703. *Possible f-Orbital Hybridization in Uranyl and Related Complexes.*

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A theoretical study is made of the possible modes of description of the bonds in certain uranyl and related complexes. If a partial sexicovalent character is desired for the uranyl–ligand bonds, then f electrons must be considered to take part in the bonding. A discussion of the sizes and energies of these f orbits shows that the $6f$ is much more effective than the $5f$ for this purpose. It is concluded that this sexicovalency is one element in the total description, with ionic contributions probably predominant. There are other alternative descriptions of the covalency, which do not involve use of f orbitals in the formation of hybrids; but although these probably play some part, it seems likely that they need to be supplemented with f hybrids.

It has been suggested that there may occur a characteristic arrangement of covalent bonds in certain complexes involving the actinide series of elements. This arrangement is illustrated by the uranyl nitrate complex, $UO_2(NO_3)_3^-$. Here the uranyl group may be thought of as representing the polar axis of a sphere, along the equatorial plane of which (or, perhaps, close to the equatorial plane) there lie six equivalent coplanar bonds to the oxygen atoms of the co-ordinated nitrate ions. Crystallographic data for this system have been reported by Hoard and Stroupe,[1] by Jander and Wendt,[2] and by Zachariasen.[3] The last has shown that among the various U–O bonds in a large series of molecular complexes there is a complete gradation from the short (or " primary ") bonds typical of the uranyl ion whose length is 1·8—2·1 Å to the long (or " secondary ") bonds typical of the equatorial ligands, where the length may be as great as 2·6—2·7 Å. It is on the basis of this gradual change that the description " bond " is here applied to the equatorial linkages.

Other evidence in favour of bond formation has recently been advanced by Glueckauf, McKay, and co-workers,[4-8] who made the suggestion that the peculiar nature of these equatorial bonds in compounds in solution might be due to f-orbital hybridization and

[1] Hoard and Stroupe, *Atomic Energy Project Report*, 1943, *A*, 1229.
[2] Jander and Wendt, *Z. anorg. Chem.*, 1949, **258**, 1.
[3] Zachariasen, *Acta Cryst.*, 1954, **7**, 795.
[4] McKay and Mathieson, *Trans. Faraday Soc.*, 1951, **47**, 428.
[5] Glueckauf, McKay, and Mathieson, *ibid.*, p. 437.
[6] Gardner, McKay, and Warren, *ibid.*, 1952, **48**, 997.
[7] Glueckauf, *Nature*, 1949, **163**, 414.
[8] Glueckauf and McKay, *ibid.*, 1950, **165**, 594.

partial covalency. However, Katzin [9] has objected to this interpretation on the grounds that there is insufficient evidence to distinguish these systems from other complexes which are usually admitted to be mainly ionic in character. Yet if the equatorial bonds are purely ionic, it is not easy to understand: (*a*) The very definite stereochemical distribution of the ligands, where the secondary oxygen atoms never seem to deviate by more than 0·5 Å from the mid-plane, and not infrequently lie in it. (*b*) The partition experiments by Glueckauf and McKay, which showed a strong tendency for the uranyl group to surround itself with six adjacent oxygen atoms, some of which may be nitrate oxygens and others water oxygens. It is a natural conclusion from this evidence that there is present at least some degree of covalent bonding, conferring particular stability on certain numbers of ligands and on certain valency angles.

Others beside Glueckauf and McKay have drawn attention to the possible role of *f* electrons in bonding. Thus Hugus [10] has described a way in which *f* electrons may be used in some of the higher oxidation states of iodine, tellurium, and antimony; and Scott [11] has also employed 4*f* orbitals in the descriptions of the iodine compounds IF_5 and IF_7. Further, Connick and Hugus [12] have used the greater stability of the 5*f* as compared with the 6*d* orbitals in the region of the Periodic Table above thorium and protactinium to suggest the intervention of 5*f* orbitals in the bonding of UO_3, UO_2^{2+} and some of the transuranic elements. R. J. Elliott,[13] from an analysis of the paramagnetic susceptibility of salts involving NpO_2^{2+} and PuO_2^{2+} ions in compounds isomorphous with sodium uranyl acetate $Na(UO_2)(OAc)_3$, has shown convincingly that the susceptibility is compatible with uranium 5*f* rather than 6*d* electrons, so that if the uranyl group is bonded by other than ionic forces, it must presumably be partly by means of *f* electrons. A similar discussion of the magnetic susceptibility of a series of 8-co-ordinated complexes of U(IV), which is close to the spin-only value, has been given by Sacconi,[14] who again is led to suppose that some of the electrons are in atomic and not molecular 5*f* orbitals, though a clear-cut decision between 6*d* and 5*f* does not seem possible. This argument has been criticized by Dawson,[15] who shows that an equally satisfactory interpretation can be obtained if $6d^2$ are involved in atomic orbitals and the 5*f* in bonding. Quite recently Eisenstein and Pryce [16] have reconsidered the paramagnetism of uranyl and neptunyl ions in great detail, and have shown that the so-called " high-frequency terms " in the susceptibility of an isolated UO_2^{2+} or NpO_2^{2+} group lead to a strong presumption of *f* electrons even in these bonds. We shall show later that if *f* electrons play a part in primary U–O bonds, they are even more likely to do so in secondary bonds.

There is yet other evidence from thermochemistry. Thus Kapustinskii and Baranova [17] have drawn attention to the large ΔH—of the order of 13 kcal.—involved in the bonding of each hydrated water molecule in $UO_2(NO_3)_x$, where $x = 2$ or 3 and in addition either 2 or 3 water molecules are tightly fastened to the complex. The greater ability of UO_2^{2+} as compared, for example, with Ba^{2+}, for holding water molecules, and the more specific nature of these forces in the case of UO_2^{2+}, have been stressed by Crandall.[18]

There are yet other arguments for the participation of 5*f* electrons in bonds. Thus Diamond, Street, and Seaborg,[19] from a very careful study of the elution behaviour of a series of actinides and lanthanides, have shown that in high concentrations of hydrochloric acid the actinides may form complex ions with chloride ions to a greater extent than do the lanthanides. To explain this additional stability a partial covalent character is ascribed to the bonding in the transuranic elements. Such bonding would appear to involve the 5*f* electrons, though these authors did not discuss the precise way in which

[9] Katzin, *Nature*, 1950, **166**, 605.
[10] Hugus, *J. Amer. Chem. Soc.*, 1952, **74**, 1076.
[11] Scott, *J. Chem. Phys.*, 1950, **18**, 1420.
[12] Connick and Hugus, *J. Amer. Chem. Soc.*, 1952, **74**, 6012.
[13] R. J. Elliott, *Phys. Rev.*, 1953, **89**, 659.
[14] Sacconi, *R. C. Accad. Lincei*, 1949, **6**, 639.
[15] Dawson, *Nucleonics*, 1952, **10**, 39.
[16] Eisenstein and Pryce, *Proc. Roy. Soc.*, 1955, *A*, **229**, 20.
[17] Kapustinskii and Baranova, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1952, 1122.
[18] Crandall, *J. Chem. Phys.*, 1949, **17**, 602.
[19] Diamond, Street, and Seaborg, *J. Amer. Chem. Soc.*, 1954, **76**, 1461.

this would occur. They did, however, show (we shall return to this later) that the relative sizes of the 5f orbitals would be approximately suitable for this purpose.

It is clear from this survey that f covalency must be considered seriously.

It does not seem possible to settle this matter of f covalency by experiment. We propose, therefore, to discuss what is involved in the hypothesis; and to see whether, on the basis of conventional theories of the chemical bond, a satisfactory description of this kind of bonding can be given. Much of our discussion, while given with particular reference to the uranyl complexes, will of course apply to other possible situations in which f bonding may occur. Let us provisionally admit the experimental evidence as indicating some degree of sexicovalent co-ordination in the equatorial plane (see Fig. 1). It is at once clear that such a system of bonds cannot be described in conventional terms by invoking hybridization among the familiar s-, p-, and d-type atomic orbitals of uranium. Nor will f electrons alone be sufficient. We must look for hybrids in which some, or all, of the possible s, p, d, and f atomic orbitals participate.

There are two general reasons why we may expect an f-type contribution to a hybrid. They are associated with Pauling's criterion of the strength of a hybrid orbital, and with Maccoll and Mulliken's criterion of the overlapping power of a hybrid. It will be convenient to discuss them separately.

Pauling[20] has defined the strength of an orbital in terms of the angular dependence of its non-radial part, a similar radial factor in all the contributing atomic orbital wave functions being assumed (see later). Thus if we normalize the angular factors to 4π, the appropriate σ-type angular terms and strengths are as shown in the Table. This Table

Atomic orbital	s	p	d	f
Angular term	1	$\sqrt{3}\cos\theta$	$\sqrt{5}(3\cos^2\theta - 1)/2$	$\sqrt{7}(5\cos^3\theta - 3\cos\theta)/2$
Strength	1	$\sqrt{3} = 1\cdot732$	$\sqrt{5} = 2\cdot236$	$\sqrt{7} = 2\cdot646$

would lead us to suppose that f electrons were capable of stronger bonding than s, p, or d. Such a conclusion may seem to indicate that the strength criterion is not a completely satisfactory one; but it is likely to give indications of the true situation, and we shall use it shortly to compare the strengths of various possible hybrids of s, p, d, and f. As we may expect from the familiar case of s, p, and d, these hybrids may have strengths which are greater than that of any of their components.

The particular combinations of s, p, d, and f orbitals which may be allowed can be found by group-theoretical considerations of the kind discussed by Kimball.[21] Let us define * the 7 possible distinct normalized f orbitals in terms of their angular factors as follows :

$$f_z = \frac{\sqrt{7}}{2}(5\cos^3\theta - 3\cos\theta), \qquad f_{z(x+y)} = \sqrt{\frac{105}{4}}\sin^2\theta\cos\theta\cos 2\phi$$

$$f_x = \sqrt{\frac{21}{8}}\sin\theta(5\cos^2\theta - 1)\cos\phi, \quad f_{zxy} = \sqrt{\frac{105}{4}}\sin^2\theta\cos\theta\sin 2\phi$$

$$f_y = \sqrt{\frac{21}{8}}\sin\theta(5\cos^2\theta - 1)\sin\phi, \quad f_+ = \sqrt{\frac{35}{8}}\sin^3\theta\cos 3\phi$$

$$f_- = \sqrt{\frac{35}{8}}\sin^3\theta\sin 3\phi$$

$$\qquad\qquad\qquad\qquad\qquad (1)$$

in which the z-direction coincides with the polar axis. Then if we consider the case of six equivalent directions around the central atom, all in the equatorial plane, and two equivalent directions along the polar axis, the group symmetry is D_{6h}, and the basic atomic orbitals fall into the following representations of this group :

Representation	a_{1g}	a_{2u}	b_{1u}	b_{2u}	e_{1g}	e_{2g}	e_{1u}	e_{2u}
Atomic orbitals	s, d_z	p_z, f_z	f_+	f_-	d_{zz}, d_{zy}	d_{x+y}, d_{xy}	p_x, p_y, f_x, f_y	$f_{z(x+y)}, f_{zxy}$

* f_+ and f_- are used as being more convenient to write than the conventional $2^{-\frac{1}{2}}\{f_3 \pm f_{-3}\}$.

[20] Pauling, " Nature of the Chemical Bond," Cornell Univ. Press, 1939, p. 78.
[21] Kimball, *J. Chem. Phys.*, 1940, **8**, 188.

Following Kimball's methods, we imagine six equivalent coplanar hybrid bond orbitals, denoted collectively by χ, directed along the equatorial directions. These may be used as a reducible representation of D_{6h}, with the following character system :

Group operation ...	E	C_2	$2C_3$	$2C_6$	$3C_2'$	$3C_2''$	iE	iC_2	$2iC_3$	$2iC_6$	$3iC_2'$	$3iC_2''$
$\Gamma(\chi)$	6	0	0	0	2	0	0	6	0	0	0	2

This implies that $\chi \subset a_{1g} + b_{1u} + e_{1u} + e_{2g}$. Since f_+ is the only atomic orbital of representation b_{1u}, it follows that f_+ must appear in these hybrids, if they are equivalent. This argument provides the necessary justification of our earlier assertion that f electrons are necessary if we want to preserve the old idea of bond orbitals.

Similar arguments to this have been given by Shirmazan and Dyatkina [22] though they did not consider our particular symmetry, D_{6h}; and by Fumi and Castellan [23] who showed that f electrons were necessary in most cases of six equivalent bonds, though again they did not consider D_{6h}. Previously Van Vleck [24] had shown that sp^3d^3f are needed with some, though not with all, types of 8-co-ordination. Certain other cases have been studied by Fumi.[25] In several of these structures f electrons could be used, though it may be possible to obtain the necessary hybrids without them.
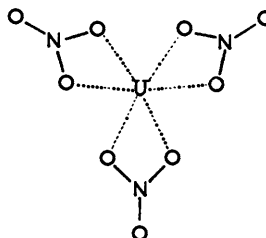

FIG. 1. *The equatorial " bonds " in uranyl nitrate.*

In many cases the X-ray analysis shows that in Fig. 1 the six equatorial bonds, although equivalent, are not at equal angles; but the angles between neighbouring bonds are alternately greater and less than 60°, as suggested by the fact that in the nitrate complexes adjacent pairs of attached oxygen atoms are bonded to a nitrogen atom. The symmetry is now D_{3h}, but an argument precisely equivalent to that used above for D_{6h} shows that again f_+ orbitals must be used.

The resolution of χ for the D_{6h} situation shows that the constituent atomic orbitals ψ_i ($i = 1 \ldots 6$) must be of the form

$$\begin{rcases} \psi_1 = s + c_1 d_z & , & \psi_4 = p_y + c_2 f_y \\ \psi_2 = f_+ & , & \psi_5 = d_{x+y} \\ \psi_3 = p_x + c_2 f_x & , & \psi_6 = d_{xy} \end{rcases} \quad \cdots \quad (2)$$

where c_1 and c_2 are two arbitrary constants, and normalization factors have been omitted for convenience.

The definitions of the angular terms in the p and d functions are as follows :

$$\begin{rcases} p_x = \sqrt{3} \sin\theta \cos\phi & , & d_{x+y} = \sqrt{\dfrac{15}{4}} \sin^2\theta \cos 2\phi \\[2mm] p_y = \sqrt{3} \sin\theta \sin\phi & , & d_{xy} = \sqrt{\dfrac{15}{4}} \sin^2\theta \sin 2\phi \\[2mm] d_z = \sqrt{5}(3\cos^2\theta - 1)/2 & , & d_{yz} = \sqrt{\dfrac{15}{4}} \sin\theta \cos\theta \sin\phi \\[2mm] & & d_{xz} = \sqrt{\dfrac{15}{4}} \sin\theta \cos\theta \cos\phi \end{rcases} \quad \cdots \quad (3)$$

[22] Shirmazan and Dyatkina, *Zhur. fiz. Khim.*, 1953, **27**, 491.
[23] Fumi and Castellan, *J. Chem. Phys.*, 1950, **18**, 762.
[24] Van Vleck, *ibid.*, 1935, **3**, 803.
[25] Fumi, personal communication.

Presumably the least amount of f-type orbitals will occur if we are able to choose $c_2 = 0$. In general the total number of f electrons in the ψ_i amounts to $1 + 2c_2^2/(1 + c_2^2)^{\frac{1}{2}}$.

It is instructive to write the explicit relation between the atomic orbitals ψ_i in (2) and the resulting hybrid orbitals χ_i. The matrix relation between them may be written, symbolically

$$\boldsymbol{\chi} = \boldsymbol{T}\boldsymbol{\psi} \qquad \ldots \ldots \ldots \ldots \quad (4)$$

where $\boldsymbol{\chi}$ is the column matrix χ_i, $\boldsymbol{\psi}$ is the column matrix ψ_i, and $\boldsymbol{T}$ is the square orthogonal matrix

$$\boldsymbol{T} = \begin{pmatrix} a & a & 2b & 0 & 2b & 0 \\ a & -a & b & \frac{1}{2} & -b & \frac{1}{2} \\ a & a & -b & \frac{1}{2} & -b & -\frac{1}{2} \\ a & -a & -2b & 0 & 2b & 0 \\ a & a & -b & -\frac{1}{2} & -b & \frac{1}{2} \\ a & -a & b & -\frac{1}{2} & -b & -\frac{1}{2} \end{pmatrix}$$

In the above expression for convenience we have put a for $1/\sqrt{6}$ and b for $1/\sqrt{12}$.

For example

$$\chi_1 = a(\psi_1 + \psi_2) + 2b(\psi_3 + \psi_5) \qquad \ldots \ldots \ldots \quad (5)$$

The inverse relation to (4) may be put in the form

$$\boldsymbol{\psi} = \boldsymbol{T}^{-1}\boldsymbol{\chi} = \boldsymbol{T}^{\dagger}\boldsymbol{\chi} \qquad \ldots \ldots \ldots \ldots \quad (6)$$

where $\boldsymbol{T}^{\dagger}$ is the adjoint matrix obtained from $\boldsymbol{T}$ by interchanging rows and columns.

FIG. 2.   *Polar diagram for* spdf-*hybrid. There are six of these, with coplanar axes of symmetry, arranged at* 60° *intervals in the equatorial plane.*

It is readily shown that the hybrids χ_i are of unusually high strength. For example if, in (2), we put $c_1 = c_2 = 0$, so that the hybrids are obtained from $s\ f_+\ p_x\ p_y\ d_{x+y}\ d_{xy}$, their strength, from eqns. (1) and (5), is $a\left(1 + \sqrt{\frac{35}{8}}\right) + 2b\left(\sqrt{3} + \sqrt{\frac{15}{4}}\right) = 3\cdot381$. This may be compared with the familiar sp^3 tetrahydral orbitals whose strength is $2\cdot0$. By making c_1 and c_2 in (2) very large so that the hybrids are derived from $d_z f_+ f_x f_y d_{x+y} d_{xy}$ the strength becomes $3\cdot364$. An even bigger value can be found by suitable choice of c_1 and c_2; in fact, when $c_1 = \frac{\sqrt{5}}{2} = 1\cdot118$, $c_2 = \sqrt{\frac{7}{8}} = 0\cdot935$, we obtain the greatest possible strength, $3\cdot954$. Since, however, it is usually considered undesirable to introduce d_z and f_x orbitals if s and p_x can be used instead, it seems more reasonable to return to the first case, where the strength is still as great as $3\cdot381$. We show, in Fig. 2, the polar diagram for this particular hybrid. A comparison of this diagram with the conventional ones for sp^3 tetrahedral and other similar hybrids, shows how very strongly directed this hybrid is. Its overlapping power (see later), as expressed by overlap integrals between it and some ligand, is exceedingly large.

The last paragraph has been concerned with the case D_{6h} when all secondary O–U–O angles are 60°. It is not difficult to apply it to the D_{3h} situation. The chief alteration is that ψ_1 must be taken in the form $ns + \sqrt{(1 - n^2)}f_-$ instead of just s. Thus the ideal hexagonal configuration of hybrids results when $n = 1$. When $n \neq 1$, the total amount of f character in the hybrids is $2 - n^2$ (with $c_1 = c_2 = 0$ as urged above). This increases

with the angle subtended by adjacent bonds, for this angle depends on n according to the Table below.

n	1·00	0·90	0·75	0·50	0
Orbital strength	3·381	3·381	3·381	3·352	3·202
Bond angle	60°	50·6°	46·0°	42·2°	40°

The angle subtended by adjacent pairs of bonds may therefore be reduced from 60° to 46° without any appreciable reduction in the strength of the bond orbitals, though further increase in the f-orbital content causes the strength to fall more rapidly. It is interesting that the minimum possible angle that can be obtained in this way is 40°, so that if the actual angle is ever less than 40° it may be supposed that appreciable strain energy will occur, due to the inability of the various charge clouds to overlap effectively. Ionic Coulomb forces between the ligands are not likely to allow very small angles of this kind, and crystallographic data do, in fact, suggest a bond angle in the region of 46°. Presumably this value is largely determined by the bond distances and the shape of the attached groups, usually carbonate or nitrate.

So far no account has been taken of the axial bonds (primary U–O bonds) which lie normal to the equatorial plane. Their existence places certain restrictions on the possible types of in-plane hybridization, for the uranyl bonds will invoke some of the representations otherwise available for in-plane bonding. This is particularly true of the representations a_{1g} and a_{2u}, both of which may be used in σ-bonds along the z-axis. Eisenstein and Pryce [16] give reasons for supposing that these axial bonds may be made from uranium $5f_z$, $6d_z$, and $7s$ orbitals, though there may be a little $7p_z$ also. In such a case we must be careful not to put $c_1 = 0$ in eqn. (2) since then our various hybrids will not all be mutually orthogonal. Until we can be more explicit about the amount of hybridization in the primary bonds, it does not seem worthwhile to make detailed calculations, especially as we have shown that a small amount of mixing of s and d_z orbitals slightly increases the orbital strength.

This is about as far as it seems practicable to go by working in terms of Pauling's strength criterion. So let us now consider the overlap criterion of Maccoll [26] and Mulliken.[27] According to this, we may judge the bond-forming power of a hybrid by the magnitude of its overlap integral with the orbital on the ligand with which it is to be paired, and the smallness of its overlap with any other ligand.

The outer electrons in the ground state of uranium occupy the orbitals $(5s)^2$ $(5p)^6$ $(5d)^{10}$ $(6s)^2$ $(6p)^6$ $(5f)^3$ $(6d)$ $(7s)^2$. The precise self-consistent-field wave functions for these orbitals have not been calculated. We may therefore begin with Slater functions. In order to test the suitability of any or all of these orbitals for the polar and equatorial bonds we have calculated their overlap integrals with a hypothetical hydrogen $1s$ orbital placed $3·3a_0$ and $4·64a_0$ away. These are approximately the primary and secondary bond distances, if hydrogen atoms are replacing oxygen as ligands, and the overlap integrals thus calculated should give some general indication of the degree of overlapping of more accurate atomic orbitals with oxygen $2p$σ orbitals. [After our calculations were complete, we realized that a rather smaller value of about $3·0a_0$ instead of $3·3a_0$ might have been better for the primary bond distance: but as our chief concern here is with the secondary bonds, for which $4·64a_0$ is a reasonable value, we have not felt it was worthwhile to recalculate the overlap integrals shown in column (a) of the Table.] In order to make these integrations we had to use the Bessel-function technique developed by Barnett and Coulson.[28] The values in column (b) were obtained by direct integration in spheroidal co-ordinates for which, however, it is necessary that the power of r in the radial factor shall be integral. It was verified by accurate calculations for several of the six-quantum orbitals that the overlap integrals thus calculated with r^3 instead of the exact non-integral Slater powers of r (3·2 and 3·3) were not materially different from the exact values given in column (a). This less laborious procedure was therefore used in deriving the values in column (b). The orbitals, whose radial parts are shown in the Table, are only orthogonal as regards their

[26] Maccoll, *Trans. Faraday Soc.*, 1950, **46**, 369.
[27] Mulliken, *J. Amer. Chem. Soc.*, 1950, **72**, 4493.
[28] Barnett and Coulson, *Phil. Trans.*, 1951, A, **243**, 221.

angular dependence. It would have been possible to orthogonalize the orbitals of a given class (*e.g.*, s-type), but in view of the large difference in overlap between orbitals with differing principal quantum number, this process would hardly alter the final values; and as the Slater rules for the orbitals are themselves increasingly approximate for heavier atoms, further precision is not warranted. This Table shows that of the five-quantum

Overlap integrals between hydrogen 1s and various uranium orbitals obtained by using Slater wave functions.

Atomic orbital	Radial factor	Overlap integral		Atomic orbital	Radial factor	Overlap integral	
		(a)	(b)			(a)	(b)
$5s$	$1795r^3 \exp{-8.59r}$	0.041	—	$6d_{x+y}$	$1.13r^{3\cdot2} \exp{-1.74r}$	0.345	0.199
$5p_x$	$1795r^3 \exp{-8.59r}$	0.016	—	† $6d_z$	$1.13r^{3\cdot2} \exp{-1.74r}$	0.398	0.229
$5d_{x+y}$	$190r^3 \exp{-5.21r}$	0.021	—	$6f_+$	$0.063r^{3\cdot2} \exp{-0.94r}$	0.231	0.296
$5f_+$	$28.23r^3 \exp{-3.41r}$	0.041	—	† $6f_z$	$0.063r^{3\cdot2} \exp{-0.94r}$	0.292	0.374
$6s$	$23.68r^{3\cdot2} \exp{-3.32r}$	0.203	0.057	$6f_x$	$0.063r^{3\cdot2} \exp{-0.94r}$	0.179	0.229
$6p_x$	$23.68r^{3\cdot2} \exp{-3.32r}$	0.184	0.059	$7s$	$0.00707r^3_z{}^3 \exp{-0.62r}$	0.203	0.249

(a) Internuclear distance = $3.3a_0$.   (b) Internuclear distance = $4.64a_0$.
† Hydrogen orbital on the polar axis.

orbitals only the $5f_+$ needs to be considered. Even then, its overlap is considerably less than either the $6d$ or $7s$. If we agree to form the hexagonal hybrids as in eqn. (2) with $c_1 = c_2 = 0$, the overlap integral of one of the hybrids with its ligand hydrogen is as large as 0.486. This is much greater than its overlap with the remaining hydrogen atoms associated with the other hexagonal hybrids χ_2, χ_3, and χ_4 (*i.e.*, the unfavourable overlaps), for which the overlap integrals, in order, are -0.058, 0.019, and 0.082. The maximum overlap of 0.486 is rather less than the tetrahedral overlap in methane, where it is 0.701; but the other overlaps in methane are 0.157, suggesting that in this case the hexagonal hybrids have a more highly directional character, and are more suited to pairing with appropriate ligands, in the formation of localized bonds than are the tetrahedral hybrids in methane.

It is obvious that different choices of atomic orbital for the hybrids will lead to different sets of overlap integrals. In particular, it makes a difference whether $5f_+$ or $6f_+$ is used. But fortunately the general directional character of the hybrids does not appear to depend greatly on choices such as these. We have made a series of calculations of these overlaps, varying both the internuclear distance and the orbitals. In addition to the overlap of a hydrogen 1s with χ_1, χ_2, χ_3, and χ_4 quoted above (set 1 say) we give three other sets so that comparison may be made. These are, in order : set (2) 0.371, -0.059, 0.148, 0.062; set (3) 0.292, -0.138, 0.069, -0.017; and set (4) 0.469, -0.010, 0.099, -0.036. With our present knowledge there is no particular reason for rejecting any of these. Fortunately they are sufficiently similar in general behaviour.

Our ignorance may be put in another way, as follows. If, as we shall later be led to conclude, the true bonding is only partly of the covalent kind we are now considering, we have no grounds for deciding what exponents to use in the various atomic orbitals. This is because the total energy of the complex is determined not wholly by the overlap of the hybrids, but also by the valency-state energy, and the ionic energy, and by resonance between covalent and ionic wave functions. Fortunately again, the overlap integrals do not appear to be highly sensitive to the valency state selected. For example, instead of the set of atomic orbitals used in column (a) of the Table, we have considered overlaps where the least conceivable degree of excitation to a valency state is supposed to occur. The $6s$ overlap changes from 0.203 to 0.25, the $6p$ from 0.184 to 0.24, the $6d$ from 0.345 to 0.34. It does not seem, therefore, as if our ignorance of the particular nature of the valency state were in any real sense critical in our conclusions.

It is obvious from the Table of overlap integrals that the $6f_+$ orbital is much more effective than the $5f_+$ orbital. This situation raises several questions requiring answer. In the first place there is singularly little difference in energy between many possible levels of the uranium atom. For example the spectroscopic data of Kiess, Humphreys, and Laun [29] show that there exist a number of configurations where a $7s$ electron has been

[29] Kiess, Humphreys, and Laun, *J. Res. Nat. Bur. Stand.*, 1946, **37**, 57.

promoted to a $6d$ orbit, and which lie within 1 ev of the ground state. Further, De Bruin, Klinkenberg, and Schuurmans [30] have found a similar order of energy differences associated with the transition $6d$–$5f$ for thorium in its oxidation states. Moreover, theoretical estimates of the differences in energy between f electrons in various shells suggest (Wu [31]) that as little as 0·3 ev separates the $5f$ and $6f$ levels in uranium. Thus it would seem as if, on energy grounds, there were no really serious objection to using $6f_+$ orbitals in the secondary bond hybrids instead of $5f_+$. Part of our trouble is that, without adequate self-consistent-field orbitals, we are ignorant of the true sizes of the f orbitals. The situation here is more serious than with s, p, or d orbitals. For, as Goeppert-Mayer [32] has shown, there is a break in the slow change of size of a $5f$ orbital which occurs somewhere near $Z = 92$, such that for higher atomic numbers the $5f$ orbital is much smaller than before, and has its maximum density well within one Bohr radius of the nucleus. It is the existence of this break, which, by bringing the $5f$ electrons close to the nucleus, prevents them from affecting chemical properties of the atom, and leads to the existence of an actinide series. According to Seaborg it is between $Z = 90$ and $Z = 91$ that the $5f$ level crosses the $6d$ level and becomes the lower.
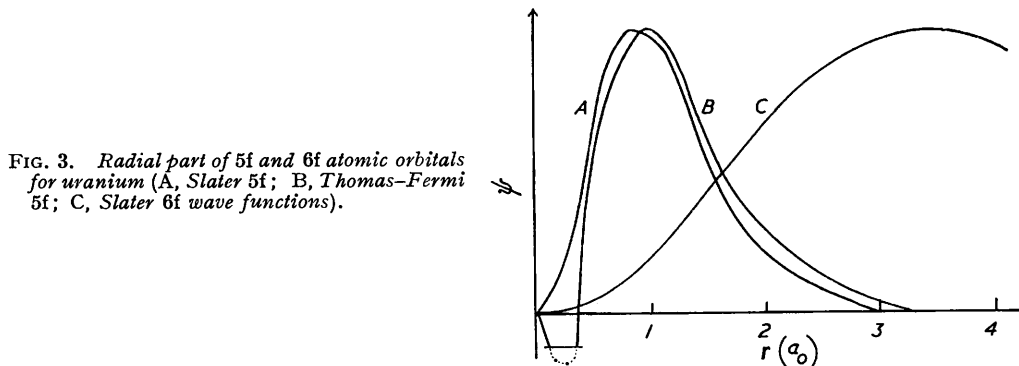

FIG. 3. *Radial part of* 5f *and* 6f *atomic orbitals for uranium* (A, *Slater* 5f; B, *Thomas–Fermi* 5f; C, *Slater* 6f *wave functions*).

It is certainly true that the Slater wave functions are likely to be particularly unreliable at these large atomic numbers. But Fig. 3 shows that, for our purposes, the error may be less than might have been expected. We have shown the variation with r of the radial part of the atomic orbital, both for the $5f$ and $6f$ Slater functions, and for the $5f$ function calculated by Eisenstein and Pryce [16] on the basis of a Thomas–Fermi statistical field in which the $5f$ electron moves. All these curves have been normalized in such a way that the peak value is 1·0. It is most gratifying that the Thomas–Fermi function agrees so closely with the Slater function. These curves show the greater overlapping power of the $6f$ as compared with the $5f$ orbital, in a striking fashion.

There is one other argument for preferring the $6f$ orbital. According to Fig. 3 this orbital appears rather too diffuse for maximum overlapping with the appropriate ligands : the $5f$ orbital, however, is too compressed. Now Craig [33] has shown, for the particular case of the d electron in transition-metal complexes, that the presence of electron-attracting groups surrounding the central ion results in an additional potential field acting on the outer electrons of this ion, and the effect of this field is to contract their charge clouds. The more diffuse the cloud was initially, the greater the relative contraction. As the Table of overlap integrals shows, the $6f$ is one of the most " outer " electrons in the uranium atom, and will therefore be contracted most in the co-ordinated state. It seems not unreasonable to suppose that if Fig. 3 gives the approximate size of the free-atom function, the co-ordinated-atom $6f$ function would be of about the right size for maximum overlapping.

We are now in a position to state our conclusions, even though these are to some extent still tentative. In the first place, if we believe that, in the secondary U–O bonds of

[30] De Bruin, Klinkenberg, and Schuurmans, *Z. Physik*, 1944, **122**, 23.
[31] Wu, *Phys. Rev.*, 1933, **44**, 727.
[32] Goeppert-Mayer, *ibid.*, 1941, **60**, 184.
[33] Craig, *Rev. Pure Appl. Chem.*, 1954, **4**, 4.

complexes such as the uranyl nitrates, there is some degree of simultaneous sexicovalent bonding, this can be achieved only with the help of f electrons. On the grounds of energy these could be either $5f$, which are not particularly good since they do not overlap very strongly at the distances involved, or $6f$ which overlap much better. More probably, however, we may believe that such sexicovalent bonding is only one element in the complete account, and the ionic element is at least as important, or even more important. In this case the size and shape of the orbitals will be dominated by the ionic element, and there is no particular reason to suppose that any f-covalent character would need to be dependent exactly on isolated-atom $5f$ and $6f$ orbitals; probably all that we have any right so say is that there is some f character in the hybrids, and this f character will be such as to give best overlap with least expenditure of promotion energy. It is worth drawing attention to a situation which is not always as well recognized as it deserves to be (see, *e.g.*, Coulson [34]). If an electron is in the hybrid orbital shown in Fig. 2, its centre of mean position will lie somewhere near the centre of the large loop. This is already nearly half-way along the " bond " that is being formed, and it means that if we use this hybrid in what is formally a covalent bond, there will be a considerable dipole moment (due to the atomic dipole described by Coulson [35]). As a result, a formally covalent structure appears to have a large ionic distribution of charge. In this way we can begin to see that the conventional language of covalent and ionic character is breaking down. The situation here with f electrons in the hybrids is not unlike that recently discussed by Orgel,[36] for the octahedral and square complexes involving d electrons, where similar conclusions about spectral transitions are arrived at, independently of whether the starting point is Van Vleck's ionic model and the resulting crystal field, or Pauling's octahedral and square hybrids and the language of covalency is used.

There are at least three ways in which our earlier discussion could be modified. In the first place the secondary oxygen atoms have non-bonding (or almost non-bonding) π electrons. These could take part in weak π-type bonding, using the empty orbitals of the central uranium atom. Although the overlap integrals are not very large, it seems probable that this back-bonding may partially off-set the ionic character of the σ-type U–O bonds. Secondly, we may feel inclined to abandon the requirement of simultaneous sexicovalent bonding in the equatorial plane. Thus we could imagine resonance between a number of bond structures, in each of which only two, or four, bonds were drawn to the secondary oxygens. Resonance of this kind would be compatible with the hexagonal symmetry, and would require no use of f orbitals. It would be analogous to the way in which, in methane, the s^2p^2 bivalent state of carbon plays a fairly significant role, although it would appear to lead to bivalency and not quadrivalency. No doubt something of this sort occurs in uranium, though the larger energy difference in carbon (sp^3–s^2p^2 is about 4 ev) would tend to favour the lower valency in carbon more than in uranium, and in any case it is difficult to see how Eisenstein and Pryce's conclusions, that f electrons participate in the primary U–O bonds, could be fitted into this scheme. Thirdly, we may abandon the two-centre bond picture, and interpret the covalency, whether partial or complete, in terms of three-centre bonds, as is not infrequently done for the electron-deficient boron hydrides. Some recent work by W. C. Hamilton [37] shows that this is a useful method, even at a quantitative level. In such a case we should presumably use sd^2 hybrids at the uranium atom. These hybrids are equivalent and coplanar, but since both s and d are of gerade symmetry, so also are their mixtures; hence the three hybrids are directed not in three but in six directions, and the hexagonal arrangement could take place by the use of something like Rundle's half-bonds [38,39] without the need to use f electrons at all. This description can be regarded as a restricted type of resonance, though it has the great advantage of greater simplicity, and a more natural explanation for the existence of 6 rather than 4 ligands in the equatorial plane.

[34] Coulson, *Discuss. Faraday Soc.*, 1955, **19**, 65.
[35] *Idem, Trans. Faraday Soc.*, 1942, **38**, 433.
[36] Orgel, *J. Chem. Phys.*, 1955, **23**, 1004.
[37] Hamilton, *Proc. Roy. Soc.*, 1956, *A*, **235**, 395.
[38] Rundle, *J. Amer. Chem. Soc.*, 1947, **69**, 1327.
[39] *Idem, J. Chem. Phys.*, 1949, **17**, 671.

It is hard to avoid the conclusion that in heavy atoms, where there are many electrons in the same valency shell, or at comparable distances from the nucleus, the simple language that has been devised to account for bonding between light atoms is no longer applicable. There is—so it would appear—no uniquely compelling description, but rather there are several alternative descriptions which could be employed.

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