A thesis entitled

d-ORBITALS IN LATER SECOND ROW ELEMENTS

submitted by

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The work described in this thesis is the candidate's own work, except as otherwise stated.

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UNITS AND ACCURACY OF CALCULATED VALUES

Unless otherwise stated all values quoted are in atomic units. The unit of energy is the Rydberg. Where calculated values are quoted in other units, the conversion factors used, taken from the review of Cohen and DuMond[1] were:

$$\begin{aligned} a_o &= 0.529167_2 \text{ Å} \\ 1 \text{ Rydberg} &= 13.60535_{13} \text{ eV} \\ &= 109{,}737.199 \text{ cm}^{-1} \\ &= 313.6305 \text{ kcals/mole} \end{aligned}$$

K and L shell orbital exponents were calculated to ± 0.001. Unless otherwise stated M shell orbital exponents were calculated to ± 0.001. The mixing parameter λ used in the two term 3d orbital basis set was calculated to ± 0.0001. The energies calculated are quoted to an accuracy of ± 0.00001 a.u. Changing an M shell orbital exponent by 0.001 will generally change the energy by less than 1.0×10^{-6} a.u. When energies were converted into other units they are generally quoted to less precision than could be possible as the greater precision was not needed for the purpose the number was quoted.

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CHAPTER 1

d ORBITALS IN LATER SECOND ROW ELEMENTS - A SURVEY

The concept of an electron-pair bond comes from the work dating from 1916, of Lewis,[2] Langmuir[3] and Kossel.[4] As Pauling[5] showed in his classic paper on the nature of the chemical bond, their theories survived the impact of the advent of quantum mechanics remarkably unscathed and are still the basis of much of our understanding of the phenomenon of chemical bonding. They also introduced the "octet rule". However, their theory is incomplete. The octet rule breaks down for molecules such as SF_6 and PF_5 which possess an "expanded octet" - there are twelve and ten electrons respectively involved in bonding. The ground state of the sulphur atom is the $1s^22s^2p^63s^2p^4\ ^3P$ term. Only two of the electrons are unpaired. According to the electron pair theory the sulphur atom could only form two, not six, single bonds. The classic example of this situation is the tetrahedral carbon atom. There is thermochemical evidence that the bonds in molecules like SF_6 and PF_5 are different. In PCl_5 the P-Cl bond energy[160] is 63 kcals/mole whilst in PCl_3 where the octet rule is obeyed, it is 78 kcals/mole. In PF_5 and PF_3 the P-F bond energies are 110 and 117 kcals/mole respectively. Many attempts have been made to rationalise this seemingly anomalous situation.

A feature of many of these is the use of 3d orbitals in describing the electron distribution in these molecules. The description of the electron distribution is the primary purpose of their quantum mechanical analysis. A knowledge of the electron distribution permits the interpretation of physical properties, prediction of further molecular types etc. It is described by a basis set of atomic orbitals. This set is not infinite but is cut off after a few terms. As a result no basis set is unique. The choice between basis sets must be made on the criterion of how well they describe the electron density in real molecules and how convenient they are as models, allowing straightforward interpretation of chemical behaviour and enabling predictions for the guidance of experimental work. This is no problem for the first row atoms since usually one basis, e.g., that derived from the $2sp^3$ configuration for carbon, is so much better than any other that it so to speak chooses itself. This is not the case for second row elements. Thus for a given molecule there have been put forward a number of possible basis sets, in some of which 3d orbitals are ignored whilst in others they are included. The 3d orbitals are seen as being used in forming both σ and π bonds. We shall first discuss the formation of σ bonds and then look at π bonds in compounds of the later second row elements.

σ Bonds

As is the case for most valence problems, the formation of σ bonds with these elements has been considered using both the molecular orbital method and valence-bond type approaches. Of the latter, the most important is the hybrid orbital method.

Hybrid Orbital Method

To obtain six unpaired electrons required by the electron pair theory to form the six S-F bonds in SF_6, it is necessary to excite the sulphur atom. The lowest lying configuration of sulphur which would give six unpaired electrons is $3sp^3 4s4p$. However this is ruled out by symmetry considerations. SF_6 is octahedral. The representation Γ_σ for which the six σ orbitals of SF_6 form a basis reduces as

$$\Gamma_{\sigma} = A_{1g} + E_{g} + T_{1u} \tag{1.1}$$

The only possible combination of atomic orbitals so that one is of A_{1g} symmetry, two of E_g symmetry and three of T_{1u} symmetry is s, p_x, p_y, p_z, d_{z^2}, $d_{x^2-y^2}$. The lowest lying configuration of sulphur with all six of these atomic orbitals is the $3sp^3d^2$ configuration. Thus in this hybrid orbital model it is necessary to invoke the participation of 3d orbitals if the sulphur atom is uncharged. (As we shall show later the problem is not necessarily resolved by giving some positive charge to the sulphur atom.) Whilst this set satisfies the symmetry requirements of the problem, individually the six sulphur orbitals do not form bonds that are equivalent or necessarily directed towards the corners of a regular octahedron. These requirements are met by the six equivalent wavefunctions (1.2) formed by a linear combination of the six orbitals:

$$\begin{aligned}
\phi_1 &= \frac{1}{\sqrt{6}}\, s + \frac{1}{\sqrt{2}}\, p_z + \frac{1}{\sqrt{3}}\, d_{z^2} \\
\phi_2 &= \frac{1}{\sqrt{6}}\, s - \frac{1}{\sqrt{2}}\, p_z + \frac{1}{\sqrt{3}}\, d_{z^2} \\
\phi_3 &= \frac{1}{\sqrt{6}}\, s + \frac{1}{\sqrt{2}}\, p_x - \frac{1}{\sqrt{12}}\, d_{z^2} + \tfrac{1}{2} d_{x^2-y^2} \\
\phi_4 &= \frac{1}{\sqrt{6}}\, s - \frac{1}{\sqrt{2}}\, p_x - \frac{1}{\sqrt{12}}\, d_{z^2} + \tfrac{1}{2} d_{x^2-y^2} \\
\phi_5 &= \frac{1}{\sqrt{6}}\, s + \frac{1}{\sqrt{2}}\, p_y - \frac{1}{\sqrt{12}}\, d_{z^2} - \tfrac{1}{2} d_{x^2-y^2} \\
\phi_6 &= \frac{1}{\sqrt{6}}\, s - \frac{1}{\sqrt{2}}\, p_y - \frac{1}{\sqrt{12}}\, d_{z^2} - \tfrac{1}{2} d_{x^2-y^2}
\end{aligned} \tag{1.2}$$

These hybrid orbitals form the strongest possible octahedral bonds having a bond strength as defined by Pauling[5] of 2.923. The bonding in other compounds of later second row elements may be considered similarly.

There are several objections to this approach which, if valid, make the theory untenable. As there is no spectroscopic data available for S (sp^3d^2) the atomic hydrogen-like wavefunctions are usually obtained using Slater's rules.[6] These give an effective nuclear charge of 1.65 for the d orbitals of sulphur in the sp^3d^2 configuration. The mean radius of these orbitals is 5.45 a.u., whereas the S-F bond length is 2.96 a.u. Unless the orbital size is reduced in molecular formation or Slater's rules are not adequate for dealing with the valence state of atoms, the orbitals are too diffuse to be useful in bonding. The 3d electrons are also considered to be too weakly bound. The energy of double promotion from the s^2p^4 to the sp^3d^2 configuration has been variously estimated. Both calculated and experimental results suggest a value greater than 25 eV and probably greater than 30 eV leading to what is thought to be an unattainably large promotion energy contribution to the total molecular energy. One should also remember that this approach completely ignores the partial ionic character of the S-F bonds. These objections have been the subject of a considerable amount of study. The greater part of the work described in this thesis is on this subject.

The idea that the d orbitals might be modified by the molecular environment was first put forward in a qualitative way by Craig, Maccoll, Nyholm, Orgel and Sutton.[8] Their suggestion resulted from an examination of overlap integrals involving 3s, 3p and 3d orbitals. The overlap integral $S_{AB} = \int \phi_A \phi_B d\tau$ had been used successfully as a criterion of bond strength by Mulliken[9] and Maccoll.[10] Using this criterion, Craig et al. were able to show that the diffuse d orbitals predicted by Slater's rules were unlikely to form useful bonds. The overlapping power of the d orbitals could only be made compatible with bond formation if the orbitals were contracted so that they gave overlaps comparable with those of 3s and 3p orbitals. This it was considered, could well happen in the field of a fairly highly electronegative atom.

The study of the mechanism of this contraction was commenced by Craig and Magnusson.[11-14] The first model they used was that of a single d electron moving in the field of a nucleus of charge Z_a surrounded by six positive charges of magnitude Z_s (simulating electronegative legand atoms) in a regular octahedral array of radius 3-4 a.u. The energy minimised effective nuclear charge for the d electron is increased from an assumed free atom value of 1 unit to 3 units of charge, reducing the mean radius of the orbital from 10.5 to 3.5 a.u. This would certainly seem to make d orbital bonding feasible. However, it should be realised that the energy of promotion of the electron into a 3d orbital is increased slightly by this contraction in size, the orbital exponents no longer being those that minimise the promotion energy. This model only involved a single d electron. With two equivalent d electrons they found that the screening correction for interelectronic repulsion is reduced by the perturbing field. In fields with symmetry lower than octahedral, where both charge and charge-nucleus separations vary, they concluded that the charge variations may, in general, be neglected. If only charges vary, the consequent variations in orbital size are small. In this model d_π and d_δ d orbitals as well as d_σ orbitals are substantially contracted. Overlap integrals, involving these contracted d orbitals, indicate that d orbital bonding is feasible. On examination of the use of a more flexible 3d wavefunction involving the mixing in of a 4d term into the wavefunction, it was found that the 3d term still dominated the properties of the mixed wavefunction. The mixing in of other wavefunctions with the correct symmetry is characteristic of perturbation theory; it also helps to improve the Slater functions which, it was known, were not very close approximations to self-consistent field d orbitals.[15] The point charge model is a simple model. Its use was due to the mathematical complexity of complete calculations on large molecules and the fact that, until very recently, computers were not available or powerful enough to perform the calculations required when the mathematical problems had been overcome.

A better approximation to the field of a ligand atom is that of a point dipole. For ligand atoms like F in SF_6 these are positive inward dipoles. Craig and Magnusson[13] showed that in the field of these dipoles, a contraction similar to that in a monopole field occurs. However there is a smaller promotion energy in the dipole case. With negative inward pointing dipoles expansion, not contraction, occurs.

A more realistic model is one which uses a potential calculated from numerical SCF calculations.[15] Magnusson found that a field of six fluoride ions always led to expansion, as expected. For d orbitals of low initial exponent some contraction occurs with Cl^-. This was ascribed to the larger, more diffuse electron cloud of Cl shielding the nucleus less efficiently.

Calculations on a hypothetical diatomic molecule, AB, with two electrons whose atomic orbitals were chosen to resemble the fluorine $2p_z$ and sulphur $3d_{z^2}$ orbitals in SF_6 gave an optimum $3d_{z^2}$ orbital exponent of 1.7. This would make the participation of d orbitals in bonding important. Again, the optimum d orbital exponent depended heavily on the internuclear distance.

Thus the work of Craig and Magnusson showed that modification of d orbital size was likely to occur. The models used were primitive but the results are convincing. The most important objection to their approach was that they considered the d orbitals in isolation from the other electrons of the atom.

A more complete model was used in work by Craig and Zauli.[16-18] Fairly extensive calculations were done, especially on SF_6. The electrostatic potential due to the fluorine atoms was calculated using atomic SCF wavefunctions for the fluoride ion. The potential due to the fluorine atom was obtained by subtracting the potential due to the $2p_\sigma$ orbital, calculated from the appropriate SCF wavefunction,[19] from that calculated for the fluoride ion. This is a good approximation to the ligand field. Their results are summarised in Table 1.1. The lowest lying configuration is that with the configuration of sulphur being $3sp_xp_yp_zd_{z^2}d_{x^2-y^2}$ followed by the $3sp_xp_yp_zd_{x^2-y^2}$ configuration where the sulphur atom is singly charged. The d orbitals are all well contracted. The 3s and 3p orbitals are slightly expanded. The effect of the use of 2s-2p hybrid orbitals of fluorine of the form

$$\Phi = \cos\theta \; 2p_\sigma + \sin\theta \; 2s \quad , \qquad (1.3)$$

in bonding was to give slightly more contracted orbitals than obtained with pure $2p_\sigma$ orbitals; the effect being greatest for the 3p orbital. The variation in the 3d orbital exponent was only 0.03. In this model all electrostatic or "coulombic" interactions have been taken into account. However there remain two important objections to this approach - the neglect of intra- and inter-atomic exchange interactions and the non-orthogonality of the sulphur orbitals with the fluorine orbitals. Craig

Table 1.1

Calculations by Craig and Zauli on SF_6

Designation	Configuration	$E-E_{S_{core}}-E_F$ a.u.	α_{3s}	α_{3p}	α_{3d}
SF_6	$3sp_xp_yp_zd_{z^2}d_{x^2-y^2}$	-20.36	2.00	1.59	1.22
$S^+F_6^-$	$3sp_xp_yp_zd_{x^2-y^2}$	-20.04	2.02	1.60	1.22
$S^-F_6^+$	$3s\bar{s}p_xp_yp_zd_{z^2}d_{x^2-y^2}$	-19.36	2.09	1.49	1.19
$S^{++}F_6^=$ cis	$3sp_xp_yp_z$	-19.76	2.04	1.61	---
trans	$3sp_xp_yp_z$	-19.90	2.04	1.61	---
S_{atom}	$3s^2p^4$	-18.04	2.14	1.66	---

and Zauli considered that the variation in orbital exponent due to the inclusion of intra-atomic exchange (which they underestimated to be only of the order of 0.1) was not significant. Philips[20] had shown that the energetic consequence of orthogonalisation was equivalent to putting a repulsive term in the potential energy. These repulsive terms would be to some degree offset by the attractive exchange terms so that it was considered inconsistent to include one without the other. These assumptions should be tested.

If we can equate the ability of a second-row or third-row element to raise its covalency with the ability of its d orbitals to take part in bonding, we must conclude that a wide variety of elements can facilitate d orbital promotion in an atom to which they are bound. Fluorine, chlorine and bromine certainly do so, and oxygen and nitrogen do also. Even carbon has to be included by virtue, for example, of the occurrence of pentacovalent phosphorus in $P(C_6H_5)_5$. The surprising thing is the large number of ligand elements which can act in this way, and also the fact that they are not only the highly electronegative elements, although the bonds formed do seem stronger the more electronegative the ligand atom. To try to understand the relation between the electronegativity of a ligand and its ability to raise the covalency of a second row element atom, Craig and Zauli studied how d orbitals were contracted in the field of H,C(sp^3), Cl and F atoms for various arrangements of ligand atoms. Their calculations in this case were not as extensive, e.g., 3s and 3p orbital exponents were kept constant. They found that fluorine is the most effective, chlorine and carbon less effective and roughly equal to one another, whilst hydrogen has only a very small effect. This is the order of the electronegativities except for the unexpected position of carbon. There is a strong dependence of the perturbing power on bond length. In comparing the orbital contraction obtained with different numbers and spatial arrangements of the same ligand atom it was found that the first atom attached is responsible for most of the orbital contraction, the contributions of the other ligands being successively less. This suggests that in mixed ligand systems, the presence of only one or two strongly perturbing atoms is sufficient for d orbitals to contribute to all bonds. Hydrides of the later second row elements in higher covalent states are thus able to occur in mixed systems, e.g., H_3PO_2, H_3PO_3 whilst PH_5 is unlikely to be stable.

In the electrostatic field of the ligand atoms they found that π and δ d orbitals contracted negligibly. This is the opposite to a result of Craig and Magnusson who found significant contraction in a monopole field. The difference can be explained by the fact that the monopole field falls off more slowly than the actual field of the atom. Exchange terms should be more important for these orbitals.

A critical examination of Craig and Zauli's approach has been made by Webster.[21,22] He investigated the effect of the neglect of intra-atomic exchange on the 3d orbital exponent. For the ^7F term of the sp^3d^2 configuration of sulphur a value of 0.596 for the optimum 3d orbital exponent was obtained without including exchange terms.[27] This is almost equal to the value of 0.599 obtained for the $3sp_xp_yp_zd_{z^2}d_{x^2-y^2}$ valence state. On including exchange, a value of 1.18 was obtained for the ^7F term. The neglect of intra-atomic exchange is obviously a serious defect in the Craig-Zauli approach. This result poses the important question - is orbital contraction by ligand field a necessary condition for 3d participation in bonding? This will be discussed later. Webster also pointed out that the use of two sets of core functions - SCF functions and their best superimposable Slater functions - could lead to errors. In the case of SF_6 they are negligible. Cruickshank, Webster and Spinnler[22] have pointed out that the neutral penetration integral terms are very important. They certainly cannot be ignored as is often the case in performing semi-empirical molecular orbital calculations. Another possibly important defect in the Craig-Zauli method is the neglect of the non-orthogonality of the sulphur valence orbitals with the ligand core orbitals. The correction to the energy has been reported as being significant.[22]

The Craig-Zauli approach was used by Mitchell[24,25] in studying orbital modification of phosphorus d orbitals in phosphonitrilics $(PNX_2)_n$ X = F, CL, =0, C etc. The d orbitals are seen to be principally engaged in $3d_{xz} - 2p_z\ \pi$ bonding. The d orbitals are contracted by the field of the σ bonding ligand atoms. The phosphorus d orbital sizes in these phosphonitrilics are slightly smaller than those calculated for sulphur in SF_6. Using approximate expressions for the interatomic exchange integrals he found a slight reduction in 3d orbital exponent as compared with that obtained in a purely electrostatic calculation. The inclusion of exchange slightly reduces the energy of the other d orbitals thus reducing the differences between the individual orbital energies. Exchange interactions are obviously important.

The modification of the size of d orbitals by the ligand field as a prerequisite for d orbital participation in bonding would be unnecessary if in the free atom they had a favourable size, i.e., if Slater's rules are inadequate to describe the orbitals in the valence state. This question was first investigated by Cruickshank, Webster and Mayers.[23] Using the Hartree Fock method[15] they obtained numerical wavefunctions for a number of terms of sulphur. They found that for the ^7F term of the sp^3d^2 configuration of sulphur, the 3d orbital is contracted, having a mean radius of 1.18Å compared with 3.36Å predicted by Slater's rules. This is one of the lowest terms in the configuration manifold; higher terms will be more diffuse. The ^5D term of $3s^2p^3d$ has a mean radius of 4.00Å.

This orbital size is probably too diffuse to be at all useful without further contraction by the field of the ligands, but that for the ^7F term is certainly the right size. The question of the size of the orbitals in the valence state still remained. This was taken up by Craig and Thirunamachandran[26,27] who used the two term double-zeta analytical 3d wavefunction first used by Richardson, Nieuwpoort, Powell and Edgell.[28] They found close agreement with Cruickshank, Webster and Mayer's SCF results for atomic terms. For the single configurational $3sp_xp_yp_zd_{z^2}d_{x^2-y^2}$ valence state they found that the 3d orbital had a mean radius of 2.39Å - too diffuse for orbital contraction not to be required. However for the multiconfigurational valence state involving equivalent octahedral hybrid orbitals, the mean radius of the 3d orbitals is 1.45Å. This is sufficiently contracted that orbital contraction need not be invoked.

The question of the size of d orbitals in the free atom has consequently been extensively investigated by several groups.

Webster[21] has examined a large number of d orbital containing configurations of the series of elements silicon → argon using Hartree, Hartree-Fock and Hartree-Fock-Slater methods. Some orbital features which he found are worth noting. The d orbitals are more contracted in a d^2 configuration than in a d^1 configuration. In a d^1 configuration the shape of the d orbital is almost independent of the occupancy of the 3s and 3p orbitals. There is a definite variation in the case of d^2 configurations. Variations between different elements, not expected on the basis of Slater's rules, are evident. Scarcely any variation occurs using the Hartree method which neglects exchange. His consideration of the neglect of exchange has already been mentioned. A parameter he used in discussing the shapes of orbitals was

$$A = \mathrm{Lt}_{r \to 0} \left(\frac{R_{n\ell}(r)}{r^{\ell}} \right) \tag{1.4}$$

which is a measure of the initial slope of the wavefunction. It is particularly useful in showing the difference between the wavefunctions obtained with and without using exchange and the variations between various elements. Webster was able to show conclusively that for a reasonably contracted orbital, such as that for the ^7F term of the sulphur $3sp^3d^2$ configuration, the Slater orbital bears little resemblance to the SCF orbital.

Coulson and Gianturco[29] have used Mayer's SCF program[30] to examine some states of sulphur. They re-examined some of the spectroscopic terms, investigated a number of single configurational and multiconfigurational valence states and the effect of adding some charge to the sulphur atom. Their work mainly complements the work of Cruickshank, Webster and Mayers and Craig and Thirunamachandran. They found a significant decrease in 3d orbital size when the sulphur atom is positively charged. However the configuration of the charged sulphur atom $s^{0.9}p^{2.7}d^{1.8}$ they used overestimates the d orbital occupancy giving a larger contraction than in fact occurs. One interesting hypothesis they put forward is that charge transfer and associated back donation are necessary for the higher valences in molecules like SF_6. This could explain the non-existence of the hydrides of the later second-row elements, e.g., SH_6.

The two term analytic wavefunctions were used by Craig and Thirunamachandran[27] to study several spectroscopic terms of the $3sp^3d^2$ configuration of sulphur. These calculations included intra-atomic exchange. Quite a large variation in d orbital size occurs as one spans the configuration manifold. Thus the ^1S term which would be expected to be one of the higher terms has a mean radius of 2.65Å and a radial maximum at 2.33Å, whilst the ^7F term which by Hund's rule[103] should be one of the lowest terms, has a mean radius of 1.85Å and a radial maximum at 1.17Å. The ratio of the mean radius to the radial maximum varies from 1.65 to 1.14. This is to be compared with the value of 7/6 for a Slater orbital. The Slater orbitals are fairly similar in shape to the two term functions for diffuse orbitals, but, as Webster pointed out, are a bad approximation for contracted orbitals. Similar studies have been made by Chandler and Thirunamachandran[31,32] on some phosphorus configurations, in particular the $3sp^3d$ configuration invoked for the bonding in the PF_5 molecule. My work on the chlorine atom is described in Chapter 2. Stokes and Thirunamachandran[33] have studied the silicon atom.

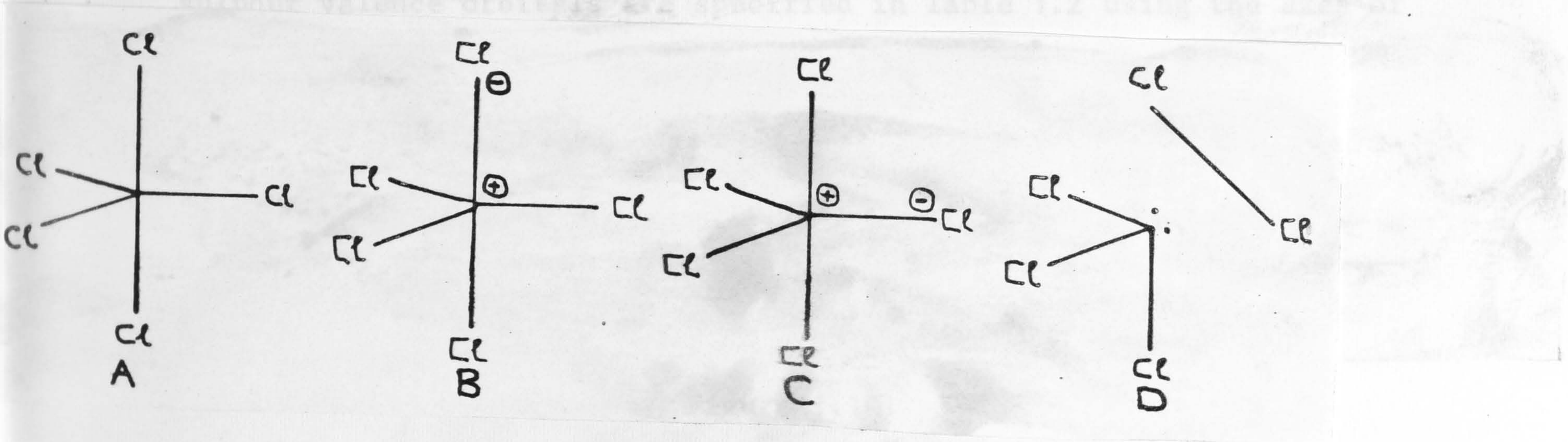
Calculations using a one term analytical wavefunction have been performed by Bendazzoli and Zauli[34] on a number of spectroscopic terms and single configurational valence states of sulphur. Similar calculations have been done by Mitchell[35] for phosphorus, sulphur and chlorine.

Whilst as far as orbital size is concerned, the case for d orbital participation in bonding would appear to be fairly good, the important question of the energetics of the promotion of an s or p electron into a d orbital cannot be ignored. Webster[21] in his SCF work obtained values of configuration average energies and one-electron orbital energies for the series of atoms silicon → argon. He was able to compare some of the configuration average energies with values calculated from spectroscopic data. The agreement between theory and experiment was good enough for him to be confident that the theoretical energies were of the right order of magnitude. Agreement was best for silicon and worsened as one traversed the periodic table. The promotion energy is obviously considerable. For instance, Webster gives a value of 24.48 eV for the ^7F term of the sulphur sp^3d^2 configuration. For the $3sp_xp_yp_zd_{z^2}d_{x^2-y^2}$ single configurational valence state Bendazzoli and Zauli[34] get a value of 31.72 eV using just a single term analytical wavefunction, whilst Coulson and Gianturco[29] obtained the value 32.96 eV using numerical SCF methods. These values can be compared with the value of 7-8 eV for the quadrivalent carbon atom.[36] The d orbital one electron energies are much smaller than those for the 3s or 3p orbitals. For the sulphur $^7F\ sp^3d^2$ term ϵ_{3s} ϵ_{3p} ϵ_{3d} are 35.48 eV, 20.58 eV and 3.32 eV respectively. This Webster showed was due to a different effective potential energy for the 3d electron. The d orbital energy is almost independent of atomic number. When the atom becomes positively charged ϵ_{3d} increases significantly. By contrast the one electron energies of a negatively charge ligand atom would be expected to decrease. This lends weight to the charge conjecture or polarisation hypothesis. In regarding this rather discouraging result, we should not discard the probability that the energy of molecular formation is sufficient to provide easily the energy required for promotion into the valence state.

This is where the hybrid orbital method stands at present in describing the bonding in molecules like SF_6 or PF_5. As far as d orbital size is concerned the situation is encouraging. I think it is safe to state that d orbitals in the valence state are sufficiently contracted to contribute significantly to bonding or if they are not, they will be contracted by the field of the ligand atoms. The promotion energy is obviously an important factor. How crucial this is to the participation of d orbitals in bonding has not yet been settled. Similarly the problem of the charge on the sulphur atom remains mainly unstudied using this approach.

Valence Bond Approach

The use of structures involving a charged central atom is an important part of the usual valence-bond description of molecules as propounded by Pauling.[37] PCl_5, for instance, is described as involving resonance between the structures shown in Figure 1.1.



The d orbital contribution would be expected to be smaller, the larger the contribution of structures B and C.

Molecular Orbital Method

We now turn to the molecular orbital approach. This is best described using SF_6 as an example. The molecular orbitals have the form

$$\phi_\ell = a_\ell\chi(S)_\ell + b_\ell\chi(F)_\ell \quad , \tag{1.5}$$

where ℓ defines the symmetry species and $\chi(S)_\ell$ and $\chi(F)_\ell$ represent the sulphur orbitals and combined fluorine orbital for that symmetry. A particular case of importance is that in which the mixing coefficients a_ℓ and b_ℓ are independent of the symmetry species of the six bonding molecular orbitals involving combinations of fluorine z orbitals. For this special case we can arrange the one electron molecular orbitals into the form

$$\psi_m = an_m + bz_m \quad , \qquad (1.6)$$

where $m = 1,2,\ldots,6$ and n_m represent the sp^3d^2 octahedral hybrid orbitals. The symmetry determined ligand orbital combinations for interaction with sulphur valence orbitals are specified in Table 1.2 using the axes of Figure 1.2.

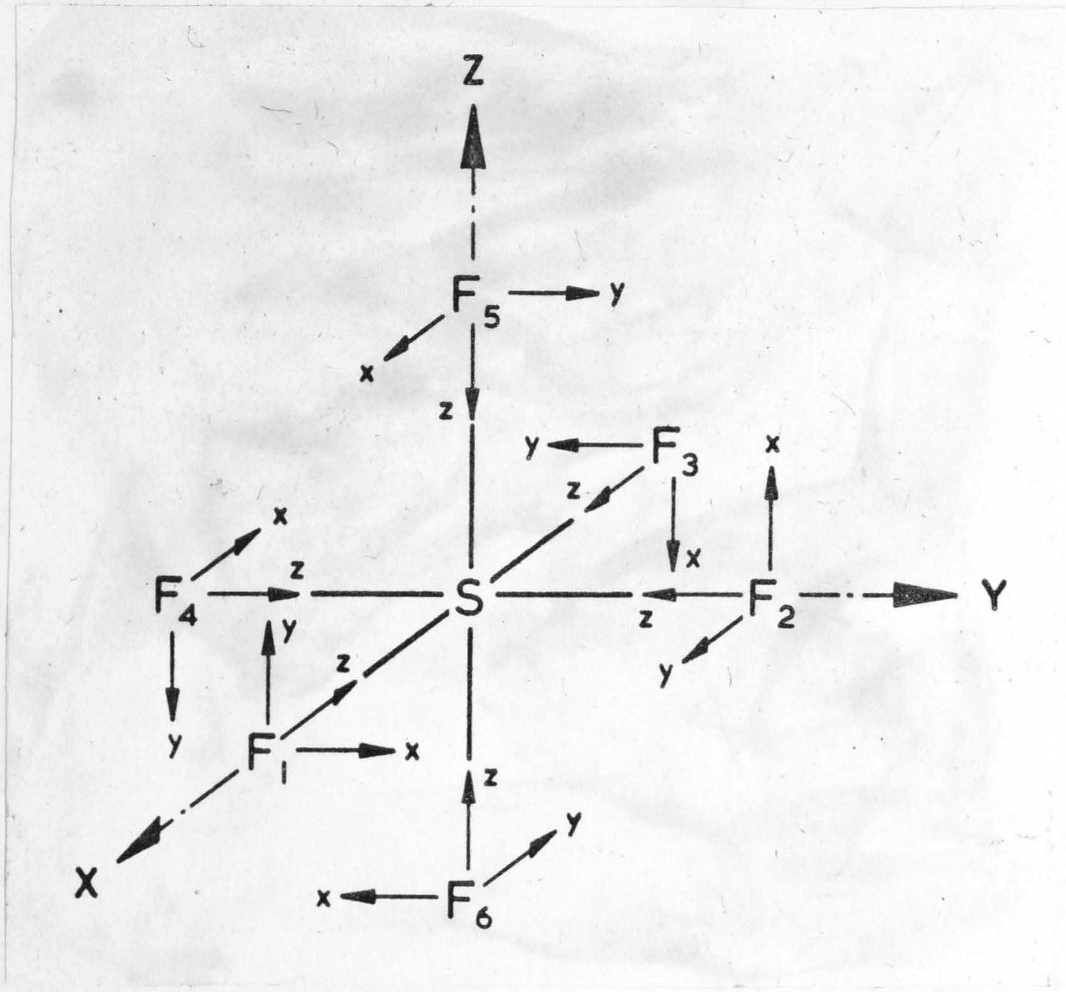


Figure 1.2

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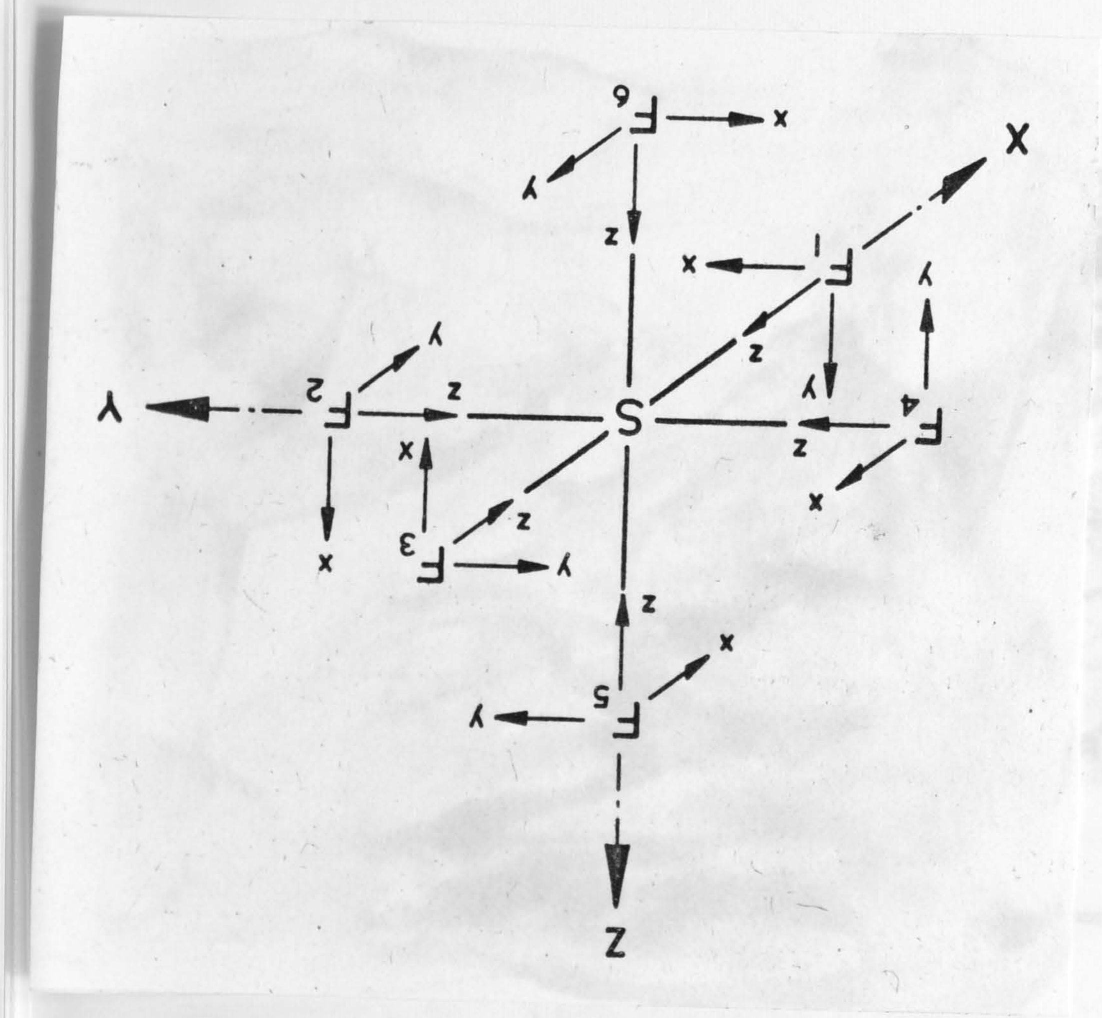


Figure 1.2

Table 1.2

Sulphur Orbitals and Symmetry Combined Fluorine Orbitals for Octahedral SF_6

Representation	Sulphur Orbital	Fluorine Orbitals
a_{1g}	3s	$\frac{1}{\sqrt{6}}(z_1+z_2+z_3+z_4+z_5+z_6)$
t_{1u}	$3p_x$	$\frac{1}{\sqrt{2}}(z_1-z_3)$ and $\frac{1}{2}(y_2+x_5-x_4-y_6)$
	$3p_y$	$\frac{1}{\sqrt{2}}(z_2-z_4)$ and $\frac{1}{2}(x_1+y_5-y_3-x_6)$
	$3p_z$	$\frac{1}{\sqrt{2}}(z_5-z_6)$ and $\frac{1}{2}(y_1+x_2-x_3-y_4)$
e_g	$3d_{x^2-y^2}$	$\frac{1}{2}(z_1-z_2+z_3-z_4)$
	$3d_{z^2}$	$\frac{1}{2\sqrt{3}}(2z_5+2z_6-z_1-z_2-z_3-z_4)$
t_{2g}	$3d_{xz}$	$\frac{1}{2}(y_1+x_5+x_3+y_6)$
	$3d_{yz}$	$\frac{1}{2}(x_2+y_5+y_4+x_6)$
	$3d_{xy}$	$\frac{1}{2}(x_1+y_2+y_3+x_4)$
t_{1g}		$\frac{1}{2}(y_1-x_5+x_3-y_6)$
		$\frac{1}{2}(x_2-y_5+y_4-x_6)$
		$\frac{1}{2}(x_1-y_2+y_3-x_4)$
t_{2u}		$\frac{1}{2}(y_2-x_5-x_4+y_6)$
		$\frac{1}{2}(x_1-y_5-y_3+x_6)$
		$\frac{1}{2}(y_1-x_2-x_3+y_4)$

Four atomic orbitals are included at each fluorine. These may be taken as pure $2p_x$ and $2p_y$ orbitals (x and y in Table 1.2) and two $2s$-$2p_z$ hybrids. The degree of hybridisation need not be specified but in each S-F bond one hybrid (designated z in Table 1.2) points towards the sulphur atom and the other hybrid may, in the simplest approximation, be considered to contain a non-bonding electron pair. If we ignore the lone pair and the sulphur $1s^2 2s^2 p^6$ core and the fluorine $1s^2$ cores which are also regarded as non-bonding we have a total of 36 electrons to accommodate in molecular orbitals.

The ground state electronic configuration of SF_6 as determined by a molecular orbital SCF calculation depends heavily upon whether or not d orbitals are invoked. If we choose to ignore in the first approximation, the involvement of d orbitals - the sp approximation (as do Rundle[38] and others) - we obtain a ground state electronic configuration of $(a_{1g})^2(t_{1u})^6(e_{1g})^4$. If d orbitals are included (e.g., the spd calculation of Santry and Segal[39]) the ground state configuration is $(a_{1g})^2(e_{1g})^4(t_{1u})^6$. The e_g and a t_{2g} orbitals involving the sulphur d_{xz}, d_{yz} and d_{xy} orbitals and fluorine $2p_\pi$ orbitals are necessarily non-bonding when d orbitals are excluded. They are strongly stabilised when d orbitals are included in the basis set used. When one compares the results obtained including and neglecting sulphur d orbitals one of the most striking features is the large charge on the sulphur atom obtained when d orbitals are neglected. Santry and Segal obtained a value of +2.06. A recent calculation of Brown and Peel[40,41] gave a charge of 2.34 units. This high charge is physically unlikely. In the spd approximation Santry and Segal obtained the lower value of 1.04 units. The lowering of the charge in the spd approximation may be explained by noting that the fluorine atoms are able to back donate charge through their π orbitals to the sulphur 3d t_{2g} orbitals. Holmes, Carter and Petersen[159] give experimental evidence from NMR and NQR studies of phosphorus chlorofluorides which indicate that a π bonding contribution is significant. One should remember also that the molecular orbital method tends to overestimate the contribution of ionic terms.

The first molecular orbital calculation on SF_6 was that of Duncan.[42] He used Slater orbital exponents for the 3d orbitals. He considered only six fluorine $2p_\sigma$ orbitals and one 3s, three 3p and two 3d sulphur orbitals. The calculation was one of the first to use the SCF methods developed by Roothaan[43] and Mulliken[44] and preceded the advent of computers into the field of molecular calculations. Mainly due to the poor basis set the results he obtained are unsatisfactory. For instance he obtained a physically unreasonable negative charge on the sulphur atom. Semi-empirical calculations on SF_6 and related compounds of the later second row elements have been recently performed by Santry and Segal[39] and Brown and Peel.[40] Santry and Segal investigated the neglect of d orbitals and the use of d orbitals with an orbital exponent equal to that for the 3s and 3p orbitals and with a slightly smaller value, using the CNDO/2 method.[45] The optimum orbital exponent lies between these two values. A slightly more reasonable exponent was used by Brown and Peel in a VESCF-MO calculation. Berry, Tamres, Ballhausen and Johansen[46] have recently done calculations on PF_5, BrF_5 and AsF_5 using a modified Wolfsberg-Helmholz approximation.[47] They particularly investigated the difference between a trigonal bipyramidal and square pyramidal structure. An extended Hückel calculation[48] was made on some phosphorus (V) chlorofluorides by Van der Voorn and Drago.[49] Carter[50] and Issleib and Grundler[51] have studied the non-existent PH_5. Manne[52] has done a calculation neglecting d orbital participation in ClF_3. A similar calculation on a large number of interhalogens was done by Havinga and Wiebenga.[53] The correct bond angles and bond lengths are predicted without the use of d orbitals. Mention should be made of a recent SCF calculation on PH_3, PO, PO^- and P_2 by Boyd and Lipscomb.[54] They used a minimal basis set which included 3d orbitals. The optimised 3d orbital exponents were 1.40 in PO and 1.10 in PO^-. These are very contracted. They conclude that 3d orbitals, though not required by symmetry considerations were important in the bonding of these molecules. In a recent calculation[55] on PO_2^- they found 3d orbitals played a very important part in the P-O bond formation. Inclusion of d orbitals was found to be important in calculations by Jordan on the radicals SiH, SiH_2, SiH_3, PH and PH_2.[56,57]

Thus a start has been made on studying molecules like SF_6 and PF_5 using the molecular orbital method but various factors such as the choice of basis sets, the number and nature of the approximations used, the inherent inadequacies of the SCF-MO method etc., give a picture best described as slightly confused. When ab initio calculations including configuration interaction, electron correlation etc., have been performed we should be able to really understand the bonding in these molecules. However this will be a tremendous undertaking.

Electron-Pair Repulsion Theory

A qualitative approach to bonding which has been widely applied is the electron pair repulsion model of Gillespie and Nyholm.[58] The forms of the orbitals are ignored and the trends correlated through consideration of geometry, with the magnitudes of repulsions between various valence shell electron-pairs. The electrostatic repulsion between the electron pairs decrease in the order: lone pair - lone pair > lone pair - bond pair > bond pair - bond pair. Its successful application to simple molecules like SF_6 and PF_5 is well known. Recently its application to methyl substituted phosphorus (V) fluorides was considered by Bartell and Hansen,[59] Gillespie[60] and Bartell.[61] Gillespie claimed that his theory explained the structural trends better than Rundle's M.O. theory[38] (which used only 3p orbitals) used by Bartell. There are valid objections to both theories. However both succeed in explaining most of the structural phenomena. A recent success of the Gillespie model over the Rundle model concerns the fact that Gillespie's theory predicts the molecule XeF_6[59] to be a distorted octahedron whilst the MO model predicts a regular octahedron. The main objection to the Gillespie model, yet perhaps its greatest strength, is that it is only qualitative.

Π Bonds

So much for the formation of σ bonds by later second row elements. In molecules like $POCl_3$, $HClO_4$, H_2SO_4 later second row elements exhibit higher covalences and are involved in π bonding. The π molecular orbitals are seen as being superimposed upon the basic σ framework. The question of d orbital participation is far less controversial. In fact, Rundle,[38] perhaps the chief antagonist of the d orbital hypothesis, has written: "I conclude that outer d orbitals must have some role at least in providing π bond character to these compounds" (i.e., chlorates, phosphates, silicates and their nitrogen derivatives). There is considerable experimental evidence to support the hypothesis that d orbitals contribute to π bonds. This has come especially from structural and spectroscopic information but also from other physical measurements and chemical evidence. Theoretical evidence is beginning to accumulate.

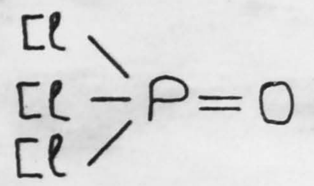
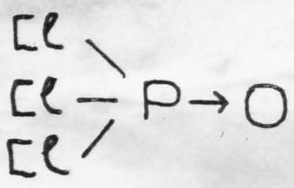
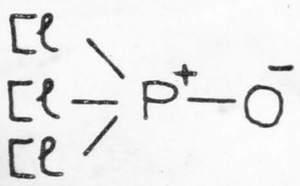
Spectroscopic methods have been used in investigating the electron distribution in these molecules. N.Q.R.[62] measurements, especially of chlorine compounds and ESR measurements[63] on some phenyl radicals have been interpreted to support 3d orbital participation in bonding. Other methods such as NMR chemical shifts and U.V. spectroscopy are not particularly sensitive to 3d orbital participation. However Goodman, Konstan and Sommer[64] claim that the U.V. spectra of phenylsilanes shows that 3d orbitals of silicon must interact with the π orbitals of the phenyl ring.

It is generally agreed that the most reliable support for the hypothesis that 3d orbitals participate in bonding comes from stereochemical evidence. The stereochemistry of phosphoryl compounds, e.g., POF_3, fits in with the model emphasising d_π-p_π interactions between phosphorus and oxygen superimposed upon a σ framework formed by sp^3 hybrids at phosphorus. The stereochemistry is essentially tetrahedral and the P-O bond length[65] of 1.45Å is much shorter than 1.55-1.65Å found in single bonds in phosphates. The bond stretching constant[66] and the bond energy[67] also indicate that the P-O bond is very strong. The bond must have multiple character. Cruickshank[68] has reviewed much structural information in which second row atoms are bonded approximately tetrahedrally to strongly electronegative atoms and has interpreted the evidence in terms of d_π-p_π bonding. This analysis is mainly of bond length changes and in the partial shortening that can be correlated with π bond effects. First row elements (especially nitrogen and oxygen) tend to show larger valence angles when bonded to second row elements. These larger angles have been related to a partial back donation of electronic charge from the lone pair orbitals of the first row atom into the 3d orbitals of the second row atom. Thus the lone pair electrons formally in the valence shell of the nitrogen or oxygen should be less localised when these atoms are bound to second row elements. There is chemical evidence also to support this, e.g., the low basicity of trisilylamine.

In the phosphonitrilic compounds $(PNX_2)_n$ delocalised p_π-d_π bonds are invoked.[69,70] These molecules have been extensively studied experimentally. Mitchell has done some theoretical studies on them.[24,25]

In some organic sulphur compounds there is evidence for 3d orbitals being involved in bonding. In particular where the central sulphur atom is assumed to be positively charged, e.g., sulphoxides, sulphones and sulphonium salts resonance involving 3d orbitals is generally accepted. When the central sulphur atom is uncharged, e.g., sulphides, the possibility of 3d orbital contribution to S-C bonds is controversial. Cilento[71] has reviewed this part of the subject. The question of d orbital participation in these compounds is being extensively examined by Zauli's group at Bologna.[72]

In addition to the d_π-p_π double-bond formulation there are other possible formulations for bonds such as the P-O bond in $POCl_3$. It could also be described as a coordinate or an ionic bond.

Attempts have been made to distinguish between these formulations but the experimental evidence tends to be conflicting.[73,74] The coordinate bond and the ionic bond formulations are similar but even the d_π-p_π double bond formulation gives some polarity in the same direction. The discussion of the experimental evidence makes use of many simplifying assumptions, so that single items of evidence for or against a particular model are not in themselves convincing. What is required is a theoretical model which provides the best basis for understanding the experimental evidence as a whole.

There has been considerable theoretical work done on these compounds in which π bonding is invoked. Attention has focussed especially on thiophene and the sulphate anion $SO_4^=$ as these are representative of large sub-classes of these compounds.

Thiophene has been treated by both molecular orbital and valence-bond methods. The use of 3d orbitals in thiophene was postulated by Schomaker and Pauling[75] and Longuet-Higgins[76]. This explained easily the similarity in properties of benzene and thiophene. The involvement of 3d orbitals in the bonding of thiophene has been challenged by some authors, e.g., Mangini and Zauli.[77] Calculations on the molecule have been done by Magnusson.[14] He found a small contribution to the ground state by the

3d orbitals which were contracted in the molecular environment with an orbital exponent of 0.9. A semi-empirical LCAO-SCF calculation by Bielefeld and Fitts[78] found again only a small contribution by the $3d_{xz}$ and $3d_{yz}$ orbitals but that their inclusion affected the electronic properties of the molecule to a great extent. Work was also done on it by Yates.[79] Christie and Selinger[80] have recently performed Pople SCF[81] and VESCF[82] calculations on the 3-hydroxyisothiazole system. They found that the inclusion of 3d orbitals gave a general lowering of the orbital energies, and a general enhancement of aromaticity.

Jordan, Smith, Lohr and Lipscomb[83] concluded from a semi-empirical LCAO-MO calculation that d orbitals were important in understanding the barrier to rotation in α-sulphonyl carbon ions. Moffitt[84] in some early work using Mulliken's molecular orbital method concluded that 3d orbitals had an important part to play in the bonding of SO_2, SO_3 and molecules of the type R_2SO_2 and R_2SO. Zauli's group[72] has also done considerable theoretical work on sulphone sulphides and sulphoxides. SO_2, SO_3, SO_3^{2-}, SO_4^{2-} and $S_2O_3^{2-}$ were studied by Porai-Koshits and Ionov[85] using semi-empirical SCF-LCAO-MO method. They concluded that 3d orbitals played a large part in π bond formation, but little in σ bonds. Bishop Randic and Morton[86] performed a Wolfsberg-Helmholz type calculation on $SO_4^=$ and $S_2O_3^=$. They obtained a very large 3d orbital participation in the bonding. This result was challenged by Manne[87], who obtained results from a calculation which ignored 3d orbitals which gave good agreement with X-Ray spectra and inner shell photo-electron spectra. Bishop obtained as the configuration of sulphur in $SO_4^=$

$$a_1^2 t_2^6 t_2^6 e^4 t_1^6 t_2^6 a_1^4 ,$$

whilst Manne and Santry and Segal[39] (using a spd basis set - which includes d orbitals) obtained

$$a_1^2 t_2^6 a_1^2 t_2^6 e^4 t_2^6 t_1^6 \quad .$$

In a more recent set of calculations Bishop[38] concluded that the highest occupied levels should be triply degenerate - either t_1 or t_2 but that energy level orders could not be definitely predicted with the type of calculation he used. Santry and Segal concluded that d orbitals must be used, otherwise the sulphur atom is given too large a positive charge. Increased π bonding is accompanied by back donation from the oxygen to the sulphur. Santry and Segal found a low 3s electron density on the sulphur. This was also found for SF_6. Results from calculations on SO_2 by them are inconclusive as regards d orbital participation. Cruickshank and Spinnler[22] have done some theoretical calculations on some tetrahedrally coordinated oxyanions.

Chlorine-oxygen compounds have also been studied. Wolfsberg and Helmholz[47] in their pioneering semi-empirical LCAO-MO calculation studied ClO_4^- and concluded that 3d orbitals were not appreciably involved in bonding. Wagner[89] studied the series of compounds ClO^-, Cl_2O, ClO_2^-, ClO, ClO_3^-, ClO_2 and ClO_4^-. He concluded that 3d orbitals played a significant role in π bonding. Calculations were done by Manne[87] on some chlorine compounds with results similar to those he obtained for sulphur compounds.

All these calculations made up to date have been semi-empirical. This should be remembered. In comparing theoretical predictions with experimental results it is likely that especially with the oxyanions crystal field effects cannot be ignored.[90]

The consensus of opinion, both experimental and theoretical, would then point to d orbital participation in d_π-p_π bonding in compounds of the later second row elements. The whole of this subject has been reviewed by Mitchell.[91]

Conclusion

So to conclude this survey we have the situation, at present, where there is general agreement that d orbitals contribute to π bonds. For σ bonds the matter is still controversial, but support for the d orbital hypothesis appears to be increasing as more accurate wavefunctions, energies and other properties are obtained. The work described in this thesis is a contribution, in this sense, which should help resolve some of the problems associated with σ bonding. Any definitive conclusions connected with σ bonding should help to further clarify questions posed with respect to π bonding.

CHAPTER 2

ORBITAL WAVE FUNCTIONS FOR SOME EXCITED STATES OF THE CHLORINE ATOM

Introduction

The chlorine atom in its ground state has the configuration $1s^2 2s^2 p^6 3s^2 p^5$ (or simply s^2p^5). From the Lewis-Langmuir Electron Pair theory we would expect chlorine to be univalent (needing to "share" only one electron to form a closed shell). This is the case for fluorine with the same ground state configuration s^2p^5. However, as the existence of molecules such as ClF_3, ClO_2, ClF_5 and Cl_2O_7 shows, chlorine exhibits higher covalencies. In such compounds, the usual symmetry arguments which give the valence state configuration of phosphorus in PF_5 to be $3sp^3d$ tell us that the s^2p^5 configuration is not the valence state configuration when chlorine exhibits higher covalencies - excited state configurations must be invoked. The valence state of an atom in a molecule can be built up from spectroscopic states of the free atom. A study of the free atom therefore provides an important guide to the situation in the valence state. As in similar studies of other later second row atoms we are particularly interested in the diffuseness of the "outer" orbitals and the magnitude of the promotion energy to the excited state. These are important factors in judging whether "outer" orbital participation in bonding is feasible. We are mainly interested in excited states involving d orbitals. Thus this work is the logical extension of the work of Craig and Thirunamachandran[26,27] on sulphur and Chandler and Thirunamachandran[31,32] on phosphorus. Silicon has been studied by Stokes and Thirunamachandran.[33]

In all this work we have used hydrogenlike wavefunctions for all but 3d orbitals. For 3d orbitals we have used either hydrogenlike (or Slater type) wavefunctions, for which use the term single-zeta or double-zeta wavefunctions in which the radial part of the wavefunction has been replaced by the two term function

$$R(3d) = N[\sin(\Pi\lambda_{3d})\phi(3d, \alpha_{3d}) + \cos(\Pi\lambda_{3d})\phi(3d, \beta_{3d})] \quad , \qquad (2.1)$$

where

$$\phi(3d, \gamma) = \sqrt{\frac{8\gamma^7}{45}}\ r^2\ e^{-\gamma r} \quad , \qquad (2.2)$$

N is the normalising factor,

$$\{1 + [128(\alpha_{3d}\beta_{3d})^{7/2}\ \sin(2\Pi\lambda_{3d})]/(\alpha_{3d}+\beta_{3d})^7\}^{-\frac{1}{2}} \quad , \qquad (2.3)$$

λ is a mixing parameter.

These were first used by Richardson et al.[28] in work on first row transition metal atoms. They possess much greater flexibility than the single zeta wave functions. We are particularly interested in comparing the use of the two functions.

The energy expressions were written in terms of Slater's I(nl), F^k and G^k integrals.[93] Details of the computation of these integrals are given in Appendix 1.

The energies were minimised with respect to the orbital exponents α_{3s}, α_{3p}, α_{3d}, β_{3d} and λ_{3d}. Stokes[33] has shown that for a single-zeta calculation the energy surface is such that any three dimensional section is a parabola of revolution about the energy axis. For this simple function surface no sophisticated minimisation techniques like the method of steepest descents are necessary. The surface for double-zeta calculations is not as simple but a crude minimisation technique sufficed. The energy was not minimised with respect to the 1s, 2s or 2p exponents. These were calculated by "Clementi's Rules".[94] That part of the energy expression which depends only upon these parameters - the core energy - was calculated separately.

Average Energies of Configurations

To get a general picture of what happens when an electron in a 3s or 3p orbital is excited to an "outer" orbital we have firstly examined the "state" corresponding to the average energy for several configurations. Following Shortley,[95] the average energy of a configuration is defined as the weighted mean of energies of all the multiplets, the weight factor being (2L+1)(2S+1), equal to the number of separate component wavefunctions of the multiplet. The expression for the average energy has the form

$$\sum I(nl) + \sum(\text{pairs})\ \text{Interaction Energy} \quad . \qquad (2.4)$$

Formulae for the interaction energy of pairs of electrons are given by Slater[93] in terms of the F^k and G^k integrals. The calculation of the average energies was thus straightforward.

The results of these single-zeta average energy calculations are given in Table 2.1.

For the neutral chlorine atom the 1s and 2s orbital exponents calculated by Clementi's rules do not depend upon the configuration of the M shell. Only the 2p exponent varies from configuration to configuration. These are not the optimum exponent values. However, they are a sufficiently good approximation that the errors introduced thereby in the M shell orbital exponents and the energy are not significant, especially when considering

Table 2.1

Energy Minimised Orbital Exponents, Energies and Radii
Average Energies of Configurations - Single Zeta Calculations

$\alpha_{1s} = 16.5239 \qquad \alpha_{2s} = 5.7152$

$E_{s^2p^5-{}^2P^\circ} = -917.00899$ a.u.

Configuration	α_{2p}	α_{3s}	α_{3p}	α_{3d}	$\bar{r}_{3d}$ a.u.	$E-E_{s^2p^5-{}^2P^\circ}$ a.u.
s^2p^5	6.4966	2.3558	2.0315	---	---	0
sp^6	6.4661	2.385	2.036	---	---	1.09287
s^2p^4d	6.4911	2.426	2.138	0.349	10.029	0.74401
sp^5d	6.4605	2.452	2.142	0.351	9.972	1.80238
$s^2p^3d^2$	6.4854	2.495	2.234	0.650	5.385	2.00302
sp^4d^2	6.4548	2.519	2.236	0.666	5.255	3.01463
p^5d^2	6.4242	---	2.239	0.688	5.087	4.27645
sp^3d^3	6.4492	2.557	2.279	1.064	3.289	4.42666

Configuration	α_{2p}	α_{3s}	α_{3p}	nl	α_{nl}	$E-E_{s^2p^5-{}^2P^\circ}$ a.u.
$3s^2p^4 4s$	6.4966	2.432	2.134	4s	0.786	0.60054
$3sp^5 4s$	6.4661	2.468	2.138	4s	0.787	1.65553
$3s^2p^4 4p$	6.4844	2.426	2.140	4p	0.601	0.67795
$3sp^5 4p$	6.4538	2.452	2.143	4p	0.604	1.73944

.../

/... Table 2.1 (continued)

$\alpha_{1s} = 16.5476$ $\alpha_{2s} = 5.7607$

Charge	Configuration	α_{2p}	α_{3s}	α_{3p}	$E-E_{s^2p^5\ ^2P^{\circ}}$ a.u.
+1	s^2p^4	6.4887	2.415	2.138	0.86571

the accuracy of the results. The 2p orbitals expands slightly as more outer orbitals are filled. More marked is the expansion as the 3s subshell becomes empty.

The 3s and 3p orbitals contract as more outer orbitals are filled. The size of the 3p orbital seems to depend only upon the number of outer orbitals filled and not upon the nature of the outer orbital or whether the 3s orbital is full, half empty or empty. The 3s orbital contracts when it becomes half empty, indicative of the mutual shielding by the 3s electrons.

The 3d orbital exponents are not very different from those predicted by Slater's Rules[6] - d^1 0.33, d^2 0.55 and d^3 0.77, the departure being greater as the d orbital contracts. Both Burns' Rules[96] and Clementi's Rules[94] predict far more contracted d orbitals. For the s^2p^4d configuration they predict exponent values of 1.17 and 1.37 respectively. The difference between these values and those predicted by Slater's rules is most striking. Slater would seem to overestimate the shielding contribution of 3s and 3p electrons (complete shielding - a contribution to the shielding constant of 1.0) whilst Burns and Clementi underestimate the shielding contribution (Burns gives the contribution of the 3s and 3p electrons to be 0.75 and 0.5 respectively). The d orbitals are more contracted when the 3s subshell is half empty or empty, indicative of the better shielding properties of the 3s orbital as compared with the 3p orbital. The mutual shielding by the 3d electrons is very small indeed.

The 4s- and 4p-containing configurations have energies below that for the corresponding 3d configurations. This is in agreement with spectroscopic observations for the s^2p^4nl series. In the average energy "state" of the $3s^2p^44s$ and $3s^2p^44p$ configurations the 4s and 4p orbitals are both diffuse, their mean radii being 5.8 and 7.5 a.u. respectively. These are less than the mean radius of the corresponding d orbital. A mean radius of about 3.0 a.u., at least, is necessary for the use of an "outer" orbital in bonding.

The average energies of the sp^6, sp^5d and $s^2p^3d^2$ configurations are above that for the ground state of Cl^+ but below the second ionisation limit.

The ground state energy for neutral chlorine calculated here can be compared with other values in the literature. According to Clementi,[34] Slater's rules give an energy of -915.7176 a.u. He gives the energy corresponding to his screening constants as -917.0474 a.u. However his parameters do not yield this energy. They are not those corresponding to the minimum energy. Stokes[33] has found that in all Clementi's screening constant calculations for second row elements a similar error has occurred. The Hartree-Fock energy is -918.9594 a.u.

Thus we should not place too much emphasis on the absolute numerical values of energies quoted. The difference between them and the Hartree-Fock energy is really quite large - almost 2.0 a.u. However it is a significant improvement on the energies calculated using Slater's rules.

$3s^2p^4d$ Configuration

We then investigated the spectroscopic terms of the $3s^2p^4d$ configuration. This is the lowest lying 3d containing configuration of chlorine. There are only twelve L-S coupled terms - ^4F, ^4D, ^4P, ^2G, $^2F(2)$, $^2D(3)$, $^2P(2)$, ^2S. Every term contributes to the valence state of chlorine in ClF_3. The terms were built up according to the $s^2p^4 + d$ coupling scheme. There are other coupling schemes which might have been used, all of which lead to complete sets of orthonormal eigenfunctions of L^2, S^2 and their z components. They are related to each other and the $s^2p^4 + d$ coupling scheme by unitary transformations. However, the $s^2p^4 + d$ coupling scheme is the most obvious and the simplest. The "parent" multiplets from the s^2p^4 configuration are ^3P, ^1D and ^1S. The expressions for the energies of the multiplets were determined using the tables given by Slater;[97] a similar table is given by Möller.[98] These give the term energies referred to the average energy of the configuration. The energy expressions are given in Table 2.2. The term energy levels fall into three fairly distinct clusters according to the parentage of the multiplets. The separation of the clusters depends upon the $F^2(3p,3p)$ integral. It is worthy of note also that the separation of the quartet terms, which all appear only once, depends only upon the $F^2(3p,3d)$ integral. There are non-diagonal elements in the energy matrix between the terms of ^2F, ^2D and ^2P symmetry which occur twice, thrice and twice, respectively. The s^2p^4d

Table 2.2

$3s^2p^4d$ Configuration-Multiplets   Energy Expressions

Diagonal Matrix Components

Parent Multiplet	Multiplet	
^3P	^4F	$E_{av} - 3/25[F^2(3p,3p)] + 2/35[F^2(3p,3d)] -$ $- 2/15[G^1(3p,3d)] - 3/35[G^3(3p,3d)]$
	^4D	$E_{av} - 3/25[F^2(3p,3p)] - 1/5[F^2(3p,3d)] -$ $- 2/15[G^1(3p,3d)] - 3/35[G^3(3p,3d)]$
	^4P	$E_{av} - 3/25[F^2(3p,3p)] + 1/5[F^2(3p,3d)] -$ $- 2/15[G^1(3p,3d)] - 3/35[G^3(3p,3d)]$
	^2F	$E_{av} - 3/25[F^2(3p,3p)] + 2/35[F^2(3p,3d)] -$ $- 2/15[G^1(3p,3d)] + 69/245[G^3(3p,3d)]$
	^2D	$E_{av} - 3/25[F^2(3p,3p)] - 1/5[F^2(3p,3d)] +$ $+ 23/30[G^1(3p,3d)] + 6/35[G^3(3p,3d)]$
	^2P	$E_{av} - 3/25[F^2(3p,3p)] + 1/5[F^2(3p,3d)] +$ $+ 11/30[G^1(3p,3d)] - 3/35[G^3(3p,3d)]$
^1D	^2G	$E_{av} + 3/25[F^2(3p,3p)] - 4/35[F^2(3p,3d)] -$ $- 2/15[G^1(3p,3d)] + 24/245[G^3(3p,3d)]$
	^2F	$E_{av} + 3/25[F^2(3p,3p)] + 8/35[F^2(3p,3d)] -$ $- 2/15[G^1(3p,3d)] - 6/245[G^3(3p,3d)]$
	^2D	$E_{av} + 3/25[F^2(3p,3p)] + 3/35[F^2(3p,3d) +$ $+ 1/10[G^1(3p,3d)] - 18/245[G^3(3p,3d)]$

.../

/... Table 2.2 (continued)

Parent Multiplet	Multiplet	
	^2P	$E_{av} + 3/25[F^2(3p,3p)] - 1/5[F^2(3p,3d)] + 11/30[G^1(3p,3d)] - 3/35[G^3(3p,3d)]$
	^2S	$E_{av} + 3/25[F^2(3p,3p)] + 2/5[F^2(3p,3d)] + 8/15[G^1(3p,3d)] - 3/35[G^3(3p,3d)]$
^1S	^2D	$E_{av} + 13/25[F^2(3p,3p)]$

Non-Diagonal Matrix Components

Multiplets	Parent Multiplets	
^2F	$^3P \rightarrow {}^1D$	$-3\sqrt{6}/49[G^3(3p,3d)]$
^2D	$^3P \rightarrow {}^1D$	$\sqrt{21}/10[G^1(3p,3d)]-3\sqrt{21}/245[G^3(3p,3d)]$
	$^3P \rightarrow {}^1S$	$\sqrt{3}/5[G^1(3p,3d)]-3\sqrt{3}/35[G^3(3p,3d)]$
	$^1D \rightarrow {}^1S$	$-4\sqrt{7}/35[F^2(3p,3d)]+\sqrt{7}/15[G^1(3p,3d)]+3\sqrt{7}/245[G^3(3p,3d)]$
^2P	$^3P \rightarrow {}^1D$	$1/2[G^1(3p,3d)]$

configuration of ArII has been studied by L. Minnhagen[99] and J.L. Tech and R.H. Garstang.[100] Both give tables for the electrostatic energies of the multiplets, so providing us with a useful check of our calculations. Tech and Garstang note a typographical error in Slater's tables for the non-diagonal matrix element between ^2F terms.

The results of a single zeta calculation on all the terms are given in Table 2.3. The calculation is straightforward for those terms which occur only once - ^4F, ^4D, ^4P, ^2G and ^2S. However, for those terms which occur more than once, the minimisation of the term energies poses a problem. In the process of minimisation of the energy with respect to the orbital exponents, the orthagonality between the wavefunctions of the different terms is lost. This problem, always present in calculations on excited states is discussed by Bethe and Salpeter.[101] We have ignored the error introduced in this way for the terms which only occur once. Chandler and Thirunamachandran[32] have discussed the problem when more than one term of a given symmetry occurs, in their paper on the sp^3d configuration of phosphorus. The approximation we have adopted here is to use the orbital exponents appropriate to the term whose energy is being minimised to calculate the other diagonal elements. This naturally leads to a spread in the values of the matrix elements from term to term, but it is not large. In the work on the configuration interaction between two ^2S multiplets discussed later a similar problem arises. Here we used the value of the diagonal elements appropriate to the minimum energy of the other term in calculating the energy of the term in question. This is probably more satisfactory. For the ^2D terms which occur thrice, the cubic equations involved were solved using the methods outlined by Neumark.[102] Because of the approximations made we should place less emphasis on the

Table 2.3

Energy Minimised Orbital Exponents, Energies and Radii

$3s^2p^4d$ Configuration-Multiplets Single Zeta Calculations

$\alpha_{1s} = 16.5239$ $\alpha_{2s} = 5.7152$ $\alpha_{2p} = 6.4911$

$E_{s^2p^5\ ^2P^o} = -917.00899$ a.u.

Parent Multiplet	Multiplet	α_{3s}	α_{3p}	α_{3d}	$\bar{r}_{3d}$	$E-E_{s^2p^5\ ^2P^o}$ a.u.	cm^{-1}
^3P	^4F	2.425	2.142	0.349	10.029	0.67511	74,085
	^4D	2.425	2.141	0.376	9.309	0.67026	73,553
	^4P	2.425	2.142	0.337	10.386	0.67743	74,339
	^2F	2.425	2.142	0.344	10.174	0.67571	74,151
	^2D	2.426	2.144	0.344	10.174	0.65176	71,522
	^2P	2.424	2.147	0.316	11.076	0.61172	67,129
^1D	^2G	2.426	2.134	0.362	9.669	0.81095	88,991
	^2F	2.426	2.135	0.335	10.448	0.81656	89,606
	^2D	2.427	2.133	0.351	9.972	0.85821	94,178
	^2P	2.427	2.130	0.378	9.259	0.87585	96,114
	^2S	2.426	2.135	0.314	11.146	0.82014	89,999
^1S	^2D	2.427	2.125	0.348	10.057	0.99876	109,601
Average Energy		2.426	2.138	0.349	10.029	0.74401	81,647

results for the terms which occur more than once. The numerical values of the matrix elements are given in Table 2.4.

The 3s orbital exponent is fairly constant over the configuration. A slight increase occurs in higher terms. The 3p orbital exponent is fairly constant for the set of terms arising from a given parent multiplet. The orbital expands as we go to the higher sets of multiplets. This can be linked to the variation in the contribution of the $F^2(3p,3p)$ integral to the term energies.

No large contraction in d orbital size occurs. The most contracted is still diffuse. The spread of d orbital size is not large either, the mean radius going from 9.3 to 11.1 a.u.; a change of about 1Å. The orbital exponent values are still close to the 0.33 predicted by Slater's rules. For the quartets, a contraction in d orbital size as we go to lower terms can be observed. This trend is probably true for the doublets also, but it is more difficult to discern due to the effect of non-diagonal elements on the term energy.

For the terms arising from the ^3P parent multiplet, two of the doublets have energies below those of the quartets. This is not to be expected. The diagonal elements for the doublets are almost equal to those for the quartets. The reversal of the expected order can be ascribed to the non-diagonal elements. Hund's rule[103] is not obeyed. Even amongst the quartets the ^4D term is lower than the ^4F term. This agrees with the order observed experimentally. The order of the clusters of terms arising from a given parent multiplet is in the same order as the order experimentally observed with about the same spacing. The spread in the values of the term energies is quite large - about 42,000 cm^{-1}. The

Table 2.4

$3s^2p^4d$ Configuration - ^2F ^2D ^2P Multiplets Energy Matrices

$$E' = E - E_{1s^2 2s^2 p^6} \text{ Core}$$

^2F

	$(^3P)^2F$	$(^1D)^2F$
$(^3P)^2F$	-28.590 - E'	-2.25×10^{-4}
$(^1D)^2F$	-2.25×10^{-4}	-28.449 - E'

^2D

	$(^3P)^2D$	$(^1D)^2D$	$(^1S)^2D$
$(^3P)^2D$	-28.592 - E'	1.2×10^{-3}	7.3×10^{-4}
$(^1D)^2D$	1.2×10^{-3}	-28.451 - E'	-4.6×10^{-3}
$(^1S)^2D$	7.3×10^{-4}	-4.6×10^{-3}	-28.245 - E'

^2P

	$(^3P)^2P$	$(^1D)^2P$
$(^3P)^2P$	-28.586 - E'	1×10^{-3}
$(^1D)^2P$	1×10^{-3}	-28.454 - E'

$(^1S)^2D$ term is above the ionisation limit. The $(^1D)^2P$ and ^2D terms are very close to it.

Chandler and Thirunamachandran[32] have shown for phosphorus that the role of intra-atomic exchange in determining the size of a d orbital in a d^1 configuration, whilst important, is small in comparison to the role played in a d^2 configuration. There is no reason to expect chlorine to behave differently.

The average energy of the $3s^2p^4d$ configuration and those multiplets which occur only once in the manifold were re-examined using double-zeta 3d wavefunctions. The results are given in Table 2.5. We did not minimise the energy with respect to the 3s or 3p orbital exponents - the values used were those obtained in the single zeta calculations. These are a good approximation for a d^1 configuration. There are two 3d orbital exponents - α and β. α, whose value is close to that of the single-zeta orbital exponent, governs the behaviour of the wavefunction at r greater than 3-4 a.u. Its value is greater than the single-zeta α_{3d}. This is the opposite of the behaviour in d^2 configurations. β only governs the behaviour of the wavefunction at small r, say 0 to 3 or 4 a.u. For this d^1 configuration the value of λ, the mixing coefficient, is quite close to 0.5 - indicating that the correction to the single term function is only small. The amount of correction, as indicated by the value of λ is greater the more contracted the orbital. For a diffuse orbital such as that for the $(^1D)^2S$ term the double-zeta function is almost identical to the single-zeta function.

The double zeta energies are lower than the single zeta energies. However the differences are not large - the biggest is 0.009 a.u. The

Table 2.5

Energy Minimised Orbital Parameters and Energies

Double Zeta Calculations $3s^2p^4d$ Configuration

Parent Multiplet	Multiplet	α	β	λ	$E-E_{s^2p^5\,{}^2P^o}$ a.u.	$E_{s.z.}-E_{d.z.}$ a.u.
^3P	^4F	0.366	1.748	0.471	0.67138	0.00373
	^4D	0.420	1.742	0.446	0.66097	0.00929
	^4P	0.348	1.791	0.479	0.67507	0.00236
^1D	^2G	0.383	1.740	0.467	0.80631	0.00464
	^2S	0.314	2.681	0.497	0.82001	0.00014
Average Energy		0.359	1.773	0.479	0.74161	0.00294

difference is greatest for the most contracted and least for the most diffuse orbital. All this supports the hypothesis that Slater orbitals are satisfactory to describe a diffuse orbital but not for even a slightly contracted orbital.

The mean radii and radial maxima for these double-zeta orbitals and the corresponding single-zeta orbitals are given in Table 2.6. The double-zeta orbitals are more contracted than the single-zeta orbitals, the difference in the size being greater the more contracted the orbital.

Table 2.6

Mean Radius and Radial Maximum - $3s^2p^4d$ Configuration

Multiplet	$\bar{r}_{3d}$ a.u.		r_{max} 3d a.u.		$\bar{r}_{3d}/r_{max}$
	Single Zeta	Double Zeta	Single Zeta	Double Zeta	Double Zeta
^4F	10.029	9.307	8.60	8.19	1.136
^4D	9.309	7.757	7.98	7.10	1.093
^4P	10.386	9.895	8.90	8.62	1.148
^2G	9.669	8.829	8.29	7.82	1.129
^2S	11.146	11.140	9.55	9.55	1.167
Av. Energy	10.029	9.582	8.60	8.35	1.148

The mean radius for the most contracted orbital, the ^4D term, has changed by 1.55 a.u. (~ 0.8Å). For a single-zeta orbital the ratio ($\bar{r}/r_{max}$) of the mean radius to the radial maximum has the value 7/6. For all these terms, $\bar{r}/r_{max}$ is less than this value. This is the opposite of the case for the more contracted d orbitals in d^2 configurations. Both $\bar{r}$ and r_{max} are smaller for the double-zeta wavefunction in a d^1 configuration. This is not always the case for a d^2 configuration. Craig and Thirunamachandran[27] found that for the sp^3d^2 configuration of sulphur $\bar{r}$ was greater for the double-zeta wavefunction. The main correction to a Slater type wavefunction is an increase in electron-density in the region 0-4 a.u. leading to a decrease in the value of r_{max} - the radial coordinate of the maximum of the function $D(r) = r^2R^2(r)$. For a d^1 configuration this correction leads to a decrease in $\bar{r}$ which is proportionally greater than that of r_{max} giving $\bar{r}/r_{max}$ a value less than 7/6. However in the more contracted d orbitals of a d^2 configuration stronger interelectronic repulsion prevents much if any contraction of change as measured by $\bar{r}$. Thus $\bar{r}/r_{max}$ is greater than 7/6 in these more contracted orbitals.

In Figure 2.1 the single-zeta and double-zeta wavefunctions for the ^4D terms are plotted. We can see that the double-zeta wavefunction increases more quickly than the single-zeta function, achieving a large maximum value at a smaller radius and then falling off to zero more quickly. The hump at about 2.0 a.u. is due to the β part of the wavefunction. Its occurrence demonstrates that even a two term analytical function does not perfectly describe a 3d orbital.

Comparison of Theory and Experiment

Most of the configurations of importance to the valence state of the later second row elements cannot be studied spectroscopically. However there are some levels of the $3s^2p^4d$ configuration of neutral chlorine which have been experimentally determined. We can thus compare these with our calculated results. None of the terms are given in Moore.[104] However, Humphreys and Paul[105] have determined the energies for the six terms arising from the ^3P multiplet → ^4F, ^4D, ^4P, ^2F, ^2D, ^2P. They are compared with our calculated values in Table 2.7. The experimental values are larger than those calculated. Slater[93] quotes results by Roothaan and Tubis for the first row elements where the reverse occurs. The double-zeta levels are lower than the single-zeta levels and thus not

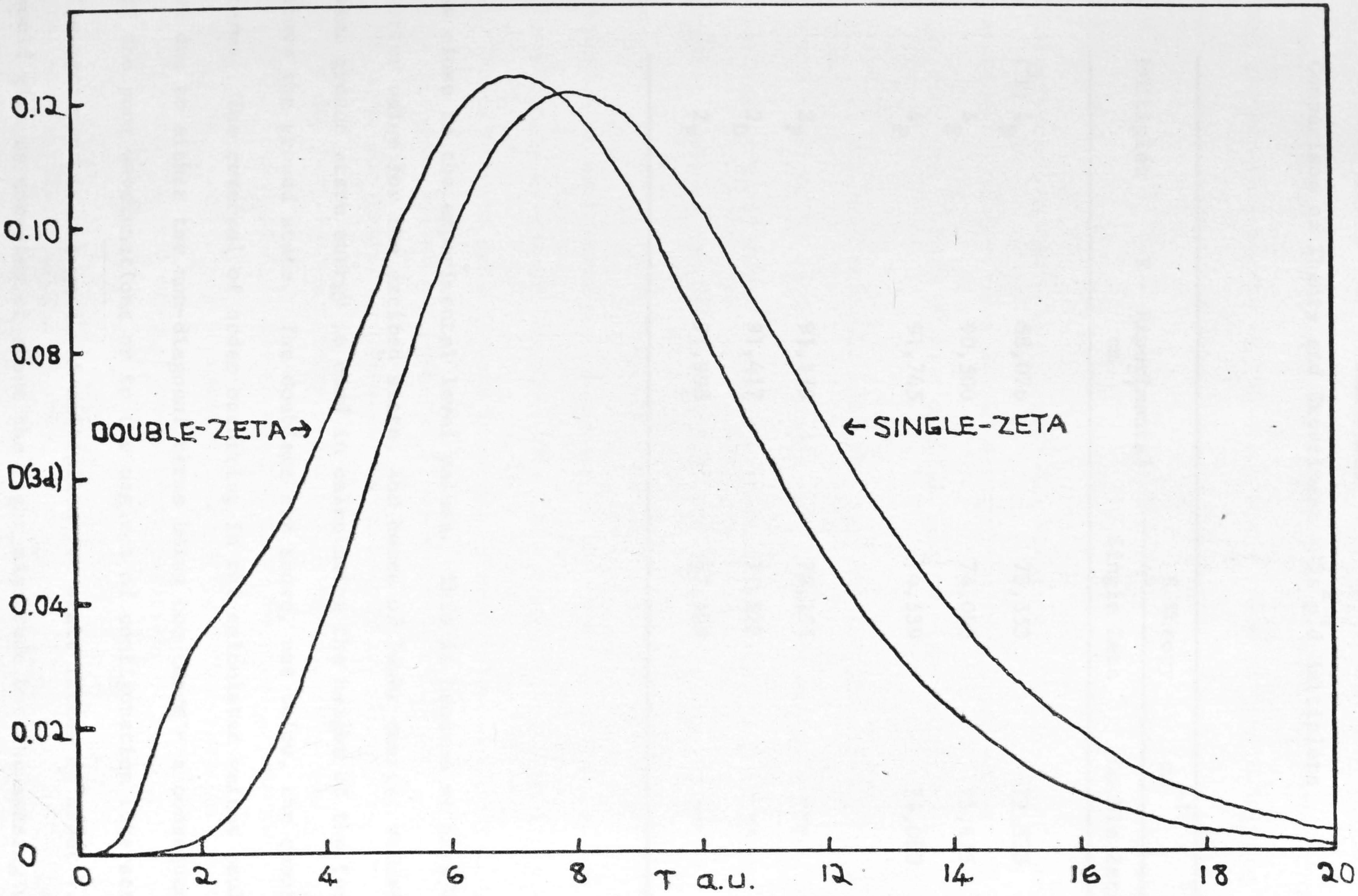


FIGURE 2.1 COMPARISON OF SINGLE-ZETA AND DOUBLE-ZETA 3d WAVEFUNCTIONS ^4D $3s^2p^4d$ CONFIGURATION CHLORINE

Table 2.7

Comparison of Theory and Experiment - $3s^2p^4d$ Multiplets

Multiplet	E - Experimental cm^{-1}	E Theory cm^{-1} Single Zeta	Double Zeta
$(^3P)\,^4D$	88,076	73,553	72,533
^4F	90,500	74,085	73,675
^4P	91,745	74,339	74,080
^2F	91,179	74,151	---
^2D	91,417	71,522	---
^2P	91,998	67,129	---

as close to the experimental level values. This is because we have a better value for the excited state, and hence of lower energy, whilst the same ground state energy is used in calculating the height of the terms above the ground state. The doublets are above, not below, the quartet terms. The reversal of order occurring in the calculated values could be due to either the non-diagonal terms being too large - a consequence of the poor wavefunctions or to the neglect of configuration interaction. The agreement is not good. A multiplicative scale factor of about 1.2 would give us energies of about the right magnitude but the spacing would still be too close.

As mentioned previously the spacing between the quartet terms depends only upon the integral $F^2(3p,3d)$. Thus from the spacing between any two of the quartets we can calculate a value of this integral. These are compared with those calculated in Table 2.8. The fairly small spread in the values calculated from the experimental term energies indicates that there is very little perturbation due to configuration interaction. The agreement is bad. The single-zeta values are $\frac{1}{4}$ to $\frac{1}{5}$ of the experimental values. The double zeta values are better - the best is that from the ^4D term whose d orbitals are the most contracted.

The isoelectronic ArII has been studied extensively by Minnhagen[99]. We can compare our calculated order with his experimental order. For the six terms arising from ^3P parent multiplet the order in ArII is the same as that observed for ClI except that the ^4P term is above the ^2P term and not ^2F or ^2D. In making the comparison with the calculated term energies we again have the phenomena of the reversal of the doublets and the quartets in the ^3P cluster. The order in the ^1D cluster is the same as the calculated order except that the ^2S term is above the ^2P term. Kjollerström, Möller and Svensson[106] were able to show that this is due to configuration interaction between the ^2S multiplets of the $3s^2p^44s$, $3s^2p^4d$ and $3sp^6$ configurations. The $(^1S)^2D$ term is below the $(^1D)^2S$ term in ArII. This could be due to configuration interaction between $(^1S)3d\,^2D$ and $(^3P)4d\,^2D$ terms. It is obvious that configuration interaction cannot be neglected if the order of terms if of interest.

Configuration Interaction

To determine the effect of configuration interaction on the wavefunctions, we have examined the configuration interaction between

Table 2.8

Comparison of Theory and Experiment

Quartet Multiplets $3s^2p^4d$ Configuration - Value of $F^2(3p,3d)$

Combination	$F^2(3p,3d)$ Exptl cm^{-1}
^4P - ^4F	8712
^4P - ^4D	9171
^4F - ^4D	9426

Multiplet	$F^2(3p,3d)$ cm^{-1} Single Zeta	Double Zeta
^4F	1867	3210
^4D	2309	6147
^4P	1689	2493

the ^2S terms in the sp^6 and s^2p^4d configurations. For the sake of computational simplicity we have not included the ^2S term from the $3s^2p^44s$ configuration. Its effect on the s^2p^4d term would be the opposite of that of the sp^6 ^2S term. Thus the effects we found are exaggerated and may even be in the wrong direction when compared with a more complete calculation. The theory of configuration interaction is outlined in Chapter 15 of Condon and Shortley.[107] The wavefunctions for the two terms are:

$$^2S(sp^6) = |sp_1\bar{p}_1p_o\bar{p}_op_{-1}\bar{p}_{-1}| \tag{2.5}$$

$$\begin{aligned} ^2S(s^2p^4d) = \frac{1}{6}\sqrt{5}\,\{3\sqrt{2}\ [|s\bar{s}p_1\bar{p}_1\bar{p}_op_{-1}d_{-1}| - |s\bar{s}p_1\bar{p}_1p_o\bar{p}_{-1}d_{-1}|] + \\ + \sqrt{6}\ [|s\bar{s}\bar{p}_1p_o\bar{p}_op_{-1}d_o| - |s\bar{s}p_1p_o\bar{p}_o\bar{p}_{-1}d_o|] + 3\sqrt{2}\ [|s\bar{s}\bar{p}_1p_op_{-1}\bar{p}_{-1}d_1| - \\ - |s\bar{s}p_1p_op_{-1}\bar{p}_{-1}d_1|] + 6|s\bar{s}p_1\bar{p}_1p_o\bar{p}_od_{-2}| + 2\sqrt{6}\ |s\bar{s}p_1\bar{p}_1p_{-1}p_{-1}d_o| + \\ + 6|s\bar{s}p_o\bar{p}_op_{-1}p_{-1}d_2|\} \quad . \end{aligned} \tag{2.6}$$

Using these we obtain the non-diagonal term

$$\langle {}^2S(sp^6) \mid \frac{2}{r_{12}} \mid {}^2S(s^2p^4d)\rangle = \frac{2}{\sqrt{6}} R^1(3s, 3p; 3p, 3d) \quad . \tag{2.7}$$

The results of our calculations are given in Table 2.9. There is negligible change in the 3s or 3p exponents. The 3d orbital has contracted slightly. The change in the energy of the $^2S\ s^2p^4d$ term is 0.002 a.u. - an improvememt better than that for the change from a single-zeta to a double-zeta wavefunction. Thus whilst the effect of configuration interaction is important, it is by no means dramatic; its neglect at least for a d^1 configuration is certainly permissible.

$3sp^5d$ Configuration

The next highest d containing configuration of neutral chlorine is the sp^5d configuration. It has 9 L-S coupled terms:

Table 2.9

Energy Minimised Orbital Exponents, Energies and Radii

Configuration Interaction - ^2S Multiplets of $3sp^6$ and $3s^2p^4d$ Configurations

$\alpha_{1s} = 16.5239$ $\alpha_{2s} = 5.7152$

Configuration	α_{2P}	α_{3s}	α_{3p}	α_{3p}	$\bar{r}_{3d}$	$E-E_{s^2p^5\,{}^2P^o}$ a.u.
^2S sp^6	6.4661	2.386	2.037	---	---	1.095969
W/O C.I.	6.4661	2.385	2.036	---	---	1.092867
^2S s^2p^4d	6.4911	2.426	2.135	0.335	10.448	0.817915
W/O C.I.	6.4911	2.426	2.135	0.314	11.146	0.820135

Non-Diagonal Term = 2.82×10^{-2} a.u.

$$\begin{array}{ll} sp^5(^3P)d & {}^4F\,{}^4D\,{}^4P\,{}^2F\,{}^2D\,{}^2P \\ sp^5(^1P)d & {}^2F\,{}^2D\,{}^2P\ . \end{array} \tag{2.8}$$

We have investigated the wavefunctions for the average energy "state" and the three quartets which occur only once in the manifold. The energy expressions for the quartets as determined from Slater's Tables[97] are:

$$
\begin{aligned}
({}^3P)\ {}^4F &= E_{av} - 2/35[F^2(3p,3d)] - 1/15[G^1(3p,3d)] - 3/70[G^3(3p,3d)] - \\
&\quad - 1/6[G^1(3s,3p)] - 1/10[G^2(3s,3d)] \quad , \\
{}^4D &= E_{av} + 1/5[F^2(3p,3d)] - 1/15[G^1(3p,3d)] - 3/70[G^3(3p,3d)] - \\
&\quad - 1/6[G^1(3s,3p)] - 1/10[G^2(3s,3d)] \quad , \\
{}^4P &= E_{av} - 1/5[F^2(3p,3d)] - 1/15[G^1(3p,3d)] - 3/70[G^3(3p,3d)] - \\
&\quad - 1/6[G^1(3s,3p)] - 1/10[G^2(3s,3d)] \quad .
\end{aligned}
\tag{2.9}
$$

The results of a single-zeta calculation are given in Table 2.10. The features and trends are the same as those noted for the $3s^2p^4d$ configuration. Hund's rule is again not obeyed - this time the ${}^4P$ quartet is the lowest. It also has the most contract d orbital.

These calculations were repeated using a double-zeta 3d wavefunction. The results are given in Table 2.11. This time the 3s and 3p orbital exponents were also optimised. The results justify the approximation made in the $3s^2p^4d$ configuration calculations - i.e., that the 3s and 3p orbital exponents do not change appreciably if a two term wavefunction is used for the 3d orbital. If anything, there is a slight expansion due to better shielding by the d orbitals. The contraction in the 3d orbitals as we go from a one term to a two term wavefunction is slightly greater than that observed in the $3s^2p^4d$ configuration. We find that the values of λ are commensurately smaller. Also the change in the energy is greater - being 0.0108 a.u. for the ${}^4P$ term.

Table 2.10

Energy Minimised Orbital Exponents, Energies and Radii

Chlorine-3sp^{5}d Configuration - Multiplets   Single Zeta Calculation

$\alpha_{1s} = 16.5239$ $\alpha_{2s} = 5.7152$ $\alpha_{2p} = 6.4605$

$E_{s^2p^5\text{-}{}^2P^o} = -917.00899$

Parent Multiplet	Multiplet	α_{3s}	α_{3p}	α_{3d}	$\bar{r}_{3d}$	$E-E_{s^2p^5\text{-}{}^2P^o}$ a.u.	cm^{-1}
^3F	^4F	2.453	2.146	0.360	9.722	1.67150	183,425
^3D	^4D	2.453	2.146	0.338	10.355	1.67584	183,902
^3P	^4P	2.453	2.145	0.376	9.309	1.66868	183,116
Average Energy		2.452	2.142	0.351	9.972	1.80238	197,789

Table 2.11

Energy Minimised Orbital Parameters, Energies and 3d Orbital Radial Properties

Chlorine-$3sp^5d$ Configuration - Double Zeta Calculation

$\alpha_{1s} = 16.5239$ $\alpha_{2s} = 5.7152$ $\alpha_{2p} = 6.4605$

	Average Energy	^4F	^4D	^4P
α_{3s}	2.452	2.451	2.452	2.449
α_{3p}	2.142	2.144	2.146	2.141
α	0.364	0.391	0.350	0.432
β	1.774	1.757	1.809	1.778
λ	0.476	0.459	0.478	0.440
$E-E_{s^2p^5\,-\,^2P^o}$ a.u.	1.74161	1.66523	1.67320	1.65788
$E_{s.z.} - E_{d.z.}$ a.u.	0.00240	0.00627	0.00264	0.01080
$\bar{r}$ a.u.	9.415	8.612	9.852	7.562
r_{max} a.u.	8.24	7.655	8.57	6.89
$\bar{r}/r_{max}$	1.143	1.125	1.150	1.098

$3s^2p^3d^2$ Configuration

We now turn to the d^2 configurations of chlorine. The lowest of these is the $s^2p^3d^2$ configurations. There are 55 multiplets in the manifold. Hund's rule predicts that the lowest term should be the ^6F term. It is represented by a single determinantal wavefunction:

$$^6F\ (M_L = 3\ M_S = 5/2) = |s\bar{s}p_1p_op_{-1}d_1d_2| \quad . \tag{2.10}$$

Using this wave function we obtain the energy of the term

$$^6F = E_{av} - 9/25[F^2(3p,3p)] - 2/5[G^1(3p,3d)] - 9/35[G^3(3p,3d)] - \\ - 58/441[F^2(3d,3d)] + 5/441[F^4(3d,3d)] \quad . \tag{2.11}$$

The results of the calculations on the average energy state and the ^6F term are given in Table 2.12. Unlike the results for the d^1 configurations, the difference between the single-zeta and double-zeta calculations is significant. They are greater, the lower the term in the manifold. The 3s and 3p orbital exponents are smaller in the double-zeta calculations, i.e., the orbital is expanded due to better 3d shielding. Unlike the case for a d^1 configuration, α in the two term function is less than the single-zeta α_{3d}. The values of β are larger than those in the more diffuse orbitals in a d^1 configuration. The smaller values of λ indicate a more equal mixing of the α and β terms of the wavefunction. The more contracted the orbital, the more the β part contributes. The behaviour of the α and β parts may be rationalised as follows: The β part of the two term wavefunction has a similar size to the 3s and 3p orbitals. The mutual shielding is not great. The α part, by contrast, is well shielded as it lies mainly outside the 3s and 3p

Table 2.12

Energy Minimised Orbital Parameters, Energies and 3d Orbital Radial Properties

Chlorine-$3s^2p^3d^2$ Configuration

	Average Energy		^6F Multiplet	
	Single Zeta	Double Zeta	Single Zeta	Double Zeta
α_{1s}	16.5239			
α_{2s}	5.7152			
α_{2p}	6.4854			
α_{3s}	2.495	2.478	2.485	2.457
α_{3p}	2.234	2.209	2.218	2.186
α	0.650	0.642	0.868	0.757
β	---	2.063	---	2.154
λ	---	0.409	---	0.369
$E-E_{s^2p^5\,^2P^o}$ a.u.	2.00302	1.91859	1.72327	1.56344
$E_{s.z.} - E_{d.z.}$ a.u.	0.08443		0.15983	
$\bar{r}$ a.u.	5.385	4.768	4.032	3.747
r_{max} a.u.	4.615	4.325	3.456	2.145
$\bar{r}/r_{max}$	1.167	1.102	1.167	1.747

orbitals and the β part of the 3d orbital. Thus it is fairly diffuse. When the β part contributes very little to the wavefunction, as is the case in a d^1 configuration, the α part being not so well shielded by the β part may contract slightly in obtaining a better shaped wavefunction. However as the contribution of the β part increases, the improved shielding leads to α being less than the single-zeta value. The range of energies spanned by the configuration manifold is evidently quite large - there is a spread of about 39,000 cm^{-1} between the average energy and the ^6F term which we expect to be one of the lowest terms. The difference between the single-zeta and double-zeta energies is appreciable, being over 2 eV for the ^6F term. Unlike the results reported for sulphur (sp^3d^2) and phosphorus (sp^2d^2 and p^3d^2) we find that both $\bar{r}$ and r_{max} decrease when we replace a single term wavefunction with a two term wavefunction. The decrease in r_{max} for the ^6F term is spectacular. $\bar{r}$ does not decrease as much as r_{max}. The ratio $\bar{r}/r_{max}$ has widely different values for the two states considered. The radial probability distributions for the single-zeta and double-zeta functions of the ^6F term are compared in Figure 2.2. As is the case for the other contracted d^2 terms that have been studied the single-zeta curve has a higher peak and tails off more slowly. This is the opposite of the case for a d^1 configuration. The bump in the double-zeta curve is not at a radius smaller than r_{max} but at a larger distance. In Figure 2.3 the curves of D(r) for the ^6F term and "average energy" state of the $s^2p^3d^2$ configuration and the ^4D term of the s^2p^2d configuration are given from the two term wavefunctions. The value of D(r) at r_{max} is seen to rise as the orbital contracts and to fall off more quickly the more contracted the orbital. For all curves there is a turning point at about 2.0 a.u. For the ^6F term this is the

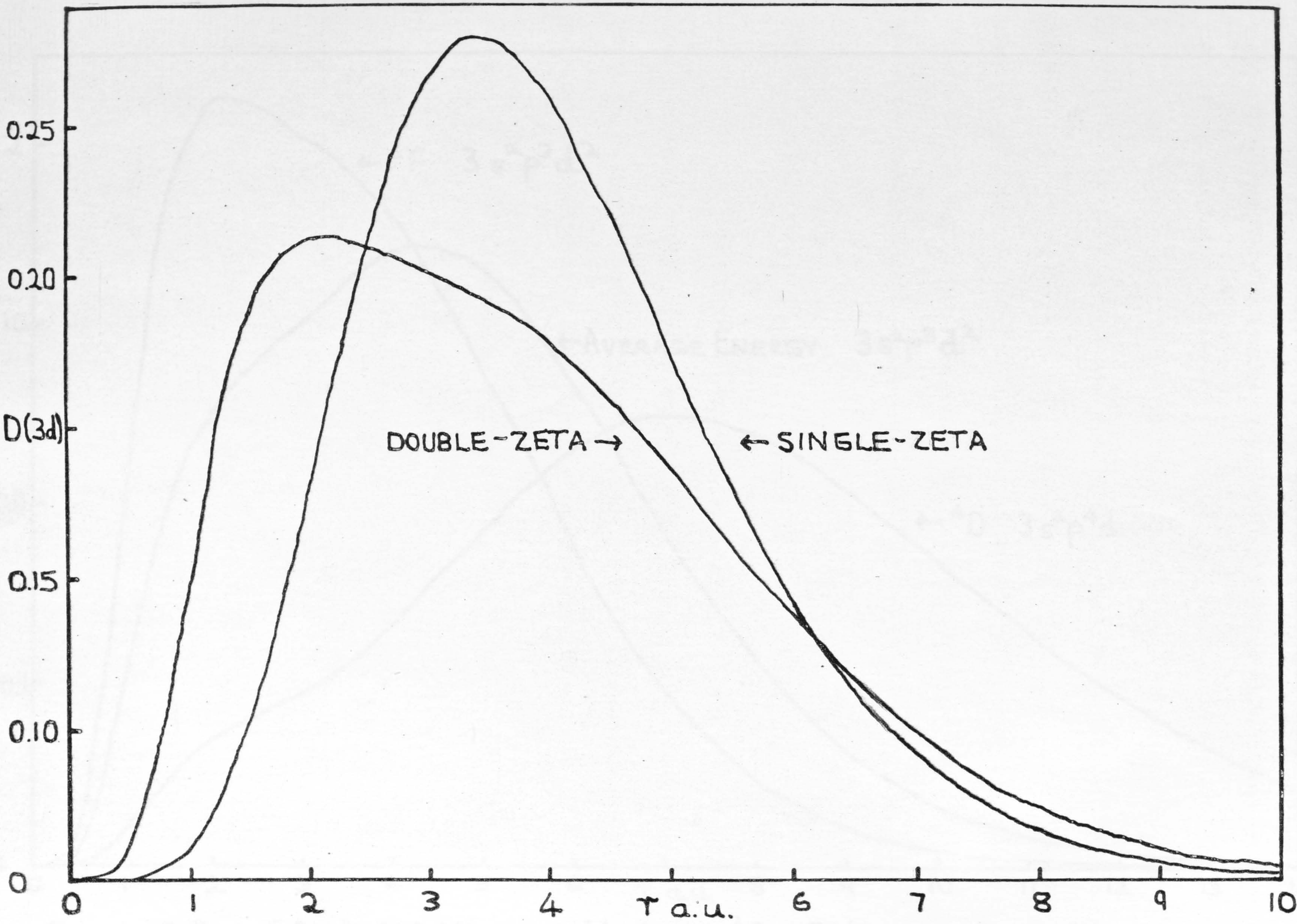


FIGURE 2.2 COMPARISON OF SINGLE-ZETA AND DOUBLE-ZETA 3d WAVEFUNCTIONS ^6F $3s^2p^3d^2$ CONFIGURATION CHLORINE

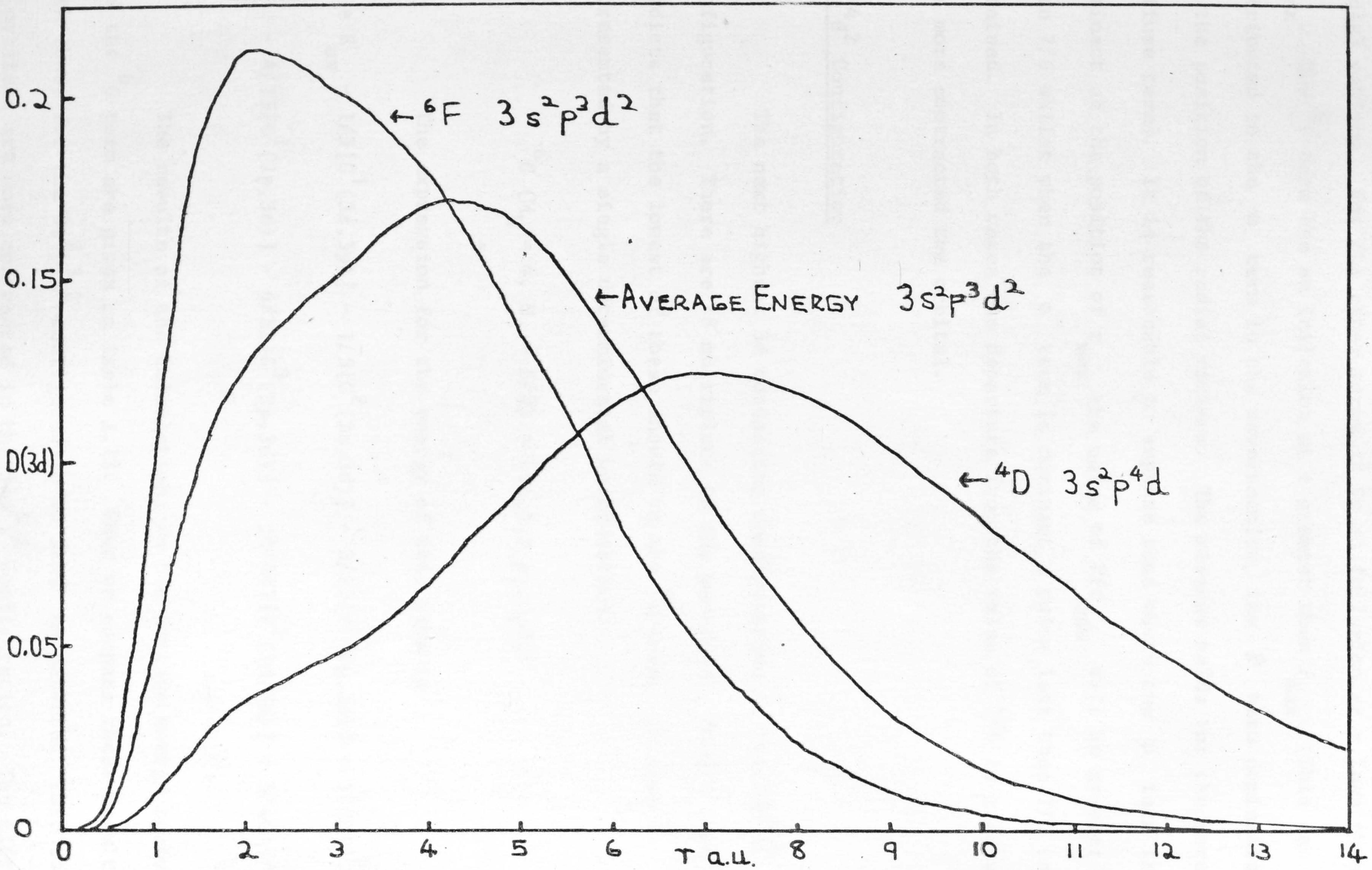


FIGURE 2.3 COMPARISON OF d^1 AND d^2 3d WAVEFUNCTIONS

radial maximum. For the other terms it is an inflexion at r less than r_{max}. The ^6F term has an inflexion at r greater than r_{max}. This can be attributed to the α term in the wavefunction, the β term dominating at the position of the radial maximum. The reverse holds for the more diffuse terms. It is reasonable to suppose that where the β term is dominant at the position of r_{max} the value of $\bar{r}/r_{max}$ will be greater than 7/6 whilst when the α term is dominant a value less than 7/6 is obtained. In both cases the departure from the value of 7/6 is greater the more contracted the orbital.

$3sp^4d^2$ Configuration

The next highest 3d containing configuration is the $3sp^4d^2$ configuration. There are 78 multiplets in the manifold. Hund's rule predicts that the lowest of these should be the ^6G term. It also is represented by a single determinantal wavefunction.

$$^6G\ (M_L = 4,\ M_S = 5/2) = |s p_1 \bar{p}_1 p_0 p_{-1} d_1 d_2| \qquad (2.12)$$

The expression for the energy of this term is

$$^6G = E_{av} - 1/3[G^1(3s,3p)] - 1/5[G^2(3s,3d)] - 3/25[F^2(3p,3p)] + 1/35[F^2(3p,3d)] - 4/15[G^1(3p,3d)] - 6/35[G^3(3p,3d)] - 58/441[F^2(3d,3d)] + 5/441[F^4(3d,3d)]\ . \qquad (2.13)$$

The results of the calculations on the average energy state and the ^6G term are given in Table 2.13. When we compare these results with those for the $3s^2p^3d^2$ configuration we find, as expected, that the 3d orbitals are more contracted in the $3sp^4d^2$ configuration. The differences

Table 2.13

Energy Minimised Orbital Parameters, Energies and 3d Orbital Radial Properties

Chlorine $3sp^4d^2$ Configuration

	Average Energy		^6G Multiplet	
	Single Zeta	Double Zeta	Single Zeta	Double Zeta
α_{1s}	16.5239			
α_{2s}	5.7152			
α_{2p}	6.4548			
α_{3s}	2.519	2.499	2.507	2.479
α_{3p}	2.236	2.207	2.225	2.189
α	0.666	0.657	0.883	0.770
β	---	2.092	---	2.183
λ	---	0.400	---	0.365
$E-E_{s^2p^5\,{}^2P^o}$ a.u.	3.01463	2.91594	2.61682	2.44560
$E_{s.z.} - E_{d.z.}$ a.u.	0.09869		0.01712	
$\bar{r}$ a.u.	5.255	4.585	3.964	3.656
r_{max} a.u.	4.505	4.14	3.398	2.06
$\bar{r}/r_{max}$	1.167	1.107	1.167	1.775

between the single-zeta and double-zeta energies are larger for the $3sp^4d^2$ configuration. The spread of energy values is larger too - there being a difference of over 50,000 cm^{-1} between the "average energy" state and the low lying ^6G term. The ratio $\bar{r}/r_{max}$ varies greatly - 1.11 for the average energy to 1.78 for the ^6G term.

$3p^5d^2$ Configuration

The other possible d^2 configuration, the p^5d^2 configuration has 19 multiplets. The lowest of these according to Hund's Rules is the ^4G term. Its wavefunction is:

$$^4G\ (M_L = 4,\ M_S = 3/2) = |p_1\bar{p}_1p_op_{-1}d_1d_2| \quad . \qquad (2.14)$$

Using this wavefunction we obtain the energy expression for this term:

$$^4G = E_{av} - 1/3[F^2(3p,3d)] - 2/15[G^1(3p,3d)] - 3/35[G^3(3p,3d)] - 58/441[F^2(3d,3d)] + $$
$$+ 5/441[F^4(3d,3d)] \quad . \qquad (2.15)$$

The results of the calculations on the "average energy" state of the configuration and the ^4G term are given in Table 2.14. Although the d orbital for the average energy state is more contracted than that for the sp^4d configuration, that for the ^4G term is less contracted than the ^6G term of the sp^4d^2 configuration. A similar situation occurs when we compare the differences between the single-zeta and double-zeta energies. The ratio $\bar{r}/r_{max}$ for the average energy of the p^5d^2 configuration is greater than that for the sp^4d^2 configuration, which, in turn, is less than that for the $s^2p^3d^2$ configuration although the p^5d^2 configuration

Table 2.14

Energy Minimised Orbital Parameters, Energies and 3d Orbital Radial Properties

Chlorine $3p^5d^2$ Configuration

	Average Energy		^4G Multiplet	
	Single Zeta	Double Zeta	Single Zeta	Double Zeta
α_{1s}		16.5239		
α_{2s}		5.7152		
α_{2p}		6.4242		
α_{3p}	2.239	2.205	2.230	2.189
α	0.688	0.682	0.787	0.750
β	---	2.138	---	2.210
λ	---	0.391	---	0.377
$E-E_{s^2p^5-{}^2P^o}$ a.u.	4.35737	4.24025	4.23536	4.08558
$E_{s.z.} - E_{d.z.}$ a.u.	0.11712		0.14979	
$\bar{r}$ a.u.	5.087	4.343	4.447	3.841
r_{max} a.u.	4.36	3.855	3.812	2.23
$\bar{r}/r_{max}$	1.167	1.127	1.167	1.722

has the most contracted d orbitals. This behaviour is the opposite of the case for d^1 configurations where $\bar{r}/r_{max}$ is also less than 7/6. It is in keeping with the trend for the more contracted d orbital d^2 configuration terms.

Variation of Size and Shape of 3d Orbitals with Nuclear Charge

We have now available from various workers[27,32,33] information about the size and shape of the radial part of the 3d orbital wavefunction for the lower lying configurations involving d orbitals of the later second row elements. These double-zeta results are summarised for d^1 configurations in Table 2.15 and for d^2 configurations in Table 2.16. For each configuration the information is arranged in blocks consisting of three columns and two rows. In the first row is given the symbol for the element, the mean radius of the state corresponding to the average energy and the value of $\bar{r}/r_{max}$; in the second row is given the symbol for the lowest term or where it is not known, that predicted by Hund's Rule, its mean radius and the value of $\bar{r}/r_{max}$.

For the d^1 configurations, Chandler and Thirunamachandran[31] noted that the ^5D term of the sulphur $3s^2p^3d$ configuration is more diffuse than the ^6D term of the phosphorus $3sp^3d$ configuration. This they attributed to the more efficient screening by the 3s and 3p orbitals in sulphur in harmony with the large 3s and 3p orbital exponents for sulphur. In addition to being more contracted the phosphorus orbitals deviate more from the single-zeta shape. This trend is also true of the average energy states of the two configurations and for the Si $3sp^2d$ P $3s^2p^2d$ and S $3sp^4d$ Cl $3s^2p^4d$ pairs. For a given element the d orbitals in the s^1 configurations

Table 2.15

Comparison of $\bar{r}$ and $\bar{r}/r_{max}$ for Various d^1 Configurations

p^j s^i		s^1			s^2	
p^1				Si	9.41	1.145
				^1D	7.84	1.143
p^2	Si	9.05	1.138	P	9.38	1.143
	^5F	6.33	1.329	^4F	7.52	1.111
p^3	P	8.01	1.137	S	9.45	1.146
	^6D	6.91	1.106	^5D	8.37	1.114
p^4	S	9.25	1.140	Cl	9.58	1.148
	^5D	6.18	1.081	^4D	7.76	1.093
p^5	Cl	9.42	1.143			
	^4P	7.56	1.098			

Configuration is $3s^ip^jd$

Table 2.16

Comparison of $\bar{r}$ and $\bar{r}/r_{max}$ for Various d^2 Configurations

p^j s^i	s^o			s^1			s^2		
p^1				Si	5.52	1.248	P	5.31	1.187
				^5G	4.48	1.378	^4G	4.46	1.371
p^2	Si	5.24	1.294	P	5.10	1.227	S	5.02	1.143
	^5G	4.19	1.374	^6G	3.87	1.464	^5G	3.92	1.548
p^3	P	4.84	1.293	S	4.59	1.209	Cl	4.77	1.102
	^6F	3.84	1.450	^7F	3.50	1.581	^6F	3.75	1.747
p^4	S	4.53	1.214	Cl	4.59	1.107			
	^5G	3.81	1.564	^6G	3.66	1.775			
p^5	Cl	4.34	1.127						
	^4G	3.84	1.722						

Configuration is $3s^i p^j d^2$

are more contracted than those in the s^2 configurations - attributable to the better shielding of the 3d orbitals by 3s orbitals than 3p orbitals. When we examine the orbital sizes for the lowest term of the configurations with given s occupancy - s^1 or s^2 but different p occupancy we observe the trend that the d orbitals are more contracted in atoms with higher atomic number. This is the opposite of the trend for a given p occupancy. It is again indicative of the better shielding properties of the 3s orbitals. However the lowest terms of the P sp^3d and S s^2p^3d configurations have more diffuse 3d orbitals than the sp^2d or sp^4d and s^2p^2d or s^2p^4d configurations respectively. This is a result of the better shielding by the spherically symmetrical arrangement of p orbitals in a half-filled shell. This does not occur with the average energy states. The general trend with them seems to be that the orbital is more diffuse the higher the 3p orbital occupancy. The shape factor $\bar{r}/r_{max}$ is remarkably similar for all the average energy states.

Slightly different trends can be discerned for the d^2 configurations. For the average energy states the d orbitals are more diffuse, the lower the occupancy of the p sub-shell for a given s orbital occupancy. This trend did not appear in the case of a d^1 configuration. It is indicative of the poorer shielding of the d orbitals when two d orbitals are occupied. The deviation of the orbital shape from that of a Slater-type orbital follows the opposite trend. It is greater the more diffuse the orbital. The shape factor $\bar{r}/r_{max}$ was always less than 7/6 for a d^1 configuration, but for a d^2 configuration it is usually greater. Within a d^1 configuration manifold this ratio tends to be smaller the more contracted the orbital but for a d^2 configuration it is greater the more contracted the orbital. For a given p sub-shell occupancy it is difficult to see any correlation between size of the 3d orbital and the s orbital occupancy. The ratio $\bar{r}/r_{max}$ is larger the less the s orbital occupancy. Slightly different correlations can be made for the lowest terms of the various configurations. Perhaps the most marked is that d orbitals in a s^1 configuration are more contracted than those in the s^o or s^2 configuration with the same p orbital occupancy. The difference between s^1 and s^2 configurations can be explained in the same way as was done for the difference between the ^6D term of the phosphorus $3sp^3d$ configuration and the ^5D term of the sulphur $3s^2p^3d$ configuration. The difference between the s^o and s^1 configurations is due to a greater charge on the nucleus in a s^1 configuration from which the d orbitals are not as well shielded. Similarly the d orbitals tend to be more diffuse the lower the p sub-shell occupancy for a given s sub-shell occupancy. The p orbital occupancy follows the order of the nuclear charges. There are some exceptions to this trend. The most contracted d orbital was that of the ^7F term of the $3sp^3d^2$ configuration of sulphur - the configuration having two half-filled sub-shells which tends to lead to lower energies and more contracted d orbitals. The shape factor for these lowest terms follows the opposite trend to that of the average energy states. It is, with one exception, greater the higher the occupancy of the s or p sub-shell. In d^1 configurations hardly any variation occurred. Thus d orbitals in a d^2 configuration are not shielded to the same extent as those in a d^1 configuration and their size and shape depends more on the nuclear charge.

Virial Theorem

The virial theorem furnishes a valuable way to see how good are our calculated wavefunctions. For inverse square laws of force it has the form[93]

$$\begin{aligned} \text{Potential Energy} &= -2\,(\text{Kinetic Energy}) \\ \text{Total Energy} &= -\text{Kinetic Energy} \quad . \end{aligned} \tag{2.16}$$

We have tested the calculation done on the average energy state of the $3s^2p^4d$ configuration. The results are given in Table 2.17. The first table lists the kinetic energies of the various atomic orbitals, using the optimum parameters from the single zeta calculation. We find that the virial theorem is not strictly obeyed. The sum of the total energy and the kinetic energy is not zero. The ratio of the potential energy to the kinetic energy is not + 2.0 . It is possible by multiplying all the parameters involved in the energy calculation - the orbital exponents, by a scaling factor λ and by varying λ - to get the virial theorem obeyed as closely as one wants. This was done and the results are also given in Table 2.17. The scaling factor was calculated to a precision of ± 0.00001. The virial theorem is then reasonably well obeyed. The orbital exponents for $\lambda = 1.0$ and $\lambda = 0.99934$ are listed. We find that the scaling factor has not significantly changed the orbital exponents of the 3s, 3p or 3d orbitals but it has for the core orbitals. These were not optimised but the values used were calculated by Clementi's rules. The energy is lower for the scaled set of orbital exponents. The 1s-2p orbital exponents used were thus not the optimum ones but they are sufficiently close to them not to affect significantly the optimum size of the 3s, 3p or 3d orbitals or their contribution to the total energy. The contributions of the 3s, 3p and 3d orbitals would not therefore seem to be the cause of the virial theorem being not obeyed. This stems from the choice of the orbital exponents for the core orbitals.

Table 2.17

$3s^2p^4d$ Configuration - Average Energy   Virial Theorem

nl	KE a.u.
1s	273.0393
2s	43.8126
2p	42.1344
3s	7.3050
3p	4.0577
3d	0.1218

Total KE = 917.472751 a.u.
Total PE = -1,833.737729 a.u.
Total Energy = -916.264978 a.u.

Total KE + Total Energy = 1.207773 a.u.
PE/KE = -1.998684

Scaling Factor λ = 0.99934

Total KE = 916.262087 a.u.
Total PE = -1,832.527462 a.u.
Total Energy = -916.265375 a.u.

Total KE + Total Energy = -0.003288 a.u.
PE/KE = -2.000004

nl	Orbital	Parameters
	λ = 1.0	λ = 0.99934
1s	16.5239	16.5130
2s	5.7152	5.7114
2p	6.4911	6.4868
3s	2.426	2.424
3p	2.138	2.137
3d	0.349	0.349

Conclusion

Thus in this part of our work we have gained a reasonable idea of the size of 3d orbitals appropriate to excited states of the chlorine atom and an idea of the energetics of the promotion. We have been able to make a good comparison between the use of single-zeta and double-zeta basis sets for 3d orbitals and the size and shape of 3d orbitals in d^1 and d^2 configurations. Calculations performed on the "average energy" states gave optimum orbital exponents fairly close to those predicted by Slater's Rules. The departure being greater the more contracted the 3d orbital. Slater's rules were found to be better than Burns' rules, or Clementi's rules for these 3d orbitals. Configurations involving 4s and 4p orbitals were found to have a smaller promotion energy. However they are fairly diffuse and are not as polarisable as 3d orbitals. Comparison between theory and experiment gave only fair results. The virial theorem was not strictly obeyed, mainly due to the fact that the chlorine core orbital exponents were not optimised. The energies calculated differ by a significant amount from those calculated using the Hartree-Fock method. The method used does not give orbital energies as do Hartree-Fock calculations. Only a small variation was found in 3d orbital size as one spanned a d^1 configuration manifold. For the quartet terms from the same parent term one could discern the trend that the 3d orbital was more contracted the lower the energy of the term. For doublets this trend was masked by the effect of cross terms. In comparing the two basis sets used it was found that for d^1 configurations there is little difference between them - as indicated by the fact that the orbital exponent α is close to the single-zeta exponent and the mixing parameter λ has a value close to 0.5. The correction to the single-zeta function is greater the more contracted the orbital. The use of the double-zeta basis set gave lower energies. A significant difference between the results obtained using single- and double-zeta basis sets was found for d^2 configurations. For d^2 configurations the shape of the double-zeta 3d orbital does not resemble that of a Slater-type orbital. The mixing parameter λ has a value nearer 0.4. The orbital exponent α does not have a value close to that of the single-zeta orbital exponent. We were able to rationalise the difference between the single-zeta and double-zeta results for d^1 and d^2 configurations. The ratio $\bar{r}/r_{max}$ increases the more contracted an orbital for d^2 configurations whilst for a d^1 configuration the reverse is true. A comparative study was made on the effect of the nuclear charge on the size and shape of 3d orbitals in d^1 and d^2 configurations. In d^1 configurations an increase in nuclear charge leads to more contracted 3s and 3p orbitals which as a result shield 3d orbitals better and thus lead to more diffuse orbitals. In d^2 configurations the 3d orbitals are not as well shielded and thus can be seen to contract with increased nuclear charge. 3s orbitals were shown to shield better than 3p orbitals. The effect of half-filled 3s and 3p shells was to tend to give greater stability to the lower terms and hence lead to more contracted 3d orbitals. Thus we have obtained a good feeling for what factors determine the size and shape of 3d orbitals in excited states of later second row atoms.

CHAPTER 3

THE VALENCE STATE OF SOME LATER SECOND ROW ELEMENTS

Introduction - The Valence State

The "state" of an atom in a molecule is manifestly not well defined, because the typically atomic quantisation is broken down by molecular formation. The problem of the valence state of an atom A bound by equivalent σ bonds to a set of n identical ligand atoms X has been studied by Van Vleck,[108] Mulliken,[109] Voge[36] and Moffitt[110,111] in examples such as methane. They have shown that the total molecular energy can be divided into parts, some purely atomic in character, and others interatomic. The total molecular energy can therefore be taken to be made up of the energies of the constituent atoms in isolation together with two-centre molecular energy terms. An atom in a state for which the energy is exactly that given by the atomic energy terms in the molecular energy is said to be in a valence state. This definition is general and can be applied to a variety of molecular descriptions. Other definitions have been discussed by Webster.[21] The exact nature of the valence state and its energy will, of course, depend upon the model used.

In the perfect pairing form of valence bond theory[112] the atomic orbitals of A, for the spherical field, are first combined into n equivalent hybrid orbitals $\sigma_1,\ldots,\sigma_n$ directed to ligands $\ell_1,\ldots,\ell_n$ the molecular wavefunction is the linear combination of Slater determinants,

$$\Psi_{P.P.} = 1/\sqrt{2^n}\,\{|\sigma_1\sigma_2\ldots\sigma_n\,\bar{\ell}_1\bar{\ell}_2\ldots\bar{\ell}_n| - |\bar{\sigma}_1\sigma_2\ldots\sigma_n\,\ell_1\bar{\ell}_2\ldots\bar{\ell}_n| - |\bar{\sigma}_1\bar{\sigma}_2\ldots\sigma_n\,\ell_1\ell_2\ldots\ell_n| + |\bar{\sigma}_1\bar{\sigma}_2\ldots\bar{\sigma}_n\,\ell_1\ell_2\ldots\ell_n|\}\quad, \qquad (3.1)$$

where the hybrid orbital σ_i is paired with ℓ_i. It is an eigenfunction of both S^2 and S_z possessing zero eigenvalues. The energy may be partitioned according to

$$E_{P.P.} = E(A) + E(A,X) + nE(X) \quad , \tag{3.2}$$

where E(A,X) contains all the interatomic terms and E(A) and E(X) the atomic energy terms belonging to A and X respectively. The valence state, then, is the state of the isolated atom A with energy E(A). Such a state may be realised by the non-physical process of separating the ligands A without any change in the spin coupling. Craig and Thirunamachandran[27] showed that the valence state wavefunction could be written in the form

$$\Psi_{P.P.} = 1/\sqrt{2^n}\,[\,|\sigma_1\sigma_2\ldots\sigma_n| + e^{i\Phi_1}|\bar{\sigma}_1\sigma_2\ldots\sigma_n| + e^{i\Phi_2}|\sigma_1\bar{\sigma}_2\ldots\sigma_n| + \\ + e^{i\Phi_n}|\bar{\sigma}_1\bar{\sigma}_2\ldots\bar{\sigma}_n|\,] \quad , \tag{3.3}$$

where the $e^{i\Phi_i}$ functions are arbitrary phase factors introduced to keep random spin coupling. The valence state energy obtained from this wavefunction is

$$E(A) = \sum_i w_i + \sum_{i<j} J_{ij} - \tfrac{1}{2}\sum_{i<j} K_{ij} \tag{3.4}$$

The total molecular energy is

$$E(P.P.) = \sum w_i + \sum_{i<j} J(\sigma_i\sigma_j) + \sum_{i<j} J(\ell_i\ell_j) - \tfrac{1}{2}\,\underset{i<j}{K}(\sigma_i\sigma_j) - \tfrac{1}{2}\,\underset{i<j}{K}(\ell_i\ell_j) + \\ + \sum_{ij} J(\sigma_i\ell_j) + nK(\sigma_i\ell_i) - \tfrac{1}{2}\sum_{ij} K(\sigma_i\ell_j) \quad , \tag{3.5}$$

where w_i are one-electron terms and J and K are the coulombic and exchange terms. The valence state wavefunction (3.3) may be expanded into natural atomic orbitals using the appropriate expressions for the hybrid orbitals. One finds that the new determinantal wavefunction is built up from terms from several configurations of the free atom. For instance the tetrahedral sp^3 wavefunction comes from s^2p^2, sp^3 and p^4 configurations.[36] We shall use the term multiconfigurational valence state[27] to describe the valence state obtained in this way. It is these multiconfigurational valence states of later second row elements that we are concerned with in this part of the work.

Instead of using hybrid orbitals (i.e., linear combinations of natural orbitals) to form a valence state, it is also possible to use a set of natural orbitals obtained from a single-configuration which collectively satisfy the symmetry requirements of the problem. This state would have random spins but the orbitals used would not be equivalent under the symmetry imposed by the ligand atoms. Such a "single configurational valence state" is the $3sp_xp_yp_zd_{z^2}d_{x^2-y^2}$ valence state studied by Craig and Thirunamachandran.[27]

Another valence state involving only one configuration is the 'Resonance Valence State' recently formulated by Craig and Thirunamachandran.[113] In this equivalence of bonds is secured by allowing resonance among pairing schemes for ligand orbitals paired to natural orbitals of the central atom. The valence state of the central atom is either the lowest term of the valence configuration or a linear combination of terms of the highest multiplicity. The valence state energy is thus directly available from spectral term values in many important examples.

Since the perfect pairing valence state wavefunction may be expanded into a linear combination of the wavefunction for spectroscopic terms, the valence state energy can be calculated from experimental term values. (In doing this one assumes that the orbital wavefunctions do not vary from term to term.) The ability to calculate the valence state energy from measured term values is the main reason why the valence state concept has an important place in the theory of the electronic structure of molecules. However a large number of terms are usually required, some of which may not be observed experimentally.

The molecules SF_6, PF_5 and ClF_3 are typical compounds of the later second row elements. Others have extensively studied single configurational valence states of the later second row elements[27,34,35] in these compounds. Work such as that by Cruickshank, Webster and Mayers,[23] Craig and Thirunamachandran,[27] Chandler and Thirunamachandran[31,32] and Coulson and Gianturco[29] provides us with information about the resonance valence states. Hybrid orbitals are a good approximation to the actual molecular orbitals. Because of this, studies of multiconfigurational valence states are particularly useful. The multiconfigurational valence states of second row atoms in SF_6, PF_5 and ClF_3 were investigated in order to obtain information on the size of the excited state orbitals involved in the hybrid orbitals and the energetics of the promotion into the valence state. The size of an orbital is invariably connected with its energy - the more favourable the size, the larger the orbital energy and hence the strength of the bonds formed. Naturally the basis sets obtained are more applicable to molecular calculations than those from free atom calculations.

$3sp^3d^2$ Multiconfigurational Valence State - S in SF_6

The first general discussion and application of the method of constructing hybrid orbitals from natural atomic orbitals using the methods of group theory was given by Kimball[114]. This technique is well described by Cotton.[115] For neutral sulphur in SF_6 one obtains the well known set of hybrid orbital functions given in the set of equations 1.2. Using equation 3.4 the energy expression for the multiconfigurational valence state is obtained:

$$E(V) = E(\text{core}) + 6E(\text{core - valence electrons}) + 3(J - \tfrac{1}{2}K)_{\text{trans}} + 12(J - \tfrac{1}{2}K)_{\text{cis}} \tag{3.6}$$

where expressed in terms of Slater's F^k, G^k and R^k integrals[93]

$$\begin{aligned}(J - \tfrac{1}{2}K)_{\text{trans}} = {} & 1/72[F^o(3s,3s)] + 1/8[F^o(3p,3p)] + 1/50[F^2(3p,3p)] + \\ & + 1/18[F^o(3d,3d)] + 2/441[F^2(3d,3d)] + 2/441[F^4(3d,3d)] + \\ & + 1/4[F^o(3s,3p)] - 1/9[G^1(3s,3p)] + 1/18[F^o(3s,3d)] + \\ & + 1/45[G^2(3s,3d)] + 1/2[F^o(3p,3d)] + 2/35[F^2(3p,3d)] - \\ & - 8/45[G^1(3p,3d)] - 18/245[G^3(3p,3d)] - 4\sqrt{10}/45[R^1(3s,3p;3p,3d)] + \\ & + \sqrt{10}/25[R^2(3s,3p;3d,3p)] + 2\sqrt{10}/315[R^2(3s,3d;3d,3d)] \quad ,\end{aligned} \tag{3.7}$$

and

$$\begin{aligned}(J - \tfrac{1}{2}K)_{\text{cis}} = {} & 1/72[F^o(3s,3s)] + 1/4[F^o(3p,3p)] - 7/200[F^2(3p,3p)] + \\ & + 7/72[F^o(3d,3d)] - 4/441[F^2(3d,3d)] + 1/1176[F^4(3d,3d)] + \\ & + 5/36[F^o(3s,3d)] - 1/36[G^2(3s,3d)] + 1/6[F^o(3s,3p)] - \\ & - 1/36[G^1(3s,3p)] + 1/3[F^o(3p,3d)] - 2/105[F^2(3p,3d)] - \\ & - 1/96[G^1(3p,3d)] - 3/245[G^3(3p,3d)] - \sqrt{10}/315[R^2(3s,3d;3d,3d)] - \\ & - \sqrt{10}/75[R^2(3s,3p;3d,3p)] + \sqrt{10}/90[R^1(3s,3p;3p,3d)] \quad .\end{aligned} \tag{3.8}$$

The energy was minimised with respect to the 3s, 3p and 3d orbital exponents. Both single- and double-zeta basis sets were used for the 3d orbitals. As in our atomic calculations we have used 1s, 2s and 2p orbital exponents calculated by Clementi's Rules.[94] The results of the calculation are given in Table 3.1. Craig and Thirunamachandran[27] have done a similar calculation in which they minimised the energy with respect to only the 3d orbital exponents. They used values of 2.25 and 1.91 for the 3s and 3p orbital exponents, chosen from the results of Bendazzoli and Zauli[34] for the single configurational valence state. More recently Coulson and Gianturco[29] have done Hartree-Fock SCF calculations on this and some other valence states of sulphur. The values we obtained for the 3d orbital exponents agree very well with those obtained by Craig and Thirunamachandran despite the fact that the 3s and 3p orbital exponents used differ slightly. Agreement with the results of Coulson and Gianturco is satisfactory. We obtain a value of -791.2 a.u. for the total energy whilst they give a value of -792.6 a.u. The lower energy from the SCF calculation is to be expected. The energy of promotion is less than that to the second ionisation limit of sulphur but well above the first ionisation limit. The difference between the single-zeta and double-zeta energies is quite large. Coulson and Gianturco obtained values of 3.02 and 2.00 a.u. for the mean radius and radial maximum of the 3d orbitals. These are slightly smaller than the values obtained by Craig and Thirunamachandran and myself.

Craig and Thirunamachandran have made a comparison of the size of the 3d orbital in the multiconfigurational valence state with that in the single configurational valence state and in free atomic terms, especially the ^7F term which is expected to be the lowest in the configuration manifold.

Table 3.1

Energy Minimised Orbital Parameters, Energies and 3d Orbital Radial Properties

Sulphur $3sp^3d^2$ Multiconfigurational Valence State

	Single Zeta	Double Zeta
α_{1s}	15.5409	
α_{2s}	5.3144	
α_{2p}	5.9468	
α_{3s}	2.191	2.189
α_{3p}	1.914	1.926
α	1.271	0.860
β	---	2.048
λ	---	0.337
$E - E_{s^2p^4\,^3P}$ a.u.	2.11064	1.98551
$E_{s.z.} - E_{d.z.}$ a.u.	0.12514	
$\bar{r}$ a.u.	2.754	3.165
r_{max} a.u.	2.360	2.06
$\bar{r}/r_{max}$	1.167	1.536

It is interesting to compare the orbital exponents obtained in this complete calculation on the valence state with those obtained in a calculation in which all exchange interactions are ignored. The exchange terms referred to, involve real orbitals. In certain examples the partition between Coulomb and exchange interactions depends on whether one uses real or complex orbitals. The orbital exponents obtained in a single-zeta calculation were 2.022, 1.815 and 1.340 for the 3s, 3p and 3d orbitals respectively, giving a mean radius of 2.612 a.u. and a radial maximum at 2.239 a.u. In the double-zeta calculation the values of α_{3s}, α_{3p}, α_{3d}, β_{3d} and λ_{3d} were 2.029, 1.825, 0.880, 1.932 and 0.299 respectively. The mean radius of the 3d orbitals was 2.957 a.u. and the radial maximum was at 2.01 a.u. Thus the inclusion of exchange in the energy expression leads to an expansion of the 3d orbital and a contraction of the 3s and 3p orbitals. Similar work on the free atom terms of sulphur[27] and phosphorus[32] found that the 3d orbital also is contracted by the inclusion of exchange. The difference between the two sets of results shows that intra-atomic exchange interactions should not be neglected.

To permit us to judge how significantly these very contracted 3d orbitals contribute to the bonding in SF_6 we have calculated the overlap integrals between the 3s, 3p and 3d orbitals of the sulphur and the 1s, 2s and 2p orbitals of fluorine. Details of the computation of these integrals are given in Appendix 3A. These are given in Table 3.2. The use of the overlap integral as a criterion of bond strength was mentioned in Chapter 1. The orbital exponents used for fluorine were $\alpha_{1s} = 8.6501$, $\alpha_{2s} = 2.5639$, $\alpha_{2p} = 2.5500$. These were obtained by minimising the energy of the fluorine ground state $2s^2p^5\ {}^2P$ term. They are in agreement with the values obtained by Clementi and Raimondi.[94] Except for the $2p_\sigma$-$3d_{z^2}$

Table 3.2

Overlap Integrals Sulphur-Fluorine

Sulphur $3sp^3d^2$ Multiconfigurational Valence State

S \ F	1s	2s	$2p_\sigma$
3s	0.0151	0.1874	0.1775
$3p_\sigma$	0.0343	0.3215	0.2485
$3d_{z^2}$	0.0575	0.4003	0.0829

S \ F	$2p_\pi$
$3p_\pi$	0.1008

R = 2.96 a.u.

overlap the overlap integrals for the $3d_{z^2}$ orbital are very favourable to bonding. The smaller magnitude of the $2p_\sigma$-$3d_{z^2}$ overlap is to be expected - overlaps of different sign coming from the two lobes of the $2p_\sigma$ orbital partially cancel each other. The 1s-$3d_{z^2}$ overlap is not negligible. It is also worth noting that the 2s orbital of the fluorine gives a better overlap than the $2p_\sigma$ orbital - the natural orbital of fluorine usually regarded as involved in bonding. This would suggest that some hybridisation of the fluorine could be energetically favourable. Thus the d orbitals appropriate to the sp^3d^2 multiconfigurational valence state of sulphur in SF_6 are sufficiently contracted to play a significant part in bonding. Further discussion of the energetics involved in the promotion into the valence state is best left until we consider the energetics appropriate to the atom in the molecular situation.

$3sp^3d_{x^2-y^2}$ Multiconfigurational Valence State S^+ in $S^+F_6^-$

As we outlined in Chapter 1 the sulphur atom in SF_6 is generally considered not to be neutral but to carry a formal positive charge. The valence-bond wavefunction has the form

$$\Psi = c_1\psi_1(SF_6) + c_2\psi_2(S^+F_6^-) + c_3\psi_3(S^{++}F_6^{=}) + \ldots.. \qquad (3.9)$$

The series can definitely be cut off after at least three terms. In the model using the sp^3d^2 hybrid orbitals we considered only the first term. This is physically unreasonable as it ignores the contributions of the charge-transfer structures. In order to obtain some feeling for the contribution of the other terms we have studied the valence state of sulphur in SF_6 when the sulphur atom carries a formal positive charge of +1. The wavefunction $\psi_2(S^+F_6^-)$ has the form

$$\psi_2(S^+F_6^-) = 1/\sqrt{6}(\phi_x + \phi_{-x} + \phi_y + \phi_{-y} + \phi_z + \phi_{-z}) \quad , \qquad (3.10)$$

where ϕ_z, for example, is the determinantal wavefunction corresponding to the situation where the fluorine atom lying on the positive z-axis carries a unit negative charge.

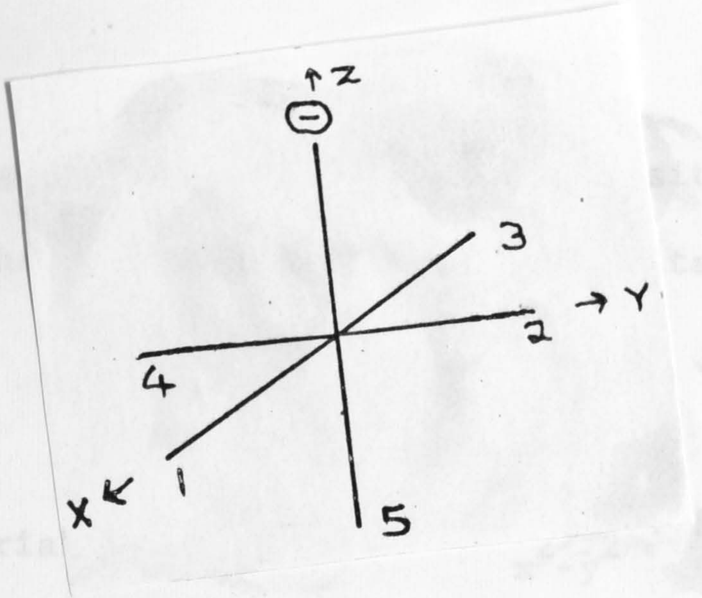


Figure 3.1

The symmetry of the molecule in this state is reduced from O_h to C_{4v} symmetry. Overall O_h symmetry is maintained by the resonance between the various charge-transfer states as indicated in equation 3.10. The representation Γ_σ for which the five σ bonding orbitals of the sulphur form a basis reduces as

$$\Gamma_\sigma = 2A_1 + B_1 + E \quad (3.11)$$

$$\Gamma_{\sigma\ \text{axial}} = A_1 \quad (3.12)$$

$$\Gamma_{\sigma\ \text{equatorial}} = A_1 + B_1 + E \ . \quad (3.13)$$

There are the following orbitals in the required symmetry classes

A_1	B_1	E
s	$d_{x^2-y^2}$	(p_x, p_y)
p_z		(d_{xz}, d_{yz})
d_{z^2}		

The valence-state configuration is obviously $3sp_xp_yp_zd_{x^2-y^2}$. d orbitals are still required by symmetry when the sulphur atom is charged.

When the charged fluorine atom is on the positive z axis as in Figure 3.1 one obtains the following set of hybrid orbitals:

$$\begin{aligned}
\phi_{\text{axial}} &= -3p_z \\
\phi_{\text{equatorial 1}} &= 1/2\ 3s + 1/2\ 3d_{x^2-y^2} + 1/\sqrt{2}\ 3p_x \\
\phi_{\text{equatorial 2}} &= 1/2\ 3s - 1/2\ 3d_{x^2-y^2} + 1/\sqrt{2}\ 3p_y \\
\phi_{\text{equatorial 3}} &= 1/2\ 3s + 1/2\ 3d_{x^2-y^2} - 1/\sqrt{2}\ 3p_x \\
\phi_{\text{equatorial 4}} &= 1/2\ 3s - 1/2\ 3d_{x^2-y^2} - 1/\sqrt{2}\ 3p_y \quad .
\end{aligned} \qquad (3.14)$$

Similar sets may be obtained for the other five components of the valence state wavefunction. It is possible to show that no atomic integral terms occur in cross terms between the various components of the wavefunction in the energy expression. The energy expression has the form

$$\begin{aligned}
E(V) = {} & E_{\text{core}} + E_{(\text{core - valence - electrons})} + 4J_{\text{axial - equatorial}} - \\
& - 2K_{\text{axial - equatorial}} + 4J_{\text{equatorial - equatorial (cis)}} - \\
& - 2K_{\text{equatorial - equatorial (cis)}} + 2J_{\text{equatorial - equatorial (trans)}} - \\
& - K_{\text{equatorial - equatorial (trans)}} ,
\end{aligned} \qquad (3.15)$$

where expressed in terms of Slater's F_k, G_k and R_k integrals,

$$\begin{aligned}
J_{\text{axial - equatorial}} = {} & 1/4[F^o(3s,3p)] + 1/4[F^o(3p,3d)] - 1/35[F^2(3p,3d)] + \\
& + 1/2[F^o(3p,3p)] - 1/25[F^2(3p,3p)] \quad ,
\end{aligned} \qquad (3.16)$$

$$K_{\text{axial - equatorial}} = 1/2[G^1(3s,3p)] + 3/196[G^3(3p,3d)] + 3/50[F^2(3p,3p)], \tag{3.17}$$

$$\begin{aligned} J_{\text{equatorial - equatorial (cis)}} = {} & 1/16[F^0(3s,3s)] + 1/4[F^0(3s,3p)] + \\ & + 1/8[F^0(3s,3d)] - 1/20[G^2(3s,3d)] + \\ & + 1/4[F^0(3p,3p)] - 1/50[F^2(3p,3p)] + \\ & + 1/4[F^0(3p,3d)] + 1/70[F^2(3p,3d)] + \\ & + 1/16[F^0(3d,3d)] + 1/196[F^2(3d,3d)] + \\ & + 1/196[F^4(3d,3d)] - 1/10\sqrt{3/5}\ [R^2(3s,3p;3d,3p)] , \end{aligned} \tag{3.18}$$

$$\begin{aligned} K_{\text{equatorial - equatorial (cis)}} = {} & 1/16[F^0(3s,3s)] + 3/100[F^2(3p,3p)] + \\ & + 1/16[F^0(3d,3d)] + 1/196[F^2(3d,3d)] + \\ & + 1/196[F^4(3d,3d)] - 1/8[F^0(3s,3d)] + \\ & + 1/12[G^1(3s,3p)] + 1/20[G^1(3p,3d)] + \\ & + 6/245[G^3(3p,3d)] , \end{aligned} \tag{3.19}$$

$$\begin{aligned} J_{\text{equatorial - equatorial (trans)}} = {} & 1/16[F^0(3s,3s)] + 1/4[F^0(3s,3p)] - \\ & - 1/6[G^1(3s,3p)] + 1/8[F^0(3s,3d)] + \\ & + 1/20[G^2(3s,3d)] + 1/4[F^0(3p,3p)] + \\ & + 1/25[F^2(3p,3p)] + 1/4[F^0(3p,3d)] + \\ & + 1/70[F^2(3p,3d)] - 1/10[G^1(3p,3d)] - \\ & - 12/245[G^3(3p,3d) + 1/16[F^0(3d,3d)] + \\ & + 1/196[F^2(3d,3d)] + 1/196[F^2(3d,3d)] - \\ & - 1/\sqrt{15}\ [R^1(3s,3d;3p,3p)] + \\ & + 1/10\sqrt{3/5}\ [R^2(3s,3p;3d,3p)] , \end{aligned} \tag{3.20}$$

$$\begin{aligned} K_{\text{equatorial - equatorial}} = {} & 1/16[F^{o}(3s,3s)] - 1/4[F^{o}(3s,3p)] + 1/8[F^{o}(3s,3d)] + \\ & + 1/20[G^{2}(3s,3d)] + 1/4[F^{o}(3p,3p)] + \\ & + 1/25[F^{2}(3p,3p)] - 1/4[F^{o}(3p,3d)] - \\ & - 1/70[F^{2}(3p,3d)] + 1/16[F^{o}(3d,3d)] + \\ & + 1/196[F^{2}(3d,3d)] + 1/196[F^{4}(3d,3d)] - \\ & - 1/10\sqrt{3/5}\,[R^{2}(3s,3p;3d,3p)] \quad . \qquad (3.21) \end{aligned}$$

The results of the calculation on the $3sp^{3}d_{x^2-y^2}$ multiconfigurational valence-state of S^{+} are given in Table 3.3. All the orbitals are more contracted than in the $3sp^{3}d^{2}$ valence-state for neutral sulphur. The 3d orbitals are the most contracted. The shapesof the 3d orbital wavefunctions are compared in Figure 3.2. The more contracted 3d orbital for S^{+} has a much steeper peak in the wavefunction and falls off to small values of D(r) very rapidly. Hence the value of $\bar{r}/r_{max}$ is closer to the single-zeta value of 7/6 than is usual for contracted d orbitals. In comparing the two sets of energies one finds that for the single-zeta calculations the energy is lower for the S^{+} valence-state whilst a lower energy is obtained for the neutral $3sp^{3}d^{2}$ valence-state in the double-zeta calculations. The latter set is a better guide to the actual situation. In any case the energy difference is not large - less than 1 eV. In comparing the two energies one should consider with the energy of promotion for the S^{+} valence-state,the energy required to form F^{-} which we have calculated to be 0.49122 a.u. The inter-atomic component of the energy would be expected to be greater with this ionic structure. Thus this structure could be more stable than that in which the sulphur atom is uncharged, despite the greater promotion energy.

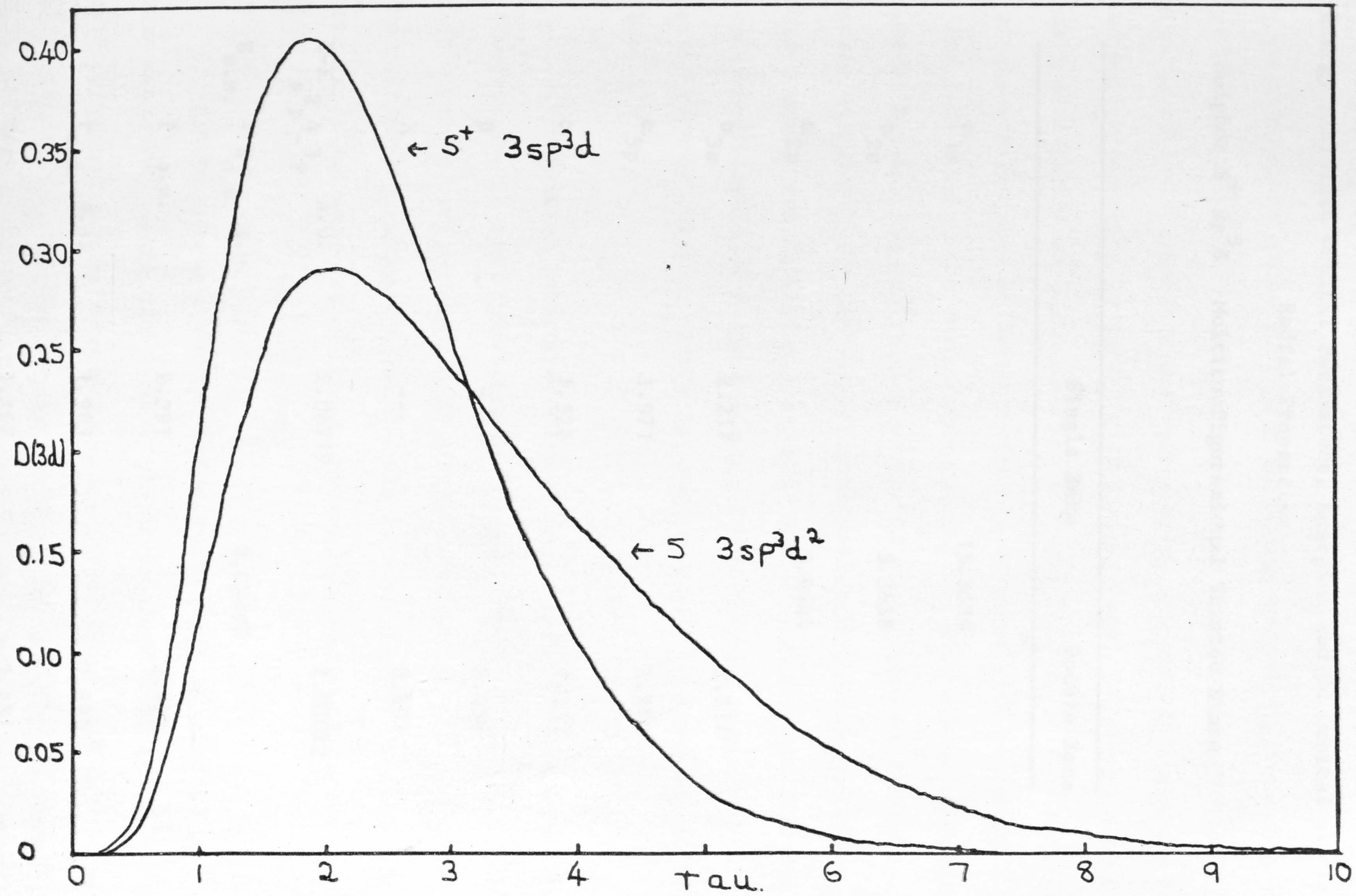


FIGURE 3.2 COMPARISON OF 3d WAVEFUNCTIONS
S $3sp^3d^2$ AND S^+ $3sp^3d$ MULTICONFIGURATIONAL VALENCE-STATES

Table 3.3

Energy Minimised Orbital Parameters, Energies and 3d Orbital Radial Properties

Sulphur S^+ sp^3d Multiconfigurational Valence State

	Single Zeta	Double Zeta
α_{1s}	15.5634	
α_{2s}	5.3638	
α_{2p}	5.9444	
α_{3s}	2.217	2.217
α_{3p}	1.971	1.972
α	1.528	1.253
β	---	2.556
λ	---	0.397
$E-E_{s^2p^4-{}^3P}$ a.u.	2.06719	2.03022
$E_{s.z.} - E_{d.z.}$ a.u.	0.03697	
$\bar{r}$ a.u.	2.291	2.422
r_{max} a.u.	1.963	1.890
$\bar{r}/r_{max}$	1.167	1.281

As calculations on the $3sp^3d_{x^2-y^2}$ single configurational valence-state had not been carried out the appropriate calculation was done for purposes of comparison. In comparing the results with those for the multiconfigurational valence-state we find that the 3s orbital is slightly more contracted in the single configurational valence-state - it has an orbital exponent of 2.253, whilst the 3d orbital is much more diffuse - it has a mean radius of 3.260 a.u. and a radial maximum of 2.61 a.u. in the single configurational valence-state as compared with values of 2.422 a.u. and 1.89 a.u. in the multiconfigurational valence-state. The biggest difference between the two valence-states is the difference in the two promotion energies. For the single-configurational valence-state the promotion energy was 2.73421 a.u. - about 9.5 eV greater than that for the multiconfigurational valence-state. The promotion energy is well above the second ionisation limit for the single configurational valence-state.

The overlap integrals between the sulphur 3s, 3p and 3d orbitals and fluorine 1s, 2s and 2p orbitals are given in Table 3.4. The $2p_\sigma$-$3d_{z^2}$ overlap with the very contracted 3d orbital obtained in this calculation on the multiconfigurational valence-state is much greater than that obtained for the $3sp^3d^2$ valence-state. The other overlaps are close in magnitude to those for the $3sp^3d^2$ valence-state.

The effect of oxidation number on the size of orbitals in sulphur was investigated very recently by Coulson and Gianturco.[29] Using single configurational valence-states they investigated such configurations as $s^{0.9}p^{2.7}d^{1.8}$. They also found the d orbital greatly contracted and the 3s and 3p orbitals not significantly changed from the situation in the

Table 3.4

Overlap Integrals Sulphur Fluorine

Sulphur S^+ $3sp^3d$ Multiconfigurational Valence State

$S \backslash F$	1s	2s	$2p_\sigma$
3s	0.0146	0.1838	0.1766
$3p_\sigma$	0.0327	0.3117	0.2487
$3d_\sigma$	0.0599	0.4015	0.1430

$S \backslash F$	$2p_\pi$
$3p_\pi$	0.0976

R = 2.96 a.u.

neutral atom. The use of such configurations as the one above for $S^{+0.6}$ is unreasonable. Any electrons lost from the sulphur atom in charge transfer would be expected to come from the highest occupied natural orbitals in the molecular field, i.e., the d orbitals. The configuration $sp^3d^{1.4}$ is more appropriate.

One can conclude from all these calculations, that from the size and overlapping power of the 3d orbitals, they should play a significant part in the bonding, when the central sulphur atom is positively charged and from the promotion energy for the valence-state, that the charge transfer component of the valence bond wavefunction cannot be neglected for energetic reasons.

$3sp^3d_{z^2}$ Multiconfigurational Valence State P in PF_5 (Trigonal Bipyramidal)

The structure of PF_5 has been shown by electron diffraction[59] to be a trigonal bipyramid. The vibrational spectrum[116,117] is compatible with the electron diffraction D_{3h} symmetry.

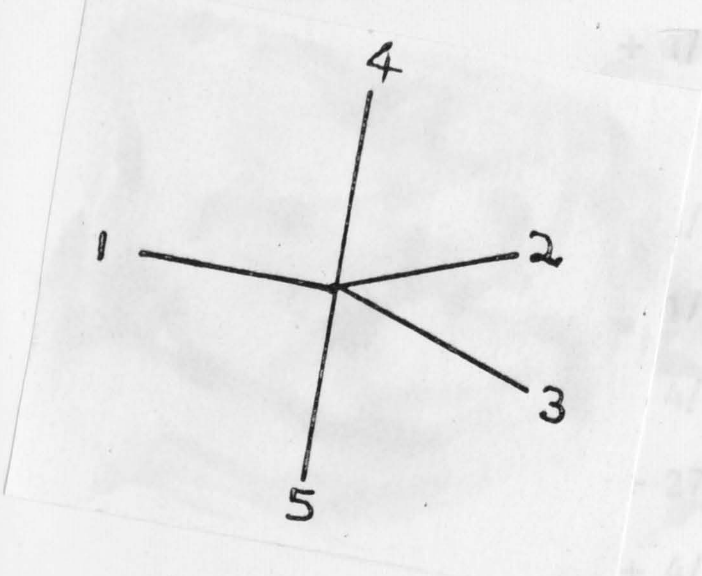


Figure 3.3

Duffey[118] and Cotton[119] have shown that the appropriate set of hybrid orbital wavefunctions is the following:

Equatorial

$$\phi_1 = 1/\sqrt{3}\ (\sin\alpha\ 3s - \cos\alpha\ 3d_{z^2}) + 2/\sqrt{6}\ 3p_x$$

$$\phi_2 = 1/\sqrt{3}\ (\sin\alpha\ 3s - \cos\alpha\ 3d_{z^2}) - 1/\sqrt{6}\ 3p_x + 1/\sqrt{2}\ 3p_y$$

$$\phi_3 = 1/\sqrt{3}\ (\sin\alpha\ 3s - \cos\alpha\ 3d_{z^2}) - 1/\sqrt{6}\ 3p_x - 1/\sqrt{2}\ 3p_y$$

Axial

$$\phi_4 = 1/\sqrt{2}\ (\cos\alpha\ 3s + \sin\alpha\ 3d_{z^2}) + 1/\sqrt{2}\ p_z$$

$$\phi_4 = 1/\sqrt{2}\ (\cos\alpha\ 3s + \sin\alpha\ 3d_{z^2}) - 1/\sqrt{2}\ p_z\ .$$

α is the mixing parameter between the 3s and $3d_{z^2}$ orbitals, both of which have A_1' symmetry. It has units of π radians. The energy expression for the $3sp^3d_{z^2}$ multiconfigurational valence-state is:

$$\begin{aligned} E(V) = {} & E(\text{core}) + E(\text{core - valence - electrons}) + (J - \tfrac{1}{2}K)_{\text{axial - axial}} + \\ & + 6(J - \tfrac{1}{2}K)_{\text{axial - equatorial}} + 3(J - \tfrac{1}{2}K)_{\text{equatorial - equatorial}} \, , \end{aligned} \tag{3.23}$$

where

$$\begin{aligned} (J - \tfrac{1}{2}K)_{\text{axial - axial}} = {} & 1/8 \cos^4\alpha \, F^0(3s,3s) + 1/8 \, F^0(3p,3p) + 1/50 \, F^2(3p,3p) + \\ & + 1/8 \sin^4\alpha \, [F^0(3d,3d) + 4/49 \, F^2(3d,3d) + \\ & + 4/49 \, F^4(3d,3d)] + 1/4 \sin^2\alpha \cos^2\alpha \, [F^0(3s,3d) + \\ & + 2/5 \, G^2(3s,3d)] + \cos^2\alpha \, [3/4 \, F^0(3s,3p) - \\ & - 1/3 \, G^1(3s,3p)] + 3/4 \sin^2\alpha \, [F^0(3p,3d) + \\ & + 4/35 \, F^2(3p,3d)] - \sin^2\alpha \, [4/15 \, G^1(3p,3d) + \\ & + 27/245 \, G^3(3p,3d)] + 1/7\sqrt{5} \sin^3\alpha \cos\alpha \, R^2(3s,3d;3d,3d) + \\ & + 4/3\sqrt{5} \sin\alpha \cos\alpha \, R^1(3s,3p;3p,3d) + \\ & + 3/5\sqrt{5} \sin\alpha \cos\alpha \, R^2(3s,3p;3d,3p) \quad . \end{aligned} \tag{3.24}$$

$$\begin{aligned} (J - \tfrac{1}{2}K)_{\text{axial - equatorial}} = {} & 1/12 \sin^2\alpha \cos^2\alpha \, F^0(3s,3s) + 1/3 \, F^0(3p,3p) - \\ & - 7/150 \, F^2(3p,3p) + 1/12 \sin^2\alpha \cos^2\alpha \, [F^0(3d,3d) + \\ & + 4/49 \, F^2(3d,3d) + 4/49 \, F^4(3d,3d)] + 1/6 \, [\sin^4\alpha + \\ & + \cos^4\alpha + 2 \sin^2\alpha \cos^2\alpha] \, F^0(3s,3d) - 1/60 \, [\sin^4\alpha + \\ & + \cos^4\alpha + 6 \sin^2\alpha \cos^2\alpha] \, G^2(3s,3d) + [1/3 \cos^2\alpha + \\ & + 1/6 \sin^2\alpha] \, [F^0(3s,3p) - 1/6 \, G^1(3s,3p)] + \\ & + 1/3 \sin^2\alpha \, [F^0(3p,3d) - 2/35 \, F^2(3p,3d) - \\ & - 1/30 \, G^1(3p,3d) - 9/245 \, G^3(3p,3d)] + 1/6 \cos^2\alpha \\ & [F^0(3p,3d) + 4/35 \, F^2(3p,3d) - 2/15 \, G^1(3p,3d) - \end{aligned}$$

$$
\begin{aligned}
&- 27/490\ G^3(3p,3d)] + 1/21\sqrt{5}\ [\cos^3\alpha\ \sin\alpha - \\
&- \sin^3\alpha\ \cos\alpha]\ R^2(3s,3d;3d,3d) - 4/15\sqrt{5}\ \sin\alpha \\
&\cos\alpha\ R^2(3s,3p;3d,3p) + 2/9\sqrt{5}\ \sin\alpha\ \cos\alpha \\
&R^1(3s,3p;3p,3d) \quad , \qquad (3.25)
\end{aligned}
$$

$$
\begin{aligned}
(J - \tfrac{1}{2}K)_{\text{equatorial - equatorial}} = {} & 1/18\ \sin^4\alpha\ F^o(3s,3s) + 1/18\ F^o(3p,3p) + \\
& + 2/225\ F^2(3p,3p) + 1/18\ \cos^4\alpha[F^o(3d,3d) + \\
& + 4/49\ F^2(3d,3d) + 4/49\ F^4(3d,3d)] + \\
& + 1/3\ F^o(3p,3p) - 7/150\ F^2(3p,3p) + \\
& + 1/9\ \sin^2\alpha\ \cos^2\alpha\ F^o(3s,3d) + 2/45\ \sin^2\alpha \\
& \cos^2\alpha\ G^2(3s,3d) + 5/9\ \sin^2\alpha\ F^o(3s,3p) - \\
& - 5/27\ \sin^2\alpha\ G^1(3s,3p) + 5/9\ \cos^2\alpha \\
& [F^o(3p,3d) - 2/35\ F^2(3p,3d)] - 5/9\ \cos^2\alpha \\
& [1/15\ G^1(3p,3d) + 18/245\ G^3(3p,3d)] - \\
& - 4/63\sqrt{5}\ \sin\alpha\ \cos^3\alpha\ R^2(3s,3d;3d,3d) + \\
& + 10/27\sqrt{5}\ \sin\alpha\ \cos\alpha\ R^1(3s,3p;3p,3d) + \\
& + 2/9\sqrt{5}\ \sin\alpha\ \cos\alpha\ R^2(3s,3p;3d,3p) \quad . \\
& \qquad (3.26)
\end{aligned}
$$

The energy was minimised with respect to the 3s, 3p and 3d orbital exponents for a set of fixed values of α and also with respect to α. The results of the single-zeta calculations are given in Table 3.5. The double-zeta results are given in Table 3.6. There is a very strong dependence of the size of the 3d orbitals on the mixing parameter α. When either the axial or equatorial bonds contain no d character - $\alpha = 0, 0.5$ respectively - the d orbitals are diffuse. As more mixing of s and d character in the two types of bonds occurs, the orbital becomes more contracted. The value of α for which the d orbital is most contracted

Table 3.5

Energy Minimised Orbital Exponents, Energies and Radii

Phosphorus $3sp^3d$ Multiconfigurational Valence State

Single Zeta Calculations

$\alpha_{1s} = 14.5578$ $\alpha_{2s} = 4.9125$ $\alpha_{2p} = 5.4444$

						α for E_{min}
α	0.0	0.125	0.25	0.375	0.5	0.3125
α_{3s}	1.979	1.958	1.934	1.947	1.976	1.936
α_{3p}	1.693	1.675	1.660	1.668	1.699	1.661
α_{3d}	0.485	0.761	0.956	0.874	0.495	0.951
$\bar{r}_{3d}$ a.u.	7.216	4.599	3.661	4.005	7.071	3.680
$E-E_{s^2p^3-{}^4S}$ a.u.	1.22667	1.19197	1.13929	1.13822	1.16655	1.13033

Table 3.6

Energy Minimised Orbital Parameters, Energies and 3d Orbital Radial Properties

Phosphorus $3sp^3d$ Multiconfigurational Valence State

Double Zeta Calculations

$\alpha_{1s} = 14.5578$ $\alpha_{2s} = 4.9125$ $\alpha_{2p} = 5.4444$

α	0.0	0.125	0.25	0.375	0.5	α for E_{min} 0.3106
α_{3s}	1.973	1.952	1.938	1.946	1.968	1.938
α_{3p}	1.683	1.673	1.666	1.671	1.686	1.666
α	0.478	0.564	0.622	0.600	0.496	0.628
β	1.472	1.560	1.596	1.581	1.477	1.605
λ	0.420	0.370	0.343	0.359	0.406	0.347
$E-E_{s^2p^3-{}^4S}$ a.u.	1.20875	1.14710	1.09232	1.09284	1.14383	1.08414
$E_{s.z.} - E_{d.z.}$ a.u.	0.01792	0.04488	0.04697	0.04538	0.02272	0.04619
$\bar{r}$ a.u.	6.518	5.047	4.379	4.657	6.122	4.370
r_{max} a.u.	5.795	3.05	2.65	2.84	5.30	2.68
$\bar{r}/r_{max}$	1.125	1.655	1.652	1.640	1.155	1.631

is close to, but does not coincide with, the value for the minimum energy. Both the 3s and 3p orbitals expand slightly as the 3d orbital contracts. As is to be expected, the axial bonds contain more 3d character than the equatorial bonds - the values of sin α and cos α being 0.828 and 0.561 $\alpha = 0.3106$. As with the sulphur $sp^3d_{x^2-y^2}$ multiconfigurational valence-state the difference in the energies obtained between the single-zeta and double-zeta calculations is not large - it is considerably smaller than that found in some calculations on free atom terms or the sulphur sp^3d^2 multiconfigurational valence-state. However the shape of the 3d orbitals differs greatly as shown in Figure 3.4. The values of $\bar{r}/r_{max}$ for values of α close to the optimum value of α are particularly big. The electron distribution in the double-zeta orbitals is more evenly distributed. The radial maximum is less than the P-F bond distance of 2.931 a.u. (average value).

The energy expression for the single configurational balance state is identical to that for the average energy of the $3sp^3d$ configuration. This has been studied by Chandler and Thirunamachandran.[31,32] The 3s and 3p orbitals are more diffuse in the multiconfigurational valence-state. The mean radius and radial maxima of the 3d orbitals in the single configurational valence-state are 9.11 a.u. and 8.01 a.u. respectively. Thus the 3d orbitals are much more contracted in the multiconfigurational valence-state. The difference in the two valence-state energies is about 3.0 eV - the multiconfigurational valence-state being lower.

The lowest term of the $3sp^3d$ configuration is the $^6D^o$ term. Chandler and Thirunamachandran found that the d orbitals had a mean radius of 6.92 a.u. and a radial maximum at 6.26 a.u. The $^6D^o$ term energy is

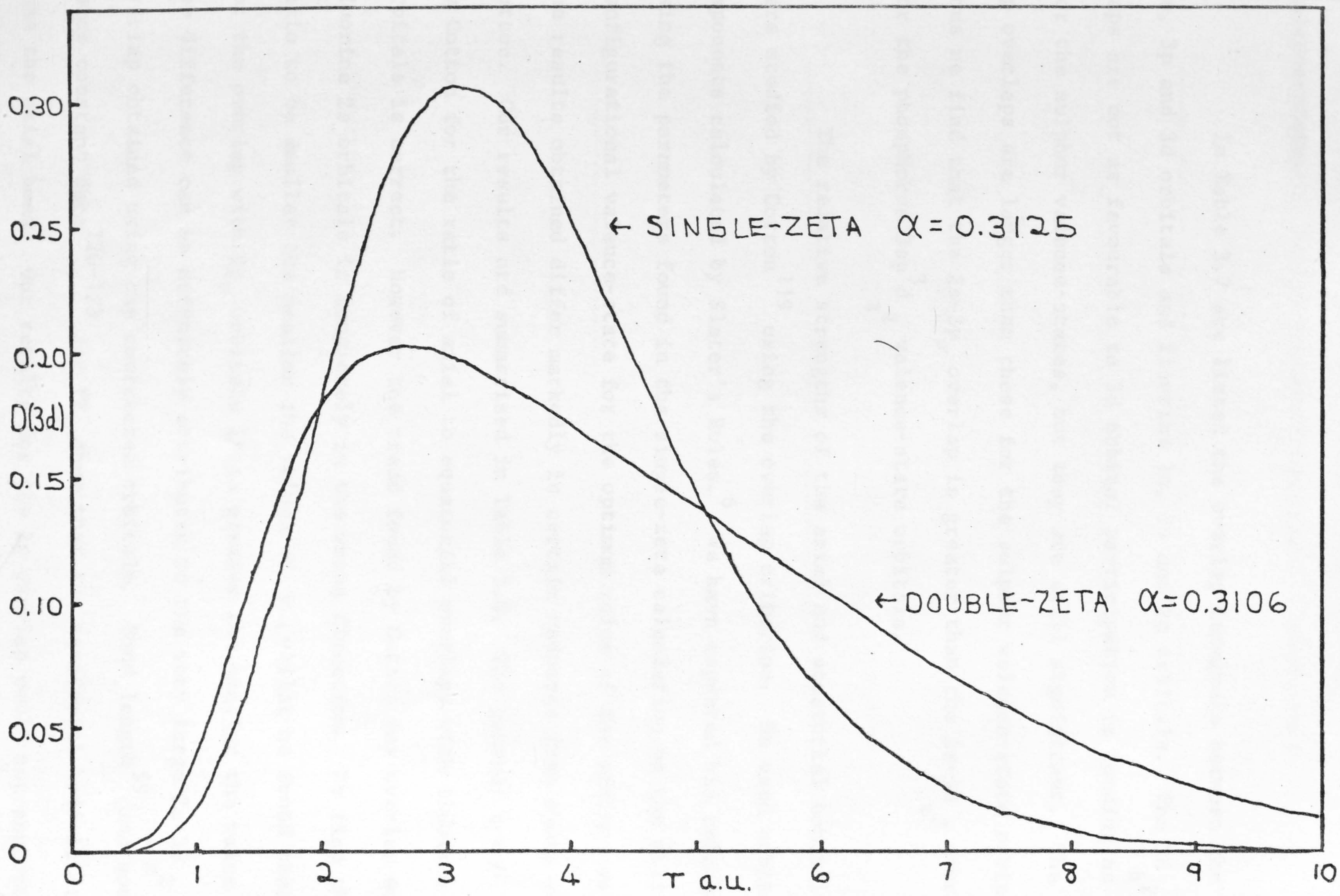


FIGURE 3.4 COMPARISON OF SINGLE-ZETA AND DOUBLE-ZETA 3d WAVEFUNCTIONS
PHOSPHORUS $3sp^3d_{z^2}$ MULTICONFIGURATIONAL VALENCE-STATE

less than that energy of the multiconfigurational valence-state. Despite the lower energy the d orbitals are more contracted in the multiconfigurational valence-state.

In Table 3.7 are listed the overlap integrals between the phosphorus 3s, 3p and 3d orbitals and fluorine 1s, 2s and 2p orbitals. The $3d_{z^2}$ overlaps are not as favourable to 3d orbital participation in bonding as those for the sulphur valence-states, but they are still significant. The 3s and 3p overlaps are larger than those for the sulphur valence-state orbitals. Thus we find that the $2s$-$3p_\sigma$ overlap is greater than the $2s$-$3d_{z^2}$ overlap for the phosphorus $3sp^3d_{z^2}$ valence-state orbitals.

The relative strengths of the axial and equatorial bonds in PF_5 were studied by Cotton[119] using the overlap criterion. He used orbital exponents calculated by Slater's Rules.[6] We have repeated his calculations using the parameters found in the single-zeta calculation on the multiconfigurational valence-state for the optimum value of the mixing coefficient. The results obtained differ markedly in certain respects from those of Cotton. Our results are summarised in Table 3.8. The general trend found by Cotton for the ratio of axial to equatorial overlaps with fluorine $2p_\sigma$ orbitals is correct. However the trend found by Cotton for overlap with fluorine 2s orbitals is completely in the wrong direction. We find the ratio to be smaller the smaller the values of α, whilst he found that as for the overlap with $2p_\sigma$ orbitals it is greater the smaller the value of α. The difference can be definitely attributed to the very large $2s$-$3d_{z^2}$ overlap obtained using the contracted orbitals. Bond length[59] and bond force constant data[120-123] for PF_5 show that the equatorial bond is stronger than the axial bond. Our results for the 2s overlap would not support this

Table 3.7

Overlap Integrals Phosphorus-Fluorine

Phosphorus $3sp^3d$ Multiconfigurational Valence State

$_{P}{}^{F}$	1s	2s	$2p_{\sigma}$
3s	0.0210	0.2264	0.1835
$3p_{\sigma}$	0.0451	0.3849	0.2359
$3d_{z^2}$	0.0523	0.3638	0.0347

$_{P}{}^{F}$	$2p_{\pi}$
$3p_{\pi}$	0.1231

$R = 2.931$ a.u.

Table 3.8

Overlap as a Function of Mixing Coefficient

$3sp^3d_{z^2}$ Multiconfigurational Valence State

Electron Pair Model

$n\ell_F$	α for max Total Overlap	S_{axial}	$S_{equatorial}$	$S_{axial}/S_{equatorial}$
$2p_\sigma$	0.28	0.259	0.277	0.935
2s	0.31	0.610	0.492	1.241
1s	0.31	0.078	0.057	1.355

$\alpha = 0.3125$

Position of F atom	P Orbital	$n\ell_F$ Overlap Integral $2p_\sigma$	2s
Axial	Axial	0.249	0.611
	Axial	-0.084	0.065
	Equatorial	0.082	-0.027
Equatorial	Axial	0.067	-0.035
	Equatorial	0.283	0.492
	Equatorial	-0.005	0.019

Π Orbitals

Position of F atom	P Orbital	Overlap Integral $2p_\pi$
Axial	Equatorial	0.101
Equatorial	Axial	0.087
	Equatorial	0.087

conclusion. These results tend to invalidate some of Cotton's arguments in his paper with respect to the hybridisation of the fluorine atoms. It may be that the overlap criterion breaks down in certain cases when 3d orbitals are involved. The overlaps of the fluorine 2s and 2p orbitals with both the phosphorus orbitals directed towards them and in other directions are also given in Table 3.8. The non-bonding overlaps are generally at least an order of magnitude less than the bonding overlaps. The value of the axial fluorine $2p_\pi$ - phosphorus equatorial orbital overlap - is significantly large.

Certainly we can say in conclusion that the contracted 3d orbitals found in the multiconfigurational valence-state must be taken into consideration when the bonding in PF_5 is being investigated.

$3sp^3d_{x^2-y^2}$ Multiconfigurational Valence State P in PF_5 (Square Pyramidal)

Electron diffraction[59] and infra-red[116,117] spectral studies have indicated that the PF_5 molecule is a trigonal bipyramid. However NMR studies[124] point to the five fluorines being equivalent. This suggests that the fluorine atoms may exchange at a rate slow compared with the time necessary to establish sharp vibrational levels and fast compared with the inverse line widths associated with nuclear resonance experiments. Berry[125] has proposed a mechanism for the intramolecular exchange of fluorine atoms in PF_5. The pathway is indicated in Figure 3.5.

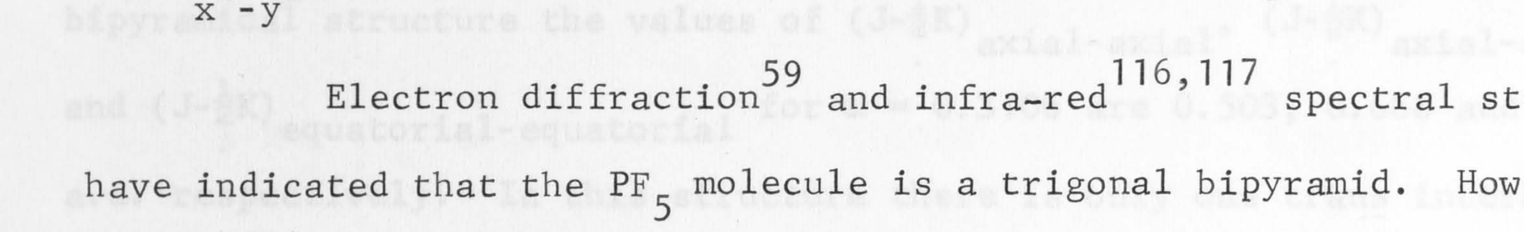


Figure 3.5

The molecule goes through an intermediate structure with C_{4v} symmetry. The high exchange rate indicates that the C_{4v} intermediate structure must have an energy close to that of the D_{3h} structure. This led us to investigate the valence-state of phosphorus in a square pyramidal structure. This has C_{4v} symmetry. Thus the hybrid orbitals and energy expression for the valence-state are the same as for the $3sp^3d_{x^2-y^2}$ multiconfigurational valence-state of S^+. The results of the calculation are given in Table 3.9. In comparing the results for the two valence-states we find that the 3s and 3p orbitals are slightly more expanded but the 3d orbitals are more contracted for the square pyramidal valence state. What is unexpected is the fact that the square pyramidal valence-state has a lower energy than the trigonal bipyramidal valence-state - the difference being about 1.3 eV. Orbitals trans to each other interact less strongly than two at an angle less than 180°, in particular 90°. For the trigonal bipyramidal structure the values of $(J-\frac{1}{2}K)_{\text{axial-axial}}$, $(J-\frac{1}{2}K)_{\text{axial-equatorial}}$ and $(J-\frac{1}{2}K)_{\text{equatorial-equatorial}}$ for $\alpha = 0.3106$ are 0.503, 0.668 and 0.690 a.u. respectively. In this structure there is only one trans interaction whilst in the square pyramidal structure there are two such interactions. This difference between the cis and trans interactions explains why the square pyramidal valence-state has a lower energy. Further discussion on this anomaly will be deferred until the next chapter.

$3sp^34s$ Multiconfigurational Valence State P in PF_5 (Trigonal Bipyramidal)

The representation Γ_σ for which the five σ orbitals of P in the trigonal bipyramidal form of PF_5 form a basis reduces as

$$\Gamma_\sigma = 2A_1' + A_2'' + E' \quad .$$

Table 3.9

Energy Minimised Orbital Parameters, Energies and 3d Orbital Radial Properties

Phosphorus $3sp^3d_{x^2-y^2}$ Multiconfigurational Valence State

	Single Zeta	Double Zeta
α_{3s}	1.918	1.924
α_{3p}	1.650	1.658
α	1.110	0.709
β	---	1.649
λ	---	0.316
$E-E_{s^2p^3-{}^4S}$ a.u.	1.02867	0.98770
$E_{s.z.} - E_{d.z.}$ a.u.	0.04096	
$\bar{r}$ a.u.	3.153	3.718
r_{max} a.u.	2.703	2.420
$\bar{r}/r_{max}$	1.167	1.536

The orbitals of the A_1' symmetry class are S and d_{z^2} orbitals. In the $3sp^3d_{z^2}$ valence-state we chose the 3s and $3d_{z^2}$ orbitals. However this set is not the only possible choice - we could equally well have chosen 3s and 4s orbitals. The choice allowed with the D_{3h} symmetry contrasts with the case of the O_h symmetry of the neutral sulphur atom in SF_6 where the S, p_x, p_y, p_z, d_{z^2}, $d_{x^2-y^2}$ combination is the only possible one allowed by symmetry. The orbital energy of a 4s orbital is less than that of a 3d orbital. Thus the $3sp^34s$ configuration of phosphorus should not be ignored as a possible valence-state configuration. The appropriate hybrid orbital wavefunctions are the following:

Equatorial

$$\phi_1 = 1/\sqrt{3}\ [\sin\alpha\ 3s - \cos\alpha\ 4s] + 2/\sqrt{6}\ 3p_x$$

$$\phi_2 = 1/\sqrt{3}\ [\sin\alpha\ 3s - \cos\alpha\ 4s] - 1/\sqrt{6}\ 3p_x + 1/\sqrt{2}\ 3p_y$$

$$\phi_3 = 1/\sqrt{3}\ [\sin\alpha\ 3s - \cos\alpha\ 4s] - 1/\sqrt{6}\ 3p_x - 1/\sqrt{2}\ 3p_y$$

Axial

$$\phi_4 = 1/\sqrt{2}\ [\cos\alpha\ 3s + \sin\alpha\ 4s] + 1/\sqrt{2}\ 3p_z$$

$$\phi_5 = 1/\sqrt{2}\ [\cos\alpha\ 3s + \sin\alpha\ 4s] - 1/\sqrt{2}\ 3p_z \quad . \qquad (3.2)$$

The energy expression for the $3sp^34s$ multiconfigurational valence-state is identical to that given in equation 3.23 for the $3sp^3d_{z^2}$ valence-state but where

$$\begin{aligned}(J-\tfrac{1}{2}K)_{\text{axial-axial}} = {} & 1/8\cos^4\alpha\ F^o(3s,3s) + 1/8\sin^4\alpha\ F^o(4s,4s) + 1/8F^o(3p,3p) + \\ & + 1/50\ F^2(3p,3p) + 1/4\sin^2\alpha\cos^2\alpha\ F^o(3s,4s) + 1/2\sin^2\alpha \\ & \cos^2\alpha\ G^o(3s,4s) + 3/4\cos^2\alpha\ F^o(3s,3p) - 1/3\cos^2\alpha \\ & G^1(3s,3p) + 3/4\sin^2\alpha\ F^o(4s,3p) - 1/3\sin^2\alpha\ G^1(4s,3p) + \\ & + 1/2\cos^3\alpha\sin\alpha\ R^o(3s,4s;3s,3s) + 1/2\cos\alpha\sin^3\alpha \\ & R^1(3s,3p;3p,4s) + 3/2\sin\alpha\cos\alpha\ R^o(3s,3p;4s,3p)\end{aligned}$$

(3.28)

$$\begin{aligned}
(J-\tfrac{1}{2}K)_{\text{axial-equatorial}} = {} & 1/12 \sin^2\alpha \cos^2\alpha\, F^0(3s,3s) + 1/12 \sin^2\alpha \cos^2\alpha\, F^0(4s,4s) + \\
& + 1/3\, F^0(3p,3p) - 7/150\, F^2(3p,3p) + 1/6\, [\sin^4\alpha + \\
& + \cos^4\alpha + \sin^2\alpha \cos^2\alpha]\, F^0(3s,4s) - 1/12\, [\sin^4\alpha + \\
& + \cos^4\alpha + 6 \sin^2\alpha \cos^2\alpha]\, G^0(3s,4s) + [1/3 \cos^2\alpha + \\
& + 1/6 \sin^2\alpha]\, [F^0(3s,3p) - 1/6\, G^1(3s,3p)] + [1/3 \sin^2\alpha + \\
& + 1/6 \cos^2\alpha]\, [F^0(4s,3p) - 1/6\, G^1(4s,3p)] + \\
& + [1/6 \sin^3\alpha \cos\alpha - 1/6 \sin\alpha \cos^3\alpha]\, R^0(3s,4s;3s,3s) + \\
& + [1/6 \cos^3\alpha \sin\alpha - 1/6 \cos\alpha \sin^3\alpha]\, R^0(3s,4s;4s,4s) + \\
& + 1/3 \sin\alpha \cos\alpha\, R^0(3s,3p;4s,3p) - 1/18 \sin\alpha \cos\alpha \\
& R^1(3s,3p;3p,4s) \qquad (3.29)
\end{aligned}$$

$$\begin{aligned}
(J-\tfrac{1}{2}K)_{\text{equatorial-equatorial}} = {} & 1/18 \sin^4\alpha\, F^0(3s,3s) + 1/18 \cos^4\alpha\, F^0(4s,4s) + \\
& + 7/18\, F^0(3p,3p) - 17/450\, F^2(3p,3p) + \\
& + 1/9 \sin^2\alpha \cos^2\alpha\, [F^0(3s,4s) - 2G^0(3s,4s)] + \\
& + 5/9 \sin^2\alpha\, F^0(3s,3p) - 5/27 \sin^2\alpha\, G^1(3s,3p) + \\
& + 5/9 \cos^2\alpha\, F^0(4s,3p) - 5/27 \cos^2\alpha\, G^1(4s,3p) - \\
& - 2/9 \sin^3\alpha \cos\alpha\, R^0(3s,4s;3s,3s) - 2/9 \sin\alpha \\
& \cos^3\alpha\, R^0(3s,4s;4s,4s) - 10/9 \sin\alpha \cos\alpha \\
& R^0(3s,3p;4s,3p) + 10/27 \sin\alpha \cos\alpha\, R^1(3s,3p;3p,4s) \\
& \qquad (3.30)
\end{aligned}$$

The valence-state energy was minimised with respect to the 3s, 3p and 4s orbital exponents for a set of fixed values of the mixing parameter α and also with respect to α. The results of the calculations are given in Table 3.10. The 4s orbitals are far less polarisable than 3d orbitals. Hence their size does not have the strong dependence on the mixing parameter

Table 3.10

Energy Minimised Orbital Exponents, and Energies

Phosphorus $3sp^34s$ Multiconfigurational Valence State

$\alpha_{1s} = 14.5578$ $\alpha_{2s} = 4.9125$ $\alpha_{2p} = 5.4500$

α	α_{3s}	α_{3p}	α_{4s}	$E-E_{s^2p^3-{}^4S}$ a.u.
0.0	1.998	1.688	0.766	1.09103
0.125	1.993	1.687	0.791	1.08962
0.250	1.986	1.689	0.794	1.09046
0.375	1.993	1.694	0.757	1.06797
0.50	1.995	1.697	0.747	1.04060
0.625	1.981	1.696	0.781	1.05059
0.750	1.971	1.694	0.801	1.08460
0.875	1.986	1.691	0.775	1.09969
1.0	1.998	1.688	0.766	1.09103
0.5329	1.992	1.697	0.753	1.03900

α which was found in the $3sp^3d_{z^2}$ valence-state. The 3s and 3p orbitals vary only slightly with α - the 3p orbitals tending to expand slightly when the 4s orbitals contract whilst for the 3s orbitals, being coupled to the 4s orbitals by an orthogonality relationship, it is difficult to discern a definite trend. The behaviour of the energy of the valence-state as a function of the mixing parameter is unusual. An initial amount of mixing of 4s character into the axial bonds leads to an initial increase in energy until a maximum is reached and the energy then decreases until the minimum energy is reached close to $\alpha = 0.5$. The 4s orbitals tend to expand as the energy lowers- the opposite of the trend for the 3d orbitals in the $3sp^3d_{z^2}$ valence-state. The promotion energy for the $3sp^34s$ multiconfigurational valence-state is less than that for the $3sp^3d_{z^2}$ valence-state but greater than that for the $3sp^3d_{x^2-y^2}$ valence-state. The 4s orbitals are diffuse having mean radii varying from 5.76 a.u. for $\alpha = 0.75$ to 6.14 a.u. for $\alpha = 0.5$; the mean radius for the optimum value of α being 6.10 a.u. The values of $\sin\alpha$ and $\cos\alpha$ for $\alpha = 0.5329$ are 0.995 and -0.103 respectively. Thus the axial bond has the more 4s character whilst the equatorial bond has more 3s character.

The overlap integrals between the phosphorus 3s, 3p and 4s orbitals and fluorine 1s, 2s and 2p orbitals are given in Table 3.11. The overlaps with the phosphorus 4s orbitals are very small. Thus on the basis of the overlap criterion the 4s orbitals would not be expected to contribute very significantly to the bonding in PF_5.

A study of overlap as a function of mixing coefficient for the $3sp^34s$ multiconfigurational valence-state hybrid orbitals was also made. The results are similar to those obtained by Cotton[119] for the $3sp^3d_{z^2}$

Table 3.11

Overlap Integrals Phosphorus-Fluorine

Phosphorus $3sp^3 4s$ Multiconfigurational Valence State

$\overset{F}{P}$	1s	2s	$2p_\sigma$
3s	0.0199	0.2195	0.1839
$3p_\sigma$	0.0441	0.3787	0.2391
4s	0.0091	0.0930	-0.0691

$\overset{F}{P}$	$2p_\pi$
$3p_\pi$	0.1210

R = 2.931 a.u.

valence-state using orbital exponents calculated by Slater's rules. The maximum overlap with fluorine $2p_\sigma$ and 2s orbitals give a ratio of $S_{axial}/S_{equatorial}$ of 0.922 and 0.916. These numbers are in keeping with the observed ratio of the strengths of the two types of bond. When we compare the value of the total overlap when it has its maximum value for the $3sp^3d_{z^2}$ and $3sp^3 4s$ valence-states we find that for overlap with fluorine 2s orbitals and $3sp^3 4s$ hybrid orbitals has about 3/4 the value that found with $3sp^3d_{z^2}$ hybrid orbitals. This is due to the difference between the $2s$-$3d_{z^2}$ and $2s$-$4s$ overlaps. It is safe to say that the $3sp^3d$ model is better than the $3sp^34s$ model because of the poor bonding properties of the $4s$ orbitals.

$3s^2p^4d$ Multiconfigurational Valence State Cl in ClF_3

Analysis of the microwave spectra of ClF_3 by Smith[126] and an X-Ray diffraction study on it at -120°C by Burbank and Bensey[127] have shown unequivocally that its structure is a slightly distorted T-shape. The Nyholm and Gillespie electron repulsion theory[58] describes the molecule as being built up from a basic trigonal bipyramidal structure with two of the equatorial bonds doubly occupied, which leads to the observed distortions. The symmetry group of the molecule is C_{2v}.

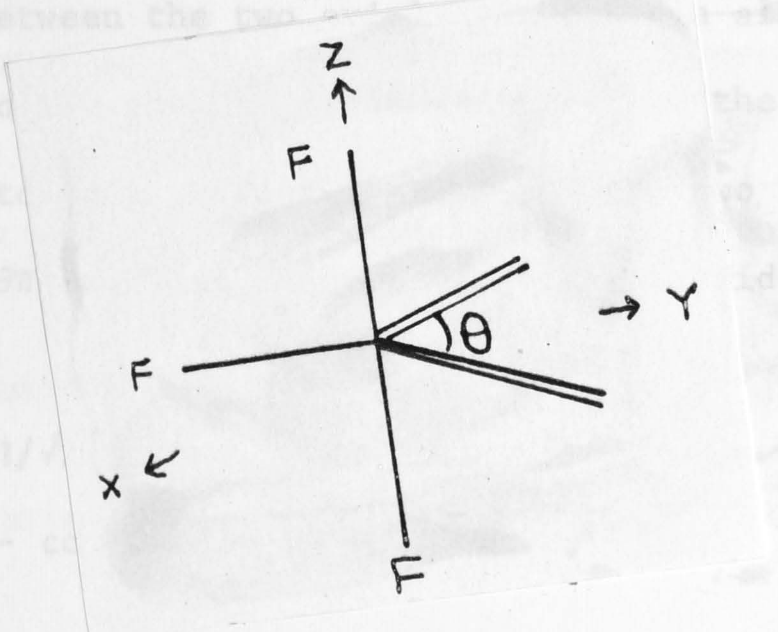


Figure 3.6

The representation Γ_σ for which the three bonding orbitals and two lone pair orbitals form a basis reduces as

$$\Gamma_\sigma = 4A_1 + 2B_1 + B_2 \tag{3.31}$$

$$\Gamma_{\sigma\ \text{axial}} = A_1 + B_2 \tag{3.32}$$

$$\Gamma_{\sigma\ \text{equatorial}} = A_1 \tag{3.33}$$

$$\Gamma_{\sigma\ \text{lone-pair}} = 2A_1 + 2B_1 \, . \tag{3.34}$$

There are the following orbitals in the required symmetry classes:

A_1	B_1	B_2
s	p_x	p_y
p_z		
d_{z^2}		
$d_{x^2-y^2}$		

(3.35)

The combination of atomic orbitals is not uniquely defined as in the case of SF_6. The lone pair-lone pair angle is not known and so becomes a variable parameter in a calculation on the molecule. Similarly the angle between the two axial orbitals can also be varied. The first model chosen for the ClF_3 valence-state was the one in which the molecule is assumed to be a perfect T-shape and the two lone pair orbitals are at an angle $\theta\pi$ radians. The appropriate hybrid orbitals are

$$\phi_{L.P.(1)} = 1/\sqrt{2}\ \{\sqrt{1-\cot^2 \theta/2}\ [\sin\alpha\ 3s + \cos\alpha\ [\sin\beta\ 3d_{z^2} + \cos\beta\ 3d_{x^2-y^2}] - \cot\theta/2\ 3p_z + 3p_x\}$$

$$\phi_{L.P.(2)} = 1/\sqrt{2}\ \{\sqrt{1-\cot^2 \theta/2}\ [\sin\alpha\ 3s + \cos\alpha\ [\sin\beta\ 3d_{z^2} + \cos\beta\ 3d_{x^2-y^2}] - \cot\theta/2\ 3p_z - 3p_x\}$$

$$\phi_{\text{equatorial}} = \cot\theta/2\ [\sin\alpha\ 3s + \cos\alpha\ [\sin\beta\ 3d_{z^2} + \cos\beta\ 3d_{x^2-y^2}] + \sqrt{\cot^2 \theta/2}\ 3p_z$$

$$\phi_{\mathrm{axial}(1)} = 1/\sqrt{2}\ [\cos\alpha\ 3s + \sin\alpha\ [\sin\beta\ 3d_{z^2} + \cos\beta\ 3d_{x^2-y^2}] + 3p_y]$$

$$\phi_{\mathrm{axial}(2)} = 1/\sqrt{2}\ [\cos\alpha\ 3s - \sin\alpha\ [\sin\beta\ 3d_{z^2} + \cos\beta\ 3d_{x^2-y^2}] - 3p_y] \qquad (3.36)$$

α and β are the mixing parameters for the orbitals of A_1 symmetry - α being the mixing parameter between 3s and 3d orbitals and β being that between $3d_{z^2}$ and $3d_{x^2-y^2}$ orbitals. The valence-state configuration is

$$s^{(2-\cot^2\theta/2)\sin^2\alpha + \cos^2\alpha}\ p_x^{2}\ p_y\ p_z^{1 + \cot^2\theta/2}$$

$$d_{z^2}^{\sin^2\beta[2-\cot^2\theta/2]\cos^2\alpha + \sin^2\alpha}\ d_{x^2-y^2}^{\cos^2\beta[2-\cot^2\theta/2]\cos^2\alpha + \sin^2\alpha}. \qquad (3.37)$$

It is thus a function of the mixing parameters occurring in the hybrid orbital functions. The energy expression has the form

$$\begin{aligned} E(V) = {} & E(\mathrm{core}) + E(\mathrm{core - valence\ electrons}) + J_{\mathrm{axial\text{-}axial}} - \tfrac{1}{2}K_{\mathrm{axial\text{-}axial}} + \\ & + 2J_{\mathrm{axial\text{-}equatorial}} - K_{\mathrm{axial\text{-}equatorial}} + 8J_{\mathrm{axial\text{-}lone\text{-}pair}} - \\ & - 4K_{\mathrm{axial\text{-}lone\text{-}pair}} + 4J_{\mathrm{equatorial\text{-}lone\text{-}pair}} - 2K_{\mathrm{equatorial\text{-}lone\text{-}pair}} + \\ & + 4J_{\mathrm{lone\text{-}pair\text{-}lone\text{-}pair}} - 2K_{\mathrm{lone\text{-}pair\text{-}lone\text{-}pair}} + \\ & + 2J_{\mathrm{lone\text{-}pair\text{-}lone\text{-}pair}} \end{aligned} \qquad (3.38)$$

Because of the complex form of the hybrid orbitals an exact expansion of the J and K integrals in terms of Slater's F^k, G^k and R^k integrals was not carried out but the appropriate coefficients were substituted into a general formula for the coulomb and exchange integrals between two hybrid orbitals $\phi_1 \phi_2$ of the form

$$\phi_1 = a\ 3s + b\ 3d_{z^2} + c\ 3d_{x^2-y^2} + d\ 3p_z + e\ 3p_x + f\ 3p_y$$

$$\phi_2 = A\ 3s + B\ 3d_{z^2} + C\ 3d_{x^2-y^2} + D\ 3p_z + E\ 3p_x + F\ 3p_y \quad . \qquad (3.39)$$

The expansions of $J(\phi_1,\phi_2)$ and $K(\phi_1,\phi_2)$ are given in Appendix 5. The energy was minimised with respect to the 3s, 3p and 3d orbital exponents and with respect to α , β and θ . A calculation was also done where θ was set equal to 2/3 - i.e., the orbitals are arranged in a trigonal bipyramidal arrangement. The results of the calculation are given in Table 3.12. The valence-state is characterised by the diffuseness of the d orbitals and a fairly low promotion energy. The valence state configuration is

$$3s^{1.9999984}\ 3p_x^{\ 2}\ 3p_y\ 3p_z\ 3d_{z^2}^{\ 0.414}\ \ 3d_{x^2-y^2}^{\ 0.585}$$

i.e., as the 3s orbital occupancy indicates almost exactly $3s^2p^4d$. The d orbitals are slightly more contracted than those for the free atom terms of the $3s^2p^4d$ configuration. As was found for the d^2 configurations of the chlorine atom, both the mean radius and the radial maximum decrease when double-zeta 3d wavefunctions are used instead of Slater-type functions. In other valence-states studied the mean radius increases. The valence energy state is higher than the lowest terms of the $3s^2p^4d$ configuration being about the same as those arising from the $3s^2p^4(^1D)$ parent term. The 3s and 3p orbitals have almost exactly the same size as those found for the free atom terms from the $3s^2p^4\ (^1D)$ parent term. The value of 1.0000

Table 3.12

Energy Minimised Orbital Parameters, Energies and 3d Orbital Radial Properties

Chlorine ClF_3 Multiconfigurational Valence State

$\alpha_{1s} = 16.5239$ $\alpha_{2s} = 5.7152$ $\alpha_{2p} = 6.4911$

	Single Zeta	Double Zeta
α_{3s}	2.427	2.423
α_{3p}	2.131	2.126
α_{3d}	0.442	0.466
β_{3d}	---	1.785
λ_{3d}	---	0.448
α	0.5002	0.4996
β	1.2675	1.2225
θ	1.0000	1.0000
$E-E_{s^2p^5-{}^2P^o}$ a.u.	0.81189	0.80092
$E_{s.z.} - E_{d.z.}$ a.u.	0.01098	
$\bar{r}$ a.u.	7.919	7.068
r_{max} a.u.	6.787	6.365
$\bar{r}/r_{max}$	1.167	1.110

Table 3.12 (continued)

$\theta = 2/3$

	Single Zeta	Double Zeta
α_{3d}	0.444	0.475
β_{3d}	---	1.811
λ_{3d}	---	0.442
α	0.4999	0.4976
β	1.2426	1.1698
$E-E_{s^2p^5-{}^2P^o}$	1.17414	1.16173

for the parameter θ means that the lone pair orbitals are at 180° to each other and at right angles to all three bonding orbitals.

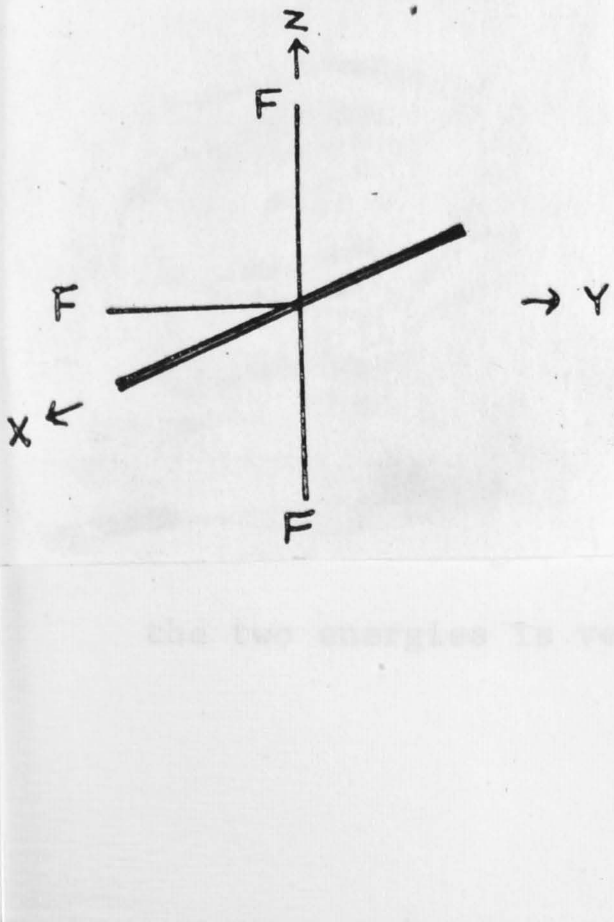


Figure 3.7

This is a marked departure from the trigonal bipyramidal structure, from which it is suggested in the textbooks, the structure is derived. The lone-pair-lone-pair repulsion, as the Nyholm-Gillespie Electron Pair repulsion theory correctly states is very strong. The values of $(J-\frac{1}{2}K)$ for the axial-axial, axial-equatorial, axial-lone-pair, equatorial-lone-pair and lone-pair-lone-pair interactions are 0.438, 0.672, 0.674, 0.998 and 0.885 a.u. respectively. The lone-pair-lone-pair repulsion is much greater than that between two bond forming orbitals. The relative magnitude of the lone-pair-equatorial repulsion is at first sight unexpected from Nyholm-Gillespie's Electron Pair repulsion theory. However we should remember that the lone pair orbitals are doubly occupied whilst in the valence-state the bond-forming orbitals are only singly occupied. Intermolecular interaction must also be considered. From the value of $\alpha \sim 0.5$ we see that the 3s orbitals contribute almost exclusively to the lone pair orbitals whilst the 3d orbitals are mainly confined to the axial hybrid orbitals. The value of θ also gives us that the equatorial hybrid orbital is a pure $3p_z$ orbital. The difference in the values of α between the single-zeta and double-zeta results - in the former case it is greater than 0.5 whilst in the latter case it is less than 0.5 - is not significant. In both cases $\sin\alpha \sim 1$ and $\cos\alpha \sim 0$. Thus the bonding orbitals have a configuration of p^2d whilst the lone pairs have a s^2p^2 configuration. This bonding configuration was recognised by Kimball[114] as one possible configuration for coordination number three. When θ is set at a value of 2/3 - appropriate to a trigonal bipyramidal arrangement of orbitals we find little change in the size of the 3d orbitals - a slight contraction does occur. However the difference between the two energies is very large - about 4.91 eV - due to almost definitely stronger lone-pair-lone-pair repulsions in the trigonal bipyramidal form.

It is possible to do a similar calculation in which instead of the angle between the two lone pair orbitals being a variational parameter, the angle between the two axial bonding orbitals is varied. The appropriate set of hybrid orbitals are those given in equation 3.36 but with the axial and lone pair orbital expressions interchanged. The valence-state configuration is then

$$3s^{(1+\cos^2\alpha)}\;3p_x\;3p_y^2\;3p_z\;3d_{z^2}^{\sin^2\beta(1+\sin^2\alpha)}\;3d_{x^2-y^2}^{\cos^2\beta(1+\sin^2\alpha)} \quad .$$

The parameter θ does not appear in the expression. The calculation is identical to that in which the lone-pair-lone-pair angle is varied. The results are also identical to the former calculations - θ is again 1.0000 - except that α has different values being 0.0002 in the single-zeta calculation and -0.0004 in the double-zeta case. This is simply due to the interchange of sin α and cos α in the expressions for the axial and equatorial hybrid orbitals.

The overlap integrals between the chlorine 3s, 3p and 3d orbitals and fluorine 1s, 2s and 2p orbitals are given in Table 3.13. When compared with the values of the overlap integrals for sulphur valence orbitals, the magnitudes of these overlaps are considerably less for all the valence orbitals. The 3d overlaps are not favourable at all to the participation by 3d orbitals in bonding. The overlaps of the axial and equatorial hybrid orbitals with fluorine 2s and 2p orbitals were calculated. The overlap integrals between the equatorial and axial hybrid

Table 3.13

Overlap Integrals Chlorine-Fluorine

Chlorine ClF_3 Multiconfigurational Valence State

Cl F	1s	2s	$2p_\sigma$
3s	0.0080	0.1279	0.1401
$3p_\sigma$	0.0207	0.2337	0.2166
$3d_{z^2}$	0.0282	0.2335	-0.0114

Cl F	$2p_\pi$
$3p_\pi$	0.0677

R = 3.146

orbitals and fluorine $2p_\sigma$ orbitals were 0.2166 and 0.1505 respectively. With fluorine 2s orbitals the values were 0.2337 and 0.2193. The relative magnitudes of the equatorial and axial overlaps in both cases are in agreement with the order of the observed bond strengths. The bond lengths[126] are 1.898 Å for the axial bond and 1.698 Å for the equatorial bond. The Urey Bradley Shimanouchi Force Constants[128] are 3.72 mD/Å for the equatorial bond and 2.59 mD/Å for the axial bond.

Thus in the $3s^2p^4d$ multiconfigurational valence-state we have 3d orbitals that are not contracted. To contribute significantly to bonding they will have to be perturbed very considerably by the field of the ligand atoms. Otherwise it is fair to say that 3d orbitals do not contribute to bonding in ClF_3 or that the component of the valence bond wavefunction corresponding to the situation where the chlorine atom is neutral does not contribute very significantly to the total wavefunction. If the chlorine atom is charged an electron would be expected to be lost from a lone pair. Thus there would still be some 3d orbital participation in the valence-state. A reduction in the 3d orbital participation should occur by a greater 3d orbital contribution to the lone pair hybrid orbitals. The 3d orbital should also be more contracted due to the charge on the chlorine atom.

$3s^2p^44s$ Multiconfigurational Valence State Cl in ClF_3

As in the case of the trigonal bipyramidal orbitals of P in PF_5, it is possible to choose a configuration not involving 3d orbitals but instead 4s orbitals - $3s^2p^44s$. We have assumed that, as was found for the $3s^2p^4d$ multiconfigurational valence state, the lone pair orbitals are at 180° to each other and at right angles to the bond forming orbitals. The following are the appropriate hybrid orbitals:

$$\begin{aligned}
\phi_{ax(1)} &= 1/\sqrt{2}\,(4s + 3p_y) \\
\phi_{ax(2)} &= 1/\sqrt{2}\,(4s - 3p_y) \\
\phi_{eq} &= 3p_z \\
\phi_{LP(1)} &= 1/\sqrt{2}\,(3s + 3p_x) \\
\phi_{LP(2)} &= 1/\sqrt{2}\,(3s - 3p_x)\ .
\end{aligned} \tag{3.40}$$

The choice of a pure $3p_z$ orbital for the equatorial hybrid and the absence of mixing between the 3s and 4s orbitals came from a consideration of the results of the calculations on the $3s^2p^4d$ multiconfigurational valence-state and the $3sp^34s$ multiconfiguration valence-state of phosphorus. The energy expression is as given in equation 3.38 but where

$$J_{\text{axial-axial}} = 1/4\ F^0(4s,4s) + 1/2\ F^0(4s,3p) + 1/4\ F^0(3p,3p) - 1/25\ F^2(3p,3p) - $$
$$- 1/3\ G^1(4s,3p)$$

$$K_{\text{axial-axial}} = 1/4\ F^0(4s,4s) - 1/2\ F^0(4s,3p) + 1/4\ F^0(3p,3p) - 1/25\ F^2(3p,3p)$$

$$J_{\text{axial-equatorial}} = 1/2\ F^0(4s,3p) + 1/2\ F^0(3p,3p) - 1/25\ F^2(3p,3p)$$

$$K_{\text{axial-equatorial}} = 1/6\ G^1(4s,3p) + 3/50\ F^2(3p,3p)$$

$$J_{\text{axial-lone-pair}} = 1/4\ F^0(3s,4s) + 1/4\ F^0(3p,4s) + 1/4\ F^0(3s,3p) +$$
$$+ 1/4\ F^0(3p,3p) - 1/50\ F^2(3p,3p) + 1/12\ R^1(3s,3p;3p,4s)$$

$$K_{\text{axial-equatorial}} = 1/4\ G^0(3s,4s) + 1/12\ G^1(4s,3p) + 1/12\ G^1(3s,3p) +$$
$$+ 3/100\ F^2(3p,3p) + 1/6\ R^1(3s,3p;3p,4s) + 1/2\ R^0(3s,3p;4s,3p)$$

$$J_{\text{equatorial-lone-pair}} = 1/2\ F^0(3s,3p) + 1/2\ F^0(3p,3p) - 1/25\ F^2(3p,3p)$$

$$K_{\text{equatorial-lone-pair}} = 1/6\ G^1(3s,3p) + 3/50\ F^2(3p,3p)$$

$$J_{\text{lone-pair-lone-pair}} = 1/4\ F^0(3s,3s) + 1/2\ F^0(3s,3p) + 1/4\ F^0(3p,3p) -$$
$$- 1/25\ F^2(3p,3p) - 1/3\ G^1(3s,3p)$$

$$K_{\text{lone-pair-lone-pair}} = 1/4\ F^0(3s,3s) - 1/2\ F^0(3s,3p) + 1/4\ F^0(3p,3p) -$$
$$- 1/25\ F^2(3p,3p)$$

$$J_{\text{lone-pair-lone-pair}} = 1/4\ F^0(3s,3s) + 1/2\ F^0(3s,3p) + 1/4\ F^0(3p,3p) -$$
$$- 1/25\ F^2(3p,3p) + 1/3\ G^1(3s,3p) \quad . \qquad (3.41)$$

The valence-state energy was minimised with respect to the 3s, 3p and 4s orbital exponents. The results are given in Table 3.14. The 4s orbitals are diffuse. However the promotion energy is about 1.35 eV less than that for the $3s^2p^4d$ multiconfigurational valence-state. Because of the much greater polarisability of the 3d orbitals it would be expected that they could participate in bonding due to contraction by the ligand field whereas this would not occur to the same extent with 4s orbitals.

Expansion of Energies of Multiconfigurational Valence States in Terms of Configurational Energies

The energy of a multiconfigurational valence-state can be expanded as a linear combination of energies of spectroscopic terms of the configurations from which it is formed. It is possible by an analysis of the symmetry properties of various terms in a configuration manifold to determine which participate in the valence-state. This was done by Craig and Thirunamachandran[27] using projection operators for the $3sp^3d^2$ configuration of sulphur in SF_6. A similar analysis has been done by Webster[21] using the theory of the symmetric permutation group. However this method does not give the relative weights of the terms. To obtain these we must expand the expression

$$E = \langle \Psi_{P.P.} | H | \Psi^*_{P.P.} \rangle \quad , \tag{3.42}$$

where $\Psi_{P.P.}$ is given by equation 3.3 and $\Psi^*_{P.P.}$ is its complex conjugate in terms of the energies of various determinantal wavefunctions made up from atomic orbitals. The resultant expansion may be rearranged to give an expansion in terms of the energies of spectroscopic states. To do

Table 3.14

Energy Minimised Orbital Exponents, Energies and Radii

Chlorine ClF_3 $3s^2p^44s$ Multiconfigurational Valence State

$\alpha_{1s} = 16.5239$ $\alpha_{2s} = 5.7152$ $\alpha_{2p} = 6.4966$

α_{3s}	2.405
α_{3p}	2.149
α_{4s}	0.740
$E-E_{s^2p^5-{}^2P}$	0.70170
$\bar{r}_{4s}$	6.136

this rearrangement we must be able to expand each determinant, obtained by expanding the wavefunction in equation 3.3 in terms of complex atomic orbitals, as a linear combination of the wavefunctions of spectroscopic states of the configuration. For example

$$|p_0\bar{p}_0| = 1/\sqrt{3}\ \psi\ [p^2\,{}^1S(M_L = 0\ M_S = 0)] + \sqrt{2/3}\ \psi\ [p^2\,{}^1D(M_L = 0\ M_S = 0)] \quad . \qquad (3.43)$$

It should be possible in the near future to develop computer programs which would make this task feasible for a configuration as complex as, for example, the $3sp^3d^2$ configuration. In the meantime we have mainly confined our interest to determining the weights of the various configurations and of the terms with highest multiplicity for some of the valence-states for which we have performed numerical calculations.

For the tetrahedral carbon atom it is well known that the valence energy has the form:

$$E(V) = 5/8\ 2sp^3 + 3/16\ 2s^2p^2 + 3/16\ 3p^4 \quad , \tag{3.44}$$

and the contribution of the ^5S term of the $2sp^3$ configuration is 5/16.[36] We have obtained the corresponding information for the $3sp^3d^2$ valence-state of S in SF_6, the $3sp^3d_{z^2}$ valence-state of P in PF_5, the $3sp^3d_{x^2-y^2}$ valence-state of P in PF_5 (square-pyramidal structure) or S^+ in $S^+F_6^-$ and the $\sim 3s^2p^4d$ valence-state of Cl in ClF_3.

For the $3sp^3d^2$ multiconfigurational valence-state of S in SF_6, the energy expression obtained by expanding equation 3.42 using a simple computer programme is

$$\begin{aligned} E(V) = {} & 1/2304\ 3s^2p^4 + 19/288\ 3sp^4d + 29/576\ 3p^4d^2 + 43/288\ 3s^2p^3d + \\ & + 65/144\ 3sp^3d^2 + 43/288\ 3p^3d^3 + 29/576\ 3s^2p^2d^2 + 19/288\ 3sp^2d^3 + \\ & + 1/2304\ 3p^2d^4 \quad . \end{aligned} \tag{3.45}$$

As expected the $3sp^3d^2$ configuration is the principal contributor to the valence-state - the next most important configurations being the p^3d^3 and s^2p^3d configurations. The coefficient of the ^7F term in the expansion, as obtained in this calculation, is 7/64. This agrees with the result obtained by Craig and Thirunamachandran[27] by a symmetry analysis.

The coefficient of the ^5D term of the $3s^2p^3d$ configuration is 5/192. It is the participation of the d^3 configurations to a significant extent which leads to the 3d orbitals being more contracted than in the free atom terms of the $3sp^3d^2$ configuration. It is worthy of note that what some workers thought possible configurations, e.g., sd^5, $spd^{\overset{4}{\cancel{5}}}$, p^6, do not in fact contribute.

The energy expression for the $3sp^3d_{z^2}$ valence-state is a function of the mixing parameter α. When $\alpha = 0.3106$ the energy expression is

$$E(V) = 0.06572\ 3s^2p^3 + 0.11191\ 3s^2p^2d + 0.02083\ 3s^2pd^2 + 0.09642\ 3sp^4 + \\ + 0.41022\ 3sp^3d + 0.09642\ 3sp^2d^2 + 0.02083\ 3p^5 + 0.11191\ 3p^4d + \\ + 0.06572\ 3p^3d^2\ . \qquad (3.46)$$

To a greater extent than was the case for the sulphur valence-state the $3sp^3d$ configuration - the "valence-state configuration" - is the main contributor to the valence-state. There are no d^3 or d^4 configurations contributing to the valence-state. This could explain why the 3d orbitals are more diffuse in this valence-state than in the sulphur $3sp^3d^2$ valence-state. The $3sp^2d^2$, $3p^4d$, $3s^2p^2d$ and $3sp^4$ configurations all contribute to about the same degree. Even the ground state s^2p^3 has a significant contribution - the ^4S ground state term has a coefficient of 0.02245. For sulphur the ground state term has a coefficient of 1/4608 (= 0.000217). The ^6D term of the $3sp^3d$ configuration has a coefficient of 3/16 (= 0.1875). The ^4S term of the p^3d^2 configuration also has a contribution of 0.02245. The ^2P term of the p^5 configuration has a coefficient of 1/48 (= 0.02083).

The energy expression for the $3sp^3d_{x^2-y^2}$ valence-state is:

$$E(V) = 7/128\ 3s^2p^3 + 7/64\ 3s^2p^2d + 3/128\ 3spd^2 + 7/64\ 3sp^4 + 13/32\ 3sp^3d + {}$$
$$+ 7/64\ 3sp^2d^2 + 3/128\ 3p^5 + 7/64\ 3p^4d + 7/128\ 3p^3d^2\ , \tag{3.47}$$

$$= 0.05469\ 3s^2p^3 + 0.10938\ 3s^2p^2d + 0.02344\ 3s^2pd^2 + 0.10938\ 3sp^4 + {}$$
$$+ 0.40625\ 3sp^3d + 0.10938\ 3sp^2d^2 + 0.02344\ 3p^5 + 0.10938\ 3p^4d + {}$$
$$+ 0.05469\ 3p^3d^2\ . \tag{3.48}$$

The coefficients are very similar to those for the $3sp^3d_{z^2}$ valence-state. There is a slightly bigger contribution from the d^2 configurations. This would tend to give more contracted 3d orbitals in this valence-state. Because of the involvement of d_2 and d_{-2} complex atomic orbitals in this valence-state, we find contributions from terms with higher l quantum number which would tend to lead to more contracted 3d orbitals. The coefficient of the ^6D term is again 3/16. The ^4G term of the p^3d^2 configuration has a coefficient of 1/64. This term does not contribute to the $3sp^3d_{z^2}$ valence-state - the only quartet from that configuration is the ^4S term. The ground state term - $3s^2p^3\ ^4S$ - has a coefficient of 1/32. The contraction of the 3d orbitals in the S^+ valence-state must be attributed to mainly the charge on the atom.

Like the phosphorus $3sp^3d_{z^2}$ valence-state, the energy of the chlorine $\sim 3s^2p^4d$ valence-state depends upon mixing coefficients. However because of their optimum values the energy expression can be approximated by the relatively simple expression

$$E(V) = 3/4\ 3s^2p^4d + 1/8\ 3s^2p^5 + 1/8\ 3s^2p^3d^2\ . \tag{3.49}$$

There are insignificant contributions from the $3sp^3d^3$, $3sp^4d^2$ and $3sp^5d$ configurations. The valence-state configuration - $3s^2p^4d$ - is the principal contributor. All the significant contributing configurations have filled 3s sub-shells. This means that any 3d orbitals are always well shielded from the nucleus and would tend to be diffuse. The coefficient of the ^4F term of the $3s^2p^4d$ configuration is $1/2 \cos^2\beta = 0.07325$. The ground state term of chlorine - $3s^2p^5\ ^2P^\circ$ - has a coefficient of 1/8. This would help to give the low promotion energy. None of the lower terms, e.g., ^6F term of the $3s^2p^3d^2$ configuration contribute to the valence-state. Thus we have diffuse 3d orbitals in the $3s^2p^4d$ valence-state.

A symmetry analysis, similar to that done by Craig and Thirunamachandran[27] was done for ClF_3. The spin weights of the doublet and quartet terms were found to be equal, i.e.,

$$\psi(V) = 1/\sqrt{2}\,[\psi_{1/2} + \psi_{3/2}] \quad . \tag{3.50}$$

The spatial symmetry of the molecule ClF_3 being so low all the spectroscopic terms of the $3s^2p^4d$ configuration can contribute to the valence-state. The table corresponding to Tables 8.2 and 8.3 of Cotton[115] required in this analysis is given in Table 3.15.

Conclusion

Thus in this part of our work we have seen what is understood by the valence-state of an atom in a molecule and mentioned several formulations of the valence-state. We have chosen one of these - the multiconfigurational valence-state - and performed numerical calculations on the multiconfigurational valence-states of P, S and Cl in PF_5, SF_6 and ClF_3 respectively. These have given a good idea of the promotion energy required to put an atom into the valence-state and some idea of

Table 3.15

Splitting of One-Electron Levels in C_{2v} Symmetry

Type of Level	$\chi(E)$	$\chi(C_2)$	$\chi(\sigma_{v(xz)})$	$\chi(\sigma_{v(yz)})$	Symmetry of Environment
s	1	1	1	1	a_1
p	3	-1	1	1	$a_1 + b_1 + b_2$
d	5	1	1	1	$2a_1 + a_2 + b_1 + b_2$
f	7	-1	1	1	$2a_1 + a_2 + 2b_1 + 2b_2$
g	9	1	1	1	$3a_1 + 2a_2 + 2b_1 + 2b_2$
h	11	-1	1	1	$3a_1 + 2a_2 + 3b_1 + 3b_2$
i	13	1	1	1	$4a_1 + 4a_2 + 3b_1 + 3b_2$

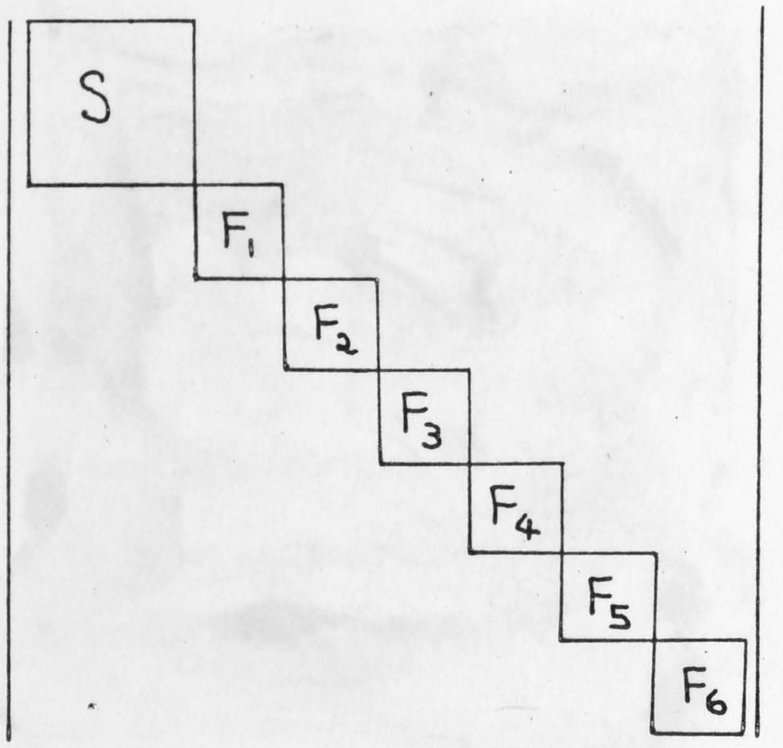
the size and shape of the atomic orbitals in the valence shell. In particular we have focussed attention on the 3d orbitals. In the valence-state of S in SF_6 studied the 3d orbitals were found to be significantly contracted - sufficient for no further contraction to be necessary for the 3d orbitals to contribute significantly to bond formation. The same is true to a lesser extent of P in PF_5. However, the valence-state of Cl in ClF_3 the 3d orbitals were found to be diffuse. 4s orbitals in valence-states were also found to be diffuse and should not be involved significantly in bond formation. The multiconfigurational valence-state was shown to be more favourable to the hypothesis that 3d orbitals are involved in the bonding in these molecules - PF_5 and SF_6 - than other formulations. There are other factors favouring its use. Amongst these it should be mentioned that the form of the hybrid orbitals leads to electron correlation being taken into account to some extent. We have examined some of the valence-states on which calculations have been performed and seen how they are built up from various configurations. This has given a feeling in particular for why the 3d orbitals are more contracted in the multiconfigurational valence-states and why they are more contracted in certain valence-states than others.

CHAPTER 4

ORBITAL MODIFICATION BY THE COULOMB FIELD OF LIGAND ATOMS

Introduction

In Chapter 3 it was shown that the 3d orbitals in the multi-configurational valence-states of phosphorus, sulphur and chlorine in PF_5, SF_6 and ClF_3 are more contracted than in the free atoms. In some cases - sulphur in SF_6 is the best example - the orbitals are sufficiently contracted that it was contended further orbital contraction need not be invoked for the 3d orbitals to play an effective part in bonding. In other cases, in particular chlorine in ClF_3, further contraction is definitely required if 3d orbitals are to participate in bond formation. Craig and Zauli[17] and Mitchell[35] have shown that the diffuse 3d orbitals found in single configurational valence-states are contracted by the electrostatic field of the ligand atoms. We have studied the orbital modification by the fluorine ligand atoms of P, S and Cl atoms in PF_5, SF_6 and ClF_3 using multiconfigurational valence-states. The aims of the calculations were to find the size of the valence shell orbitals, especially the 3d orbitals in the molecular environment, to get a better estimate of the valence-state promotion energy and an idea, remembering that not all terms of the molecular energy are included, of the relative energies of formation of the molecules. The calculations neglect interatomic exchange and the non-orthogonality of the ligand atom orbitals to the central atom orbitals. If we assume that the molecular wavefunction can be represented by a single determinantal wavefunction, total neglect of both inter- and intra-atomic exchange allows the wavefunction to be written as a simple product or diagonalised determinantal wavefunction. If we include intra-atomic exchange, the determinant has a blocked form, e.g., for SF_6.



(4.1)

Each diagonal block has the form of the appropriate atomic valence-state determinantal wavefunction. The off diagonal terms not included in the blocks on the diagonal are set equal to zero. When inter-atomic exchange is included these off diagonal terms are not zero. The value of the energy given by

$$E = \langle \Psi | H | \Psi^* \rangle \quad , \tag{4.2}$$

where Ψ is a diagonally blocked determinantal wavefunction of the form of 4.1 and H is the molecular Hamiltonian operator for the molecule, AB_n has the form

$$E = E_A + nE_B + \frac{2nZ_AZ_B}{R} + n\left[\sum_A \left(\phi_A(1) \middle| \frac{-2Z_B}{r_{a1}} \middle| \phi_A(1) \right) + \sum_B \left(\phi_B(1) \middle| \frac{-2Z_A}{r_{a1}} \middle| \phi_B(1) \right) \right] + $$

$$+ \sum_A \sum_B J(\phi_A \, \phi_B) + \sum_{BB'} E_{BB'} \quad , \tag{4.3}$$

where the terms represent, in order, the energies of the valence states of the atoms A and B, the repulsion between the nuclei of A and B, the attraction of the electrons assigned to the atom A to the nucleus of B, the attraction of the electrons of B to the nucleus of A, the coulombic repulsion between all the electrons of A and all the electrons of B and the electrostatic interactions between the ligand atoms B and B'. R is the internuclear distance r_{a1}, r_{b1} are the distances between the nuclei A and B and the electron designated as 1. It is a simple matter to show that the coulombic term for a multiconfigurational valence-state is the same as that for the corresponding single configurational valence-state. Details of the computation of the nuclear attraction integrals and the inter-atomic coulomb integrals are given in Appendices 3B and 3C respectively. Formulae for the interaction energy between the fluorine atoms in the molecules are given in Appendix 6.

SF_6 - Sulphur $3sp^3d^2$ Multiconfigurational Valence State Single Zeta Calculation

It has been shown by infra-red and Raman spectroscopy[129] that the molecule SF_6 has O_h symmetry. The S-F bond length as determined by electron diffraction[7] is $1.56_4 \pm 0.06$ Å = 2.96 a.u. Using this as the value of the S-F distance, the energy of the molecule SF_6 was minimised with respect to the 3s, 3p and 3d orbital exponents. Those parts of the energy expression which did not involve these orbitals were calculated separately, i.e., the sulphur core energy, the fluorine-fluorine interactions and the interactions of the fluorine atom with the sulphur nucleus. The results of a single-zeta calculation are given in Table 4.1. The 3s and 3p orbitals are more diffuse than in the valence-state. There is insignificant change in the size of the 3d orbital. This adds weight to the suggestion in Chapter 3, that the 3d orbital in the valence-state was

Table 4.1

Energy Minimised Orbital Exponents, Energies and Radii

SF_6 S $3sp^3d^2$ Multiconfigurational Valence State

	SF_6	S Valence State
α_{3s}	2.064	2.191
α_{3p}	1.708	1.914
α_{3d}	1.272	1.271
E_{atom} a.u.	-790.93253	
E_{S-F} a.u.	-4.03902	
E_{F-F} a.u.	0.05490	
E a.u.	-794.91665	
$E-E_{s^2p^4\,{}^3P}$ a.u.	-1.72819	
$\bar{r}$ a.u.	2.752	
r_{max} a.u.	2.358	
$\bar{r}/r_{max}$	1.167	

sufficiently contracted to contribute significantly to bonding. The valence-state promotion energy is increased by about 1.97 eV to 2.25593 a.u. The sulphur-fluorine interaction energy is fairly large whilst the contribution of the fluorine-fluorine interactions is relatively small. The interaction energy of the trans fluorine atoms is -0.02880 a.u. whilst that for two cis atoms is -0.00077 a.u. The sign of the energy in the latter case can be attributed to the fact that the $2p_\sigma$ orbital is not directed towards the other fluorine atom as it is in the trans case, but to the sulphur nucleus and so the nucleus is not as well shielded from the electrons of the other atom. The energy of formation for the molecule obtained is appreciable - in keeping with the known stability of the molecule. The calculated S-F bond energy is 90.34 kcals/mole. Experimentally it is found to be 90.98 kcals/mole.[130] This apparent agreement should, of course, be disregarded because the exchange terms neglected will further increase the calculated bond energy to give poorer agreement. We can compare our results with those obtained by Craig and Zauli[17] and Mitchell[35] in which intra-atomic exchange is neglected. In their papers they quote only the value of that part of the energy which involves the valence electrons of the central atom. For our calculation this has a value of -21.54 a.u. Craig and Zauli give a figure of -20.36 a.u. and Mitchell gives a figure of -20.80 a.u. The optimum values of the 3s, 3p and 3d orbital exponents obtained by Craig and Zauli were 2.00, 1.59 and 1.22 respectively, whilst those obtained by Mitchell were 1.93, 1.64 and 1.19 respectively. We have performed a similar calculation neglecting intra-atomic exchange but using a set of hybrid orbitals. The energy obtained was 21.01 a.u. and the 3s, 3p and 3d orbital exponents were 1.900, 1.642 and 1.282 respectively. In comparing these results with those in which intra-atomic exchange was included we find that its neglect leads to the 3s and 3p orbitals being more diffuse whilst the 3d orbital is more contracted. It is slightly more diffuse than the 3d orbital obtained for the multiconfigurational valence-state when intra-atomic exchange is neglected. The 3s and 3p orbital exponents are similar to those obtained by Mitchell. However the 3d orbitals are more contracted. All the valence shell orbitals obtained in our calculation including intra-atomic exchange are more contracted than those obtained by Craig and Zauli and Mitchell. The difference between Craig and Zauli's and Mitchell's results is a result of different potentials for the fluorine ligand atom being used - Craig and Zauli using a potential calculated from numerical Hartree-Fock wavefunctions for F^-, whilst Mitchell used a potential calculated from Clementi's[94] analytical wavefunctions for the F atom. In Table 4.2 are given the interaction energies of each of the sulphur orbitals with a fluorine ligand atom. The biggest contribution to the molecular energy comes from terms involving the $3d_{z^2}$ wavefunction. These can arise from interactions involving either $3d_{z^2}$ or $3d_{x^2-y^2}$ orbitals. (The $3d_{z^2}$ orbital and the $3d_{x^2-y^2}$ orbital are, of course, equivalent in an octahedral environment.) Large contributions also come from the 3s and $3p_\sigma$ terms. The $3p_\pi$ and $3d_{x^2-y^2}$ terms give smaller contributions than the core orbitals. Thus the interaction of the $3d_{z^2}$ orbitals with the fluorine atoms helps considerably to make the promotion into the valence-state energetically possible.

SF_6 - Sulphur $3sp^3d^2$ Multiconfigurational Valence State Double Zeta Calculation

When a double-zeta basis set was used for the 3d orbitals, the results obtained were surprising. They are summarised in Table 4.3. The energy of formation is unrealistically large. This is due to the shape of the 3d orbitals. This is shown in Figure 4.1. It resembles the shape of a 4d orbital - the node occurring very close to the position of the fluorine nucleus. The value of r'_{max} quoted in Table 4.3 is that for the inner lobe. The value of the energy obtained is a mathematical

Table 4.2

Orbital Contributions to Molecular Energy

nlm	E a.u.
1s	-0.03578
2s	-0.03604
$2p_\sigma$	-0.03824
$2p_\pi$	-0.03484
3s	-0.10225
$3p_\sigma$	-0.25465
$3p_\pi$	-0.02139
$3d_{z^2}$	-0.47808
$3d_{x^2-y^2}$	-0.00836

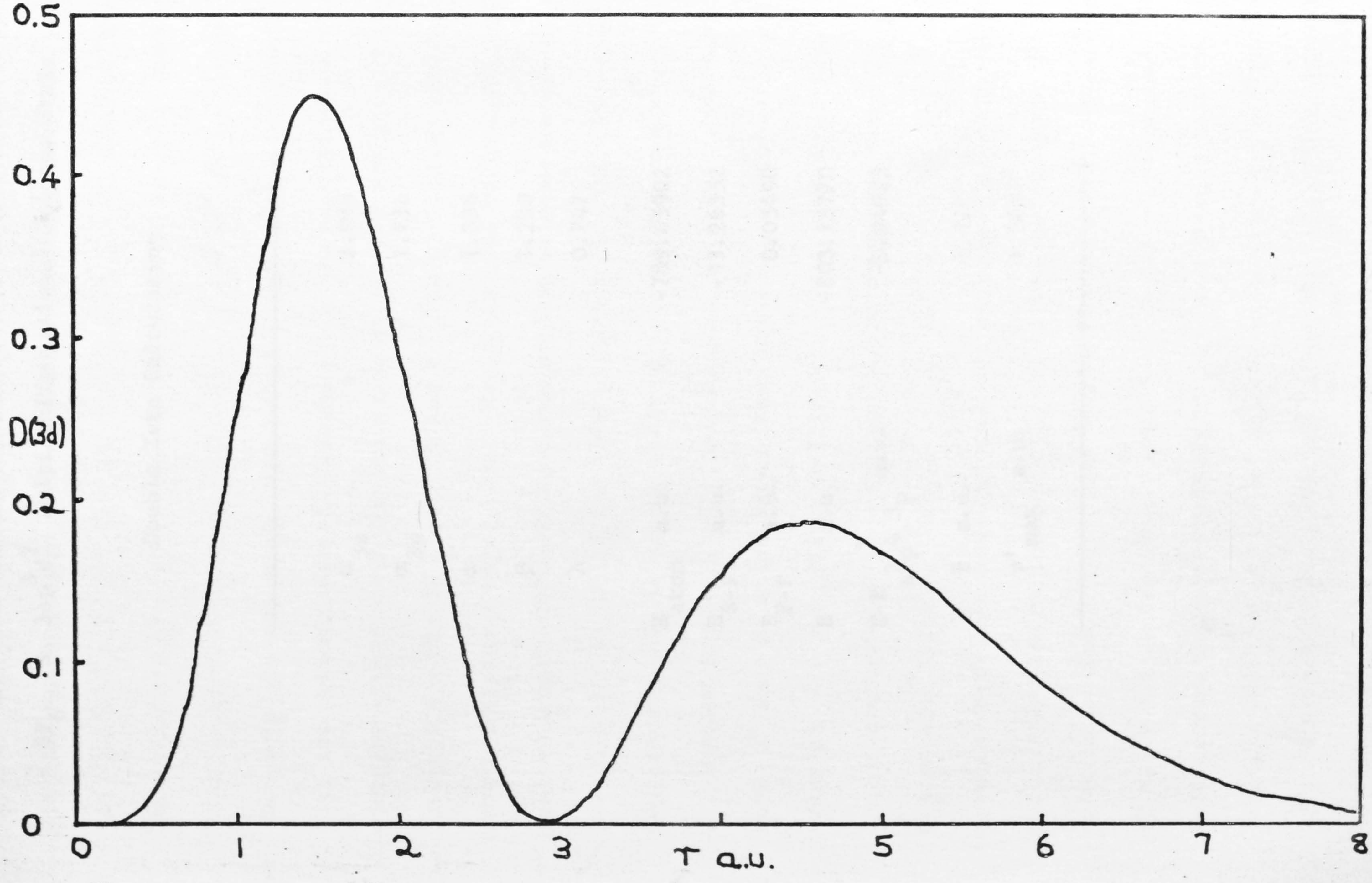


FIGURE 4.1 3d DOUBLE-ZETA WAVEFUNCTION SF$_6$

Table 4.3

Energy Minimised Orbital Parameters, Energies and Radii

SF_6 S $3sp^3d^2$ Multiconfigurational Valence State

Double Zeta Calculation

α_{3s}	2.074
α_{3p}	1.736
α	1.336
β	1.230
λ	0.747
E_{atom} a.u.	-789.65902
E_{S-F} a.u.	-13.26352
E_{F-F} a.u.	0.05490
E a.u.	-803.13770
$E-E_{s^2p^4\,{}^3P}$ a.u.	-9.94923
$\bar{r}$ a.u.	3.127
r'_{max} a.u.	1.500

artifact. Analysis of the various terms contributing to the molecular energy shows that this is confined to the terms involving 3d orbitals. The interaction energy of a $3d_{z^2}$ orbital electron with a fluorine atom was +1.15318 a.u. and that of one in a $3d_{x^2-y^2}$ orbital -3.22833 a.u. These figures are interpreted as meaning that the $3d_{z^2}$ orbital repels a fluorine atom strongly whilst a $3d_{x^2-y^2}$ orbital very strongly attracts it. Both are obviously incorrect. These values arise due to the fact that the coulomb integral $J(2s,3d_{x^2-y^2})$ has a value of -1.1018 a.u. compared with the single-zeta value of +0.5316 and the nuclear attraction integral for the $3d_{z^2}$ orbital has a value of -5.7106 as compared with a single-zeta value of -7.2194. The other coulomb integrals all have smaller magnitudes than the corresponding single-zeta values but their relative values follow the same general trend. Any integral involving a double-zeta orbital can be split up into a term involving only the exponent α, another involving only the exponent β and a cross-term involving both α and β. The latter term has a negative coefficient due to the value of λ - the mixing coefficient. This term would seem to give a larger contribution than the sum of the other two terms in the case of the coulomb integral $J(2s,3d_{x^2-y^2})$ and in the nuclear attraction integral a value which when compared with the contributions of cross-terms in other nuclear attraction integrals is relatively much larger. This result has shown us a limitation of the double-zeta basis set. This anomaly is able to arise due to the great flexibility of the two-term function. The second lobe corresponds approximately to the contribution from the fluorine orbitals when the 3d orbital is made orthogonal to the fluorine orbitals. If this were done the anomalous behaviour would not be expected to occur. It is interesting, however, to speculate whether 4d orbitals whose radial distribution would be similar to these 3d orbitals might be a better choice than 3d orbitals for bonding. The promotion energy required would be slightly greater and some of the molecular interactions would be expected to have a smaller magnitude, due to the presence of a node at about the position of the ligand atom nuclei, as do the wavefunctions found in this calculation. It would not be expected that the energy calculated would be physically unreasonable because of the involvement of a different form of wavefunction and a different set of appropriate orbital exponents. Alternatively would a two term function of the form

$$\psi(3d) = \cos\lambda\,\phi_{3d} + \sin\lambda\,\phi_{4d}\,, \qquad (4.4)$$

be better than the double-zeta basis set? Such a function was investigated by Craig and Magnusson.[12] Both suggestions should be investigated further.

The overlap integrals between the fluorine 1s, 2s and $2p_\sigma$ orbitals and the $3d_{z^2}$ orbitals have values of -0.0021, -0.0158 and 0.2852 respectively. The value of $S(2p_\sigma, 3d_{z^2})$ is much larger than is the case for the atom in the valence-state or for the 3d orbitals obtained in the single-zeta calculation; it having a value similar to those for the 3s and $3p_\sigma$ orbitals. The 1s, and 2s orbitals are almost orthogonal to the $3d_{z^2}$ orbital. The question of the orthogonality of the $3d_{z^2}$ orbitals to the fluorine core orbitals will be pursued further in the next chapter. In calculating the energy of the molecule it was assumed that all the fluorine orbitals were orthogonal to the sulphur orbitals (otherwise hybrid and resonance integrals should be included in the energy expression).

PF$_5$ - Phosphorus 3sp^{3}d$_{z^2}$ Multiconfigurational Valence State Trigonal Bipyramidal Structure

Vibrational spectra[116,117] and electron diffraction studies[59] have shown that the molecule PF$_5$ has D_{3h} symmetry. The P-F bond distances found by electron diffraction were 1.534 ± 0.004 Å for the equatorial bonds and 1.577 ± 0.005 Å for the axial bonds giving an average length of 1.551 ± 0.001 Å = 2.931 a.u. In expanding the expression as given in equation 4.3 for the molecular energy we find that for the equatorial fluorine atoms the $3d_{z^2}$ orbitals directed along the molecular three-fold axis appear to be $3d_{x^2}$ orbitals. It is simple to show

$$3d_{x^2} = -1/2\ 3d_{z^2} + \sqrt{3}/2\ 3d_{x^2-y^2} \ , \qquad (4.5)$$

hence it follows

$$J(\phi,\ 3d_{x^2}) = 1/4\ J(\phi,\ 3d_{z^2}) + 3/4\ J(\phi,\ 3d_{x^2-y^2}) \ , \qquad (4.6)$$

where ϕ is any fluorine orbital and similarly for the nuclear attraction integrals

$$\langle 3d_{x^2 a}(1) \left| \frac{-2Z}{r_{b1}} \right| 3d_{x^2 a}(1) \rangle = \tfrac{1}{4} \langle 3d_{z^2 a}(1) \left| \frac{-2Z}{r_{b1}} \right| 3d_{z^2 a}(1) \rangle +$$

$$+ \tfrac{3}{4} \langle 3d_{x^2-y^2 a}(1) \left| \frac{-2Z}{r_{b1}} \right| 3d_{x^2-y^2 a}(1) \rangle \ . \qquad (4.7)$$

Thus integrals involving $3d_{x^2-y^2}$ orbitals appear although they are not involved in the valence-state configuration. Otherwise the expansion of the energy expression is straightforward. Using for the P-F bond length the average value, for all bonds, the energy was minimised with respect to the 3s, 3p and 3d orbital exponents and the mixing parameter θ. The results of a calculation using a single-zeta 3d orbital are given in Table 4.4. Again we find that the 3s and 3p orbitals are expanded by the ligand fields. The 3d orbital is contracted significantly having a size comparable with that found for the 3d orbital in SF_6. It is slightly more diffuse. Thus ligand field contraction does play its part in allowing d orbitals to participate in bonding. This was not really shown in the case of SF_6. There is a slight decrease in the optimum value of θ - the mixing parameter between the 3s and $3d_{z^2}$ orbitals in the hybrid orbital wavefunction. This leads to slightly greater participation of the 3s orbitals in the axial bonds and 3d orbitals in the equatorial bonds. There is a fairly large P-F interaction contribution to the molecular energy although it is proportionally less than in SF_6. The fluorine-fluorine interaction is very small. The axial-axial, axial-equatorial and equatorial-equatorial fluorine-fluorine interactions were 0.03007, -0.00280 and -0.00035 a.u. respectively. The valence-state promotion energy is 1.22000 a.u. compared with 1.13033 a.u. obtained in the valence-state calculations. This energy is greater than the valence-state energy for any value of θ in the valence-state calculations. The bond energy is larger than that for SF_6. This is principally due to the lower valence-state promotion energy. The calculated P-F bond energy[130] is 98.92 kcals/mole compared with the experimental value of 109.56 kcals/mole. Again one should remember that there are terms missing from the energy expression used to obtain this calculated value.

We can compare this energy and the optimised orbital exponents with those obtained by Mitchell[35] neglecting intra-atomic exchange and

Table 4.4

Energy Minimised Orbital Exponents, Energies and Radii

PF_5 P $3sp^3d_{z^2}$ Multiconfigurational Valence State

		PF_5	P Valence State
α_{3s}		1.798	1.936
α_{3p}		1.520	1.661
α_{3d}		1.231	0.951
θ		0.2996	0.3125
E_{atom}	a.u.	-678.51166	
E_{P-F}	a.u.	-2.79427	
E_{F-F}	a.u.	-0.00280	
E	a.u.	-681.30873	
$E-E_{s^2p^3\,{}^4S}$	a.u.	-1.57708	
$\bar{r}$	a.u.	2.843	
r_{max}	a.u.	2.437	
$\bar{r}/r_{max}$	a.u.	1.167	

using a single configurational valence-state. He obtains values of 1.65, 1.45 and 1.15 for the 3s, 3p and 3d orbital exponents and a value of 13.60 a.u. for that part of the energy involving only the valence electrons, which is to be compared with a value of -14.18 a.u. obtained in this calculation. As in SF_6 the valence shell orbitals are all more contracted in our calculation.

A double-zeta calculation gave results similar to those for SF_6. The values of the 3d orbital exponents α, β and λ obtained were 1.10, 1.00 and 0.690 respectively. The mean radius was 3.248 a.u. and the maximum of the inner lobe occurred at 1.92 a.u. The value of θ was 0.2971. The energy of formation of the molecule obtained was -3.92460 a.u. This result confirms the fact that the result obtained for SF_6 was not an isolated occurrence, but a more general phenomenon.

PF_5 - Phosphorus $3sp^3d_{x^2-y^2}$ Multiconfigurational Valence State Square Pyramidal Structure

We have also studied the square pyramidal form of PF_5. This form was given by Berry[125] as an intermediate in the process of the intramolecular exchange of fluorine atoms in the trigonal bipyramidal structure. In multiconfigurational valence-state calculations the phosphorus atom in the C_{4v} structure was found to have a lower valence-state promotion energy and more contracted 3d orbitals than in the D_{3h} structure. In expanding the energy expression for the molecule with this structure the $3d_{x^2-y^2}$ orbitals appear as $3d_{z^2-y^2}$ or $3d_{x^2-z^2}$ orbitals. It can be shown that

$$3d_{z^2-y^2} = 1/2\ 3d_{x^2-y^2} + \sqrt{3}/2\ 3d_{z^2} , \qquad (4.7)$$

and hence

$$J(\phi,\ 3d_{z^2-y^2}) = \tfrac{1}{4}\, J(\phi,\ 3d_{x^2-y^2}) + \tfrac{3}{4}\, J(\phi,\ 3d_{z^2}) \quad , \qquad (4.8)$$

and similarly for the nuclear attraction integrals

$$\left\langle 3d_{z^2-y^2_a}(1) \left| \frac{-2Z_B}{r_{b1}} \right| 3d_{z^2-y^2_a}(1) \right\rangle = \tfrac{1}{4} \left\langle 3d_{x^2-y^2_a}(1) \left| \frac{-2Z_B}{r_{b1}} \right| 3d_{x^2-y^2_a}(1) \right\rangle + \tfrac{3}{4} \left\langle 3d_{z^2_a}(1) \left| \frac{-2Z_B}{r_{b1}} \right| 3d_{z^2_a}(1) \right\rangle . \qquad (4.9)$$

Using as the P-F bond distance the value used in the calculation on the trigonal bipyramidal form the energy was minimised with respect to the 3s, 3p and 3d orbital exponents. The results of the calculation are given in Table 4.5. The orbital exponents are almost identical to those obtained for the trigonal bipyramidal form of PF_5. The 3d orbital is slightly more contracted in this structure. As before, the 3s and 3p orbitals are more diffuse than in the valence-state of the isolated atom whilst the 3d orbital is more contracted. The magnitude of the P-F interaction is slightly larger. This is due to a proportionally larger contribution for the $3d_{z^2}$ terms. In the D_{3h} structure the ratio of the contributions to the molecular energy of the $3d_{z^2}$ terms to the $3d_{x^2-y^2}$ terms is 11:9 whilst for this C_{4v} structure it is 3:2. This is slightly offset by a bigger fluorine-fluorine interaction. The valence-state promotion energy appropriate to these orbital exponents is -1.09813 a.u. as compared with -1.02867 a.u. obtained in the calculations on the multiconfigurational valence-state. The energy of formation is larger - the P-F bond energy being 107.16 kcals/mole as compared with 98.92 kcals/mole

Table 4.5

Energy Minimised Orbital Exponents, Energies and Radii

PF_5 P $3sp^3d_{x^2-y^2}$ Multiconfigurational Valence State

		PF_5	P Valence State
α_{3s}		1.792	1.918
α_{3p}		1.523	1.650
α_{3d}		1.244	1.110
E_{atom}	a.u.	-678.63352	
E_{P-F}	a.u.	-2.91618	
E_{F-F}	a.u.	0.03770	
E	a.u.	-681.51200	
$E-E_{s^2p^3\,{}^4S}$	a.u.	-1.78035	
$\bar{r}$	a.u	2.814	
r_{max}	a.u.	2.416	
$\bar{r}/r_{max}$	a.u.	1.167	

calculated for the D_{3h} structure and 109.56 kcals/mole determined experimentally. The difference in energy between these two structures is 2.77 eV as compared with 1.31 eV calculated for the multiconfigurational valence-states of the isolated atoms. Thus on electrostatic grounds we would expect the molecule PF_5 to be square pyramidal and not trigonal bipyramidal. The high rate of exchange observed in NMR experiments suggests that the intermediate state of C_{4v} symmetry postulated by Berry must have an energy very close to that of the trigonal bipyramidal structure. The result, whilst striking, is thus not unreasonable in relation to the uncertainties connected with the calculations. The trigonal bipyramidal form could have a much greater contribution from exchange terms than the square pyramidal form. Alternatively the term in the valence bond wavefunction corresponding to the situation where the phosphorus atom is neutral may not be the most important term. The term corresponding to the situation where the phosphorus atom carries a unit positive charge may be more important. In this situation the trigonal bipyramidal form would be expected to be more stable as it minimises the repulsive interactions between the charged ligand atoms. The contribution of 3d orbitals to the valence-state when the phosphorus atom is positively charged would be expected to be minimal.

ClF_3 Chlorine $3s^2p^4d$ Multiconfigurational Valence State

The Cl-F bond distances in ClF_3 were found by Smith[126] to be 1.598 Å for the "equatorial" bond and 1.698 Å for the "axial" bonds giving an average of 1.665 Å = 3.146 a.u. Using this value for the Cl-F bond distance the energy of the ClF_3 molecule was minimised with respect to the 3s, 3p and 3d orbital exponents and the mixing coefficients

α, β and λ. The results of the calculation are given in Table 4.6. The 3s and 3p orbitals are expanded by the ligand field, but not to the same extent as was found for PF_5 and SF_6. The 3d orbital is greatly contracted. This result is a spectacular demonstration of contraction by the ligand field. The field causes the 3d orbital to contract so that its mean radius is about the position of the fluorine nucleus. In some cases it may expand. Hence the term electronegative is used to describe the fluorine atom. The fluorine atom is seen to exert an attractive force on the central atom electrons such that the electron density of the valence orbitals is greatest around the fluorine nuclei. There would appear to be some correlation between 3d orbital size and bond length - the 3d orbital being more contracted in PF_5 than in ClF_3. However this is also the order of the 3d orbital sizes in the valence states. The mixing parameters α and λ have values very similar to those found for the valence-state of the isolated atom. The directions of the lone pairs are still collinear. However there is a significant change in β - the mixing coefficients between the $3d_{z^2}$ orbital and the $3d_{x^2-y^2}$ orbitals. In the valence-state there was approximately equal mixing, the values of sin β and cos β being -0.7528 and -0.6772 respectively. However in the molecular valence-state the values of sin β and cos β are 0.0681 and -0.9977 respectively, i.e., the valence-state configuration is approximately $3s^2 3p_x^2 3p_y 3p_z 3d_{x^2-y^2}$. The valence-state promotion energy is 0.96772 a.u. as compared with 0.81189 a.u. for the isolated atom - a difference of 2.12 eV. This is proportionally the greatest increase found in these molecular calculations. The chlorine-fluorine interaction energy is rather small, being proportionally about half that found for SF_6. This is due to a much smaller contribution from fluorine - $3d_{z^2}$ orbital interactions - the

Table 4.6

Energy Minimised Orbital Exponents, Energies and Radii

ClF_3 Cl $3s^2p^4d$ Multiconfigurational Valence State

	ClF_3	Cl Valence State
α_{3s}	2.387	2.427
α_{3p}	2.049	2.131
α_{3d}	1.100	0.442
α	0.4911	0.5002
β	0.9782	1.2675
λ	1.0000	1.0000
E_{atom} a.u.	-916.04127	
E_{Cl-F} a.u.	-0.97041	
E_{F-F} a.u.	0.02726	
E a.u.	-916.98443	
$E-E_{S^2p^5\,{}^2P^o}$ a.u.	0.02456	
$\bar{r}$ a.u	3.182	
r_{max} a.u.	2.727	
$\bar{r}/r_{max}$	1.167	

strongest of the orbital interactions to the energy expression - it being a 1/4 of that in SF_6 and 6/11 of that in PF_5 (trigonal bipyramidal) and the effect of a larger bond length - it being 6-7% greater than in SF_6 and PF_5. The values of the trans and cis fluorine-fluorine interactions were 0.02880 and -0.00077 a.u. respectively. On electrostatic grounds our calculations suggest that the molecule ClF_3 should be unstable. This is a result of the combination of a large increase in the valence-state energy, a low interaction energy with ligand atoms and a fairly high fluorine-fluorine interaction. Since the molecule is known to be reasonably stable, we must conclude that the exchange terms neglected in the calculation contribute very significantly to the energy of the molecule or alternatively that the chlorine atom carries of fairly high positive charge so that the molecule is stabilised by the ionic interactions. There does not appear in the literature, any determination of the heat of formation of ClF_3 and so the bond energy can not be calculated. However estimates give it a fairly small value. We can compare our result with that obtained by Mitchell[35] neglecting intra-atomic exchange and using a single configurational valence-state. He obtained values of 2.22, 1.90 and 1.10 for the 3s, 3p and 3d orbital exponents and an energy of -28.42 a.u. which is to be compared with a figure of -29.26 a.u. from our calculations. However his energy gives an energy of formation of -0.84 a.u., i.e., the molecule is stable on electrostatic grounds. In his calculations he assumed a Cl-F bond distance of 3.0 a.u. as compared with 3.146 a.u. in our calculation. The Cl-F interaction energy in his calculation is at least 1.90 a.u. - a value which seems unreasonably high. His S-F and P-F interaction energies are much less than those obtained in our calculations. This may be due to an incorrect positioning of the z axis. If the axis was positioned along the axial bonds of ClF_3 and the valence-state configuration was assumed to be $3sp^3d_{z^2}$, a greater $3d_{z^2}$ orbital contribution would result. A calculation using the alternative formulation of the valence-state of chlorine, i.e., in which the lone pairs are assumed to be collinear and the axial-axial bond angle is used as a variational parameter gave the same result except for the appropriate change in the value of the mixing parameter α - it being -0.0089.

Conclusion

Thus the effect of the electrostatic field of the ligand atoms in molecules like SF_6, PF_5 and ClF_3 is important. 3s and 3p orbitals are expanded by the ligand field 3d orbitals are generally contracted. The field tends to cause the size of the orbital to change so that its mean radius is close to the internuclear separation. The valence-state promotion energy is generally increased by about 2-3 eV. This is due mainly to the significant increase in the size of the 3s and 3p orbitals. The energy thus obtained is of more significance than that obtained in calculations on the multiconfigurational valence-state of the isolated atom as the parameters used are more appropriate to the molecular situation. The fact that the valence-state orbitals are perturbed strongly suggests that free atom data should not be used in semi-empirical calculations on molecules containing second row elements without some corrections being made to take account of these effects. The interactions between the ligand atoms are not very significant. Their magnitude is greatest for trans interactions where the ligands repel each other. In other cases the interaction is a small nett attraction. By far the strongest interaction between a fluorine ligand atom and a central atom orbital was that for the $3d_{z^2}$ orbital. Correlation between the amount of the contribution and the magnitude of the intermolecular interaction made possible the explanation of certain trends and unexpected results. The effect of the inclusion of intra-atomic exchange was to give a lower energy. The difference between the size of the 3d orbitals in single and multi-configurational valence-states is not as great as in the isolated atom. Reasonable agreement between experimental and calculated bond energies was obtained. The use of a double-zeta basis set for the 3d orbitals led to physically unrealistic energies. The orbitals developed nodes to resemble 4d orbitals. However the overlaps between the 1s and 2s orbitals of fluorine and these $3d_{z^2}$ orbitals are very small - approaching the value of zero assumed in the calculation of the energy. Certain anomalies were found in some of these calculations. In all of them the central atom is assumed to be uncharged. These anomalies could be explained by the occurrence of a significant interatomic exchange contribution to the molecular energy - greater in one case than in another. However the exclusion of ionic terms from the molecular wavefunction is probably a more likely cause of the anomalies. At least the term corresponding to the situation where the central atom carries a unit positive charge should be included. In some cases, e.g., $P^+F_5^-$ this would lead to a minimal contribution from d orbitals to the valence-state configuration. In others, e.g., $S^+F_6^-$ they are still demanded by the symmetry of the problem, as we showed in Chapter 3.

CHAPTER 5

CONSIDERATION OF THE NEGLECT OF INTERATOMIC EXCHANGE AND NON-ORTHOGONALITY OF LIGAND-CENTRAL ATOM ORBITALS

Introduction

There are two main objections that can be raised to the calculations given in Chapter 4. Firstly interatomic exchange terms were not included in the energy expression. It was assumed that the optimum orbital exponents do not depend strongly on them and so would not be significantly altered by their being dropped from the energy expression. Secondly, it was assumed that the fluorine orbitals were orthogonal to the sulphur, phosphorus or chlorine orbitals. As the tables of overlap integrals given in Chapter 3 show, they are not orthogonal and as a result additional terms should appear in the energy expression, when interatomic exchange is included, with overlap integrals between the non-orthogonal orbitals involved as coefficients. Allied to the neglect of non-orthogonality is the fact that the wavefunctions are not normalised when intermolecular exchange is included. The computation involved in a calculation on a molecule of the size of SF_6, PF_5 or ClF_3 is increased by at least an order of magnitude if these omissions are rectified. Because the wavefunction used is unsatisfactory due to factors such as the neglect of ionic terms, a computation of so great a magnitude is not worthwhile. To see how significant are these omissions and how they effect the size of the 3d orbitals and the calculated molecular energy investigations were made on the effect of including the exchange terms involving the 3d orbitals in SF_6 and of allowing for non-orthogonality of the $3d_{z^2}$ orbitals. In this we have made use of the fact that the double-zeta orbitals have three parameters determining their size and shape, any one of which can be varied to meet either an orthogonality or an energy minimisation condition.

Inclusion of Exchange Terms Involving 3d Orbitals

Intermolecular exchange terms occur in the energy expression for a molecule if the determinantal wavefunction is not of the form of 4.1, but has non-zero terms that are not in the diagonal blocks. The molecular energy then has the form

$$E = E' + \sum_{i} K(\sigma_i\ \ell_i) - \tfrac{1}{2} \sum_{i \neq j} K(\sigma_i\ \ell_j) - \tfrac{1}{2} \sum_{i \neq j} \sum_{A \neq B} K(\ell_{iA}\ \ell_{jB}) \quad , \qquad (5.1)$$

where E' is the energy as given in equation 4.3, the K's are intermolecular exchange integrals and the hybrid orbital σ_i is assumed to be paired to the ligand orbital ℓ_i. The summation is over all orbitals of the central atom and the ligand atoms. The effect of the inclusion of the intermolecular exchange terms on the energy and size of 3d orbitals in SF_6 was investigated. The intermolecular exchange contribution to the molecular energy involving 3d orbitals has the form:

$$\begin{aligned} E_{\text{exchange-3d}} = {} & 3\sqrt{2}\ \langle 3s,\ 2p_\sigma;2p_\sigma,\ 3d_{z^2}\rangle + 3\sqrt{6}\ \langle 3p_z,\ 2p_\sigma;2p_\sigma,\ 3d_{z^2}\rangle - \\ & -3\ \langle 3d_{x^2-y^2},\ 2p_\sigma;2p_\sigma,\ 3d_{x^2-y^2}\rangle - 6\ \langle 3d_{z^2}, 1s;1s,\ 3d_{z^2}\rangle - \\ & -6\ \langle 3d_{z^2},\ 2s;2s,\ 3d_{z^2}\rangle - 12\ \langle 3d_{z^2},\ 2p_\pi;2p_\pi,\ 3d_{z^2}\rangle - \\ & -6\ \langle 3d_{x^2-y^2},\ 1s;1s,\ 3d_{x^2-y^2}\rangle - 6\ \langle 3d_{x^2-y^2},\ 2s;2s,\ 3d_{x^2-y^2}\rangle - \\ & -12\ \langle 3d_{x^2-y^2},\ 2p_\pi;2p_\pi,\ 3d_{x^2-y^2}\rangle \quad . \end{aligned} \qquad (5.2)$$

Details of the computation of the exchange integrals are given in Appendix 3D. The energy of the molecule was minimised with respect to the 3d orbital exponent - all other parameters were taken from the molecular calculation in which exchange was neglected. The results of the calculation are given in Table 5.1. The 3d orbital is more diffuse than that found when intermolecular exchange was neglected. The molecular energy is lowered by the inclusion of the exchange contributions by about 6.30 eV. This represents an increase in the S-F bond energy at 24.206 kcals/mole. Thus the inclusion of the intermolecular exchange terms considerably lowers the energy and tends to cause the 3d orbitals to expand slightly. The expansion found in this calculation in which only the 3d orbital exponent is optimised may be countered by an expansion of the 3s and 3p orbitals. These orbitals would then shield the 3d orbitals less efficiently and hence the 3d orbitals would contract. The computation of values of intermolecular exchange integrals is very tedious. There is a need for the formulation of some form of exchange potential for use in molecular calculations analogous to that obtained by Slater for a free-electron gas.[161]

Effect of Non-Orthogonality of $3d_{z^2}$ Orbitals to Ligand Core Orbitals

Even with all the exchange terms included in the energy expression, the expression so obtained is not rigorous as it neglects non-orthogonality in some places and not in others. This question has been discussed by Van Vleck and Sherman.[131] In the Heitler-London[132] treatment of the hydrogen molecule the energy is given by

$$E = 2E_H + \frac{J \pm K}{1 \pm S^2} \quad , \qquad (5.3)$$

Table 5.1

Energy Minimised Orbital Parameters, Energies and 3d Orbital Radial Distribution Properties

SF_6 S $3sp^3d^2$ Multiconfigurational Valence State

Inclusion of Interatomic Exchange Involving 3d Orbitals

α_{1s}	15.5409		
α_{2s}	5.3144	α_{2p}	5.9468
α_{3s}	2.064	α_{3p}	1.708

α_{3d}		1.256
$E-E_{s^2p^4\,{}^3P}$ w/o exchange	a.u.	-1.72651
$E_{exchange}$	a.u.	-0.46308
$E-E_{s^2p^4\,{}^3P}$ w/ exchange	a.u.	-2.18959
$\bar{r}$	a.u.	2.787
r_{max}	a.u.	2.389
$\bar{r}/r_{max}$		1.167

where E_H is the energy of the two isolated hydrogen atoms, J and K are the coulomb and exchange terms obtained using the complete interaction Hamiltonian - not just the electron-electron interaction part - and S is the overlap integral between the bonding electrons. It has often been customary to neglect the term S^2 in the denominator - assuming it to be negligible as compared to unity. The bonding orbitals are thus assumed to be orthogonal although in practice they are not. For the H_2 molecule the value of S is about 0.42. It is easy to generalise this approximation for the n-electron problem as has been done in the calculation including some interatomic exchange just described. Also neglected are integrals involving higher order permutations. These are integrals involving product wavefunctions which differ from each other by more than a simple permutation. Their coefficients always involve a factor of the overlap integral and so would vanish were there complete orthogonality. Thus there arise integrals such as the resonance integral, e.g.,

$$\left\langle 1s_A(1) \left| \frac{-2Z_A}{r_{b1}} \right| 3d_{z^2_B}(1) \right\rangle ,$$

the kinetic energy integral, e.g.,

$$\left\langle 1s_A(1) \right| -\nabla_1^2 \left| 3d_{z^2_B}(1) \right\rangle ,$$

and hybrid integrals, e.g.,

$$\left\langle 1s_A(1) 2p_{\sigma_A}(2) \left| \frac{2}{r_{12}} \right| 3d_{z^2_B}(1) 2p_{\sigma_A}(2) \right\rangle .$$

With all these examples, the integrals occur with a factor of $S(1s, 3d_{z^2})$ in the coefficient. The same integrals occur if one imposes the orthogonality condition by writing the wavefunction for say, the $3d_{z^2}$ orbital, in the form

$$\psi_{3d_{z^2}} = C_1\phi_{3d_{z^2}} + C_2\phi_{1s_B} + C_3\phi_{2s_B} + C_3\phi_{2p_{\sigma_B}} \tag{5.4}$$

Van Vleck[162] has shown that the neglect of higher order permutations is partially cancelled by a neglect of normalisation. Coolidge and James[133] showed that the activation energy of the process $H + H_2 = H_2 + H$ is radically changed when corrections are made for higher order permutations and non-orthogonality. Philips[20] considered the effect of orthogonalisation on the calculation of crystal field parameters for $Cr(H_2O)_6^{3+}$. Orthogonalisation terms were included by representing them as an effective repulsive potential energy term. This was thought to approximately cancel the non-coulombic component of the ionic ligand's field, leaving only the field of the point negative charges. This can only hold if the penetration of the 3d electron into the ligand core is very slight as is likely under conditions of the tightly bound 3d electrons in a transition metal. The effect of the neglect of orthogonality was studied by Stuart and Hirst[134] using the LiH molecule. Their calculation was reasonably rigorous - including all the appropriate ionic terms in the wavefunction. They found a value for the electronic energy of -22.444 eV when the valence orbitals of one atom were not orthogonal to the core orbitals (1s) of the other atom and a value of -19.337 eV when they were orthogonal. This is to be compared with a value of -21.671 eV found experimentally. Thus the value obtained neglecting the non-orthogonality is higher than the experimental value but closer to it than that obtained when the non-orthogonality is taken into account. However this latter approach gives a better value for the dipole moment of the molecule. Neglecting non-orthogonality they obtained a value of -4.141 D. When it is taken into account a value of -6.586 D is obtained. This is to be compared with an experimental value of -5.882 D. Thus it had been shown that the non-orthogonality of valence oribtals with ligand core orbitals should not be neglected.

We have investigated the effect of imposing the orthogonality of $3d_{z^2}$ orbitals to fluorine core orbitals in SF_6. Use was made of the fact discovered in the work described in Chapter 4 that the double-zeta orbitals are approximately orthogonal to the 1s and 2s orbitals of the fluorines. One of the 3d orbital parameters was varied so that the overlap integral was approximately zero. The energy was minimised with respect to the 3s and 3p orbital exponents and the other 3d orbital parameters. In Table 5.2 are given the results obtained when the 1s-$3d_{z^2}$ overlap was minimised using the mixing coefficient λ as a variational parameter. In all these calculations the orbital exponents were calculated to an accuracy of ± 0.005 and the mixing coefficient λ' to an accuracy of ± 0.0005. The $3d_{z^2}$ orbital was found to have a larger mean radius than that found when the orthogonality condition is not imposed. The energy is increased by over 5.0 a.u. However the energy of formation is still too large to be physically realistic. In Table 5.3 are given the results obtained when the energy was minimised with the 2s-$3d_{z^2}$ overlap minimised. Again λ was used as the variational parameter. The 3d orbital is slightly less diffuse and the energy is lower by about 2 a.u. than that obtained when S(1s, $3d_{z^2}$) was minimised. In Figure 5.1 are drawn the radial distribution functions for the double-zeta orbitals obtained without any orthogonality conditions imposed, with S(1s, 3d) minimised and with S(2s,3d) minimised.

Table 5.2

Optimum Orbital Parameters, Energy and Mean Radius of 3d Orbitals

Effect of Imposing Orthogonality of Sulphur $3d_{z^2}$ Orbitals
With Fluorine 1s Orbitals

SF_6 $3sp^3d^2$ Multiconfigurational Valence State

Double Zeta Calculation

α_{3s}	2.145
α_{3p}	1.800
α	1.090
β	1.040
λ	0.753
$E-E_{s^2p^4-{}^3P}$ a.u.	-4.67790
S(1s,3d)	0.00029
$\bar{r}$ a.u.	4.773

Table 5.3

Optimum Orbital Parameters, Energy and Mean Radius of 3d Orbital

Effect of Imposing Orthogonality of Sulphur $3d_{z^2}$

Orbitals with Fluorine 2s Orbitals

SF_6 $3sp^3d^2$ Multiconfigurational Valence State

Double Zeta Calculation

α_{3s}	2.120
α_{3p}	1.790
α	1.140
β	1.085
λ	0.751
$E-E_{s^2p^3-{}^3P}$ a.u.	-6.90477
S(2s,3d)	0.00511
$\bar{r}$ a.u.	4.248

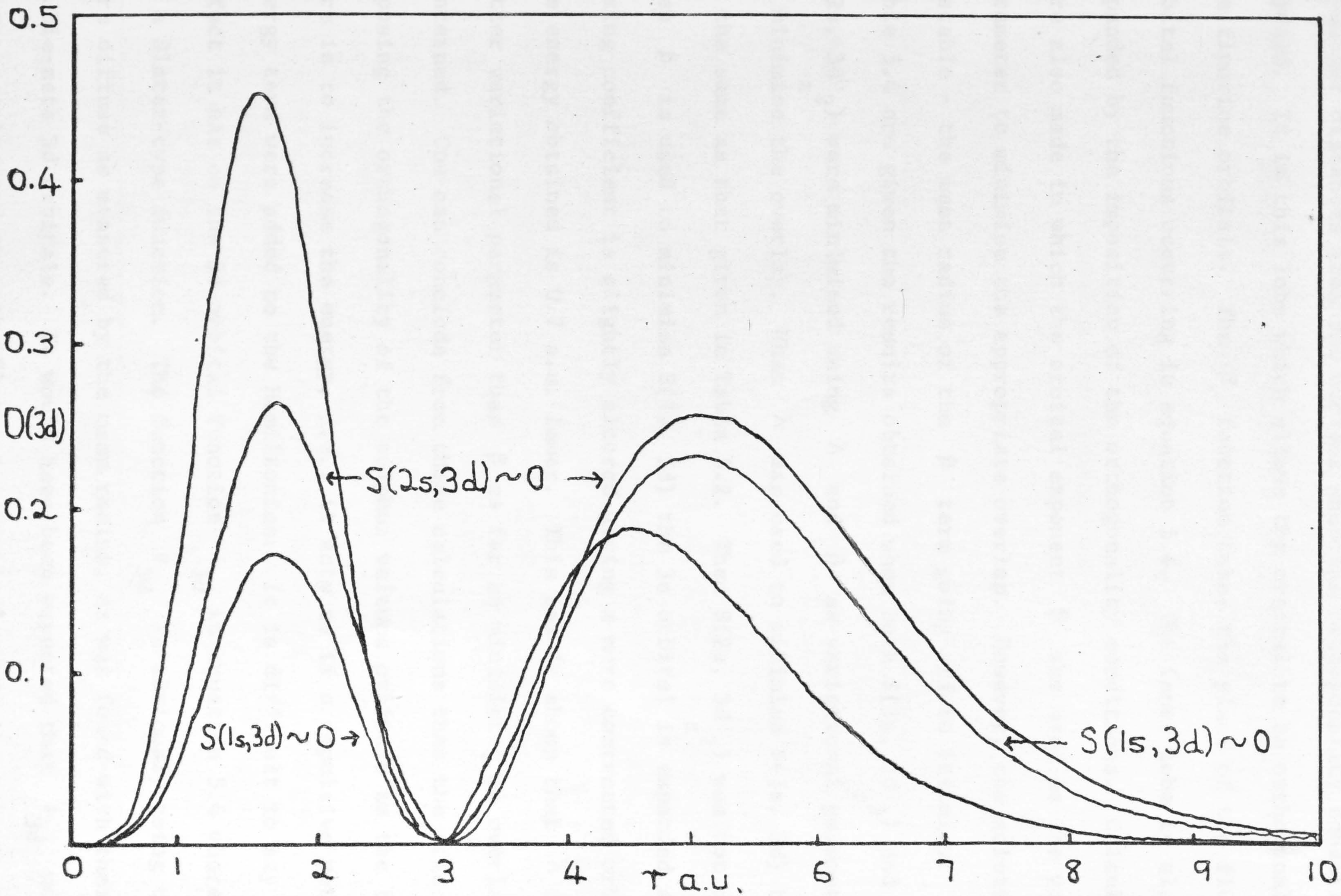


Figure 5.1 Effect of Imposing Orthogonality Conditions
3d Double-Zeta Wavefunctions SF$_6$

One can see that the outer lobe is increased in size and has a maximum at larger distances from the nucleus when the orthogonality conditions are imposed. It is this lobe which allows the orbital to be orthogonal to the fluorine orbitals. The β function takes the place of the fluorine orbital functions occurring in equation 5.4. The inner lobe is also expanded by the imposition of the orthogonality conditions. Calculations were also made in which the orbital exponent β was used as the variational parameter to minimise the appropriate overlap. However, the solution is unstable - the mean radius of the β term going off to infinity. In Table 5.4 are given the results obtained when both S(1s, $3d_{z^2}$) and S(2s, $3d_{z^2}$) were minimised using λ and β as variational parameters to minimise the overlap. When λ was used to minimise S(1s, 3d) the result is the same as that given in Table 5.2. Then S(2s, $3d_{z^2}$) was not minimised. When β is used to minimise S(1s, 3d) the 3s orbital is expanded and the mixing coefficient is slightly altered giving a more contracted orbital. The energy obtained is 0.7 a.u. lower. This result shows that λ is a better variational parameter than β as far as minimising an overlap is concerned. One can conclude from these calculations that the effect of imposing the orthogonality of the sulphur valence orbitals to the fluorine core is to increase the energy, i.e., it acts as if a repulsive potential energy term were added to the Hamiltonian. It is difficult to say what effect it has on the 3d orbital function ϕ_{3d} in equation 5.4 where ϕ_{3d} is a Slater-type function. The function ψ_{3d} is obviously going to be more diffuse as measured by the mean radius, as was found with these double-zeta 3d orbitals. It would have been expected that ϕ_{3d} would be more contracted than the Slater-type orbital not orthogonal to the core orbitals. This would give a total charge distribution given by ψ_{3d}

Table 5.4

Optimum Orbital Parameters, Energy and Mean Radius of 3d Orbital

Effect of Imposing Orthogonality of Sulphur $3d_{z^2}$ Orbitals
With Both 1s and 2s Fluorine Orbitals

SF_6 $3sp^3d^2$ Multiconfigurational Valence State

Double Zeta Calculation

Variational Parameter S(1s,3d)	β	λ
Variational Parameter S(2s,3d)	λ	β
α_{3s}	2.125	2.145
α_{3p}	1.800	1.800
α	1.090	1.090
β	1.040	1.040
λ	0.752	0.753
$E-E_{s^2p^4-{}^3P}$ a.u.	-5.37999	-4.67790
S(1s,3d)	0.00710	0.00029
S(2s,3d)	0.00219	0.00414
$\bar{r}$ a.u.	4.587	4.773

with about the same mean radius as was obtained without imposing the orthogonality conditions.

Conclusion

These calculations have shown that the inclusion of intermolecular exchange terms in the molecular energy and the allowance for the non-orthogonality of ligand orbitals to the central atom orbitals are important. The calculations described were exploratory in character. Despite this fact the essential trends looked for were discernible. Because of the nature of the 3d basis set used it is difficult to state exactly how great an energy increase occurs when the orthogonality conditions are imposed. This increase is countered by a large decrease in energy, i.e., increase in the energy of formation, when the intermolecular exchange terms are included. These results give numerical confirmation for the principle stated by Craig and Zauli[17] that it would be inconsistent to include one set of terms without the other. How nearly these two terms of opposite sign cancel each other is still to be settled. The effect on the size of the 3d orbitals is probably very small in the case of the inclusion of the exchange terms. Some contraction should occur when the ligand core orbitals are made orthogonal to the central atom valence orbitals - the latter being understood to be Slater type orbitals like ϕ_{3d} in equation 5.4. If one calculates for the 3d orbitals the contributions to ψ_{3d} of the fluorine orbitals using the overlap integrals in Table 3.2 one finds that if ψ_{3d} is orthogonal to the fluorine 1s orbital:

$$\psi_{3d} \sim 1.002\ \phi_{3d} - 0.068\ \phi_{1s} \quad . \tag{5.5}$$

If it is orthogonal to the 2s orbital we find:

$$\psi_{3d} \sim 1.283\ \phi_{3d} - 0.543\ \phi_{2s} \quad . \qquad (5.6)$$

If it is to be orthogonal to the $2p_\sigma$ bonding orbital:

$$\psi_{3d} \sim 1.015\ \phi_{3d} - 0.1243\ \phi_{2p_\sigma} \quad . \qquad (5.7)$$

Thus a wavefunction of the form given in equation 5.4 will contain a very significant contribution from the fluorine 2s orbitals. The contribution of the 1s orbital is not very large. The neglect of the non-orthogonality with the fluorine 2s orbitals is thus expected to have an important effect on the energy and size of the 3d orbital ϕ_{3d}. A more complete investigation of these two effects should be made. However it is reasonably to be expected, that they will justify the conclusions based on the calculations described in this chapter.

CONCLUSION

d ORBITALS IN LATER SECOND-ROW ELEMENTS - DO THEY OR DON'T THEY?

At the outset the aim of this work was to investigate further the importance of 3d orbitals in basis sets used to describe the electron distribution in molecules of the later second row elements exhibiting higher covalencies. In the course of the work much has been learnt about 3d orbitals in atoms and molecules. For convenience there are collected below the main conclusions reached about the 3d orbitals. Some of these had been reached by other workers, being confirmed in this work by new examples; others had not been made previously.

Size of 3d Orbitals

Free atom studies show that 3d orbitals in d^2 configurations are more contracted than in d^1 configurations.

For d^2 configurations there is a large variation in 3d orbital size within the configuration manifold. For d^1 configurations the range of 3d orbital sizes is much smaller.

Within a configuration manifold the 3d orbitals tend to be more contracted the lower the energy of the term.

Comparative studies of one and two term wavefunctions showed that the radial distribution of a contracted 3d orbital is not well described by a one term function; it is a fair approximation for very diffuse orbitals.

When algebraic analysis showed that there was a large contribution to a multiconfigurational valence-state by d^2 and d^3 configurations, numerical studies correspondingly showed that the 3d orbitals were sufficiently contracted to contribute significantly to bonding.

3d orbitals in multiconfigurational valence-states are more contracted than any of the terms of the valence-state configuration.

The size of 3d orbitals in free atoms is decreased by the inclusion of intra-atomic exchange. In the valence-state this is not necessarily the case.

The most important factor determining the size of the 3d orbitals in molecules is the coulombic field of the ligand atoms. This invariably led to 3d orbitals being sufficiently contracted for bonding.

Inclusion of intermolecular exchange terms do not alter the 3d orbital size greatly.

Thus the supposed difficulty with 3d orbital participation in bonding based upon the size of the 3d orbital is confirmed as unfounded.

Energetics

The promotion energy into the valence-state is high - ranging from 13.2 eV for Cl in ClF_3 to 30.7 eV for S in SF_6. These values quoted are from the promotion energies found in molecular calculations in which intermolecular exchange terms are neglected. These are more appropriate than those calculated for the isolated atom.

Valence-states involving 4s orbitals have a lower promotion energy but the 4s orbitals, being diffuse and less polarisable than 3d orbitals, are unlikely to contribute significantly to bonding.

The $3d_{z^2}$ orbital gives a larger contribution to the molecular energy than any of the other valence orbitals. The electrostatic interaction of a $3d_{z^2}$ orbital with a fluorine atom is greater than that for a 3s or $3p_\sigma$ orbital.

The overlap integral $S(2s,3d_{z^2})$ is greater than $S(2s,3s)$ or $S(2s,3p_\sigma)$ for the contracted $3d_{z^2}$ orbitals.

A simple calculation using Mulliken's approximation[135] shows that the contributions of the $3d_{z^2}$ orbitals to the intermolecular exchange component of the molecular energy will be greater than that for the 3s or $3p_\sigma$ orbitals. For example, the values of $K(2s,3d_{z^2})$, $K(2s,3p_\sigma)$ and $K(2s,3s)$ are about 0.18, 0.13 and 0.04 in this approximation. These terms have negative coefficients in the energy expression.

Thus despite the high promotion energy into the valence-state it is likely that 3d orbitals will contribute significantly to the molecular energy.

Charge

It was found in each of the molecules studied that it was difficult to justify the neglect of ionic terms in the valence bond wavefunction.

In some cases where the central atom is charged, e.g., P^+ in $P^+F_5^-$, whilst symmetry allows d orbital participation, it is likely to be minimal on energetic grounds. The valence-state configuration for P^+ in $P^+F_5^-$ is approximately $3sp^3$.

In other cases, e.g., S^+ in $S^+F_6^-$, 3d orbital participation is demanded by the symmetry of the problem - the valence-state configuration being $3sp^3d$ instead of $3sp^3d^2$ in the neutral atom.

The symmetry of the arrangement of the bonding orbitals is lower when the central atom is charged. This lower symmetry does not in general require as great a contribution from 3d orbitals, as the above examples show.

Thus it can be said that in choosing a basis set to describe the electron distribution in compounds of the later second row elements, 3d orbitals should be included. Their size or the energetics involved do not make it unreasonable. The actual contribution will depend on how ionic are the bonds.

APPENDIX 1

THE CALCULATION OF ATOMIC INTEGRALS

Orthogonalisation of Wavefunctions

The angular part of the wavefunction ensures that orbitals with different ℓ or m quantum numbers are orthogonal. Slater-type orbitals[6] with the same ℓ and m but different n are not orthogonal. To build up an orthogonal orbital we take a linear combination of the form

$$\Phi_{n\ell} = \sum_{i=\ell+1}^{n} c_{in\ell}\, \phi_{i\ell} \quad , \tag{A1.1}$$

where $\phi_{i\ell}$ is an unnormalised Slater-type radial wavefunction. Using the orthogonality and normalisation conditions, the coefficients $c_{in\ell}$ may be calculated. The appropriate formulae for 1s-4p orbitals are given in Table A1.1. S_{nm} is the overlap integral between unnormalised Slater-type radial wavefunctions

$$\begin{aligned} S_{nm} &= \int \phi_{n\ell}(r)\, \phi_{m\ell}(r)\, r^2 dr \quad , \\ &= \frac{(n+m)!}{(\alpha_{n\ell}+\alpha_{m\ell})^{n+m+1}} \quad . \end{aligned} \tag{A1.2}$$

I(nℓ)

The one electron integral $\int \phi_{n\ell}(-\nabla^2 - \frac{2Z}{r})\phi_{n\ell} dv$ is denoted by $I(n\ell)$. Freeman and Löwdin[136] showed that this may be put in the form

$$\int_0^\infty \left\{ r^{2\ell+2} \left[\frac{d}{dr} \left(\frac{R_{n\ell}(r)}{r^\ell} \right) \right]^2 - 2ZR^2_{n\ell}(r) \right\} dr \quad , \tag{A1.3}$$

Table A1.1

Orthogonalisation of Wavefunctions

nℓ	R(nℓ)
1s	$1/(\sqrt{S_{11}}\; e^{-\alpha_{1s} r})$
2s	$\frac{1}{\sqrt{S_{11}S_{22}-S_{12}^2}}\left[\sqrt{S_{11}}\; r e^{-\alpha_{2s} r} - \sqrt{\frac{S_{12}^2}{S_{11}}}\; e^{-\alpha_{1s} r}\right]$
2p	$1/(\sqrt{S_{22}}\; r e^{-\alpha_{2p} r})$
3s	$\frac{1}{\sqrt{S_{11}S_{22}-S_{12}^2}} \cdot \frac{1}{\sqrt{\begin{vmatrix} S_{11} & S_{12} & S_{13} \\ S_{12} & S_{22} & S_{23} \\ S_{13} & S_{23} & S_{33} \end{vmatrix}}} \times$
	$\times\; [(S_{12}S_{23}-S_{13}S_{22})e^{-\alpha_{1s} r} - (S_{11}S_{23}-S_{12}S_{13}) r e^{-\alpha_{2s} r} + (S_{11}S_{22}-S_{12}^2) r^2 e^{-\alpha_{3s} r}]$
3p	$\frac{1}{\sqrt{S_{22}S_{33}-S_{23}^2}}\left[\sqrt{S_{22}}\; r^2 e^{-\alpha_{3p} r} - \sqrt{\frac{S_{23}^2}{S_{22}}}\; r e^{-\alpha_{2p} r}\right]$
3d	$1/(\sqrt{S_{33}}\; r^2 e^{-\alpha_{3d} r})$ (Single-zeta)

...../

/.....

Table A1.1 (continued)

nℓ R(nℓ)

4s $R(4s) = c_1 e^{-\alpha_{1s} r} + c_2 r e^{-\alpha_{2s} r} + c_3 r^2 e^{-\alpha_{3s} r} + c_4 r^3 e^{-\alpha_{4s} r}$

$$\triangle = S_{11}S_{22}S_{33}S_{44} - S_{11}S_{22}S_{34}^2 - S_{22}S_{33}S_{14}^2 - S_{33}S_{44}S_{12}^2 - S_{11}S_{33}S_{24}^2 -$$

$$- S_{22}S_{44}S_{13}^2 - S_{11}S_{44}S_{23}^2 + 2S_{11}S_{23}S_{24}S_{34} + 2S_{22}S_{13}S_{14}S_{34} +$$

$$+ 2S_{33}S_{12}S_{14}S_{24} + 2S_{44}S_{12}S_{13}S_{23} + S_{12}^2 S_{34}^2 + S_{13}^2 S_{24}^2 +$$

$$+ S_{14}^2 S_{23}^2 - 2S_{13}S_{24}S_{14}S_{23} - 2S_{12}S_{34}S_{14}S_{23} - 2S_{12}S_{34}S_{13}S_{24}$$

$$\triangle' = S_{11}S_{22}S_{33} - S_{11}S_{23}^2 - S_{22}S_{13}^2 - S_{33}S_{12}^2 - 2S_{12}S_{13}S_{23}$$

$$c_1 = -(S_{12}S_{23}S_{34} - S_{12}S_{24}S_{33} + S_{13}S_{23}S_{24} - S_{13}S_{22}S_{34} + S_{14}S_{22}S_{33} -$$

$$- S_{14}S_{23}^2)/\sqrt{\triangle\triangle'}$$

$$c_2 = (S_{11}S_{23}S_{34} - S_{11}S_{24}S_{33} + S_{13}^2 S_{24} - S_{13}S_{12}S_{34} + S_{14}S_{12}S_{33} -$$

$$- S_{14}S_{23}S_{13})/\sqrt{\triangle\triangle'}$$

/.....

/..... Table A1.1 (continued)

nℓ	R(nℓ)
	$c_3 = -(S_{11}S_{22}S_{34} - S_{11}S_{24}S_{33} + S_{12}S_{13}S_{24} - S_{12}^2 S_{34} + S_{14}S_{12}S_{23} - S_{14}S_{13}S_{22})/\sqrt{\Delta\Delta'}$ $c_4 = \sqrt{\Delta'/\Delta}$
4p	$\frac{1}{\sqrt{S_{22}S_{33}-S_{23}^2}} \cdot \frac{1}{\begin{vmatrix} S_{22} & S_{23} & S_{24} \\ S_{23} & S_{33} & S_{34} \\ S_{24} & S_{34} & S_{44} \end{vmatrix}} \times$ $\times [(S_{23}S_{34} - S_{24}S_{33}) r e^{-\alpha_{2p} r} + (S_{23}S_{24} - S_{22}S_{34}) r^2 e^{-\alpha_{3p} r} +$ $+ (S_{22}S_{33} - S_{23}^2) r^3 e^{-\alpha_{4p} r}]$

which is particularly convenient for computation. Using this formula we get the general formula for hydrogen-like wavefunctions,

$$I(n\ell) = \sum_{i=\ell+1}^{n} \sum_{j=\ell+1}^{n} c_{in\ell} c_{jn\ell} \Big[\alpha_{i\ell}\alpha_{j\ell}\Big(\frac{1}{\alpha_{i\ell}+\alpha_{j\ell}}\Big)^{i+j+1}(i+j)! - [2Z + \alpha_{i\ell}(j-\ell-1) + \alpha_{j\ell}(i-\ell-1)]\Big(\frac{1}{\alpha_{i\ell}+\alpha_{j\ell}}\Big)^{i+j}(i+j-1)! + (i-\ell-1)(j-\ell-1) \times \Big(\frac{1}{\alpha_{i\ell}+\alpha_{j\ell}}\Big)^{i+j-1}(i+j-2)!\Big] , \qquad (A1.4)$$

where $c_{in\ell}$, $c_{jn\ell}$ are the normalisation and orthogonalisation coefficients defined above. The expression for I(3d) using a two term wavefunction is

$$I(3d) = N^2\{[45/8 \sin^2(\lambda\pi)\xi_1^{-5} + 720 \sin(2\lambda\pi)\xi_1\xi_2(\xi_1+\xi_2)^{-7} + 45/8 \cos^2(\lambda\pi)\xi_2^{-5}] - 2Z[15/8 \sin^2(\lambda\pi)\xi_1^{-6} + 120 \sin(2\lambda\pi)(\xi_1+\xi_2)^{-6} + 15/8 \cos^2(\lambda\pi)\xi_2^{-6}]\} \qquad (A1.5)$$

where

$$N = \left[\frac{45/8 \sin^2(\lambda\pi)}{\xi_1^7} + \frac{720 \sin(2\lambda\pi)}{(\xi_1+\xi_2)^7} + \frac{45/8 \cos^2(\lambda\pi)}{\xi_2^7}\right]^{-\frac{1}{2}} \qquad (A1.6)$$

$$R(3d) = N[\sin(\lambda\pi)r^2e^{-\xi_1 r} + \cos(\lambda\pi)r^2e^{-\xi_2 r}] \quad . \qquad (A1.7)$$

λ used here is related to the λ' tabulated in the text by the relation

$$\tan(\pi\lambda') = \tan(\pi\lambda)\Big(\frac{\xi_2}{\xi_1}\Big)^{7/2} \quad . \qquad (A1.8)$$

Two Electron Integrals

The two electron, one centre integrals can be reduced to a sum of integrals of the form

$$R^k(ij;rt) = \int_0^\infty \int_0^\infty R_{n_i \ell_i}(r_1) R_{n_j \ell_j}(r_2) R_{n_r \ell_r}(r_1) R_{n_t \ell_t}(r_2) r_1^2 r_2^2 \frac{2r(a)^k}{r(b)^{k+1}} dr_1 dr_2 \quad ,$$

$r(b) > r(a)$, i.e., $r(a)$, $r(b)$ are the smaller and larger of the pair r_1, r_2.

(A1.9)

Two particular cases of these integrals are $F^k(n_i\ell_i, n_j\ell_j) = R^k(ij;ij)$ which arises in the expansion of Coulomb integrals and $G^k(n_i\ell_i, n_j\ell_j) = R^k(ij;ji)$ which arises in the expansion of exchange integrals. In a basis set of Slater-type orbitals, the integral can be expressed as the sum

$$R^k(ij;rt) = 2 \sum_{i_1=\ell_i+1}^{n_i} \sum_{i_2=\ell_r+1}^{n_r} \sum_{i_3=\ell_j+1}^{n_j} \sum_{i_4=\ell_t+1}^{n_t} c_{i_1 n_i \ell_i} c_{i_2 n_r \ell_r} c_{i_3 n_j \ell_j} \times$$

$$\times c_{i_4 n_t \ell_t} [Srk(k, i_1, i_2, i_3, i_4, \alpha_{i_3 \ell_j} + \alpha_{i_4 \ell_t}, \alpha_{i_1 \ell_i} + \alpha_{\ell_2 \ell_r}) +$$

$$+ Srk(k, i_3, i_4, i_1, i_2, \alpha_{i_1 \ell_i} + \alpha_{i_2 \ell_r}, \alpha_{i_3 \ell_j} + \alpha_{\ell_4 \ell_t})] \quad , \qquad (A1.10)$$

where

$$Srk(k,m,n,p,q,\alpha,\beta) = (1/\alpha)^{p+q+k+1} (1/\beta)^{m+n-k} (p+q+k)!(m+n-k-1)! - \sum_{i=1}^{p+q+k+1} (1/\alpha)^i \times$$

$$\times (1/(\alpha+\beta))^{m+n+p+q+1-i} \frac{(m+n+p+q-i)!(p+q+k)!}{(p+q+k+1-i)!} \quad . \qquad (A1.11)$$

In $G^k(n_i\ell_i, n_j\ell_j)$ the two Srk terms are identical so that the Srk function need only be evaluated once per cycle. When a two term function is used another summation is included for every 3d function occurring. Some formulae for the calculation of these integrals have been given by Zauli[137] and Brown and Fitzpatrick.[138]

Mean Radius

The mean radius of an orbital is defined by the integral

$$\bar{r} = \int_0^\infty R^2(n\ell)\, r^3\, dr \quad . \qquad \text{(A1.12)}$$

For a hydrogen-like orbital it is given by

$$\bar{r}_{n\ell} = \sum_{i=\ell+1}^{n} \sum_{j=\ell+1}^{n} c_{in\ell}\, c_{jn\ell} \left(\frac{1}{\alpha_{i\ell}+\alpha_{j\ell}} \right)^{i+j+2} (i+j+1)! \quad . \qquad \text{(A1.13)}$$

For the two term 3d wavefunction it is given by

$$\bar{r} = N^2 \left[\sin^2(\pi\lambda) \left(\frac{1}{2\xi_1} \right)^8 7! + \sin(2\pi\lambda) \left(\frac{1}{\xi_1+\xi_2} \right)^8 7! + \cos^2(\pi\lambda) \left(\frac{1}{2\xi_2} \right)^8 7! \right] \quad , \qquad \text{(A1.14)}$$

where R(3d) is defined as in equation A1.7.

APPENDIX 2

TYPICAL VALUES OF ATOMIC INTEGRALS

$I(n\ell)$

n \ ℓ	s	p	d
1	-255.7892		
2	-60.2727	-59.7844	
3	-20.6110	-17.9843	-11.6013
4	-5.5203	-4.9927	

$F^{0}(n\ell,n'\ell')$

$n'\ell'$ \ $n\ell$	1s	2s	2p	3s	3p	3d	4s
1s	19.4261						
2s	5.2861	3.7162					
2p	5.8615	3.9668	4.3207				
3s	1.5621	1.4206	1.4396	1.0866			
3p	1.3233	1.2595	1.2702	1.0256	0.9754		
3d	0.8267	0.8244	0.8253	0.7394	0.7179	0.5812	
4s	0.3889	0.3828	0.3836	0.3696	0.3669		0.2961
4p	0.3030	0.3022	0.3023				

$F^2(n\ell, n'\ell')$

$n\ell$	$n'\ell'$	F^2
2p	2p	2.0907
3p	3p	0.5208
3p	3d	0.3204
3d	3d	0.2666

$F^4(n\ell, n'\ell')$

$n\ell$	$n'\ell'$	F^4
3d	3d	0.1652

$G^k(n\ell, n'\ell')$

k	$n\ell$ \ $n'\ell'$	1s	2s	3s	4s
0	1s		0.4288	0.04260	0.001806
	2s			0.07841	0.003211
	3s				0.009579
1	2p	0.7391	2.3990	0.09770	0.004052
	3p	0.02908	0.04575	0.7014	0.01643
	4p	0.000407	0.000598	0.003841	
2	3d	0.0000521	0.02580	0.2698	

$G^k(n\ell,n'\ell')$

k	$n\ell$ \ $n'\ell'$	2p	3p	4p
0	2p		0.04116	0.000531
	3p			0.002776
2	2p		0.04491	0.000585
	3p			0.003628
1	3d	0.02217	0.3868	
3	3d	0.01290	0.2290	

$R^k(n_1\ell_1,n_2\ell_2;n_3\ell_3,n_4\ell_4)$

k	$n_1\ell_1$	$n_2\ell_2$	$n_3\ell_3$	$n_4\ell_4$	R^k
2	3s	3d	3d	3d	0.2395
2	3s	3p	3d	3p	0.3731
1	3s	3p	3p	3d	0.5084
0	3s	3s	3s	4s	0.06543
0	3s	4s	4s	4s	0.00291
0	3s	3p	4s	3p	0.05389
1	3s	3p	3p	4s	0.01773

Parameters Used - Orbital Exponents and Nuclear Charges

1s-3d Integrals Sulphur $3sp^3d^2$ Multiconfigurational Valence State

1s	15.5409						
2s	5.3144	2p	5.9468				
3s	2.198	3p	1.926	3d	α	0.860	
					β	2.048	
					λ	0.337	Z = 16

4s Integrals Phosphorus $3sp^3 4s$ Multiconfigurational Valence State

1s	14.5578			
2s	4.9125	2p	5.4500	
3s	1.992	3p	1.697	
4s	0.735			Z = 15

4p Integrals Chlorine $3s^2p^4 4p$ Average Energy

1s	16.5239			
2s	5.7152	2p	6.4844	
3s	2.426	3p	2.140	
		4p	0.601	Z = 17

APPENDIX 3

THE CALCULATION OF MOLECULAR INTEGRALS

A. Overlap Integrals

The overlap integral S for a pair of overlapping atomic orbitals χ_a and χ_b of a pair of atoms a and b is defined for a given internuclear distance R by

$$S(\chi_a,\chi_b,R) = \int \chi_a \chi_b \, d\tau \quad , \tag{A3.1}$$

where

$$\chi_a(n\ell m) = \sum_{i=\ell+1}^{n} c_{in\ell}\, r^{i-1}\, e^{-\alpha_{i\ell} r_a}\, Y_{\ell m}(\theta_a,\phi) \quad . \tag{A3.2}$$

These integrals were evaluated by the method of Mulliken, Riecke, Orloff and Orloff.[139] For the integration the polar coordinates of the two atoms are transformed into elliptical coordinates

$$\xi = \frac{r_a + r_b}{R} \; , \quad \eta = \frac{r_a - r_b}{r_a + r_b} \; , \quad \phi = \phi_a = \phi_b \; ,$$

$$\cos\theta_a = \frac{1+\xi\eta}{\xi+\eta} \; , \quad \cos\theta_b = \frac{1-\xi\eta}{\xi-\eta} \quad . \tag{A3.3}$$

The integration over ξ ranges from 1 to ∞, over η from -1 to 1 and over ϕ from 0 to 2π. The element of volume is $(R/2)^3(\xi^2-\eta^2)d\xi d\eta d\phi$. Overlap integrals are usually tabulated in terms of the variables p and t, introduced by Mulliken et al, defined by

$$p = R/2\,(\alpha_a + \alpha_b) \; , \quad t = \frac{\alpha_a - \alpha_b}{\alpha_a + \alpha_b} \quad . \tag{A3.4}$$

There are rules to decide which atom is designated a or b.

On substituting one can obtain a set of master formulae for the overlap integrals between unnormalised Slater orbitals. For example,

$$S(ns_a, np_{\sigma_b}; p, t) = \int_1^{\infty}\int_{-1}^{1} (\xi+\eta)^{n_a-1} (\xi-\eta)^{n_b-2} (1-\xi\eta)(\xi^2-\eta^2) e^{-p(\xi+\eta t)} d\eta d\xi \quad . \tag{A3.5}$$

These integrals were expanded in terms of Rosen's A_k and B_k functions[140] defined by

$$A_k(p) = \int_1^{\infty} \xi^k e^{-p\xi} d\xi \quad , \tag{A3.6}$$

$$B_k(pt) = \int_{-1}^{1} \eta^k e^{-pt\eta} d\eta \quad . \tag{A3.7}$$

These functions were computed using the recursive formulae:

$$\begin{aligned} A_k(\alpha) &= 1/\alpha \; [e^{-\alpha} + kA_{k-1}(\alpha)] \quad , \\ A_o(\alpha) &= 1/\alpha \; e^{-\alpha} \\ B_k(\alpha) &= 1/\alpha \; [(-1)^k e - e^{-\alpha} + kB_{k-1}(\alpha)] \\ B_o(\alpha) &= 1/\alpha \; [e^{\alpha} - e^{-\alpha}] \quad . \end{aligned} \tag{A3.8}$$

In Table A3.1 the expansion of a number of overlap integrals between unnormalised Slater orbitals are given in terms of Slaters A_k and B_k functions. The argument of A_k is p and the argument of B_k is pt.

Tables of numerical values and various formulae may be found in the paper by Mulliken et al.[139] and also in papers by Craig et al.,[8] Jaffé,[141] Jaffé and Doak,[142] Roberts and Jaffé,[143] Liefer, Cotton and Letto[144] and Cotton.[119]

Table A3.1

Overlap Integrals

$n\ell m_a$	$n\ell m_b$	$S(n\ell m_a, n\ell m_b)$
1s	1s	$1/2(R/2)^3[A_2B_o - A_oB_2]$
1s	2s	$1/2(R/2)^4[A_3B_o - A_2B_1 - A_1B_2 + A_oB_3]$
1s	$2p_\sigma$	$\sqrt{3}/2\ (R/2)^4[-A_3B_1 + A_2B_1 + A_1B_3 - A_oB_2]$
1s	3s	$1/2(R/2)^5[A_4B_o - 2A_3B_1 + 2A_1B_3 - A_oB_4]$
1s	3p	$\sqrt{3}/2\ (R/2)^5[-A_4B_1 + A_3B_2 + A_3B_o + A_2B_3 - A_2B_1 - A_1B_4 - A_1B_2 + A_oB_3]$
1s	$3d_{z^2}$	$\sqrt{5}/4\ (R/2)^5[3A_4B_2 - A_4B_o - 4A_3B_1 - 3A_2B_4 + 3A_2B_o + 4A_1B_3 + A_oB_4 - 3A_oB_2]$
1s	4s	$1/2(R/2)^6[A_5B_o - 3A_4B_1 + 2A_3B_2 + 2A_2B_3 - 3A_1B_4 + A_oB_5]$
1s	$4p_\sigma$	$\sqrt{3}/2\ (R/2)^6[-A_5B_1 + 2A_4B_2 + A_4B_o - 2A_3B_1 - 2A_2B_4 + A_1B_5 + 2A_1B_3 - A_oB_4]$
2s	2s	$1/2(R/2)^5[A_4B_o - 2A_2B_2 + A_oB_4]$
2s	$2p_\sigma$	$\sqrt{3}/2\ (R/2)^5[-A_4B_1 - A_3B_2 + A_3B_o + A_2B_3 + A_2B_1 + A_1B_4 - A_1B_2 - A_oB_3]$

/.....

/.....

Table A3.1 (continued)

$n\ell m_a$	$n\ell m_b$	$S(n\ell m_a, n\ell m_b)$
2s	3s	$1/2(R/2)^6[A_5B_o - A_4B_1 - 2A_3B_2 + 2A_2B_3 + A_1B_4 - A_oB_5]$
2s	$3p_\sigma$	$\sqrt{3}/2\ (R/2)^6[-A_5B_1 + A_4B_o + 2A_3B_3 - 2A_2B_2 - A_1B_5 + A_oB_4]$
2s	$3d_{z^2}$	$\sqrt{5}/4\ (R/2)^6[3A_5B_2 - A_5B_o + 3A_4B_3 - 5A_4B_1 - 3A_3B_4 - 4A_3B_2 + + 3A_3B_o - 3A_2B_5 + 4A_2B_3 + 3A_2B_1 + 5A_1B_4 - 3A_1B_2 + A_oB_5 - - 3A_oB_3]$
2s	4s	$1/2(R/2)^7[A_6B_o - 2A_5B_1 - A_4B_2 + 4A_3B_3 - A_2B_4 - 2A_1B_5 + + A_oB_6]$
2s	$4p_\sigma$	$\sqrt{3}/2\ (R/2)^7[-A_6B_1 + A_5B_2 + A_5B_o + 2A_4B_3 - A_4B_1 - 2A_3B_4 - - 2A_3B_2 - A_2B_5 + 2A_2B_3 + A_1B_4 - A_oB_5 + A_1B_6]$
$2p_\sigma$	2s	$\sqrt{3}/2\ (R/2)^5[A_4B_1 - A_3B_2 + A_3B_o - A_2B_3 - A_2B_1 + A_1B_4 - - A_1B_2 + A_oB_3]$
$2p_\sigma$	$2p_\sigma$	$3/2(R/2)^5[-A_4B_2 + A_2B_4 + A_2B_o - A_oB_2]$
$2p_\sigma$	3s	$\sqrt{3}/2\ (R/2)^6[A_5B_1 - 2A_4B_2 + A_4B_o - 2A_3B_1 + 2A_2B_4 + 2A_1B_3 - - A_1B_5 - A_oB_4]$

/.....

/..... Table A3.1 (continued)

$n\ell m_a$	$n\ell m_b$	$S(n\ell m_a, n\ell m_b)$
$2p_{\sigma}$	$3p_{\sigma}$	$3/2(R/2)^6[-A_5B_2 + A_4B_3 + A_3B_4 + A_3B_o - A_2B_5 - A_2B_1 - A_1B_2 +$ $+ A_oB_3]$
$2p_{\sigma}$	$3d_{z^2}$	$\sqrt{15/4}\ (R/2)^6[3A_5B_3 - A_5B_1 - A_4B_2 - A_4B_o - 3A_3B_5 - A_3B_1 +$ $+ A_2B_4 + 3A_2B_o + A_1B_5 + A_1B_3 + A_oB_4 - 3A_oB_2]$
$2p_{\sigma}$	$4s$	$\sqrt{3/2}\ (R/2)^7[A_6B_1 - 3A_5B_2 + A_5B_o + 2A_4B_3 - 3A_4B_1 + 2A_3B_4 +$ $+ 2A_3B_2 - 3A_2B_5 + 2A_2B_3 + A_1B_6 - 3A_1B_4 + A_oB_5]$
$2p_{\sigma}$	$4p_{\sigma}$	$3/2(R/2)^7[-A_6B_2 + 2A_5B_3 + A_4B_o - 2A_3B_5 - 2A_3B_1 + A_2B_6 +$ $+ 2A_1B_3 - A_oB_4]$
$2p_{\pi}$	$2p_{\pi}$	$3/4(R/2)^5[-A_4B_2 + A_4B_o + A_2B_4 - A_2B_o - A_oB_4 + A_oB_2]$
$2p_{\pi}$	$3p_{\pi}$	$3/4(R/2)^6[-A_5B_2 + A_5B_o + A_4B_3 - A_4B_1 + A_3B_4 - A_3B_o - A_2B_5 +$ $+ A_2B_1 - A_1B_4 + A_1B_2 + A_oB_5 - A_oB_3]$
$2p_{\pi}$	$4p_{\pi}$	$3/4(R/2)^7[-A_6B_2 + A_6B_o + 2A_5B_3 - 2A_5B_1 + A_4B_2 - A_4B_o -$ $- 2A_3B_5 + 2A_3B_1 + A_2B_6 - A_2B_4 + 2A_1B_5 - 2A_1B_3 - A_oB_6 + A_oB_4$

B. Nuclear Attraction Integrals

The nuclear attraction integral is the one electron two centre integral

$$\int \chi_a \left| \frac{-2Z_b}{r_b} \right| \chi_a \, d\tau \quad , \tag{A3.9}$$

where χ_a is defined as in A3.2. It is a measure of the attraction of the electrons centred on one atom A to the nucleus of another atom B of charge Z_b. It is calculated in manner analogous to that used for overlap integrals. The parameter p becomes $R/2(\alpha+\alpha')$ and t is identically equal to unity. Master formulae similar to A3.5 can be obtained, for example,

$$\left\langle (nd_\sigma)_a \left| \frac{-2Z_b}{r_b} \right| (n'd_\sigma)_a \right\rangle = -\,5/4\; Z_u (R/2)^{n+n'} \int_1^\infty \int_{-1}^{1} (\xi+\eta)^{n+n'-5} \times$$

$$\times\, (3\xi^2\eta^2 + 4\xi\eta - \xi^2 - \eta^2 + 3)^2\, e^{-p(\xi+\eta)}\, d\eta\, d\xi \quad . \tag{A3.10}$$

These integrals are expanded in terms of Rosen's A_k and B_k functions. In Table A3.2 the expansion of a number of nuclear attraction integrals involving unnormalised Slater orbitals are given. The arguments of A_k and B_k are both $R/2(\alpha+\alpha')$. Other methods of calculating nuclear attraction integrals include that in the paper by C.C.J. Roothaan and the papers following it from the Chicago group.[145-149]

Table A3.2

Nuclear Attraction Integrals

$n\ell m_a$	$n\ell m_a{}'$	$\langle n\ell m_a \left\| \frac{-2Z_b}{r_b} \right\| n\ell m'_a \rangle$
1s	1s	$-Z_b(R/2)^2[A_1B_o + A_oB_1]$
1s	2s	$-Z_b(R/2)^3[A_2B_o + 2A_1B_1 + A_oB_2]$
1s 2s	3s 2s	$-Z_b(R/2)^4[A_3B_o + 3A_2B_1 + 3A_1B_2 + A_oB_3]$
1s 2s	4s 3s	$-Z_b(R/2)^5[A_4B_o + 4A_3B_1 + 6A_2B_2 + 4A_1B_3 + A_oB_4]$
2s 3s	4s 3s	$-Z_b(R/2)^6[A_5B_o + 5A_4B_1 + 10A_3B_2 + 10A_2B_3 + 5A_1B_4 + A_oB_5]$
3s	4s	$-Z_b(R/2)^7[A_6B_o + 6A_5B_1 + 15A_4B_2 + 20A_3B_3 + 15A_2B_4 + 6A_1B_5 +$ $+ A_oB_6]$
4s	4s	$-Z_b(R/2)^8[A_7B_o + 7A_6B_1 + 21A_5B_2 + 35A_4B_3 + 35A_3B_4 + 21A_2B_5 +$ $+ 7A_1B_6 + A_oB_7]$
$2p_\sigma$	$2p_\sigma$	$-3Z_b(R/2)^4[A_3B_2 + A_2B_3 + 2A_2B_1 + 2A_1B_2 + A_1B_o + A_oB_1]$

/.....

/.... Table A3.2 (Continued)

$n\ell m_a$	$n\ell m_a{}'$	$\langle n\ell m_a \| \frac{-2Z_b}{r_b} \| n\ell m'_a \rangle$
$2p_\sigma$	$3p_\sigma$	$-3Z_b(R/2)^5[A_4B_2 + 2A_3B_3 + 2A_3B_1 + A_2B_4 + 4A_2B_2 + A_2B_o + 2A_1B_3 + 2A_1B_1 + A_oB_2]$
$3p_\sigma$	$3p_\sigma$	$-3Z_b(R/2)^6[A_5B_2 + 3A_4B_3 + 2A_4B_1 + 3A_3B_4 + 6A_3B_2 + A_3B_o + A_2B_5 + 6A_2B_3 + 3A_2B_1 + 2A_1B_4 + 3A_1B_2 + A_oB_3]$
$2p_\pi$	$2p_\pi$	$-3/2\ Z_b(R/2)^4[-A_3B_2 + A_3B_o - A_2B_3 + A_2B_1 + A_2B_2 - A_1B_o + A_oB_3 - A_oB_1]$
$2p_\pi$	$3p_\pi$	$-3/2\ Z_b(R/2)^5[-A_4B_2 + A_4B_o - 2A_3B_3 + 2A_3B_1 - A_2B_4 + 2A_2B_2 - A_2B_o + 2A_1B_3 - 2A_1B_1 + A_oB_4 - A_oB_2]$
$3p_\pi$	$3p_\pi$	$-3/2\ Z_b(R/2)^6[-A_5B_2 + A_5B_o - 3A_4B_3 + 3A_4B_1 - 3A_3B_4 + 4A_3B_2 - A_3B_o - A_2B_5 + 4A_2B_3 - 3A_2B_1 + 3A_1B_4 - 3A_1B_2 + A_oB_5 - A_oB_3]$
$3d_{z^2}$	$3d_{z^2}$	$-5/4\ Z_b(R/2)^6[9A_5B_4 - 6A_5B_2 + A_5B_o + 9A_4B_5 + 18A_4B_3 - 7A_4B_1 + 18A_3B_4 + 28A_3B_2 - 6A_3B_o - 6A_2B_5 + 28A_2B_3 + 18A_2B_1 - 7A_1B_4 + 18A_1B_2 + 9A_1B_o + A_oB_5 - 6A_oB_3 + 9A_oB_1]$
$3d_{x^2-y^2}$	$3d_{x^2-y^2}$	$-15/8\ Z_b(R/2)^6[A_5B_4 - 2A_5B_2 + A_5B_o + A_4B_5 - 2A_4B_3 + A_4B_1 - 2A_3B_4 + 4A_3B_2 - 2A_3B_o - 2A_2B_5 + 4A_2B_3 - 2A_2B_1 + A_1B_4 - 2A_1B_2 + A_1B_o + A_oB_5 - 2A_oB_3 + A_oB_1]$

C. Coulomb Integrals

The Coulomb integral is the two centre two electron integral:

$$\iint \chi_a(1)\chi_B(2)\, 2/r_{12}\, \chi_A'(1)\chi_B'(2)\,d\tau_1 d\tau_2 \quad . \tag{A3.11}$$

Its evaluation involves two volume integrations. The integration over the coordinates of one electron, say that designated 2, amounts to calculating the potential of the corresponding charge distribution

$$U_{BB'} = \int \chi_B(2)\chi_B'(2)\, 2/r_{12}\, d\tau_2 \quad , \tag{A3.12}$$

where $1/r_{12}$ is expanded in the series

$$1/r_{12} = \sum_{k=0}^{\infty} \sum_{m=-k}^{k} \frac{(k-|m|)!}{(k+|m|)!} \frac{r_<^k}{r_>^{k+1}} P_k^{|m|}(\cos\theta_1) P_k^{|m|}(\cos\theta_2) \exp(im(\phi_1-\phi_2))$$

$$\{r_<, r_>\} \equiv \{r_1, r_2\} \quad . \tag{A3.13}$$

Analytic expressions for the potentials obtained on performing this integration for the charge distributions used in this work are given in Table 3.3. They are functions of the coordinates of the other electron, 1. The charge distribution came from unnormalised wavefunctions. Two useful expressions used in the analytic integration were

$$\int_0^{r_1} r_2^n e^{-\alpha r_2} dr_2 = \frac{n!}{\alpha^{n+1}} - \sum_{i=1}^{n+1} \frac{r_1^{n+1-i}}{\alpha^i} \frac{n!}{(n+1-i)!} e^{-\alpha r_1} \tag{A3.14}$$

$$\int_{r_1}^{\infty} r_2^n e^{-\alpha r_2} dr_2 = \sum_{i=1}^{n+1} \frac{r_1^{n+1-i}}{\alpha^i} \frac{n!}{(n+1-i)!} e^{-\alpha r_1} \quad . \tag{A3.15}$$

Table A3.3

Potentials Due to Charge Distributions

$n\ell$	$n'\ell'$	$U_{n\ell-n'\ell'}$
1s	1s	$\frac{4}{r_1} \cdot \frac{1}{(2\alpha_{1s})^3} [1 - e^{-2\alpha_{1s} r_1}] - \frac{2e^{-2\alpha_{1s} r_1}}{(2\alpha_{1s})^2}$
1s	2s	$\frac{12}{r_1} \cdot \frac{1}{(\alpha_{1s}+\alpha_{2s})^4} [1 - e^{-[\alpha_{1s}+\alpha_{2s}] r_1}] - \frac{2r_1 e^{-[\alpha_{1s}+\alpha_{2s}] r_1}}{(\alpha_{1s}+\alpha_{2s})^2} - \frac{8e^{-[\alpha_{1s}+\alpha_{2s}] r_1}}{(\alpha_{1s}+\alpha_{2s})^3}$
2s	2s	$\frac{48}{r_1} \cdot \frac{1}{(2\alpha_{2s})^5} [1-e^{2\alpha_{2s} r_1}] - \frac{2r_1^2 e^{-2\alpha_{2s} r_1}}{(2\alpha_{2s})^2} - \frac{12r_1 e^{-2\alpha_{2s} r_1}}{(2\alpha_{2s})^3} - \frac{36e^{-2\alpha_{2s} r_1}}{(2\alpha_{2s})^4}$

/.....

/.....

Table A3.3 (continued)

$n\ell$	$n'\ell'$	$U_{n\ell-n'\ell'}$
$2p_\sigma$	$2p_\sigma$	$\displaystyle \frac{48}{r_1}\cdot\frac{1}{(2\alpha_{2p})^5}[1-e^{-2\alpha_{2p}r_1}]-\frac{2r_1^2e^{-2\alpha_{2p}r_1}}{(2\alpha_{2p})^2}-\frac{12r_1e^{-2\alpha_{2p}r_1}}{(2\alpha_{2p})^3}-\frac{36e^{-2\alpha_{2p}r_1}}{(2\alpha_{2p})^4}+[3\cos^2\theta_1-1]\Big[\frac{1}{r_1^3}\,\frac{288}{(2\alpha_{2p})^7}[1-e^{2\alpha_{2p}r_1}]-\frac{2r_1^2e^{-2\alpha_{2p}r_1}}{(2\alpha_{2p})^2}-\frac{12r_1e^{-2\alpha_{2p}r_1}}{(2\alpha_{2p})^3}-\frac{48e^{-2\alpha_{2p}r_1}}{(2\alpha_{2p})^4}-\frac{144e^{-2\alpha_{2p}r_1}}{r_1(2\alpha_{2p})^5}-\frac{288e^{-2\alpha_{2p}r_1}}{r_1^2(2\alpha_{2p})^6}\Big]$
$2p_\pi$	$2p_\pi$	$\displaystyle \frac{48}{r_1}\cdot\frac{1}{(2\alpha_{2p})^5}[1-e^{-2\alpha_{2p}r_1}]-\frac{2r_1^2e^{-2\alpha_{2p}r_1}}{(2\alpha_{2p})^2}-\frac{12r_1e^{-2\alpha_{2p}r_1}}{(2\alpha_{2p})^3}-\frac{36e^{-2\alpha_{2p}}}{(2\alpha_{2p})^4}+[3\sin^2\theta_1\cos 2\phi-[3\cos^2\theta-1]]\Big\{\frac{144}{r_1^3}\times\frac{1}{(2\alpha_{2p})^7}[1-e^{-2\alpha_{2p}r_1}]-e^{-2\alpha_{2p}r_1}\Big[\frac{r_1^2}{(2\alpha_{2p})^2}+\frac{6r_1}{(2\alpha_{2p})^3}+\frac{24}{(2\alpha_{2p})^4}+\frac{72/r_1}{(2\alpha_{2p})^5}+\frac{144/r_1^2}{(2\alpha_{2p})^6}\Big]\Big]\Big\}$

/.....

/.....   Table A3.3 (continued)

$n\ell$	$n'\ell'$	$U_{n\ell-n'\ell'}$
$2p_{\pi}$	$2p_{\bar{\pi}}$	$\frac{48}{r_1} \cdot \frac{1}{(2\alpha_{2p})^5}[1 - e^{-2\alpha_{2p} r_1}] - \frac{2r_1^2 e^{-2\alpha_{2p} r_1}}{(2\alpha_{2p})^2} - \frac{12 r_1 e^{-2\alpha_{2p} r_1}}{(2\alpha_{2p})^3} -$ $- \frac{36 e^{-2\alpha_{2p}}}{(2\alpha_{2p})^4} - [3 \sin^2\theta \; \cos^2\phi - [3 \cos^2\theta - 1]] \left\{ \frac{144}{r_1^3} \times \right.$ $\times \frac{1}{(2\alpha_{2p})^7} [1 - e^{-2\alpha_{2p} r_1}] - e^{-2\alpha_{2p} r_1} \left[\frac{r_1^2}{(2\alpha_{2p})^2} + \frac{6 r_1}{(2\alpha_{2p})^3} + \right.$ $\left. \left. + \frac{24}{(2\alpha_{2p})^4} + \frac{72/r_1}{(2\alpha_{2p})^5} + \frac{144/r_1^2}{(2\alpha_{2p})^6} \right] \right\}$
$2p_{\sigma}$	$2p_{\pi}$	$6/5 \sin\theta \; \cos\theta \; \cos\phi \left[\frac{720}{r_1^3} \frac{1 - e^{-2\alpha_{2p} r_1}}{(2\alpha_{2p})^7} \right] - e^{-2\alpha_{2p} r_1} \times$ $\times \left[\frac{5 r_1^2}{(2\alpha_{2p})^2} + \frac{30 r_1}{(2\alpha_{2p})^3} + \frac{120}{(2\alpha_{2p})^4} + \frac{360/r_1}{(2\alpha_{2p})^5} + \frac{720/r_1^2}{(2\alpha_{2p})^6} \right]$

For the integration over the coordinates of the other electron, designated 1, two methods were used. Those integrals involving only electrons in a 2p orbital and those involving electrons in orbitals with an n quantum number 3 or 4 were evaluated using Gaussian quadrature. This method was proposed by Magnusson and Zauli.[150] 1152 points were used for the sub-integral involving the 2p orbitals only whilst 512 points were used in the other case. Elliptical coordinates were used. The two ranges of integration used in the zeta integration varied from integral to integral. For example for the 2p only sub-integrals the ranges used were 1 to 1.6 and 1.6 to 6 whilst for those involving the 4s(1)4s(1) distribution the ranges were 1 to 2.75 and 2.75 to 1.75. The optimum ranges for each sub-integral were determined. The other method, used for all the other integrals, was an analytic integration involving the expansion of the integral in terms of Rosen's A_k and B_k functions. For example, the sub-integral

$$\begin{aligned}\langle 1s,2p_\sigma;2s,\,3p_\sigma\rangle = {} & \frac{18(R/2)^5}{\alpha^4}\,[A_4'B_2' - 2A_3'B_3' - 2A_3'B_1' + A_2'B_4' + \\ & + 4A_2'B_2' + A_2'B_0' - 2A_1'B_3' - 2A_1'B_1' + A_0'B_2'] - \\ & - \frac{18(R/2)^5}{\alpha^4}\,[A_4B_2 - 2A_3B_3 - 2A_3B_1 + A_2B_4 + 4A_2B_2 + \\ & + A_2B_0 - 2A_1B_3 - 2A_1B_1 + A_0B_2] - \frac{12(R/2)^6}{\alpha^3}\,[A_5B_2 - \\ & - A_4B_3 - 2A_4B_1 - A_3B_4 + 2A_3B_2 + A_3B_0 + A_2B_5 + 2A_2B_3 - \\ & - A_2B_1 - 2A_1B_4 - A_1B_2 + A_0B_3] - \frac{3(R/2)^7}{\alpha^2}\,[A_6B_2 - \\ & - 2A_5B_1 - 2A_4B_4 + A_4B_0 + 4A_3B_3 + A_2B_6 - 2A_2B_2 - \\ & - 2A_1B_5 + A_0B_4]\,. \qquad \text{(A3.16)}\end{aligned}$$

$\alpha = \alpha_{1s(2)} + \alpha_{2s(2)}$ $\beta = \alpha_{2p(1)} + \alpha_{3p(1)}$

The argument of A_k' is R/2 β and of B_k' is -R/2 β. The argument of A_k is R/2 $(\alpha+\beta)$ and of B_k is R/2 $(\alpha-\beta)$. The radial parts of the wavefunctions involved were unnormalised and non-orthogonal. Similar formulae for all sub-integrals involving at least one charge distribution of S symmetry and involving 1s, 2s or 2p electrons on one atom and 1s-42 electrons on the other have been calculated. These sub-integrals, computed by either method, were combined using the appropriate coefficients to obtain the required integral involving normalised, orthogonal hydrogen-like orbitals. Of the two methods the Gaussian quadrature method is more appropriate for integrals involving higher n quantum numbers or those involving no charge distribution of S symmetry whilst for low n quantum numbers, say n = 1, 2, it is more efficient to use the method involving Rosen's A_k and B_k functions as less calculation is involved. There is considerable literature on the subject of the calculation of coulomb integrals. The two methods most commonly used are that put forward by Roothaan[145] and developed by the Chicago school, to which my methods are related and the Barnett-Coulson zeta method.[151,152] The former is far simpler in its theory. There are also other approaches, e.g., those involving the use of the Fourier transform convolution theorem.[153-155]

D. Exchange Integrals

Two centre exchange integrals were calculated using a modified form of a programme received from Quantum Chemistry Exchange[156] written by F. Bernardi and G. Paiusco - QCPE 106. Their method is based on that first put forward by Rüdenberg.[157] The basic theory involved in the calculation of these integrals is described in papers by Rüdenberg,[157] Wahl, Cade and Roothaan[148] and Bernardi and Paiusco[158] to which the reader is referred. Bernardi and Paiusco's method differs from the others in that they use Gaussian quadrature to evaluate the integrals $B_q^{m\ell}(\beta)$ and $\phi_{nn'}^{m\ell}(\alpha,\alpha')$ defined by

$$B_q^{m\ell}(\beta) = \sqrt{\frac{2\ell+1}{2}\,\frac{(\ell-m)!}{(\ell+m)!}}\int_{-1}^{1} P_\ell^{m}(\nu)(1-\nu^2)^{m/2} e^{\beta\nu}\nu^q d\nu \quad , \qquad \text{(A3.17)}$$

$$\phi^m_{nn'}(\alpha,\alpha') = (-1)^m\,\frac{(\ell-m)!}{(\ell+m)!}\int_1^\infty (\mu^2-1)^{m/2} Q_\ell^{m}(\mu_1)\{e^{-\alpha\mu_1}\mu_1^{n}\int_1^{\mu_1} d\mu_2(\mu_2^{2}-1)^{m/2}\times$$

$$\times P_\ell^{m}(\mu_2)e^{-\alpha'\mu_2}\mu_2^{n'} + e^{-\alpha'\mu_1}\mu_1^{n'}\int_1^{\mu_1} d\mu_2(\mu_2^{2}-1)^{m/2}P_\ell^{m}(\mu_2)\times$$

$$\times e^{-\alpha\mu_2}\mu_2^{n}\}d\mu_1 \quad . \qquad \text{(A3.18)}$$

Rüdenberg suggested the use of various recurrence relationships to evaluate these integrals. Wahl, Cade and Roothaan used Simpson's rule for numerical integration to evaluate them. The Gaussian method is by far the most efficient.

When $\ell = 0$ an alternative form for $\phi^m_{nn'}(\alpha,\alpha')$ not involving Legendre functions of the second kind obtained by partial integration of A3.18 is used,

$$\phi^{m\ell}_{nn'}(\alpha,\alpha') = \int_1^\infty \frac{d\mu_1}{\mu_1^2-1}\left\{\frac{1}{P_\ell^m(\mu_1)}\int_1^{\mu_1} d\mu_2 P_\ell^m(\mu_2)(\mu_2^2-1)^{m/2}e^{-\alpha\mu_2}\mu_2^n\right\}\times$$

$$\times\left\{\frac{1}{P_\ell^m(\mu_1)}\int_1^{\mu_1} d\mu_2 P_\ell^m(\mu_2)(\mu_2^2-1)^{m/2}e^{-\alpha'\mu_2}\mu_2^{n'}\right\} \quad . \qquad (A3.19)$$

The associated Legendre functions $P_\ell^m(x)$ required are calculated using a polynomial form for $\ell = 0$ to $\ell = 10$ and for larger values of ℓ by recurrence relationships. For the integrals encountered in this work $m = 0, 1, 2$ and 3.

The coefficients ω_{nq} used were taken from Table II of Rüdenberg's paper. Those required which did not appear there were easily calculated from the expansion of the appropriate product of wavefunctions in elliptical coordinates. These are used in evaluating the function

$$\omega_n^\ell(\beta) = \sum_{q=0}^{n_a+n_b-m} \omega_{nq} B_q^{m\ell}(\beta) \quad . \qquad (A3.20)$$

The two centre exchange integrals involving Slater-type orbitals are evaluated according to equation 1.16 of Rüdenberg's paper. [Equation 6 of Bernardi and Paiusco's paper.] It is a simple matter to combine these integrals involving Slater-type orbitals to give to appropriate integral involving hydrogen-like orbitals.

APPENDIX 4

TYPICAL VALUES OF MOLECULAR INTEGRALS

Parameters used:

$\alpha_{1s} = 15.5409$ $\alpha_{2s} = 5.3144$ $\alpha_{2p} = 5.9468$

$\alpha_{3s} = 2.064$ $\alpha_{3p} = 1.708$ $\alpha_{3d} = 1.272$

$Z_A = 16$

$\beta_{1s} = 8.6501$ $\beta_{2s} = 2.5639$ $\beta_{2p} = 2.5500$

$Z_B = 9$

Internuclear Distance = 2.96 a.u.

Nuclear Attraction Integrals $\left\langle \chi_a \middle| \frac{-2Z_b}{r_b} \middle| \chi_a \right\rangle$

$n\ell$	Nuclear Attraction Integrals
1s	-6.081081
2s	-6.081081
$2p_\sigma$	-6.139959
$2p_\pi$	-6.051642
3s	-6.051191
$3p_\sigma$	-7.100051
$3p_\pi$	-5.411123
$3d_{z^2}$	-7.219426
$3d_{x^2-y^2}$	-4.786765

Coulomb Integrals $J(n\ell m, n'\ell'm')$

$n\ell_A$ \ $n\ell_B$	1s	2s	$2p_\sigma$	$2p_\pi$
1s	0.675676	0.675635	0.711128	0.657887
2s	0.675676	0.675584	0.710981	0.657886
$2p_\sigma$	0.682218	0.682103	0.719509	0.663391
$2p_\pi$	0.672405	0.672350	0.706783	0.655386
3s	0.672192	0.664867	0.690251	0.652490
$3p_\sigma$	0.787917	0.756144	0.785928	0.742839
$3p_\pi$	0.601235	0.600173	0.614306	0.597452
$3d_{z^2}$	0.799538	0.734676	0.752042	0.730219
$3d_{x^2-y^2}$	0.531863	0.531624	0.538348	0.528271

$n\ell_A$ \ $n\ell_B$	$2p_\pi$
$2p_{\bar{\pi}}$	0.654871
$3p_{\bar{\pi}}$	0.588855

$$\langle 2p_\sigma(1)2p_\pi(2)\ ;\ 2p_\pi(1)2p_\sigma(2)\rangle = 0.001019$$

Exchange Integrals $\langle n\ell m_A(1)n'\ell'm'_B(2)\ ;\ n'\ell'm'_B(1)n''\ell''m''_A(2)\rangle$

1s	$3d_{z^2}$	$3d_{z^2}$	1s	0.01274250
2s	$3d_{z^2}$	$3d_{z^2}$	2s	0.00389378
$2p_\sigma$	$3d_{z^2}$	$3d_{z^2}$	$2p_\sigma$	0.05283760
$2p_\pi$	$3d_{z^2}$	$3d_{z^2}$	$2p_\pi$	0.03136002
1s	$3d_{x^2-y^2}$	$3d_{x^2-y^2}$	1s	0.00000005
2s	$3d_{x^2-y^2}$	$3d_{x^2-y^2}$	2s	0.00001405
$2p_\sigma$	$3d_{x^2-y^2}$	$3d_{x^2-y^2}$	$2p_\sigma$	0.00033235
$2p_\pi$	$3d_{x^2-y^2}$	$3d_{x^2-y^2}$	$2p_\pi$	0.00053060
3s	$2p_\sigma$	$2p_\sigma$	$3d_{z^2}$	0.00183350
3p	$2p_\sigma$	$2p_\sigma$	$3d_{z^2}$	0.00222421

APPENDIX 5

EXPANSION OF THE ATOMIC INTEGRALS $J(\phi_1,\phi_2)$, $K(\phi_1,\phi_2)$ FOR A GENERAL FORM OF THE HYBRID ORBITAL FUNCTIONS IN TERMS OF SLATER'S F^k, G^k AND R^k INTEGRALS

$$\phi_1 = a\ 3s + b\ 3d_{z^2} + c\ 3d_{x^2-y^2} + d\ 3p_z + e\ 3p_x + f\ 3p_y$$

$$_2 = A\ 3s + B\ 3d_{z^2} + C\ 3d_{x^2-y^2} + D\ 3p_z + E\ 3p_x + F\ 3p_y$$

$$\begin{aligned}
J(\phi_1,\phi_2) = {} & a^2A^2 && F^o(3s,3s)\\
& + [a^2D^2 + A^2d^2 + a^2E^2 + A^2e^2 + a^2F^2 + A^2f^2] && F^o(3s,3p)\\
& + 4/3[adAD + aeAE + afAF] && G^1(3s,3p)\\
& + [a^2B^2 + A^2b^2 + a^2C^2 + A^2c^2] && F^o(3s,3d)\\
& + 4/5[abAB + acAC] && G^2(3s,3d)\\
& + [d^2D^2 + e^2E^2 + f^2F^2 + d^2E^2 + e^2D^2 + d^2F^2 + \\
& + f^2D^2 + e^2F^2 + f^2E^2] && F^o(3p,3p)\\
& + 1/25\ [4d^2D^2 + 4e^2E^2 + 4f^2F^2 - 2d^2E^2 - \\
& - 2D^2e^2 - 2d^2F^2 - 2D^2f^2 - 2e^2F^2 - 2E^2f^2 + \\
& + 12deDE + 12dfDF + 12efEF] && F^2(3p,3p)\\
& +[b^2D^2 + B^2d^2 + b^2E^2 + B^2e^2 + b^2F^2 + B^2f^2 + \\
& + c^2D^2 + C^2d^2 + c^2E^2 + C^2e^2 + c^2F^2 + C^2f^2] && F^o(3p,3d)\\
& + 1/35[4b^2D^2 + 4B^2d^2 - 2b^2E^2 - 2B^2e^2 - 2b^2F^2 - \\
& - 2B^2f^2 - 4c^2D^2 - 4C^2d^2 + 2c^2E^2 + 2C^2e^2 + 2c^2F^2 + \\
& + 2C^2f^2 - 4\sqrt{3}[bcE^2 + BCe^2 + bcF^2 + BCf^2]] && F^2(3p,3d)\\
& + 1/15[16bdBD + 4beBE + 4bfBF + 12ceCE + \\
& + 12cfCF - 4\sqrt{3}\ [beCE + bfCF + BEce + BFcf]] && G^1(3p,3d)
\end{aligned}$$

$$
\begin{aligned}
= &+ 1/245\ [108bdBD + 72beBE + 72bfBF + 60cdCD + \\
&+ 96ceCE + 96cfCF - 12\sqrt{3}\ [beCE + bfCF + ceBE + \\
&+ cfBF]] && G^{3}(3p,3d) \\
&+ [b^{2}B^{2} + c^{2}C^{2} + b^{2}C^{2} + c^{2}B^{2}] && F^{0}(3d,3d) \\
&+ 1/49\ [4b^{2}B^{2} + 4c^{2}C^{2} - 4b^{2}C^{2} - 4c^{2}B^{2} + \\
&+ 16bcBC] && F^{2}(3d,3d) \\
&+ 1/441\ [36b^{2}B^{2} + 36c^{2}C^{2} + 6b^{2}C^{2} + 6B^{2}c^{2} + \\
&+ 60bcBC] && F^{4}(3d,3d) \\
&+ 4/7\sqrt{5}\ [abB^{2} + ABb^{2} - 2acBC - 2ACbc - \\
&- abC^{2} - ABc^{2}] && R^{2}(3s,3d;3d,3d) \\
&+ 4/3\sqrt{5}\ [2adBD + 2ADbd - aeBE - AEbe - \\
&- afBF - AFbf + \sqrt{3}\ [aeCE + AEce + afCF + \\
&+ AFcf]] && R^{1}(3s,3p;3p,3d) \\
&+ 2/5\sqrt{3}\ [2abD^{2} + 2ABd^{2} - abE^{2} - ABe^{2} - \\
&- abF^{2} - ABf^{2} + \sqrt{3}\ [acE^{2} + ACe^{2} + acF^{2} + \\
&+ ACf^{2}]] && R^{2}(3s,3p;3d,3p)
\end{aligned}
$$

$$
\begin{aligned}
K(\phi_{1},\phi_{2}) = &\ a^{2}A^{2} && F^{0}(3s,3s) \\
&+ [2adAD + 2aeAE + 2afAF] && F^{0}(3s,3p) \\
&+ 1/3\ [2adAD + 2aeAE + 2afAF + a^{2}D^{2} + A^{2}d^{2} + \\
&+ a^{2}D^{2} + A^{2}e^{2} + a^{2}E^{2} + a^{2}F^{2} + A^{2}f^{2}] && G^{1}(3s,3p) \\
&+ [2abAB + 2acAC] && F^{0}(3s,3d) \\
&+ 1/5\ [2abAB + 2acAC + a^{2}B^{2} + A^{2}b^{2} + a^{2}C^{2} + \\
&+ A^{2}c^{2}] && G^{2}(3s,3d) \\
&+ [d^{2}D^{2} + e^{2}E^{2} + f^{2}F^{2} + 2deDE + 2dfDF + \\
&+ 2efEF] && F^{0}(3p,3p) \\
&+ 1/25\ [4d^{2}D^{2} + 4e^{2}E^{2} + 4f^{2}F^{2} + 2deDE + \\
&+ 2dfDF + 2efEF + 3d^{2}E^{2} + 3D^{2}e^{2} + 3d^{2}F^{2} + \\
&+ 3D^{2}f^{2} + 3e^{2}F^{2} + 3E^{2}f^{2}] && F^{2}(3p,3p)
\end{aligned}
$$

$$= + [2bdBD + 2beBE + 2bfBF + 2cdCD + 2ceCE +$$

$$+ 2cfCF] \qquad F^0(3p,3d)$$

$$+ 1/35\ [8bdBD - 4beBE - 4bfBF - 8cdCD +$$

$$+ 4ceCE + 4cfCF - 4\sqrt{3}\ [ecBE + beCE + cfBF +$$

$$+ bfCF]] \qquad F^2(3p,3d)$$

$$+ 1/15\ [8bdBD + 2beBE + 2bfBF + 6ceCE +$$

$$+ 6cfCF + 4b^2D^2 + 4B^2d^2 + b^2E^2 + B^2e^2 +$$

$$+ b^2F^2 + B^2f^2 + 3c^2E^2 + 3C^2e^2 + 3c^2F^2 +$$

$$+ 3C^2f^2 - \sqrt{3}\ [2beEC + 2BEec + 2bfFC +$$

$$+ 2BFfc + 2bcE^2 + 2BCe^2 + 2bcF^2 + 2BCf^2]] \qquad G^1(3p,3d)$$

$$+ 1/245\ [54bdBD + 36beBE + 36bfBF + 30cdCD +$$

$$+ 48ceCE + 48cfCF + 27b^2D^2 + 27B^2d^2 + 18b^2E^2 +$$

$$+ 18B^2e^2 + 18b^2F^2 + 18B^2f^2 + 15c^2D^2 + 15C^2d^2 +$$

$$+ 24c^2E^2 + 24C^2e^2 + 24c^2F^2 + 24C^2f^2 - 6\sqrt{3}\ [beEC +$$

$$+ ecBE + cfBF + bfCF + bcE^2 + BCe^2 + bcF^2 + BCf^2]] \qquad G^3(3p,3d)$$

$$+ [b^2B^2 + c^2C^2 + 2bcBC] \qquad F^0(3d,3d)$$

$$+ 4/49\ [b^2B^2 + c^2C^2 + b^2C^2 + B^2c^2] \qquad F^2(3d,3d)$$

$$+ 1/441\ [36b^2B^2 + 36c^2C^2 + 42bcBC + 15b^2C^2 +$$

$$+ 15B^2c^2] \qquad F^4(3d,3d)$$

$$+ 4/7\sqrt{5}\ [abB^2 + ABb^2 - 2acBC - 2ACbc -$$

$$- abC^2 - ABc^2] \qquad R^2(3s,3d;3d,3d)$$

$$-2/3\sqrt{5}\ [2adBD + 2ADbd + 2abD^2 + 2ABd^2 + aeBE +$$

$$+ AEbe + abE^2 + ABe^2 + afBF + AFbf + abF^2 +$$

$$+ ABf^2 - \sqrt{3}\ [aeEC + AEec + ACe^2 + acE^2 + afCF +$$

$$+ AFcf + acF^2 + ACf^2]] \qquad R^1(3s,3p;3p,3d)$$

$$+ 2/5\sqrt{5}\ [2adBD + 2ADbd - aeBE - AEbe - afBF -$$

$$- AFbf + \sqrt{3}\ [aeEC + AEec + afFC + AFfc]] \qquad R^2(3s,3p;3d,3p)$$

APPENDIX 6

FLUORINE-FLUORINE INTERACTIONS

1. Axial-Axial (Trans)

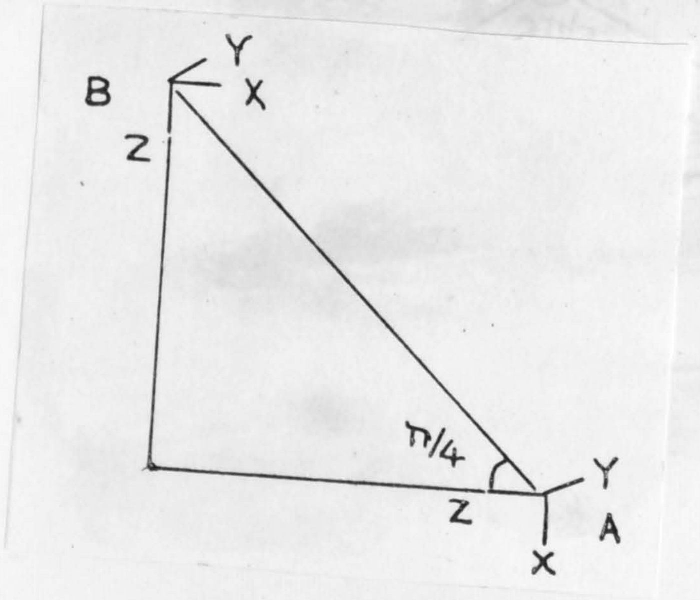
$$E = 4\left\langle 1s \left| \frac{-2Z}{r} \right| 1s \right\rangle + 4\left\langle 2s \left| \frac{-2Z}{r} \right| 2s \right\rangle + 2\left\langle 2p_{\sigma} \left| \frac{-2Z}{r} \right| 2p_{\sigma} \right\rangle +$$

$$+ 8\left\langle 2p_{\pi} \left| \frac{-2Z}{r} \right| 2p_{\pi} \right\rangle + \frac{2Z^2}{12} + 4J(1s,1s) + 8J(1s,2s) + 4J(1s,2p_{\sigma}) +$$

$$+ 16J(1s,2p_{\pi}) + 4J(2s,2s) + 4J(2s,2p_{\sigma}) + 16J(2s,2p_{\pi}) + J(2p_{\sigma},2p_{\sigma}) +$$

$$+ 8J(2p_{\sigma},2p_{\pi}) + 8J(2p_{\pi},2p_{\pi}) + 8J(2p_{\pi},2p_{\bar{\pi}}) \quad . \qquad (A6.1)$$

2. Axial-Equatorial (Cis)



A $p_{\sigma}' = 1/\sqrt{2}\ (p_{\sigma} - p_{\pi})$

$p_{\pi}' = 1/\sqrt{2}\ (p_{\sigma} + p_{\pi})$

B $p_{\sigma}' = 1/\sqrt{2}\ (p_{\sigma} + p_{\pi})$

$p_{\pi}' = 1/\sqrt{2}\ (p_{\pi} - p_{\sigma})$

$$E = 4\langle 1s \left| \frac{-2Z}{r} \right| 1s\rangle + 4\langle 2s \left| \frac{-2Z}{r} \right| 2s\rangle + 3\langle 2p_\sigma \left| \frac{-2Z}{r} \right| 2p_\sigma\rangle + 7\langle 2p_\pi \left| \frac{-2Z}{r} \right| 2p_\pi\rangle +$$

$$+ \frac{2Z^2}{R} + 4J(1s,1s) + 4J(1s,2s) + 3J(1s,\ 2p_\sigma) + 7J(1s,2p_\pi) + 4J(1s,2s) +$$

$$+ 4J(2s,2s) + 3J(2s,2p\ ) + 7J(2s,2p_\sigma) + J(1s,2p_\sigma) + J(2s,2p_\sigma) +$$

$$+ 3/4J(2p_\sigma,2p_\sigma) + 5/2\ J(2p_\sigma,2p_\pi) + 3/4\ J(2p_\pi,2p_\pi) + J(2p_\pi,2p_{\bar\pi}) +$$

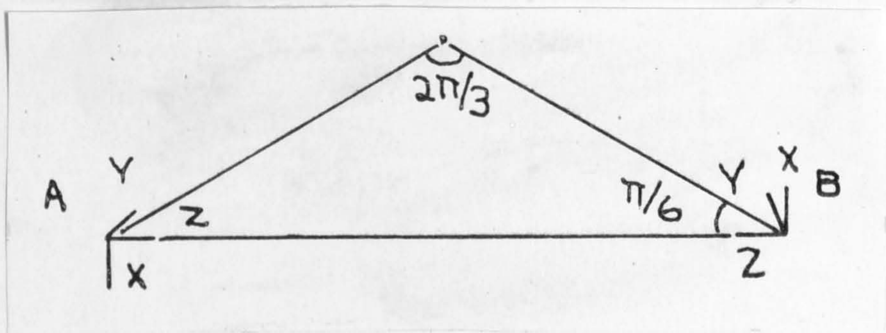
$$+ \langle 2p_\sigma,2p_\pi;2p_\pi,2p_\sigma\rangle + J(1s,2p_\pi) + J(2s,2p_\pi) + 2J(1s,2p_\sigma) + 2J(2s,2p_\sigma) +$$

$$+ 2J(1s,2p_\pi) + 2J(2s,2p_\pi) + 3/2\ J(2p_\sigma,2p_\sigma) + 5J(2p_\sigma,2p_\pi) + 3/2\ J(2p_\pi,2p_\pi) +$$

$$+ 2J(2p_\pi,2p_{\bar\pi}) - 2\langle 2p_\sigma,2p_\pi;2p_\pi,2p_\sigma\rangle + 4J(1s,2p_\pi) + 4J(2s,2p_\pi) + 3J(2p_\sigma,2p_\pi) +$$

$$+ 4J(2p_\pi,2p_\pi) + 3J(2p_\pi,2p_{\bar\pi})\ . \qquad (A6.2)$$

3. Equatorial-Equatorial



A

$$p_\sigma' = \sqrt{3}/2\ p_\sigma - 1/2\ p_\pi$$

$$p_\pi' = 1/2\ p_\sigma + \sqrt{3}/2\ p_\pi$$

B

$$p_\sigma' = \sqrt{3}/2\ p_\sigma + 1/2\ p_\pi$$

$$p_\pi' = -1/2\ p_\sigma + \sqrt{3}/2\ p_\pi$$

$$
\begin{aligned}
E = {} & 4\left\langle 1s \left| \frac{-2Z}{r} \right| 1s \right\rangle + 4\left\langle 2s \left| \frac{-2Z}{r} \right| 2s \right\rangle + 5/2\left\langle 2p_{\sigma} \left| \frac{-2Z}{r} \right| 2p_{\sigma} \right\rangle + \\
& + 15/2\left\langle 2p_{\pi} \left| \frac{-2Z}{r} \right| 2p_{\pi} \right\rangle + \frac{2Z^2}{R} + 4J(1s,1s) + 4J(1s,2s) + 5/2\ J(1s,2p_{\sigma}) + \\
& + 15/2\ J(1s,2p_{\pi}) + 4J(1s,2s) + 4J(2s,2s) + 5/2\ J(2s,2p_{\sigma}) + 15/2\ J(2s,2p_{\pi}) + \\
& + 3/2\ J(1s,2p_{\sigma}) + 3/2\ J(2s,2p) + 1/2\ J(1s,2p_{\pi}) + 1/2\ J(2s,2p_{\pi}) + \\
& + 15/16\ J(2p_{\sigma},2p_{\sigma}) + 25/8\ J(2p_{\sigma},2p_{\pi}) + 7/16\ J(2p_{\pi},2p_{\pi}) + 1/2\ J(2p_{\pi},2p_{\bar{\pi}}) + \\
& + 3/4\langle 2p_{\sigma},2p_{\pi};2p_{\pi},2p_{\sigma}\rangle + J(1s,2p_{\sigma}) + J(2s,2p_{\sigma}) + 3J(1s,2p_{\pi}) + 3J(2s,2p_{\pi}) + \\
& + 5/8\ J(2p_{\sigma},2p_{\sigma}) + 15/4\ J(2p_{\sigma},2p_{\pi}) + 21/8\ J(2p_{\pi},2p_{\pi}) + 3J(2p_{\pi},2p_{\bar{\pi}}) + \\
& + 3/2\langle 2p_{\sigma},2p_{\pi};2p_{\pi},2p_{\sigma}\rangle + 4J(1s,2p_{\pi}) + 4J(2s,2p_{\pi}) + 5/2\ J(2p_{\sigma},2p_{\pi}) + \\
& + 4J(2p_{\pi},2p_{\pi}) + 7/2\ J(2p_{\pi},2p_{\bar{\pi}}) \quad . \qquad \text{(A6.3)}
\end{aligned}
$$

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