

Contribution from the Department of Chemistry,
University College, Cardiff, Wales CF1 1XL, United Kingdom

An Angular-Overlap Treatment for Some 8-Coordinate Complexes of the Lanthanide and Actinide Series

KEITH D. WARREN

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The angular-overlap treatment is applied to the σ and π f-orbital interactions in 8-coordinate lanthanide or actinide complexes of cubic-antiprismatic (D_{4d}) or dodecahedral (D_{2d}) geometry. Predictions are made of the splittings of the ground-state manifolds for various f^x configurations ($x = 1-4$) as a function of the e_π/e_σ ratio, and for f^2 systems these are compared with the experimental data available for U(IV) species. These latter results are sufficiently encouraging to conclude that the angular-overlap model probably affords at least as good a reflection of the f-orbital bonding involvement as does the more traditional electrostatic parameterization.

Introduction

The angular-overlap model (AOM) was originally introduced by Jørgensen, Pappalardo, and Schmidtke¹ in an attempt to interpret the small 4f ligand field splittings found for various 9-coordinate lanthanide species. These authors considered only σ -bonding interactions, but more recently there has been renewed interest^{2,3} in the application of the AOM to both lanthanide and actinide complexes, and for such systems a number of geometries have been treated, especially the 6-coordinate, O_h , ML_6 arrangement. Indeed, for these latter systems it proved possible³ to derive values for both the σ - and π -bonding contributions, e_σ and e_π , and the AOM has also been utilized⁴ to investigate the magnitudes of possible f-orbital Jahn-Teller effects for these ML_6 complexes.

However, apart from the relatively small number of actinide species showing the cubic, O_h , ML_8 arrangement (for which the AOM results have already been given³), there exist a substantial number of lanthanide systems, and a probably greater number of actinide complexes, in which the central metal atom is 8-coordinate. The great bulk of these are tetrahedral species of general formula ML'_4 , where L' represents a bidentate ligand such as $CH_3COCHCOCH_3$ (acac), $C_6H_5C(O)CH(COC_6H_5)$ (DBM), etc., but although it is well-known⁵⁻¹² that one of two alternative geometries—either the cubic-antiprismatic, D_{4d} , or the dodecahedral, D_{2d} (see Figure 1)—generally constitutes the most energetically favored arrangement, only a rather small number of X-ray crystal structure determinations have actually been carried out. Thus, the β crystalline modification of $U(acac)_4$ has been found to show a slightly distorted cubic-antiprismatic structure,¹³ and the corresponding compounds of Th, Pa, Np, and Pu were shown to be isomorphous, while $U(DBM)_4$ was found to be essentially dodecahedral.¹⁴ However, in addition to these systems there exist extensive series of compounds such as $[Ln(acac)_4]^-$, $[Ln(trop)_4]^-$, $An(trop)_4$, etc. (trop = $C_8H_5O_2$) for which¹⁵⁻¹⁷

no crystallographic data are available and whose mode of 8-coordination is therefore unknown. Consequently, since the precise mode of 8-coordination will determine the nature of the ligand field splittings of the respective lowest lying f^x states, it was thought appropriate to investigate the predictions of the AOM for such complexes.

It has of course always been possible to treat the ligand field splittings of the f orbitals in these systems in terms of the familiar, and electrostatically based, $A_k^q(r^k)$ parameters (or the equivalent B_q^k quantities), but it is generally conceded that even for the 4f series an electrostatic approach is quantitatively quite inadequate (and is worse for 5f systems), so that the $A_k^q(r^k)$ parameterization is thus purely phenomenological. Consequently, an attempt is made here to apply the AOM to these two groups of 8-coordinate species, since this approach does at least purport to reflect the tendencies for weak σ and π metal-ligand bonding to occur. Moreover, if as usual, one neglects δ - and φ -type interactions, only two disposable parameters, e_σ and e_π , are required, whereas in D_{4d} symmetry three $A_k^q(r^k)$ quantities are needed in the general case, and for D_{2d} symmetry no fewer than five.

In this treatment emphasis has been placed on studying the behavior of the weak-field, $[LSJM_J]$, f^x ground-state manifolds in D_{4d} and D_{2d} environments. The results are presented explicitly for the f^x systems $x = 1-4$ (see Tables III and IV and the supplementary material) but may easily be generalized to any f^x ground state. Particular attention is paid to the f^2 U(IV) systems, for which some experimental results are available for comparison. For these latter species the ground-state predictions for D_{4d} symmetry are unequivocal and the good accord with the limited experimental data¹⁸ is most encouraging. For D_{2d} symmetry two angular parameters (θ_a and θ_b) are needed to define any given system (see Figure 1), as against only one (θ) for D_{4d} symmetry, and the ground-state predictions therefore depend in a more complex fashion on these angles. For U(IV) species of D_{2d} symmetry various ground states may be deduced,^{19,20} but the results presented here suggest that it should be possible to accommodate the ground states thus implied via small changes in θ_a and θ_b , within the range indicated experimentally.

Theory

The general theory of the AOM as applied to f-orbital systems has been given previously,³ and is therefore only briefly outlined here. The complexes now considered are all ML'_4

- (1) C. K. Jørgensen, R. Pappalardo, and H. H. Schmidtke, *J. Chem. Phys.*, **39**, 1422 (1963).
- (2) W. Urland, *Chem. Phys.*, **14**, 393 (1976).
- (3) K. D. Warren, *Inorg. Chem.*, **16**, 2008 (1977).
- (4) K. D. Warren, *Inorg. Chem.*, **19**, 653 (1980).
- (5) J. L. Hoard and J. V. Silverton, *Inorg. Chem.*, **2**, 235 (1963).
- (6) E. L. Muettterties and C. M. Wright, *Q. Rev., Chem. Soc.*, **21**, 109 (1967).
- (7) S. J. Lippard and B. J. Russ, *Inorg. Chem.*, **7**, 1686 (1968).
- (8) D. G. Blight and D. L. Kepert, *Inorg. Chem.*, **11**, 1556 (1972).
- (9) S. J. Lippard, *Prog. Inorg. Chem.*, **8**, 109 (1974).
- (10) E. L. Muettterties and L. J. Guggenberger, *J. Am. Chem. Soc.*, **96**, 1748 (1974).
- (11) U. Casellato, M. Vidali, and P. A. Vigato, *Inorg. Chim. Acta*, **18**, 77 (1976).
- (12) W. L. Steffen and R. C. Fay, *Inorg. Chem.*, **17**, 779 (1978).
- (13) H. Titzte, *Acta Chem. Scand.*, **24**, 405 (1970).
- (14) V. L. Wolf and H. Barningham, *Acta Crystallogr.*, **13**, 778 (1960).
- (15) L. R. Melby, N. J. Rose, E. Abramson, and J. C. Caris, *J. Am. Chem. Soc.*, **86**, 5117 (1964).

- (16) E. L. Muettterties and C. M. Wright, *J. Am. Chem. Soc.*, **87**, 4706 (1965).
- (17) E. L. Muettterties, *J. Am. Chem. Soc.*, **88**, 305 (1966).
- (18) J. Mulak and A. Czopnik, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, **20**, 209 (1972).
- (19) T. Yoshimura, C. Miyake, and S. Imoto, *Bull. Chem. Soc. Jpn.*, **47**, 515 (1974).
- (20) S. R. Sofen, K. Abu-Dari, D. F. Freyberg, and K. N. Raymond, *J. Am. Chem. Soc.*, **100**, 7882 (1978).

Table I. Angular-Overlap Calculations for Cubic-Antiprismatic, D_{4d} , Systems
Strong-Field f-Orbital Angular-Overlap Energies^a

orbital ^b	c/a					
	e_σ contrib			e_π contrib		
	0.9	1.0	1.1	0.9	1.0	1.1
b_2	1.4007 (+0.2578) ^c	32/27 (+0.0423)	0.9377 (-0.2051)	0.4158 (-1.8699)	8/9 (-1.3968)	1.4631 (-0.8226)
e_1	0.2079 (-0.9350)	4/9 (-0.6984)	0.7316 (-0.4113)	3.2605 (+0.9749)	28/9 (+0.8254)	2.8887 (+0.6030)
e_2	2.1904 (+1.0475)	20/9 (+1.0794)	2.1949 (+1.0521)	2.0842 (-0.2015)	20/9 (-0.0635)	2.3752 (+0.0895)
e_3	0.9014 (-0.2415)	20/27 (-0.4021)	0.6047 (-0.5382)	2.4473 (+0.1616)	20/9 (-0.0635)	2.0045 (-0.2813)

	$A_k^Q(r^k):e_\lambda$ Relationships					
	c/a			c/a		
	0.9		1.0	1.0		1.1
	e_σ	e_π	e_σ	e_π	e_σ	e_π
$A_2^0\langle r^2 \rangle$	-0.1929	-0.2899	0.0000	0.0000	+0.1868	+0.2809
$A_4^0\langle r^4 \rangle$	-0.4403	-0.1468	-0.5000	-0.1667	-0.5362	-0.1783
$A_6^0\langle r^6 \rangle$	+0.2685	-0.4026	+0.2063	-0.3095	+0.1273	-0.1909

^a All listed quantities represent diagonal matrix elements. ^b The real f-orbital basis set is as follows: f_z^3 (b_2); f_{xz^2} , f_{yz^2} (e_1); $f_z(x^2-y^2)$, f_{xy^2} (e_2); $f_x(x^2-3y^2)$, $f_y(3x^2-y^2)$ (e_3). ^c The barycentric values are shown in parentheses.

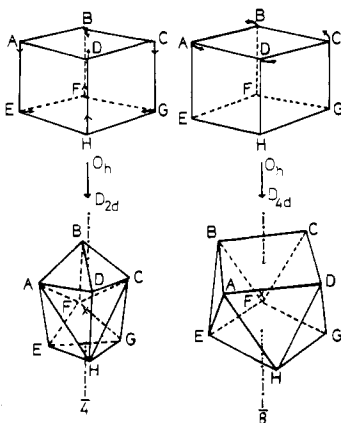


Figure 1. Cubic-antiprismatic (D_{4d}) and dodecahedral (D_{2d}) 8-coordination.

species, L' being a bidentate ligand, so that the model is here applied to ML_N species, with $N = 8$, the positions of the coordinated ligand atoms being defined by the polar angles, θ_j and φ_j ($j = 1-N$). The general ligand field matrix element is thus given by

$$\langle \psi_a | V | \psi_b \rangle = \sum_{\lambda} \sum_{\omega} \sum_{j=1}^N e_{\lambda\omega} [F_{\lambda\omega}^i(\psi_a)] [F_{\lambda\omega}^j(\psi_b)]$$

where the $F_{\lambda\omega}^i$ are the elements of the general angular transformation matrix²¹ and the other parameters as defined earlier.³ The resulting angular overlap ligand field matrix may then (if necessary) be diagonalized, so that the antibonding energies of the various f-orbital levels can be evaluated in terms of the e_σ and e_π parameters, representing respectively the contributions due to the σ and π interactions.

For 8-coordinate lanthanide and actinide complexes the most commonly occurring geometries approximate to the cubic antiprismatic arrangement, of D_{4d} symmetry, and the dodecahedral geometry, of D_{2d} symmetry, as illustrated in Figure 1. In the former case only one angular parameter, θ , is required to define the system, but for the latter case two angles, θ_a and θ_b , are needed. For the cubic antiprismatic (D_{4d}) geometry two cases may be distinguished. Thus, one may first treat the regular (or Archimedean) cubic antiprism, in which c/a , the side length ratio of the cubic antiprism,¹⁸ is unity, and

the defining angle, θ , is therefore $\cos^{-1}(1/3^{1/2})$. In general however one must consider the case $c/a \neq 1$, for both $c/a < 1$ and $c/a > 1$, corresponding to larger or smaller values of θ , respectively, and calculations are here presented for $c/a = 0.9, 1.0$, and 1.1 , thus spanning the range of values usually found. For the dodecahedral (D_{2d}) geometry, since two angular parameters are involved, one cannot adequately cover the whole range of possible structures without an excessive number of calculations, but results have been obtained for one parameter choice ($\theta_a = 35^\circ$, $\theta_b = 70^\circ$) for all f^x systems ($x = 1-4$), and for the f^2 case (corresponding to U(IV) species) calculations have been made for three other choices of θ_a and θ_b , so as to span the range of values normally encountered (see Tables I-IV and the supplementary material).

For the various D_{4d} cases the real f-orbital basis set yields via the angular overlap technique the one-electron antibonding energies listed in Table I, these values also being expressed relative to their barycenters to facilitate later comparisons. Moreover, for f-orbital systems the D_{4d} symmetry is equivalent to a pseudoaxial ($C_{\infty v}$) arrangement, so that orbitals of differing $|m_l|$ values are not mixed, and the imaginary f orbitals, defined by their m_l values, have the same one-electron energies as the real f orbitals, which are combinations of the same $\pm m_l$.

Since the ground levels of lanthanide and actinide f^x systems are known to be much better described in terms of the weak-field $[LSJM_J]$ basis than via the strong-field scheme, the one-electron energies of the real f orbitals, obtained via the AOM (the strong-field results) must now be used to express the energies of the various components of the weak-field levels of any given ground state in terms of the e_σ and e_π quantities. Happily, because D_{4d} symmetry corresponds to a pseudoaxial situation, the components of the various weak-field states will actually be defined by the M_J values, so that when the $[LSJM_J]$ functions are known the AOM energies can easily be found if the results for the individual $|m_l\rangle$ orbitals are available. Moreover, although this procedure is only really feasible for f^x systems when x is small, the splittings of any weak-field f^x ground state can readily be obtained from the strong-field results by making use of Stevens²² operator equivalent technique.

Thus, for the D_{4d} situation the effective field involves the parameters $A_2^0\langle r^2 \rangle$, $A_4^0\langle r^4 \rangle$, and $A_6^0\langle r^6 \rangle$ of the electrostatic scheme (the $A_2^0\langle r^2 \rangle$ contribution vanishes for $c/a = 1$), and the energies of the four $\pm M_J$ components of the ${}^2F_{7/2}$ state

Table II. Angular-Overlap Calculations for Dodecahedral, D_{3d} , Systems

Strong-Field f-Orbital Angular-Overlap Matrices					
case i: $\theta_a = 35^\circ, \theta_b = 70^\circ$			case ii: $\theta_a = 40^\circ, \theta_b = 65^\circ$		
orbital ^a	e_σ contrib	e_π contrib	orbital ^a	e_σ contrib	e_π contrib
b_2	0.7669 (-0.3760) ^b	2.9652 (+0.6795)	b_2	0.7954 (-0.3474)	2.3325 (+0.0468)
e'	1.4826 (+0.3398)	2.0380 (-0.2478)	e'	1.1663 (+0.0234)	2.3691 (+0.0834)
a_2	2.4576 (+1.3147)	1.7741 (-0.5116)	a_2	3.3102 (+2.1674)	1.0398 (-1.2460)
a_1	0.0000 (-1.1429)	3.2405 (+0.9548)	a_1	0.0000 (-1.1429)	3.8917 (+1.6060)
e''	0.9052 (-0.2377)	1.9721 (-0.3136)	e''	0.7809 (-0.3620)	1.9989 (-0.2868)
$\langle e' e'' \rangle$	-0.0666	-0.7599	$\langle e' e'' \rangle$	+0.2498	-1.1933
case iii: $\theta_a = 40^\circ, \theta_b = 75^\circ$			case iv: $\theta_a = 30^\circ, \theta_b = 65^\circ$		
orbital	e_σ contrib	e_π contrib	orbital	e_σ contrib	e_π orbital
b_2	0.4783 (-0.6645)	2.9374 (+0.6517)	b_2	1.2148 (+0.0719)	2.8500 (+0.5643)
e'	1.4687 (+0.3259)	1.7137 (-0.5720)	e'	1.4250 (+0.2822)	2.4984 (+0.2127)
a_2	2.3774 (+1.2345)	2.0866 (-0.1991)	a_2	2.5107 (+1.3678)	1.4190 (-0.8667)
a_1	0.0000 (-1.1429)	3.0496 (+0.7639)	a_1	0.0000 (-1.1429)	3.3421 (+1.0563)
e''	1.1034 (-0.0394)	2.2495 (-0.0362)	e''	0.7123 (-0.4306)	1.6961 (-0.5897)
$\langle e' e'' \rangle$	-0.2409	-0.6469	$\langle e' e'' \rangle$	+0.0965	-0.8586

 $A_k^q(r^k); e_\lambda$ Relationships

	case i		case ii		case iii		case iv	
	e_σ	e_π	e_σ	e_π	e_σ	e_π	e_σ	e_π
$A_2^0(r^2)$	+0.2599	+0.3900	+0.2117	+0.3174	-0.0275	-0.0413	+0.5613	+0.8419
$A_4^0(r^4)$	-0.1127	-0.0376	-0.3049	-0.1016	-0.1129	-0.0376	-0.0847	-0.0282
$A_6^0(r^6)$	-0.0941	+0.1411	-0.0045	+0.0068	-0.1302	+0.1953	-0.0279	+0.0419
$A_4^4(r^4)$	-2.4974	-0.8325	-2.3778	-0.7925	-2.9285	-0.9762	-2.0734	-0.6911
$A_6^4(r^6)$	-1.6714	+2.5070	-2.8923	+4.3383	-1.2837	+1.9255	-2.0182	+3.0273

^a The real f-orbital basis set is as follows: f_z^3 (b_2); f_{xz^2} , f_{yz^2} (e'); $f_z(x^2-y^2)$ (a_2); f_{xyz} (a_1); $f_x(x^2-3y^2)$, $f_y(3x^2-y^2)$ (e''). The e' and e'' orbitals both belong to the same D_{3d} irreducible representation, e , and the superscripts are used only for identification. All terms except $\langle e' | e'' \rangle$ [$=\langle xz^3 | x(x^2-3y^2) \rangle = -\langle yz^3 | y(3x^2-y^2) \rangle$] represent diagonal matrix elements. ^b The barycentric values are shown in parentheses.

Table III. Ground-State Splittings for f^2 , 3H_4 Systems in D_{4d} Symmetry

$\pm M_J$	c/a					
	0.9		1.0		1.1	
	e_σ	e_π	e_σ	e_π	e_σ	e_π
4	+0.4678	+0.1373	+0.3720	+0.0077	+0.2600	-0.1135
3	-0.7299	+0.4329	+0.7324	+0.2501	-0.6900	+0.0428
2	+0.2079	-0.8007	+0.1065	-0.6041	-0.0132	-0.3624
1	+0.1262	-0.0762	+0.2142	+0.0423	+0.2892	+0.1563
0	-0.1446	+0.6136	+0.0795	+0.6080	+0.3082	+0.5531

for an f^1 system may readily be written down in terms of these $A_k^q(r^k)$ quantities, with use of Stevens²² method. (Note that the sixth-degree terms vanish within $^2F_{5/2}$.) Moreover, it is simple to transform the f^1 strong-field angular-overlap results to the weak-field form without the use of the specific $|LSJM_J\rangle$ functions. Thus the matrix elements of the spin-orbit coupling operator for the f^1 system are readily evaluated in the D_{4d} strong-field scheme, and the matrix that transforms this to the diagonal weak-field $|LSJM_J\rangle$ result is easily derived. When this transformation matrix is applied to the f^1 strong-field angular-overlap matrix, the latter will be converted into the required weak-field form, the result of course agreeing with that obtained via the f^1 $|LSJM_J\rangle$ wave functions. Then finally, the diagonal elements of the weak-field angular-overlap matrix are expressed relative to their barycenters for comparison with the operator equivalent results derived by Stevens' technique.

Thus for the D_{4d} situation the energies of the four $\pm M_J$ components for the $^2F_{7/2}$ state of f^1 may be obtained both in terms of the e_σ and e_π quantities on the one hand and in terms of the $A_k^q(r^k)$ parameters on the other, and it is then easy to express these latter parameters in terms of e_σ and e_π . Consequently, since the splitting of any f^x ground state in D_{4d} symmetry can be found in terms of $A_2^0(r^2)$, $A_4^0(r^4)$, and $A_6^0(r^6)$, these same splittings can equally well be expressed in terms of the alternative e_σ and e_π parameters.

Table IV. Matrix Elements Defining Ground-State Splittings for f^2 , 3H_4 Systems in D_{3d} Symmetry

$\langle M_J M_J' \rangle$	e_σ	e_π
Case i: $\theta_a = 35^\circ, \theta_b = 70^\circ$		
$\langle 0 0 \rangle$	+0.3433	-0.0232
$\langle \pm 1 \pm 1 \rangle$	+0.1303	+0.1650
$\langle \pm 2 \pm 2 \rangle$	-0.1701	+0.2859
$\langle \pm 3 \pm 3 \rangle$	-0.0195	-0.2764
$\langle \pm 4 \pm 4 \rangle$	-0.1124	-0.1629
$\langle \pm 2 \mp 2 \rangle$	+0.5871	-0.2753
$\langle \pm 3 \mp 1 \rangle$	+0.3398	+0.0243
$\langle \pm 4 0 \rangle$	-0.1229	+0.5220
Case ii: $\theta_a = 40^\circ, \theta_b = 65^\circ$		
$\langle 0 0 \rangle$	+0.3378	+0.2036
$\langle \pm 1 \pm 1 \rangle$	+0.1962	+0.1542
$\langle \pm 2 \pm 2 \rangle$	-0.1199	+0.0155
$\langle \pm 3 \pm 3 \rangle$	-0.3074	-0.1496
$\langle \pm 4 \pm 4 \rangle$	+0.0622	-0.1220
$\langle \pm 2 \mp 2 \rangle$	+0.7590	-0.5620
$\langle \pm 3 \mp 1 \rangle$	+0.3613	-0.0336
$\langle \pm 4 0 \rangle$	-0.3560	+0.8555
Case iii: $\theta_a = 40^\circ, \theta_b = 75^\circ$		
$\langle 0 0 \rangle$	+0.2781	-0.2877
$\langle \pm 1 \pm 1 \rangle$	+0.0249	+0.0152
$\langle \pm 2 \pm 2 \rangle$	-0.2795	+0.3051
$\langle \pm 3 \pm 3 \rangle$	+0.0697	-0.2839
$\langle \pm 4 \pm 4 \rangle$	+0.0458	+0.1076
$\langle \pm 2 \mp 2 \rangle$	+0.5845	-0.1669
$\langle \pm 3 \mp 1 \rangle$	+0.3788	+0.0579
$\langle \pm 4 0 \rangle$	-0.0198	+0.4257
Case iv: $\theta_a = 30^\circ, \theta_b = 65^\circ$		
$\langle 0 0 \rangle$	+0.3460	+0.3118
$\langle \pm 1 \pm 1 \rangle$	+0.2319	+0.3151
$\langle \pm 2 \pm 2 \rangle$	+0.0060	+0.1987
$\langle \pm 3 \pm 3 \rangle$	-0.1244	-0.2047
$\langle \pm 4 \pm 4 \rangle$	-0.2865	-0.4650
$\langle \pm 2 \mp 2 \rangle$	+0.5844	-0.3739
$\langle \pm 3 \mp 1 \rangle$	+0.3004	-0.0073
$\langle \pm 4 0 \rangle$	-0.2179	+0.6071

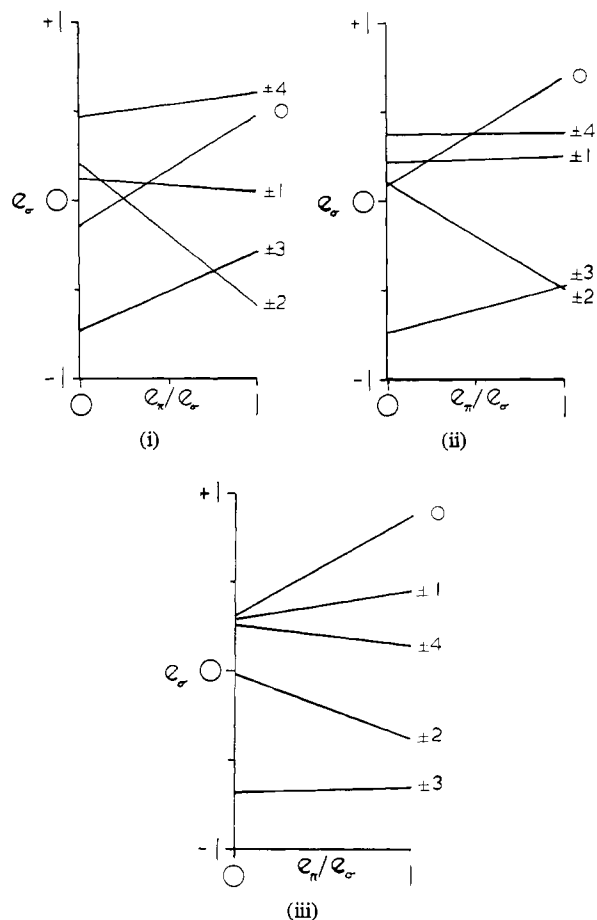


Figure 2. Ground-state splittings for f^2 , 3H_4 systems in D_{4d} symmetry: (i) $c/a = 0.9$, (ii) $c/a = 1.0$, (iii) $c/a = 1.1$.

In D_{2d} symmetry however two pairs of the real f orbitals, f_{xz^2} , f_{yz^2} and $f_{x(x^2-3y^2)}$, $f_{y(3x^2-y^2)}$, belong to the same irreducible representation (e), and may therefore in principle mix. In fact the effective potential for this symmetry permits the mixing of the imaginary f orbitals differing by ± 4 in m_l , so that in the strong-field angular-overlap matrix for D_{2d} systems there arise off-diagonal matrix elements connecting the two e representations. Nonetheless, the procedure to be followed is essentially the same as for the D_{4d} cases since it is convenient to use the same strong-field basis set as for that symmetry. Thus the same transformation may be used to convert the strong-field angular-overlap matrix to the weak-field $|LSJM_f\rangle$ form, although the strong-field matrix will now contain off-diagonal terms connecting the two e representations. Moreover, since the $f_{x(x^2-y^2)}$, $f_{y(3x^2-y^2)}$ pair of orbitals (e_2 in D_{4d}) are now in D_{2d} no longer degenerate but transform as a_2 and a_1 , respectively, there will also arise an off-diagonal matrix element between the two erstwhile degenerate e_2 components.

From the resulting weak-field D_{2d} angular-overlap matrix expressions may be obtained, in terms of e_σ and e_π , for both the diagonal and the off-diagonal elements within the $f^1 \ ^2F_{7/2}$ state; the former may then be equated to the results in terms of $A_2^0\langle r^2 \rangle$, $A_4^0\langle r^4 \rangle$, and $A_6^0\langle r^6 \rangle$, obtained via Stevens²² method, and the latter to similar relationships involving $A_4^4\langle r^4 \rangle$ and $A_6^4\langle r^6 \rangle$. Thus the ensuing results for the $A_k^q\langle r^k \rangle$ in terms of the e_λ may once more be applied to determine the ground-state splittings for any f^x configuration in D_{2d} symmetry.

The results thus derived for f^x systems ($x = 1-4$) for both D_{4d} and D_{2d} species were then used to calculate ground-state splitting patterns covering a realistic range of values for the ratio e_π/e_σ of the two angular-overlap parameters. Since the

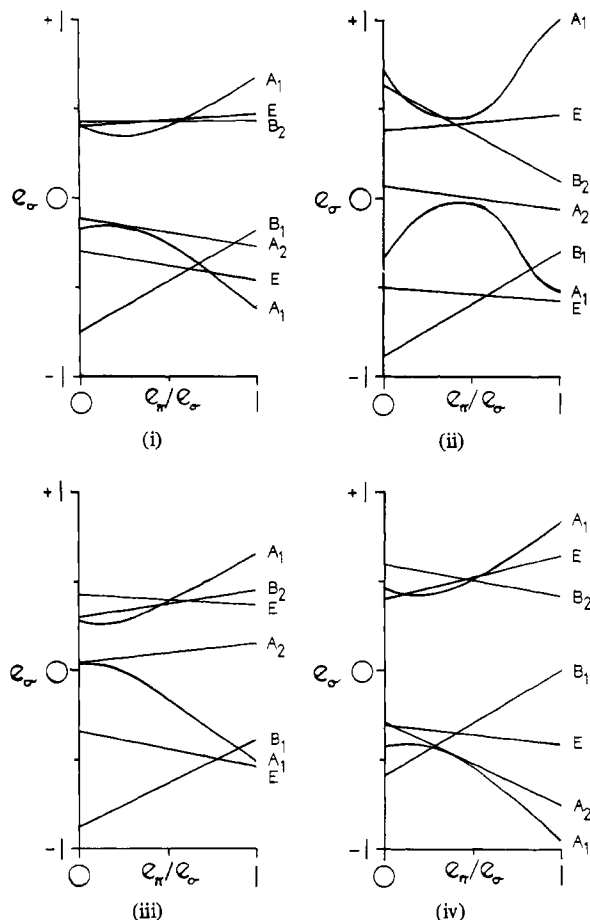


Figure 3. Ground-state splittings for f^2 , 3H_4 systems in D_{2d} symmetry: (i) $\theta_a = 35^\circ$, $\theta_b = 70^\circ$; (ii) $\theta_a = 40^\circ$, $\theta_b = 65^\circ$; (iii) $\theta_a = 40^\circ$, $\theta_b = 75^\circ$; (iv) $\theta_a = 30^\circ$, $\theta_b = 65^\circ$.

e_λ quantities should be roughly proportional²³ to the corresponding S_λ^2 values (S_λ being the relevant overlap integral) and the S_π quantities are usually substantially smaller than the S_σ values, only the range of e_π/e_σ ratios between zero and unity need be considered. In principle e_π could be negative, should the ligands themselves possess their own π^* antibonding levels of higher energy than the metal f orbitals, but the results are here collected for $e_\pi/e_\sigma = 0-1$ and may easily be extended to span the range 0 to -1 .

Finally, for simplicity, the possible effects of nonlinear ligation have been neglected, so that any possible asymmetry of π bonding in the local ligand x and y directions is disregarded, and e_π therefore strictly represents only an averaged value. Nevertheless, this may at least be partially justified since studies of the photoelectron spectra of U(IV) β -diketone complexes²⁴ suggest that the σ contribution to the metal-ligand bonding is in any case dominant. Moreover, the complexed β -diketone ring in An^{IV} species is known¹³ not to be coplanar with the An-O linkage, but to be tilted about the O-O axis; since this tilt angle (average value 143° in $U(acac)_4$) is comparable with the C-O-An angle (average value 135° in $U(acac)_4$), it would not be anticipated that the π -bonding propensities of the ligating oxygen atoms should be markedly asymmetric.

Results and Discussion

The resulting ground-state splitting patterns, covering the range $e_\pi/e_\sigma = 0-1$ for the f^2 , 3H_4 system, are now therefore

(23) D. W. Smith, *Struct. Bonding (Berlin)*, **35**, 87 (1978).

(24) I. Fragala, G. Condorelli, A. Tondello, and A. Cassol, *Inorg. Chem.*, **17**, 3175 (1978).

given diagrammatically for the D_{4d} and D_{2d} geometries in Figures 2 and 3, respectively. In Figure 2 are shown the results for $c/a = 0.9, 1.0,$ and 1.1 , while in Figure 3 are presented the data for four different choices of the pairs of defining angles, θ_a and θ_b . These latter angles are as follows: (i) $\theta_a = 35^\circ, \theta_b = 70^\circ$; (ii) $\theta_a = 40^\circ, \theta_b = 65^\circ$; (iii) $\theta_a = 40^\circ, \theta_b = 75^\circ$; (iv) $\theta_a = 30^\circ, \theta_b = 65^\circ$. The appropriate matrix elements, in terms of the e_λ parameters, are given for D_{4d} symmetry in Table III and for D_{2d} symmetry in Table IV. The corresponding results for $f^1, f^3,$ and f^4 systems are listed in the supplementary material.

Since pseudoaxial symmetry is operative in the D_{4d} situation whereas in the D_{2d} case states differing in M_J by ± 4 are permitted to mix, it is apparent that these two types of 8-coordination should lead to different splittings of the various J states constituting the ground levels of the various f^x configurations. Consequently, a study of the magnetic susceptibility and ESR properties of such 8-coordinate tetrakis lanthanide or actinide complexes would be of great value in elucidating their stereochemistry. However, despite the considerable interest in such species manifested during the 1960s, Lippard⁹ was forced to note in 1974 that there yet remained much interesting work to be done on the magnetic properties of 8-coordinate f^x complexes. At that time only the $U(acac)_4$ complex had been adequately investigated,¹⁸ and although Yoshima, Miyake, and Imoto¹⁹ did record some further experimental data for other 8-coordinate $U(IV)$ species, hardly any additional magnetic studies have since been reported for these extensive series of compounds. Examination of the AOM predictions is therefore effectively limited to those relating to these f^2 $U(IV)$ systems.

The X-ray crystal study by Titze¹³ of the β form of $U(acac)_4$ showed it to possess a monoclinic unit cell (space group $C2/c$), with the eight oxygen atoms yielding an average U–O distance of 2.32 Å and surrounding the U atom in the form of a somewhat distorted right Archimedean antiprism. Early investigations²⁵ of the magnetic susceptibility of $U(acac)_4$ showed that in the higher temperature region above about 195 K the susceptibility corresponded to a magnetic moment of some 3.2–3.3 μ_B , although the Curie–Weiss law was not closely obeyed at the lower temperature. This was confirmed by the later and more detailed work of Mulak and Czopnik,¹⁸ who found extensive deviations from Curie–Weiss behavior in the low-temperature range, culminating in the observation of temperature-independent paramagnetism (TIP) of 19850×10^{-6} cgsu below about 20 K. These authors showed that the experimental data could be satisfactorily accommodated by the assumption of effective D_{4d} symmetry, with the $M_J = \pm 3$ component of the 3H_4 ground state lying lowest; the TIP below 20 K was attributed to a small rhombic distortion from strict D_{4d} symmetry, lifting the degeneracy of the $M_J = \pm 3$ level, the separation between its two components being estimated to be about 15 cm^{-1} , while the overall splitting of the 3H_4 ground state was calculated to be some 3100 cm^{-1} .

However, an attempt to interpret the data by a theoretical treatment based on the electrostatic model gave at best only rather equivocal agreement with experiment. Thus, as pointed out by Mulak and Czopnik,¹⁸ the point-charge model is in any case inherently unreliable since it generally leads to predicted splittings several times smaller than those actually observed, and in this case the M_J component of 3H_4 predicted to lie lowest was extremely sensitive to the chosen value of the ratio c/a . For $c/a < 0.92$ $M_J = 0$ was predicted to lie lowest, with $M_J = \pm 1$ fractionally higher, but between $c/a = 0.92$ and $c/a = 0.95$ the ground level becomes $M_J = \pm 2$, followed by $M_J = \pm 3$ for c/a between 0.95 and 1.09, and finally $M_J = \pm 4$ for

$c/a > 1.09$. Moreover, although $M_J = \pm 3$ was calculated to lie lowest for the major part of the c/a range in the region of unity, the value of c/a derived from the crystallographic data¹³ for $U(acac)_4$ is significantly smaller than that which should produce $M_J = \pm 3$ as the ground component.

Thus, apart from $\beta-U(acac)_4$, crystallographic data are available for $\beta-Zr(acac)_4, \beta-Ce(acac)_4,$ and $\alpha-Ce(acac)_4$,^{26–28} all of which show the slightly distorted cubic-antiprismatic structure. If one takes the parameter a as half of the mean of the lengths s and s_r , as defined by Titze,¹³ and calculates the parameter c from the mean M–O bond lengths, the ratio c/a is found to be 0.931, 0.888, 0.920, and 0.843 for $\beta-U(acac)_4, \beta-Zr(acac)_4, \beta-Ce(acac)_4,$ and $\alpha-Ce(acac)_4$, respectively. The values thus cluster around $c/a \approx 0.90$, and that for $\beta-U(acac)_4$ is clearly too small to lead to $M_J = \pm 3$ lying lowest on the electrostatic model.

Nevertheless, the predictions of the AOM are, in contrast, in good accord with the experimental findings. Thus, as shown in Figure 2, for the $f^2, ^3H_4$ system in D_{4d} symmetry, with $c/a = 1.0$, the $M_J = \pm 3$ component remains the ground level throughout almost all of the e_π/e_σ range considered, only being superseded by $M_J = \pm 2$ at $e_\pi/e_\sigma \approx 0.99$. Moreover, although a decrease in the c/a ratio does bring this crossover point to lower e_π/e_σ values, even at $c/a = 0.90$ the $M_J = \pm 3$ component lies lowest up to $e_\pi/e_\sigma \approx 0.77$, after which, as before, $M_J = \pm 2$ takes over up to $e_\pi/e_\sigma = 1$. Consequently, since the available PES data²⁴ suggest the predominance of σ bonding in $U(IV)$ β -diketone complexes, the predictions of the AOM are satisfactorily borne out and are in addition relatively insensitive to the value of c/a assumed. Furthermore, for the $M(IV), 5f^1$ species $[PaF_6]^{2-}$ and $[PaCl_6]^{2-}$ the AOM was found³ to yield e_π/e_σ ratios of 0.429 and 0.517, respectively, while the $A_k^q(r^k)$ parameters deduced from the electronic Raman spectral data of Amberger et al.²⁹ for the $5f^2, U(IV)$ complex $[UCl_6]^{2-}$ yield the result $e_\pi/e_\sigma = 0.367$. There is therefore every reason to believe that for $U(acac)_4$ the appropriate e_π/e_σ value will be well below the ± 3 to ± 2 crossover point, thus reinforcing the AOM forecast of $M_J = \pm 3$ as the ground component.

An inspection of Figure 2 shows that for c/a in the region of 0.9–1.0 the overall splitting of the $f^2 ^3H_4$ ground state is of the order of 1.0–1.2 e_σ . For the second-row ligand Cl, values of e_σ of 1264 and 1445 cm^{-1} , respectively, were found for $[PaCl_6]^{2-}$ and $[UCl_6]^{2-}$, while for the first-row ligand F, $[PaF_6]^{2-}$ gave $e_\sigma = 2866$ cm^{-1} . Since Mulak and Czopnik¹⁸ calculate the total 3H_4 splitting for $U(acac)_4$ to be 3100 cm^{-1} , corresponding to $e_\sigma \approx 2500$ –3000 cm^{-1} , the value of e_σ that might be anticipated for the first-row oxygen ligand is clearly of the correct order of magnitude, although the available data are obviously not adequate to define the magnitude of e_π . Finally, the small splitting of the $M_J = \pm 3$ ground level, leading to the TIP below 20 K, is by no means unexpected because of the known distortions from the perfect cubic-antiprismatic geometry, and in any case this level would, even in strict D_{4d} symmetry, be susceptible to Jahn–Teller activity.

Because of the deviations from Curie–Weiss behavior the effective value of μ , the magnetic moment, for these $U(IV)$ β -diketone complexes depends to some extent upon the temperature range used, and from their data for the region 77–300 K Yoshimura et al.¹⁹ reported an effective μ value of 2.92 μ_B for the cubic-antiprismatic $U(acac)_4$. In contrast the dodecahedral $U(DBM)_4$ gave $\mu = 3.43$ μ_B over the same range, and UCl_4 (known to have dodecahedral coordination about

(25) C. A. Hutchison and N. Elliott, *J. Chem. Phys.*, **16**, 920 (1948).(26) J. V. Silverton and J. L. Hoard, *Inorg. Chem.*, **2**, 243 (1963).(27) H. Titze, *Acta Chem. Scand.*, **23**, 399 (1969).(28) B. Matkovic and D. Grdenic, *Acta Crystallogr.*, **16**, 456 (1963).(29) H.-D. Amberger, R. D. Fischer, G. G. Rosenbauer, and A. W. Spiegel, *Ber. Bunsenges. Phys. Chem.*, **80**, 495 (1976).

the U atom) yielded $\mu = 3.29 \mu_B$. Other species examined included $U(\text{tfac})_4$, $U(\text{bac})_4$, $U(\text{TTA})_4$, and $U(\text{cupf})_4$ (tfac = trifluoroacetylacetonate, bac = benzoylacetonate, TTA = thenoyltrifluoroacetate, cupf = cupferronate), for which moments of 3.16, 3.08, 3.01, and $3.50 \mu_B$, respectively, were recorded, and on the basis of these μ values Yoshimura et al. concluded that $U(\text{cupf})_4$ was probably dodecahedral but the remainder were antiprismatic. These authors also indicated that it was possible to interpret their magnetic data for the antiprismatic species on the basis of $M_J = 0$ lying lowest, with $M_J = \pm 1$ and $M_J = \pm 2$ only slightly higher, but since this ordering derives from the electrostatic model, which as previously noted is intrinsically suspect from a quantitative standpoint, the AOM interpretation, which agrees with that of Mulak and Czopnik,¹⁸ is clearly preferable.

For the U(IV) systems of D_{2d} symmetry the situation is unfortunately by no means so clear. Thus only $U(\text{DBM})_4$ and the catecholato anion $[U(\text{catech})_4]^{4-}$ (catech = $C_6H_4O_2$) have been investigated by X-ray diffraction,^{14,20} and the available magnetic data are somewhat limited since only UCl_4 and $U(\text{cupf})_4$ (assumed to be dodecahedral) were studied from room temperature down to 4 K. Both these species showed markedly nonlinear χ_M^{-1} vs. T plots in the low-temperature region, giving as T approached zero a substantial TIP of the order of $(15\,000\text{--}20\,000) \times 10^{-6}$ cgsu, which was interpreted¹⁹ as arising from an A_1 level ($|+4\rangle, |-4\rangle, |0\rangle$) lying lowest, with the A_2 component ($|+4\rangle, |-4\rangle$) only slightly higher. Thus, whereas the pseudoaxial D_{4d} symmetry of the cubic-antiprismatic systems led to the lifting of the ninefold degeneracy of the 3H_4 ground state to give four doublets and one singlet for which M_J remained a good quantum number, the dodecahedral geometry permits components differing in M_J by ± 4 to mix, giving rise to two doublets and five singlets. In this way the $M_J = +2$ and $M_J = -2$ levels are split, yielding two widely separated singlets, mixtures of $|+2\rangle$ and $|-2\rangle$, transforming as B_1 and B_2 , while the $M_J = 0$ level interacts with both $M_J = +4$ and $M_J = -4$, giving two A_1 singlets and one A_2 singlet. The two doublets of E symmetry arise from the interactions of the $M_J = \pm 1$ and $M_J = \mp 3$ levels.

However, only when a doublet level lies lowest (or very close to lowest) can the first-order Zeeman effect be expected to operate to produce temperature-dependent paramagnetism over the whole temperature range, except where the lower A_1 and the A_2 levels lie lowest and are closely juxtaposed, so that the second-order terms mimic the first-order effect. When either the B_1 or the B_2 level lies lowest, only TIP due to second-order Zeeman terms would be expected, and this should be small unless, fortuitously, an interacting level were to lie only slightly higher. Furthermore, the difficulty of interpreting the magnetic behavior of such systems is compounded by the fact that for the A_1 plus A_2 levels lying lowest a generally

substantial TIP would be expected as T approaches zero, while small distortions from strict D_{2d} symmetry, or the Jahn-Teller effect, could split any E level that might lie lowest, leading to similar behavior.

In Figure 3 are shown the splitting patterns resulting for the f^2 , 3H_4 ground state in D_{2d} symmetry for various choices of the θ_a and θ_b angles. It is clear that these splittings are quite susceptible to the e_π/e_σ ratio and highly susceptible to the choice of the angles, θ_a and θ_b . Moreover, if one accepts that π bonding is unlikely to be substantial—for example, $e_\pi/e_\sigma < 0.50$ —then nowhere in the diagrams shown will an E level lie lowest, although interpolation suggests that for $\theta_a \approx 32^\circ$ with $\theta_b = 65^\circ$, and $e_\pi/e_\sigma \approx 0.30\text{--}0.40$, the B_1 , A_1 , A_2 , and E levels will all lie within about $0.05\text{--}0.10 e_\sigma$ units, with either B_1 or A_1 plus A_2 lowest. Furthermore, the lower A_1 and the A_2 levels can only lie close together and constitute the ground level when e_π/e_σ is greater than about 0.30, with θ_a less than about 32° and θ_b less than about 67° .

Thus, for the dodecahedral systems so far studied an unambiguous interpretation of a generally temperature-dependent paramagnetism, tending toward a large TIP as T approaches zero, is hardly possible. However, the one case reported²⁰ as showing a small (870×10^{-6} cgsu) TIP in the range 4–80 K may readily be understood since the accompanying X-ray diffraction studies revealed the defining angles θ_a and θ_b to be 37.1 and 75.2° , respectively, in $[U(\text{catech})_4]^{4-}$. Thus, examination of Figure 3i and iii (the most closely comparable choices of angles) shows that at all reasonable values of e_π/e_σ the magnetically inactive singlet of B_1 symmetry lies lowest and is well separated from any other level. This therefore would be expected to yield only a small TIP over a wide temperature range, via second-order Zeeman terms, in accordance with the observed behavior. Moreover, the data of Figure 3 indicate that an A_1 singlet cannot lie lowest and well separated from the A_2 or any other level except for improbably high values of e_π/e_σ , and with both θ_a and θ_b significantly smaller than the experimental figures.

On the whole therefore the results of the AOM calculations for f^2 D_{2d} systems seem likely to be of less immediate utility than for the corresponding D_{4d} species. Further accurate magnetic susceptibility measurements extending down to 4 K are clearly desirable, especially for compounds of established dodecahedral geometry for which the θ_a and θ_b angles have been determined crystallographically, and studies of the paramagnetic anisotropy would be particularly valuable for systems of either symmetry.

Supplementary Material Available: Calculations for D_{4d} and D_{2d} systems and tables of ground-state splittings and matrix elements defining ground-state splittings for f^2 systems in D_{4d} and D_{2d} symmetry (7 pages). Ordering information is given on any current masthead page.