3s3p^33d$ configuration of phosphorus) has its radial maximum at $r_m = 9$ a.u.   In an octahedral field of unit charges at $\sigma = 3$ α is 3.2 and the radial maximum is at 2.8 a.u., a value comparable with that of the orbitals of ligand atoms such as chlorine, and therefore compatible with covalent bonding.   Typical magnitudes of orbitals before and after contraction are shown in Fig. 2.

An important point in a more general consideration of the bond possibilities is that the energy of promotion of the electron into the 3d orbital, if changed at all, is *increased* by the

perturbing field. The reason for this is that an inner, non-projecting, orbital is more stabilised than a projecting orbital, so that the excitation energy from one to the other is increased. The increase may be considerable. A $3d$ orbital of $Z_a = 1$ has a binding energy of 0·055 a.u. in the free atom and in the octahedral field of unit charges at $\sigma = 4$ it is 1·265 a.u., an increase of 1·21 a.u. A less projecting and more tightly bound $3p$ orbital is stabilised by almost the full $6Z_s/\sigma = 1\cdot5$ a.u., so that the excitation energy would be increased by 0·29 a.u., or 8·2 ev. This example is an extreme one, but it shows that the free-atom promotion energy to, say, P($3s3p^33d$) has little relevance to the conditions of molecule formation, and that an extra promotion energy of several volts may be required. This effect is illustrated in Fig. 3, which shows the incremental energy Δ for promotion to the $3d$ orbital plotted as a function of the nuclear charge Z_a.

The most important feature in Fig. 3 is the strong dependence of Δ on Z_a which shows that, although the overlap condition may be quite easy to fulfil over a considerable range of Z_a, the energy condition is not; and in particular we should not expect bonds to be formed if the free atom orbitals are very weakly bound indeed, *i.e.*, for $Z_a \rightleftharpoons 0$, even though the orbitals after contraction would overlap sufficiently. It can safely be predicted that the energy of promotion into the valence state would require more energy than is supplied by the resulting bond formation under these conditions. Also crude methods of assessing Z_a, such as Slater's rules, are not good enough for accurate energy calculations of this kind in view of the sensitivity shown in Fig. 3, although they suffice for the rather insensitive calculations of orbital size and overlap. Moreover, we find that for energies, much more than for orbital sizes, later terms in the potential (3) are important. These remarks must therefore be read in their context as applying to the zero-th order approximation.

Contraction in Fourth Quantum Level Orbitals.—The radial maximum of a fourth quantum orbital of the Slater type occurs at $r_m = 16/Z_a$, or 16/9 times farther out than for a third quantum orbital of the same nuclear charge. We expect for this reason that orbital contraction will operate more strongly for the same values of the parameters σ, Z_s, and Z_a. This expectation is supported by the results in Table 2 which, except for the last column, are for $\sigma = 4$ a.u.

TABLE 2.   *Contraction in 4f orbitals at $\sigma = 4$.*

Z_a	Z_s	α	$\alpha/4$	$\alpha^*/3$	Z_a	Z_s	α	$\alpha/4$	$\alpha^*/3$
0	0·25	1·5	0·4	0·5	1	1·0	3·9	1·0	1·1
0	0·5	2·5	0·6	0·7	1	2·0	4·6	1·15	1·3
0	1·0	3·5	0·9	0·9	2	0·25	3·0	0·75	0·9
0	2·0	4·35	1·1	1·2	2	0·5	3·6	0·9	1·0
0	4·0	5·1	1·3	1·4	2	1·0	4·2	1·05	1·2
1	0·25	2·4	0·6	0·7	2	2·0	5·0	1·25	1·4
1	0·5	3·1	0·8	0·9					

* For $3d$ orbitals at $\sigma = 3$.

Comparison with Fig. 1 shows, for example, that, for $\sigma = 4$ and $Z_s = 1$, a $3d$ orbital of unit nuclear charge has $\alpha = 2\cdot7$, compared with 3·9 for a $4f$ orbital. However a more useful comparison, shown in the last two columns of Table 2, is between the wave-function exponents α/n calculated at $\sigma = 4$ for the $4f$ orbital and at $\sigma = 3$ for the $3d$. These are close, and suggest that for other principal quantum numbers n one might estimate values of α quite well by assuming the constancy of α/n evaluated for $\sigma = n$ a.u.

Secondary Effects.—Two equivalent electrons. In this and following sections we consider a number of factors which may be expected to modify the results obtained for a single electron in a spherically symmetrical field. It will be shown that within the range of values of the actual nuclear charge Z_a for which contraction is important, the modifying factors are relatively unimportant.

In phosphorus pentafluoride with the valence-state configuration $3s3p^33d$, and in the other cases of a single exterior electron, the model already discussed can be applied. In octahedral molecules of the sulphur hexafluoride type the central atom's valence state is $3s3p^33d^2$ with two equivalent and weakly bound d electrons and it is necessary to consider the influence of interelectronic repulsion. The analogous model is a helium-like two-electron system in the field of a bare nucleus surrounded octahedrally by positive charges.

Even in the $Z_s = 0$ limit we now have to consider both the actual nuclear charge Z_a and an effective nuclear charge which we shall call simply Z. In the one-electron case the two are the same. With two electrons Z becomes the effective charge required to minimize the total electronic energy, including interelectron repulsion. Z is less than Z_a on account of screening, as is well known in the treatment of the helium atom, and in the Slater theory of complex atoms. If we are to include electron repulsion explicitly in calculations of the properties of the two-electron system we must begin with the true nuclear charge Z_a and should find that, in the absence of a perturbing field, the energy is minimized by a value of α close to the Z given by Slater's rules. Interelectron repulsion alone causes a decrease in effective charge, *i.e.*, an orbital expansion, which will be opposed and finally overcome by the octahedral perturbation.

The energy of the two-electron valence-state may be found from the energies of stationary states of the same configuration. The energy of the appropriate valence state for two $3d_\gamma$ electrons is as follows, the d_ϵ orbitals being supposed inaccessible :

$$2I + F_0 - 6F_2 - 1{\cdot}5F_4 \qquad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

in terms of the Slater parameters [6] F, and I, the single-electron binding energy. Evaluation of the F's leads to the expression $2I + 0{\cdot}0804\alpha$ for the total energy. Fig. 4 shows the

FIG. 4. *Energy terms for one of a pair of equivalent 3d electrons in the field of a nucleus of charge 1·5 surrounded by a regular octahedron of unit charges at a distance of 4 a.u. The lowest curve is the free-atom binding energy, the straight line is the interelectron repulsion term, 0·0402α, the broken curve is the zero-th order perturbation energy plus the constant 1·5 a.u., and the upper full line is the sum, showing a shallow minimum in the total energy at about α = 2·65.*
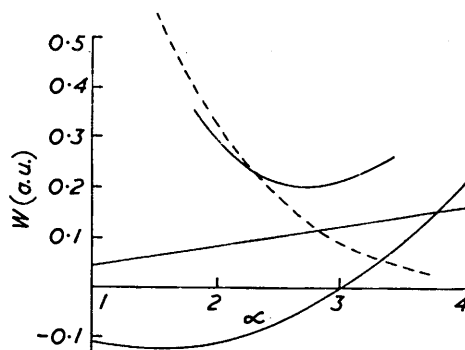
terms I, $0{\cdot}0402\alpha$ and the perturbation energy separately plotted for the case $\sigma = 4$, $Z_a = 1{\cdot}5$, $Z_s = 1$.

Without a perturbing field the energy is minimised by $\alpha = Z = 1{\cdot}14$, corresponding to a screening by one electron of the other equivalent to $1{\cdot}5 - 1{\cdot}14 = 0{\cdot}36$ electron, in close agreement with the Slater value of 0·35. The field being included, $\alpha = 2{\cdot}65$ compared with the value 2·85 for one electron, for which there is no repulsion term. One sees therefore that the screening correction for interelectron repulsion is reduced by the perturbing field. This is a general result which we shall use in the following way. Instead of using Z_a for the calculation we use the Slater value of effective nuclear charge; then α in the perturbing field is an underestimate of the formally correct value based on Z_a and explicit inclusion of interelectron repulsion. Since the under-estimation is small, usually much less than the upper limit 0·35, it is unimportant.

Higher approximations to the potential. Hitherto we have examined the effect on the the unperturbed atomic orbitals of the spherically symmetrical first term of the potential (3), which depends only upon the total charge $-6Z_s$ and its separation σ from the central nucleus. Second and later terms depend also upon the polar angles θ and φ. As is well known, an octahedral field does not remove the three-fold degeneracy of the p orbitals but splits the five d orbitals into a doublet (d_γ) and a triplet (d_ϵ) of which the doublet is lower under our conditions of positive field sources. The second term of (3) causes the major part of this splitting. The energies of the split components may differ considerably and

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[6] Condon and Shortley, " The Theory of Atomic Spectra," Cambridge Univ. Press, 1953, p. 202.

orbital contractions must be calculated separately for them. In terms of the integrals (7) we have for the perturbation energies :

$$d_\epsilon : -(Z_s/\sigma)\left\{6\sigma R_{33}^0 - (2/3)\,\sigma R_{33}^4\right\}$$

$$d_\gamma : -(Z_s/\sigma)\left\{6\sigma R_{3s}^0 + \sigma R_{33}^4\right\} \quad\quad\quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

The first term, common to both expressions, has already been discussed at length. The second term is now added and the total energy minimized, giving values of α for d_ϵ and d_γ. Typical results for $Z_a = 1\cdot5$, $\sigma = 4$ a.u., are shown in Table 3. The zero-th order term σR_{nn}^0, increases monotonically with $\alpha\sigma$, and it must increase the effective charge. The term σR_{33}^4, tabulated in an Appendix, approaches zero both at small and at very large values of $\alpha\sigma$, passing through a maximum at $\alpha\sigma = 10\cdot5$. Near this maximum it varies slowly, and its influence on the rate of change of the total energy is correspondingly small. This is the reason why Table 3 shows no change in α from the inclusion of the second term in the potential in the first example. For $\sigma = 4$ the maximum in σR_{33}^4 occurs at $\alpha = 2\cdot625$, so that if the zero-th order term gives $\alpha > 2\cdot625$ the second term of the potential will decrease α. This is too small an effect to be apparent in the first case in Table 3, but appears in the second, where the larger charges $Z_s = 4$ cause larger magnitudes throughout. This accounts for the fact that the d_γ orbitals, which are the more stable, have a lower α value. The d_ϵ orbitals, in the energy of which the σR_{33}^4 term appears with negative sign, have a greater value than the d_γ, and greater than the zero-th order value in the last column. In other cases (*viz.*, small Z_a and Z_s) in which the energy corrections are less, this trend is reversed, and, for α less than $2\cdot625$, the second term increases α values for d_ϵ and decreases them for d_ϵ. For $\sigma = 3$ the maximum in σR_{33}^4 is at the larger value $\alpha = 3\cdot5$, so that in most cases of interest d_γ will be slightly more contracted than d_ϵ. These effects of higher approximations are small because, in the interesting range of α, σR_{33}^4 is a slowly varying function. Its magnitude however is considerable, and the splitting caused by it between d_ϵ and d_γ is $4\cdot3$ ev in the first of the two examples quoted in Table 3.

TABLE 3. *Orbital contraction in an octahedral field* $Z_a = 1\cdot5$, $\sigma = 4$ a.u.

Z_s	$\alpha\ (d_\gamma)$	$\alpha\ (d_\epsilon)$	α (zero-th order)
1	2·75	2·75	2·75
4	3·5	3·75	3·6

The relative insignificance of the second term in the potential applies only to small values of Z_a. Large values of Z_a bring in large values of $\alpha\sigma$, and it becomes important that σR_{33}^4 falls off more slowly at large $\alpha\sigma$ than does σR_{33}^0 so that the former becomes predominant. For $Z_a = 6$, $\sigma = 4$, and field charges $Z_s = 4$ the values of α are $\alpha(d_\gamma) = 5\cdot6$ and $\alpha(d_\epsilon) = 6\cdot3$, both being determined by the second term in the potential. The interest in such extreme cases is only formal because at $Z_a = 6$ the orbital is already suitable for covalent-bond formation, and the change in size caused by the perturbation has a negligible effect on its overlapping power.

Values of the quantity σR_{44}^4, tabulated in an Appendix, allow the analogous calculations to be performed on orbitals of principal quantum number 4; we shall not discuss these in detail. The maximum value of σR_{44}^4 is at $\alpha = 4\cdot5$ for $\sigma = 4$, allowing the general conclusion that over most of the important range the second term in the potential will increase α for d_γ orbitals. Also because the variation is slow, the effect of this term is small as in the $3d$ calculation.

The reasons for the particular types of variation in α which higher terms induce are inherent in the problem. The point charges which surround the central atom attract the electron in the central atom's orbital. If this orbital is small compared with the radius of the charges it will tend to be expanded; if it is large it will be contracted; and the transition between these forms of behaviour will occur at a value of α for which the radial maximum of the orbital occurs at, or near, the charge radius σ. Now the radial maximum is at $r_m = n^2/\alpha$, where n is the principal quantum number of the orbital; equating r_m with σ
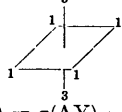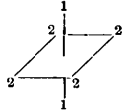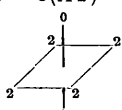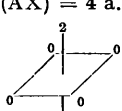
we find that the transition between orbital expansion and contraction is at $\alpha\sigma = n^2$, or at 9 a.u. for a 3 quantum orbital and 16 a.u. for a 4-quantum orbital. These values are not exact because the radial maximum is not exactly the measure of the quantity associated with the orbitals which determines whether they are drawn outward or inward by the field, but it is fairly close. A more precise measure is the value $\alpha\sigma$ at which the integrals of the later terms in the expansion have their maxima, *viz.*, $\alpha\sigma = 10\cdot5$ and 18 for third- and fourth-quantum orbitals respectively. Under the conditions of our problem the orbitals always require contraction to minimize their energy, and the zero-th term in the expansion of the potential overwhelms all others; this shows no maximum, and consequently the presence of the maximum only shows itself through the minor modifying effects which later terms in the potential exert.

Fields of lower symmetry. These may be produced by variations either in the charges Z_s or in the distances between the central atom and the ligands or in both. To simulate conditions in, for example, AX_4Y_2 molecules such as SF_4Cl_2 presumably both are required, but the effects of the variations are best examined separately. The first example is a *trans*-octahedral array consisting of two charges Z_{ax} and four Z_{rad}, all at the same distance σ. The potential is :

$$V_{r<\sigma} = -(2Z_{ax} + 4Z_{rad})/\sigma - \sqrt{(2/5)}\ \Theta_2{}^0(2Z_{ax}-2Z_{rad})(r^2/\sigma^3) -$$
$$\sqrt{(2/9)}\ \Theta_4{}^0(2Z_{ax} + 1\cdot5Z_{rad})(r^4/\sigma^5) - (35/16)\sin^4\theta\cos4\varphi\ Z_{rad}(r^4/\sigma^5) - \quad . \quad . \quad (11)$$

together with analogous expression for $V_{r>\sigma}$. The perturbation energy corresponding to the potential (11) can be found by using tables in the Appendix. One finds that in the important range of Z_a the major contribution to the energy is from the spherically symmetrical term which represents the potential of a charge $2Z_{ax} + 4Z_{rad}$ uniformly spread over a spherical surface of radius σ. The later terms in the potential (11) remove

TABLE 4. *Effective nuclear charge in* trans-AX$_4$Y$_2$ *fields.*

Field	Z_a	$\alpha(d_{z^2})$	$\alpha(d_{xz}, d_{yz})$	$\alpha(d_{x^2-y^2})$	$\alpha\ (d_{xy})$
$\sigma(AX) = \sigma(AY) = 4$ a.u.	1·5	3·0	3·2	3·05	3·25
	2·0	3·1	3·35	3·15	3·5
$\sigma(AX) = \sigma(AY) = 4$ a.u.	1·5	2·95	3·25	3·0	3·1
	2·0	3·08	3·48	3·10	3·33
$\sigma(AX) = 4$ a.u.	1·5	3·0	3·0	2·95	3·0
	2·0	3·15	3·15	3·05	3·15
$\sigma(AY) = 4$ a.u.	1·5	2·65	2·65	2·65	2·65
	2·0	2·85	2·9	2·9	2·9
Equal charges $Z_s = 2\cdot0$ .... $\sigma(AX) = 4$ a.u. $\sigma(AY) = 3$ a.u. ...	1·5 2·0	3·6 3·7	3·55 3·65	3·3 3·4	3·55 3·75
Equal charges $Z_s = 2\cdot0$ .... $\sigma(AX) = 3$ a.u. $\sigma(AY) = 4$ a.u. ...	1·5 2·0	3·65 3·8	3·8 4·1	3·75 3·9	3·85 4·1

most of the degeneracy of the orbitals, giving four components, namely d_{z^2}, d_{xy}, $d_{x^2-y^2}$, and d_{xz}, d_{yz}, the last two remaining degenerate. For each component the energy must be minimized with respect to the exponent α, for given values of the parameters Z_a, Z_s, and σ. Some values are given in Table 4. In connexion with binding in molecules,

d_{z^2} and $d_{x^2-y^2}$ are of special interest, the former being concerned mainly in the axial bond orbitals and the latter with p_x, p_y, and s in the radial orbitals.

The second extreme representation of asymmetrical molecules is in terms of variable bond lengths σ, with the same Z_s for all ligand groups. The important comparison is now between different molecules such as AX_4Y_2, AX_2Y_4, and the trend is illustrated by reference to ligands X and Y having the same charge Z_s but separated from the central atom by 3 and 4 atomic units respectively. Results are shown in the last two sets of Table 4. One sees that the effect of 2 or 4 of the more closely held ligand X on the exponent α is not too different from a linear interpolation between the extremes AX_6 and AY_6. The effect is dominantly isotropic with only minor variations between different orbitals. Thus contraction is greater in all directions for the presence of some groups held by short bonds. This might be important in molecules in which, by analogy with the properties of the model, one would expect that one or more groups held by short bonds (*e.g.*, first-row elements) would extend their influence to all the groups present and so to strengthen all the bonds.

To complete this consideration of the less symmetrical fields we should consider asymmetry developed by differences of charge and distance together. However this hardly seems necessary. The effect of charge asymmetry is small compared with the effect of the same total charge uniformly distributed, and smaller than the effect of changes in bond length. One finds that changing σ from 4 to 3 causes the same change in α as doubling the charges Z_s at a constant $\sigma = 4$. Thus where both charges and distances alter, the former may in general be neglected; and if only the charges vary it is clear that the consequent variations in α from orbital to orbital are small.

Interaction of the 3d with Other Atomic Wave Functions.—A full solution of the perturbation problem calls for an expansion in a complete set of functions, such as the hydrogen-like atomic functions of nuclear charge $Z_a + \delta$ referred to earlier. The effect of this is to allow· flexibility in the form of the radial wave function and so to distribute the electronic charge between the central nucleus and the perturbing nuclei in the manner required to minimise the energy. Such an expansion is not of course unique : variation in the radial function provides for a charge drift which could be approximated in other ways, such as by using a wave function initially which allowed some migration of the electron into orbitals at the perturbing centres.

In the regular octahedral field, the number of different atomic wave functions able to participate in the expansion is reduced by symmetry. In this field a d atomic wave function has components which transform as do the E and T_1 representations of the octahedral group. The same representations occur in wave functions of azimuthal quantum number 4, 6, 8 . . . so that the lowest wave function of other than d symmetry appearing in the expansion is the $5g$. The separation between orbitals $n = 3$ and $n = 5$ in the perturbing fields is several electron-volts and the influence of this orbital is negligible under this and the other conditions of the problem. The only important interconfigurational mixing is with other orbitals of d symmetry, and of these the $4d$ is most prominent, on account of its being closest in energy to the $3d$.

We consider the wave function (12) in terms of which the importance of $3d$ and $4d$ mixing may be studied :

$$\Psi(\alpha, \chi) = \phi_3\cos \chi + \phi_4\sin \chi \quad . \quad . \quad . \quad . \quad . \quad (12)$$

The $3d$ and $4d$ wave functions are given the same effective charge α. The energy may be expressed as follows, the new integrals $\mathfrak{A}$ and $\mathfrak{B}$ being tabulated in an Appendix.

$$W(\chi, \alpha\sigma) = \cos^2 \chi\left\{W_{3d}(\alpha\sigma) - (6z_s/\sigma)\, R_{33}^0(\alpha\sigma)\right\} +$$
$$\sin^2 \chi\left\{W_{4d}(\alpha\sigma) - (6Z_s/\sigma)\mathfrak{A}(\alpha\sigma)\right\} - \sin2\chi(6Z_s/\sigma)\mathfrak{B}(\alpha\sigma) \quad . \quad (13)$$

The values of $\cos^2 \chi$ and α which make the energy a minimum under the conditions $Z_a = 1$ and $\sigma = 4$ are given in Table 5. The examples, which are representative, show a marked energy depression by configuration mixing (1·8, 2·6, and 2·9 ev respectively) but only a

small change in α. Moreover the weight of the $3d$ function, given by $\cos^2\chi$, remains high, showing that the properties of the mixed wave function will be dominated by the $3d$ component. Thus we may expect that, for example, values of the overlap integral derived from a single contracted orbital will be close to values from the more complicated forms. In a field of lower symmetry, mixing will doubtless play a somewhat larger part.

TABLE 5. *The effect of $3d$ and $4d$ mixing for $Z_a = 1$, $\sigma = 4$.*

Z_s	α	$W_{min} + 6Z_s/\sigma$	$\cos^2\chi$	α ($\chi = 0$)	$W + 6Z_s/\sigma$ ($\chi = 0$)
1	2·65	0·17 a.u.	0·9	2·75	0·235 a.u.
2	2·85	0·245	0·9	3·05	0·34
4	3·15	0·345	0·9	3·45	0·45

Summary of Conclusions based on the Model.—(i) Slater orbitals of principal quantum numbers 3 and 4 with free-atom effective nuclear charges in the range 0—3 are strongly contracted by point charges at a distance σ equal to an average bond length. After contraction the effective nuclear charges α are usually in the range 1·5—5. Orbitals of principal quantum number $n = 4$ are more affected than $n = 3$.

(ii) It may be inferred that similar but diminishing effects will occur for orbitals $n = 2$ and $n = 1$, and increasing effects for $n = 5$ and 6.

(iii) For low values of free-atom effective nuclear charge the predominant effect is isotropic, affecting all orbitals with the same radial dependence whatever their angular properties. Secondary directional effects are small, even in fields such as the axial field of two point charges. In the secondary effect orbitals directed towards the field charges are more contracted than others if very loosely bound, and less contracted otherwise; the transition occurs for $n = 3$ orbitals at $\alpha\sigma = 10\cdot5$ and for those of $n = 4$ at $\alpha\sigma = 18$.

(iv) Because the contraction is mainly isotropic orbitals capable of π-bonding are contracted nearly to the same degree as σ-bonding orbitals.

(v) The energy of electron promotion in the presence of the field is greater than the free-atom promotion energy by an increment Δ depending on the distance σ, the charges Z_s of the field sources and the free-atom effective charge Z_a. The increment for $Z_a \simeq 0$ is probably greater than the free-atom promotion energy. For values of Z_a appropriate to the $3d$ orbitals of S and P the increment may be about 5 ev in the zero-th order approximation, but less when terms of higher order are included.

Application to Molecules.—The properties of the model systems may be calculated precisely or, if approximations are made, their effect can be foreseen. However, use of results for the model to interpret molecular properties requires assumptions of a far-reaching kind. Some of them inherent in the overlap approximation have been discussed.[1] Others concern mainly the use of Slater orbitals for the central atom and simulation of the atomic fields of the ligand atoms by the coulomb field of a point charge. Our discussion is confined to the particular question of the feasibility of covalent bonding after allowance for increase in overlap of the contracted orbital of a central atom with the orbitals of the ligand atoms. We shall not attempt to deal with the final determining factor in bonding, namely, the energy, since the relation between overlap and bond energy is not well established.

Slater functions are not very close approximations to self-consistent-field d orbitals, but this is not serious in calculations of overlap integrals which, at best, can serve only as a rough guide to the bonds likely to be formed. As applied to our present calculations the position is no worse; indeed it is likely to be somewhat better since we are concerned to establish a specific effect upon highly projecting orbitals and only the finer quantitative aspects of this depend upon the form of the orbital. Equally, it is of secondary importance for overlap calculations whether, the form of the orbitals being accepted, the exponents given by Slater's rules for free atoms have a precise quantitative significance. It will be seen in the work described in earlier sections that the value of α in the contracted orbital varies more slowly than the Z_a of the free-atom orbital, so that an error in the latter is cushioned. Finally, it has to be ensured that the Slater exponent can be identified with Z_a/n, where n is the principal quantum number, in the model. Treating this point

first, we note that the Slater exponents are in principle derived by minimizing the total energy of an atom. This includes exchange as well as coulomb-type terms. If, as for example in the $3s3p^33d$ configuration of P, we have a single electron exterior to all the rest the exchange interactions of this electron are very small, and the effect of all the other electrons on it differs little from the effect of the same total electronic charge amalgamated with the nucleus. In this case we are quite justified in identifying the Slater effective charge with the actual charge Z_a on the nucleus in the model. If there are two equivalent projecting electrons as in $3s3p^33d^2$ the Slater value of the effective charge may be identified with Z_a only when allowance is made for the mutual repulsion between the two electrons, as described earlier, and when exchange integrals of the other electrons with the outer pair may be ignored. The case would be quite different for an inner electron; there the potential field is not even roughly that of point charge but has substantial non-central coulomb and exchange contributions strongly configuration-dependent, and the behaviour of the electron could not be represented at all well in a one-electron model with the same nuclear charge. It turns out that only in the circumstances of a highly screened and loosely bound exterior electron can our model be applied; and fortunately this is the case of interest.

*The Field of Ligand Atoms.**—To apply the model to molecules also makes it necessary to represent the field of a ligand atom by that of a point charge. The approximation made in doing this can be brought out by considering a case intermediate in complexity between the model and real systems. This is a central hydrogen-like atom with, as usual, a loosely bound electron surrounded, not by point charges, but by other hydrogen-like atoms, introducing the possibility of bonding between the electron of the central atom and those of the surrounding atoms. The potential of the ligands now consists of the attraction of their nuclei minus the coulomb repulsions of the ligand's electrons plus exchange terms. Evidently the dependence on distance of this composite potential will not follow the r^{-1} law at all closely, and the parameter Z_s used in the model as the perturbing charge of the ligand can be no more than the parameter of a coulomb field which is equivalent in some sense to the true atomic field. The same holds in complex atoms. It is clear that at any point in the field of an atom there is a value of Z_s which will give the value of the potential at that point provided only that the field is spherically symmetrical, and another which will give the field strength, but the values of each vary with r. Values of these quantities are given in calculations of the self-consistent fields of atoms and may be used in a useful comparison of the halogen atoms F, Cl and Br. For this purpose Table 6 compares values of Z_p, the potential-determined nuclear charge, and Z_f, the field-determined nuclear charge for the halogens each at its single-bond covalent radius.

TABLE 6. *S.C.F. Effective charges of the halogens at the covalent radius.*

	Covalent radius (a.u.)	Z_p	Z_f	Ref.
F	1·21	0·7	2·6	8
Cl	1·87	0·8	3·1	9
Br	2·16	0·7	3·1	10

Differences between the halogen atoms should not be expressed primarily as differences in the charge parameter Z_s since at the respective covalent radii the charges are nearly the same and show no clear trend. We shall therefore assign to the halogens the same value Z_s, and treat this as a parameter, taking values in the range 0·25—4·0, which includes the likely values both of Z_p and Z_f in Table 6. The differences in behaviour between the halogens emerge as the result of different separations from the central atom and not of different perturbing charges. The contraction is quite sensitive to changes in the distance

* Clearly the effect of ligand atoms is related to their electronegativity; but electronegativities cannot be used directly, since separate values are required for effective charge and bond length. These two are amalgamated in the concept of electronegativity.[7]

[7] Pritchard and Skinner, *Chem. Rev.*, 1955, **55**, 745.
[8] Brown, *Phys. Rev.*, 1933, **44**, 214.
[9] Hartree, Kronig, and Paterson, *Physica*, 1933, **1**, 895.
[10] Arnot and McLaughlan, *Proc. Roy. Soc.*, 1934, *A*, **146**, 662.

parameter σ, as has already been pointed out, and, since the bond-length differences are considerable, the contractions vary substantially from F to Cl, and from Cl to Br. We should expect different Z_s values for elements in different Periodic Groups, but variations in bond lengths should still play the more important part. It must be emphasized that this discussion of actual values for Z_s is tentative. The fact that the ligand fields are not truly coulombic makes the choice of the " equivalent " coulomb parameter rather uncertain.

The domain of application of the model is, broadly, to those molecules for which covalent binding requires participation by loosely held d orbitals. The simplest are those with $3d$ orbitals, for example, the halides of second-row elements and certain complex ions such as AlF_6^{3-}; and with $4d$ orbitals there are analogous halides and ions and as well the large and important class of transition-metal complexes with incomplete $3d$ shells. In some of these, both $3d$ and $4d$ electrons may be concerned : the $3d$ by their electrostatic ·stabilization in the crystalline field, and the $4d$ in covalent binding. On account of their additional complexity we postpone dealing with these molecules and confine attention to the simple examples for which, moreover, overlap integrals are available.

In a following section we apply our work to two specific cases, namely, the halides of sulphur and phosphorus. The application of the model to these molecules has the following features : (i) for the central atom we use the effective nuclear charge calculated from Slater's rules as the actual nuclear charge of a hydrogen-like orbital, treating inner electrons as fused into the nucleus. This applies to a single exterior d electron as in $P(3s3p^33d)$; with two equivalent electrons, as in $S(3s3p^33d^2)$, interelectronic effects are allowed for either by using the Slater effective charge for the configuration $3s3p^33d$ and including interelectron repulsion explicitly or, a little less precisely, by using the Slater exponent straightforwardly for the two-electron case and allowing the repulsion to be taken up in the extra screening correction. (ii) For the ligand atoms we retain the fiction of a coulomb field but compute for a wide range of the coulomb parameter Z_s. The same charge parameter is used for all halogens, differences being allowed to appear through the variations in internuclear spacings σ.

Application to molecules PX_5 *and* SX_6. The bond lengths in phosphorus penta-fluoride and pentachloride are approximately 2·9 and 4·0 a.u. Ignoring small effects such as higher order terms in the potential, we work out the contractions as already discussed, for a range of charge parameters Z_s and equating σ to the bond length. The calculations are summarized in Table 7, in which $\alpha/3$ is the exponent of the contracted $3d$ orbital. Since our results depend only on the total charge $\sum Z_s$, the octahedral field results for $Z_s = 0·25$ apply directly to the trigonal bipyramid for $Z_s = 0·30$ and the same bond lengths.

TABLE 7. *Contractions and* p_z–d_{z^2} *overlaps in* PF_5 *and* PCl_5.

	PF$_5$			PCl$_5$		
Z_s	σ	$\alpha/3$	S	σ	$\alpha/3$	S
0	—	0·33	0	—	0·33	0
0·3	3	0·7	0	4	0·6	0
0·6	3	0·9	−0·01	4	0·8	0·1
1·2	3	1·1	0·05	4	0·9	0·17
2·4	3	1·3	0·12	4	1·0	0·2
4·8	3	1·5	0·17	4	1·1	0·22

In Table 7 the P–F bond length is taken as 3·0 a.u. to use values already tabulated. The overlaps are $2p_z$–$3d_{z^2}$ for PF_5 and $3p_z$–$3d_{z^2}$ for PCl_5; the latter has been tabulated [1] and the former is given in an Appendix. For all Z_s the phosphorus orbital is more contracted in the pentafluoride than in the pentachloride, and the overlap associated with the contracted orbitals is comparable in the two examples although distinctly greater in the second. Small differences in overlaps may or may not be significant for bond strengths; the more important points are, first, that contraction is bigger for the fluoride than for the chloride for the same effective charges Z_s, and, secondly, that the d overlap becomes comparable with the s–p and p–p overlaps for Z_s values within the physically reasonable range. For example in the pentachloride the P(s)–Cl(p) overlap is 0·24 and the P(p)–Cl(p)

overlap is 0·28, both little greater than the p–d values given at the end of Table 7. The sp^3d covalent bond model in phosphorus pentachloride becomes tenable therefore once the contraction has been allowed for; and similar arguments apply to the pentafluoride.

In the hexahalides of sulphur we take $\sigma = 3$ a.u. for the fluoride and $\sigma = 4$ for the hypothetical chloride. The overlaps are found by interpolation in the tabulated values (Table 8). As before, the d overlap becomes considerable when the contraction is taken into account; it is comparable to the overlap of s and p orbits of S.

Table 8.

Z_s	SF$_6$			SCl$_6$		
	σ	$\alpha/3$	S	σ	$\alpha/3$	S
0	—	0·55	0	—	0·55	0
0·25	3	0·9	0·0	4	0·7	0
0·5	3	1·0	0·05	4	0·8	0·14
1·0	3	1·1	0·07	4	1·0	0·15
2·0	3	1·3	0·12	4	1·1	0·18
4·0	3	1·5	0·17	4	1·2	0·20

π-Bonding. Even in unsymmetrical fields all the d orbitals are contracted to about the same extent. For example in the " square " field of 4 equal charges $Z_s = 2$, one finds $\alpha(d_{z^2}) = 3\cdot15$, $\alpha(d_{x^2-y^2}) = 3\cdot05$, $\alpha(d_{xz}, d_{yz}) = 3\cdot15$. The last orbitals are used for π bonding in a square molecule, and the near equality of effective charge with the σ-bond orbital shows that an environment which prepares diffuse d orbitals for participation in σ-bond formation will allow π-bonding also if other conditions are met, such as availability of orbitals on the ligand atom. An example in which such π-bonding is important is sulphur trioxide, although here it is not necessary to invoke d participation in the σ-framework. If the sulphur valence state is taken as $3s3p^43d$ or $3s^23p^33d$ three σ-bonds hold the trigonal shape, and one π-bond can be formed by using one of $3d_{xz}$ and $3d_{yz}$ or $3p_z$, the π-bond being shared between three sites. Alternatively if two electrons are to be promoted into the configuration $3s3p^33d^2$, three sp^2 bonds are supplemented by three pd^2 π-bonds. Both possibilities have of course been long recognized; but we can now support them by the consideration that the d orbitals concerned are capable of substantial overlaps with the $2p\pi$ orbitals of oxygen. With a value of $Z_s = 1\cdot0$ chosen to use available results, we find $\alpha(d_{xz}) = 2\cdot8$. The $3d_\pi$–$2p_\pi$ overlap integral for the S–O bond is 0·26, a value which would be increased in a p–d hybrid. One sees therefore that the overlap requirements implicit in the suggestion of double bonding are amply met. The gain from the second electron promotion amounts to two extra π-bonds, and a strengthening even of the first, so that one might expect the sp^3d^2 valence state to be attained in this molecule, as in the structure (A).
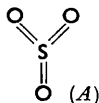
We thank Dr. I. G. Ross for his helpful comments on the manuscript.

APPENDIX 1.   *Auxiliary functions defined in equation* (7).

$\alpha\sigma$	σR_{33}^0	σR_{33}^1	σR_{33}^2	σR_{33}^3	σR_{33}^4	σR_{34}^0	σR_{44}^0	σR_{44}^2	σR_{44}^4	$\mathfrak{A}$*	$\mathfrak{B}$†
2·5	0·4133	0·1976	0·1088	0·0679	0·0470	0·3563	0·3123	0·0453	0·0110	0·3048	0·1125
3·0	0·4915	0·2723	0·1692	0·1158	0·0854	0·4261	0·3742	0·0766	0·0259	0·3571	0·1291
3·5	0·5656	0·3497	0·2368	0·1727	0·1333	0·4941	0·4357	0·1169	0·0479	0·4071	0·1411
4·0	0·6341	0·4249	0·3061	0·2334	0·1861	0·5593	0·4958	0·1655	0·0787	0·4514	0·1477
4·5	0·6961	0·4939	0·3714	0·2922	0·2385	0·6208	0·5541	0·2203	0·1175	0·4928	0·1486
5·0	0·7511	0·5538	0·4286	0·3447	0·2859	0·6778	0·6098	0·2785	0·1616	0·5317	0·1447
6·0	0·8394	0·6408	0·5098	0·4189	0·3531	0·7757	0·7107	0·3930	0·2559	0·6074	0·1257
7·0	0·9011	0·6838	0·5433	0·4467	0·3771	0·8510	0·7948	0·4879	0·3381	0·6831	0·0989
8·0	0·9416	0·6912	0·5373	0·4354	0·3639	0·9052	0·8604	0·5503	0·3917	0·7554	0·0719
9·0	0·9667	0·6743	0·5053	0·3988	0·3271	0·9419	0·9087	0·5776	0·4115	0·8211	0·0490
10·0	0·9817	0·6434	0·4598	0·3501	0·2795	0·9657	0·9424	0·5749	0·4014	0·8746	0·0316
12·0	0·9949	0·5676	0·3616	0·2511	0·1863	0·9890	0·9792	0·5126	0·3278	0·9470	0·0116
15·0	0·9994	0·4647	0·2455	0·1444	0·0929	0·9984	0·9963	0·3807	0·1958	0·9882	0·0020
20·0	1·0000	0·3500	0·1399	0·0629	0·0314	0·9999	0·9999	0·2243	0·0729	1·0000	0·0002

* $\mathfrak{A} = 4\cdot5\sigma R_{33}^0 - 10\cdot5\sigma R_{34}^0 + 7\sigma R_{44}^0.$ † $\mathfrak{B} = 1\cdot974(\sigma R_{33}^0 - \sigma R_{34}^0).$

APPENDIX 2. *Overlap integrals :* $S(2p_z-3d_{z^2})$.

p/t *	−0·5	−0·4	−0·3	−0·2	−0·1	0·0
2	−0·1688	−0·2411	−0·3106	−0·3698	−0·4124	−0·4338
3	−0·1042	−0·1349	−0·1610	−0·1831	−0·2021	−0·2183
4	−0·0216	0·0078	0·0105	0·0268	0·0346	0·0299
5	0·0382	0·0770	0·1182	0·1539	0·1770	0·1826
6	0·0675	0·1113	0·1548	0·1917	0·2175	0·2286
7	0·0740	0·1111	0·1454	0·1739	0·1949	0·2069
8	0·0675	0·0938	0·1163	0·1343	0·1484	0·1586
9	0·0558	0·0719	0·0842	0·0936	0·1017	0·1093
10	0·0433	0·0517	0·0570	0·0607	0·0646	0·0697

p/t *	0·1	0·2	0·3	0·4	0·5
2	−0·4313	−0·4040	−0·3540	−0·2859	−0·2076
3	−0·2303	−0·2352	−0·2289	−0·2077	−0·1705
4	0·0118	−0·0169	−0·0495	−0·0770	−0·0900
5	0·1684	0·1354	0·0882	0·0357	−0·0103
6	0·2226	0·1985	0·1573	0·1038	0·0473
7	0·2083	0·1968	0·1707	0·1300	0·0792
8	0·1642	0·1630	0·1519	0·1277	0·0903
9	0·1162	0·1210	0·1205	0·1106	0·0878
10	0·0761	0·0832	0·0886	0·0884	0·0777

* Notation as in ref. 1.

DEPARTMENT OF PHYSICAL CHEMISTRY,
    THE UNIVERSITY OF SYDNEY.
DEPARTMENT OF CHEMISTRY,
    THE N.S.W. UNIVERSITY OF TECHNOLOGY.