Splitting of Terms Beyond a D-Term in an Octahedral Ligand Field

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Although the procedure to calculate the ligand field energies of terms of a many d-electron configuration in cubic symmetry is known, we present a novel semiquantitative method for the splitting of d-electron terms in cubic symmetry. The method is based on quantitative calculations of one-electron orbitals of a given angular momentum.

Introduction

In the weak-field approach of ligand field theory, Russell-Saunders terms (or L, S-terms) are obtained first by taking into account electron repulsions perturbation, and the terms are then split into final energy levels by the ligand field of appropriate symmetry of the complex. The qualitative derivation of the (L, S)-terms by the use of the microstate table is well-known. The showing of the splittings of these terms by the ligand field, even qualitatively, is somewhat involved. Thus, for instance the d^2 (or d^8) electronic configuration gives rise to the ground state ^3F and the excited states ^3P, ^1G, ^1D, and ^1S. The quantitative splittings of these terms by the ligand field are derived by first forming the $|L, M_L\rangle$ wave functions of a given term either by using the ladder operator techniques [1] or by the application of the $3-j$ symbols [2]. These functions are further linearly combined to form the basis functions for cubic symmetry which are then utilized in the calculation of the ligand field energies [3]. If it is intended to show qualitatively how the terms split, this can be done by the use of symmetry and group theory. There are two ways to derive the splittings by symmetry and group theory. One procedure is by the application of Bethe's formula [4] for the character of a rotation which yields the reducible representation of a term which can then be decomposed into the irreducible representations. A second procedure is to take recourse to the fact that these terms can be considered as being equivalent to one-electron orbitals and to conclude that the terms split exactly as the one-electron orbitals. Thus, just as the d-orbitals in an octahedral symmetry split into t_{2g} and e_g orbitals, a D-term of a many d-electron configuration splits into T_{2g} and E_g levels. Similarly, f-orbitals split into t_{1u}, t_{2u}, a_{2u} and an F-term splits into T_{1g}, T_{2g}, A_{2g} levels, g-orbitals split into t_{1g}, t_{2g}, e_g, a_{1g} and a G-term splits into T_{1g}, T_{2g}, E_g, A_{1g} levels, and so on[1]. However, it still remains to be shown in this procedure how the one-electron orbitals split. Although it is a simple matter to show the splitting of the d-orbitals in an octahedral ligand field by visualising the d-orbitals, it is not such a simple procedure to show the splitting of the f-orbitals or the g-orbitals. Indeed, the f-orbitals that are used to deduce the splitting in an octahedral ligand field are not just the real orbitals but are further combinations of real orbitals which are the bases for cubic symmetry [5] or as sometimes called "cubic oriented". In other words, it is necessary to know the actual cubic based orbitals beforehand to arrive at the qualitative splittings in this procedure[2]. It is possible, however, to start from the real orbitals and deduce the splitting by the use of symmetry and eventually arrive at the cubic based orbitals, as we will show below.

There is yet another procedure which is quantitative and makes use of the ligand field potential and one-electron orbitals. It is the purpose of this paper to outline this procedure, since it brings out certain interesting aspects of the theory. Before presenting this procedure, however, we would like

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[1] It should be noted that the one-electron orbitals acquire either g or u symmetry in a centrosymmetric complex depending upon whether the l-quantum number is even or odd, respectively. However, the terms of many d-electron system always transform as levels of g symmetry regardless of whether the L value of the term is even or odd.

[2] It turns out in the case of the d-orbitals, the real orbitals are also the cubic oriented orbitals.

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to briefly review the two procedures of symmetry and group theory mentioned above.

Qualitative Splitting of Terms by the Use of Symmetry and Group Theory

Application of Bethe's Formula [4]

The formula for the character of the identity operation, E, is given by, $\chi(E) = 2L + 1$, and of a rotation φ is given by,

$$\chi(\varphi) = [\sin(L + 1/2)\varphi]/\sin(\varphi/2)\,.$$

For F and G terms, since $L = 3$ and 4, the corresponding representations have the characters:

	E	$6C_4$	$3C_4^2$	$8C_3$	$6C_2'$
Γ_F	7	-1	-1	1	-1
Γ_G	9	1	1	0	1

Thus the Γ_F reduces to the irreducible representations $A_{2g} + T_{1g} + T_{2g}$ and the Γ_G to

$$A_{1g} + E_g + T_{1g} + T_{2g}\,.$$

This procedure, however, does not result in any further information.

Application of Symmetry to One-Electron Orbitals

We will show this procedure for f-orbitals only. The real f-orbitals, excluding a common factor $\sqrt{105/4}\sqrt{\pi}\,r^3$ are as follows:

$$\begin{aligned}
Y_3^0 &= (1/\sqrt{15})(5z^3 - 3zr^2)\,,\\
Y_3^{1c} &= (1/\sqrt{2})(-Y_3^1 + Y_3^{-1})\\
&= (1/\sqrt{10})(5z^2 - r^2)\,x\,,\\
Y_3^{1s} &= (i/\sqrt{2})(Y_3^1 + Y_3^{-1})\\
&= (1/\sqrt{10})(5z^2 - r^2)\,y\,,\\
Y_3^{2c} &= (1/\sqrt{2})(Y_3^2 + Y_3^{-2}) \quad = z(x^2 - y^2)\,,\\
Y_3^{2s} &= -(i/\sqrt{2})(Y_3^2 - Y_3^{-2}) = 2zyx\,,\\
Y_3^{3c} &= (1/\sqrt{2})(-Y_3^3 + Y_3^{-3})\\
&= (1/\sqrt{6})(x^3 - 3xy^2)\,,\\
Y_3^{3s} &= (i/\sqrt{2})(Y_3^3 + Y_3^{-3})\\
&= (1/\sqrt{6})(-y^3 + 3yx^2)\,.
\end{aligned}$$

The symmetry transformation properties of these real f-orbitals under the symmetry operations of the O point group are given in Table 1[3]. Obviously, the representation of the f-orbitals transforms as $a_2 + t_1 + t_2$ irreducible representations. However, it should be noted that although the $2zyx$ orbital forms the basis for the a_2 representation, the other six orbitals which transform together as t_1 and t_2 representations either mix among themselves or produce new orbitals. It should further be noted that among these six orbitals, the

$$(1/\sqrt{15})(5z^3 - 3zr^2) \quad \text{and} \quad z(x^2 - y^2)$$

orbitals give rise to a character of $+1$ and -1, respectively, under C_4 rotation. Carrying out the symmetry operations of a quadrate point-symmetry group (C_{4v}, D_{4h}, D_4 point groups) such as D_4 on these two orbitals shows that they transform as a_2 and b_2 representations which means that they are the proper components of the octahedral t_1 and t_2 representations, respectively. Successive operation

Table 1. Symmetry Transformation Properties of Real f-orbitals in O Symmetry Point Group. (A common factor of $\sqrt{105/4}\sqrt{\pi}\,r^3$ has been excluded from the orbitals.)

	E	$6C_4$	$3C_4^2$	$8C_3$	$6C_2'$
$(1/\sqrt{15})(5z^3 - 3zr^2)$	1	1	1	$(1/\sqrt{15})(5y^3 - 3yr^2)$	-1
$(1/\sqrt{10})(5z^2 - r^2)\,x$	1	$-(1/\sqrt{10})(5z^2 - r^2)\,y$	-1	$(1/\sqrt{10})(5y^2 - r^2)\,z$	$(1/\sqrt{10})(5z^2 - r^2)\,y$
$(1/\sqrt{10})(5z^2 - r^2)\,y$	1	$(1/\sqrt{10})(5z^2 - r^2)\,x$	-1	$(1/\sqrt{10})(5y^2 - r^2)\,x$	$(1/\sqrt{10})(5z^2 - r^2)\,x$
$z(x^2 - y^2)$	1	-1	1	$y(z^2 - x^2)$	1
$2zyx$	1	-1	1	1	-1
$(1/\sqrt{6})(x^3 - 3xy^2)$	1	$(1/\sqrt{6})(-y^3 + 3yx^2)$	-1	$(1/\sqrt{6})(z^3 - 3zx^2)$	$-(1/\sqrt{6})(-y^3 + 3yx^2)$
$(1/\sqrt{6})(-y^3 + 3yx^2)$	1	$-(1/\sqrt{6})(x^3 - 3xy^2)$	-1	$(1/\sqrt{6})(-x^3 + 3xz^2)$	$-(1/\sqrt{6})(x^3 - 3xy^2)$
Γ_f	7	-1	-1	1	-1

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[3] These follow from the symmetry transformation properties of (z, y, x):

$$C_4\begin{pmatrix} z\\ y\\ x\end{pmatrix} = \begin{pmatrix} z\\ x\\ -y\end{pmatrix}; \quad C_4^2\begin{pmatrix} z\\ y\\ x\end{pmatrix} = \begin{pmatrix} z\\ -y\\ -x\end{pmatrix};$$

$$C_3\begin{pmatrix} z\\ y\\ x\end{pmatrix} = \begin{pmatrix} y\\ x\\ z\end{pmatrix}; \quad \text{and} \quad C_2'\begin{pmatrix} z\\ y\\ x\end{pmatrix} = \begin{pmatrix} -z\\ x\\ y\end{pmatrix}.$$

of C_3 rotation on each of these components produces the other two components of its representation. The four cubic based orbitals thus obtained, namely, the

$$(1/\sqrt{15})\,(5\,y^3 - 3\,y\,r^2)\,, \quad (1/\sqrt{15})\,(5\,x^3 - 3\,x\,r^2)\,,$$

$y(z^2 - x^2)$, and $x(y^2 - z^2)$ orbitals can be formed by linearly combining the four real orbitals

$$(1/\sqrt{10})\,(5\,z^2 - r^2)\,x\,, \quad (1/\sqrt{10})\,(5\,z^2 - r^2)\,y\,,$$
$$(1/\sqrt{6})\,(x^3 - 3\,x\,y^2)\,, \quad \text{and}$$
$$(1/\sqrt{6})\,(-\,y^3 + 3\,y\,x^2)\,.$$

By expressing the cubic based orbital as a linear combination of the appropriate real orbitals, the coefficients in the linear combination can be determined by equating the coefficients of the same terms on both sides of the expression. The results are

$$(1/\sqrt{15})\,(5\,y^3 - 3\,y\,r^2)$$
$$= -\,\sqrt{3/8}\,Y_3^{1\mathrm{s}} - \sqrt{5/8}\,Y_3^{3\mathrm{s}}\,,$$
$$(1/\sqrt{15})\,(5\,x^3 - 3\,x\,r^2)$$
$$= -\,\sqrt{3/8}\,Y_3^{1\mathrm{c}} + \sqrt{5/8}\,Y_3^{3\mathrm{c}}\,,$$
$$y\,(z^2 - x^2) = \sqrt{5/8}\,Y_3^{1\mathrm{s}} - \sqrt{3/8}\,Y_3^{3\mathrm{s}}\,,$$
$$x\,(y^2 - z^2) = -\,\sqrt{5/8}\,Y_3^{1\mathrm{c}} - \sqrt{3/8}\,Y_3^{3\mathrm{c}}\,.$$

From the symmetry transformation properties of these cubic based orbitals given in Table 2, it can be seen that the

$$(1/\sqrt{15})\,(5\,z^3 - 3\,z\,r^2)\,, \quad (1/\sqrt{15})\,(5\,y^3 - 3\,y\,r^2)\,,$$

and $(1/\sqrt{15})\,(5\,x^3 - 3\,x\,r^2)$ orbitals form the bases for the t_1 representation and the orbital triplet $z(x^2 - y^2)$, $y(z^2 - x^2)$, and $x(y^2 - z^2)$ spans the t_2 representation.

It may be noted at this point that the linear combinations of $|\,L,\,M_{\mathrm{L}}\rangle$ functions for cubic representations are just these combinations. Thus,

$$A_2 = Y_3^{2\mathrm{s}} = (-\,i/\sqrt{2})\,[|\,3,2\rangle - |\,3,-2\rangle]\,,$$
$$T_{1\mathrm{a}} = Y_3^0 = |\,3,0\rangle\,,$$
$$\begin{aligned} T_{1\mathrm{b}} &= -\,\sqrt{3/8}\,Y_3^{1\mathrm{s}} - \sqrt{5/8}\,Y_3^{3\mathrm{s}} \\ &= -\,\sqrt{3/8}\,\{(i/\sqrt{2})\,[|\,3,1\rangle + |\,3,-1\rangle]\} \\ &\quad -\sqrt{5/8}\,\{(i/\sqrt{2})\,[|\,3,3\rangle + |\,3,-3\rangle]\}\,, \end{aligned}$$
$$\begin{aligned} T_{1\mathrm{c}} &= -\,\sqrt{3/8}\,Y_3^{1\mathrm{c}} + \sqrt{5/8}\,Y_3^{3\mathrm{c}} \\ &= -\,\sqrt{3/8}\,\{(1/\sqrt{2})\,[-\,|\,3,1\rangle + |\,3,-1\rangle]\} \\ &\quad +\sqrt{5/8}\,\{(1/\sqrt{2})\,[-\,|\,3,3\rangle + |\,3,-3\rangle]\}\,, \end{aligned}$$
$$T_{2\mathrm{a}} = Y_3^{2\mathrm{c}} = (1/\sqrt{2})\,[|\,3,2\rangle + |\,3,-2\rangle]\,,$$
$$\begin{aligned} T_{2\mathrm{b}} &= \sqrt{5/8}\,Y_3^{1\mathrm{s}} - \sqrt{3/8}\,Y_3^{3\mathrm{s}} \\ &= \sqrt{5/8}\,\{(i/\sqrt{2})\,[|\,3,1\rangle + |\,3,-1\rangle]\} \\ &\quad -\sqrt{3/8}\,\{(i/\sqrt{2})\,[|\,3,3\rangle + |\,3,-3\rangle]\}\,, \end{aligned}$$
$$\begin{aligned} T_{2\mathrm{c}} &= -\,\sqrt{5/8}\,Y_3^{1\mathrm{c}} - \sqrt{3/8}\,Y_3^{3\mathrm{c}} \\ &= -\,\sqrt{5/8}\,\{(1/\sqrt{2})\,[-\,|\,3,1\rangle + |\,3,-1\rangle]\} \\ &\quad -\sqrt{3/8}\,\{(1/\sqrt{2})\,[-\,|\,3,3\rangle + |\,3,-3\rangle]\}\,. \end{aligned}$$

Table 2. Symmetry Transformation Properties of Cubic Oriented f-Orbitals in O Symmetry Point Group [A common factor of $(\sqrt{105}/4\sqrt{\pi}\,r^3)$ has been excluded from the orbitals.]

	E	$6C_4$	$3{C_4}^2$	$8C_3$	$6C_2'$
$2\,z\,y\,x$	1	-1	1	1	-1
$(1/\sqrt{15})\,(5\,z^3 - 3\,z\,r^2) = a$	1	1	1	b	-1
$(1/\sqrt{15})\,(5\,y^3 - 3\,y\,r^2) = b$	1	c	-1	c	c
$(1/\sqrt{15})\,(5\,x^3 - 3\,x\,r^2) = c$	1	$-b$	-1	a	b
$z\,(x^2 - y^2) = \alpha$	1	-1	1	β	1
$y\,(z^2 - x^2) = \beta$	1	$-\gamma$	-1	γ	$-\gamma$
$x\,(y^2 - z^2) = \gamma$	1	β	-1	α	$-\beta$

Quantitative Splittings of one-Electron Orbitals and Application to the Splittings of Many d-Electron Terms

Splitting of f-orbitals and of an F Term

The expansion for the ligand field potential in an octahedral complex including spherical harmonics of sixth degree can be shown to be

$$\begin{aligned} V_{\mathrm{O_h}}^{\mathrm{LF}} = e\,z\{&\varrho_0(r)\,\sqrt{4\,\pi}\,(6)\,Y_0^0 \\ &+ \varrho_4(r)\,(\sqrt{4\,\pi/9})\,(7/2) \\ &\cdot[Y_4^0 + (\sqrt{5/14})\,(Y_4^4 + Y_4^{-4})] \\ &+ \varrho_6(r)\,(\sqrt{4\,\pi/13})\,(3/4) \\ &\cdot[Y_6^0 - (\sqrt{7/2})\,(Y_6^4 + Y_6^{-4})]\}\,, \end{aligned}$$

where e and z are the electronic charge and the ligand effective charge, and $\varrho_l(r) = r_<^l/r_>^{l+1}$ with $r_<$ being the lesser of the electronic radius vector and the ligand central atom distance and $r_>$ being the greater of the two. The potential up to fourth degree spherical harmonic terms is just the potential that is used in calculations with d-electrons and the sixth degree terms are needed in calculations involving f-orbitals. However, as we will show in the following, *if our interest is in finding the splittings of terms of a many d-electron configuration, it is sufficient to use the octahedral potential that is used for a single d-electron, i.e., up to fourth degree harmonics.*

A simple and an elegant way of calculating the one-electron energies with a given potential is by the use of the expansions of products of spherical harmonics of the orbitals in terms of a combination of spherical harmonics. The coefficients in the expansion can be obtained either by the application of the $3-j$ symbols [2] or by an algebraic method in a straightforward manner by expressing a product as being equivalent to an appropriate combination of spherical harmonics and insuring that the coefficients of the same terms on both sides of the expression must be same. The necessary products for the f-orbital energy calculations obtained by these procedures are given in Table 3. By utilizing these products and the octahedral ligand field potential, the nonzero matrix elements of the ligand field energy are calculated to be[4]:

$$\begin{aligned}\langle Y_3^0|\, V_{\mathrm{O_h}}^{\mathrm{LF}}\,|Y_3^0\rangle &= (7/11)\langle\varrho_4(r)\rangle\\ &\quad+(25/143)\langle\varrho_6(r)\rangle\\ &= 6x+20y,\\ \langle Y_3^{\pm1}|\, V_{\mathrm{O_h}}^{\mathrm{LF}}\,|Y_3^{\pm1}\rangle &= (7/66)\langle\varrho_4(r)\rangle\\ &\quad-(75/572)\langle\varrho_6(r)\rangle\\ &= x-15y,\\ \langle Y_3^{\pm2}|\, V_{\mathrm{O_h}}^{\mathrm{LF}}\,|Y_3^{\pm2}\rangle &= -(49/66)\langle\varrho_4(r)\rangle\\ &\quad+(15/286)(\varrho_6(r)\rangle\\ &= -7x+6y,\\ \langle Y_3^{\pm3}|\, V_{\mathrm{O_h}}^{\mathrm{LF}}\,|Y_3^{\pm3}\rangle &= (7/22)\langle\varrho_4(r)\rangle\\ &\quad-(5/572)\langle\varrho_6(r)\rangle\\ &= 3x-y,\\ \langle Y_3^{\pm1}|\, V_{\mathrm{O_h}}^{\mathrm{LF}}\,|Y_3^{\mp3}\rangle &= (7\sqrt{15}/66)\langle\varrho_4(r)\rangle\\ &\quad+(35\sqrt{15}/572)\langle\varrho_6(r)\rangle\\ &= \sqrt{15}\,x+7\sqrt{15}\,y,\end{aligned}$$

Table 3. Products of Spherical Harmonics of Third Degree as Linear Combinations of Spherical Harmonics.

$$\begin{aligned}Y_3{}^0\cdot Y_3{}^0 &= (1/2\sqrt{\pi})\,[Y_0{}^0+(4/3\sqrt{5})\,Y_2{}^0+(6/11)\,Y_4{}^0\\ &\qquad+(100/33\sqrt{13})\,Y_6{}^0]\\ Y_3{}^{\pm1*}\cdot Y_3{}^{\pm1} &= (1/2\sqrt{\pi})\,[Y_0{}^0+(1/\sqrt{5})\,Y_2{}^0+(1/11)\,Y_4{}^0\\ &\qquad-(25/11\sqrt{13})\,Y_6{}^0]\\ Y_3{}^{\pm2*}\cdot Y_3{}^{\pm2} &= (1/2\sqrt{\pi})\,[Y_0{}^0-(7/11)\,Y_4{}^0\\ &\qquad+(10/11\sqrt{13})\,Y_6{}^0]\\ Y_3{}^{\pm3*}\cdot Y_3{}^{\pm3} &= (1/2\sqrt{\pi})\,[Y_0{}^0-(\sqrt{5}/3)\,Y_2{}^0+(3/11)\,Y_4{}^0\\ &\qquad-(5/33\sqrt{13})\,Y_6{}^0]\\ Y_3{}^{\pm1*}\cdot Y_3{}^{\mp3} &= (\sqrt{21}/11\sqrt{2\pi})\,Y_4{}^{\pm4*}-(5\sqrt{35}/11\sqrt{78\pi})\,Y_6{}^{\pm4*}\\ Y_3{}^{\pm2*}\cdot Y_3{}^{\mp2} &= (\sqrt{35}/11\sqrt{2\pi})\,Y_4{}^{\pm4*}+(5\sqrt{14}/11\sqrt{13\pi})\,Y_6{}^{\pm4*}\end{aligned}$$

$$\begin{aligned}\langle Y_3^{\pm2}|\, V_{\mathrm{O_h}}^{\mathrm{LF}}\,|Y_3^{\mp2}\rangle &= (35/66)\langle\varrho_4(r)\rangle\\ &\quad-(105/286)\langle\varrho_6(r)\rangle\\ &= 5x-42y,\end{aligned}$$

where

$$\begin{aligned}\langle\varrho_l(r)\rangle &= \langle\varrho_l(r)\rangle_f\\ &= e\,z\int_0^\infty (r_<^l/r_>^{l+1})\,R_f(r)^2\,r^2\,\mathrm{d}r,\\ x &= (7/66)\langle\varrho_4(r)\rangle,\quad\text{and}\\ y &= (5/572)\langle\varrho_6(r)\rangle.\end{aligned}$$

Thus, except for Y_3^0 which is a pure energy level, two 2×2 secular determinants result, one being a doubly degenerate determinant. The simpler determinant of Y_3^2 and Y_3^{-2} yields the energies

$$(-2x-36y)\quad\text{and}\quad(-12x+48y)$$

with the corresponding wave functions

$$(1/\sqrt{2})\,(Y_3^2+Y_3^{-2})\ \text{and}\ -(i/\sqrt{2})\,(Y_3^2-Y_3^{-2}).$$

The doubly degenerate determinant of $Y_3^{\pm1}$ and $Y_3^{\mp3}$ results in energies $(6x+20y)$ and $(-2x-36y)$ with the corresponding wave functions

$$\begin{aligned}&[(\sqrt{3/8})\,Y_3^{\pm1}+(\sqrt{5/8})\,Y_3^{\mp3}]\quad\text{and}\\ &[(\sqrt{5/8})\,Y_3^{\pm1}-(\sqrt{3/8})\,Y_3^{\mp3}]\end{aligned}$$

which are, of course, imaginary. The degenerate set of orbitals can be combined to result in real functions. The real functions thus obtained are for energy $(6x+20y)$:

$$\begin{aligned}&-\sqrt{3/8}\,[(i/\sqrt{2})\,(Y_3^1+Y_3^{-1})]\\ &-\sqrt{5/8}\,[(i/\sqrt{2})\,(Y_3^3+Y_3^{-3})],\\ &-\sqrt{3/8}\,[(1\sqrt{2})\,(-Y_3^1+Y_3^{-1})]\\ &+\sqrt{5/8}\,[(1/\sqrt{2})\,(-Y_3^3+Y_3^{-3})],\end{aligned}$$

and for energy $(-2x-36y)$:

$$\begin{aligned}&\sqrt{5/8}\,[(i/\sqrt{2})\,(Y_3^1+Y_3^{-1})]\\ &-\sqrt{3/8}\,[(i/\sqrt{2})\,(Y_3^3+Y_3^{-3})],\\ &-\sqrt{5/8}\,[(1\sqrt{2})\,(-Y_3^1+Y_3^{-1})]\\ &-\sqrt{3/8}\,[(1/\sqrt{2})\,(-Y_3^3+Y_3^{-3})].\end{aligned}$$

The energies and the wave functions are summarized below. (A common factor of $\sqrt{105}/4\sqrt{\pi}\,r^3$ has been left out of the cartesian forms.)

$E=-12x+48y$:

$$Y_3^{2s}=2zyx\,;$$

$E=-2x-36y$:

$$\begin{aligned}&Y_3^{2c}=z(x^2-y^2),\\ &(\sqrt{5/8})\,Y_3^{1s}-(\sqrt{3/8})\,Y_3^{3s}=y(z^2-x^2),\\ &-(\sqrt{5/8})\,Y_3^{1c}-(\sqrt{3/8})\,Y_3^{3c}=x(y^2-z^2);\end{aligned}$$

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[4] In what follows, the upper signs go together and the lower signs go together.

$E = 6x + 20y$:

$$Y_3^0 = (1/\sqrt{15})\,(5z^3 - 3zr^2)\,,$$
$$-(\sqrt{3/8})\,Y_3^{1\mathrm{s}} - (\sqrt{5/8})\,Y_3^{3\mathrm{s}} = (1/\sqrt{15})\,(5y^3 - 3yr^2)\,,$$
$$-(\sqrt{3/8})\,Y_3^{1\mathrm{c}} + (\sqrt{5/8})\,Y_3^{3\mathrm{c}} = (1/\sqrt{15})\,(5x^3 - 3xr^2)\,.$$

The representations spanned by these functions are a_2, t_2, and t_1, respectively, as shown above.

This procedure, of course, gives the same results as those obtained by the symmetry method above and in addition the energies.

The energies obtained above are for one-electron f-orbitals. The splittings and the energies of split levels of an F-term could have been obtained just with the restricted potential without the sixth degree harmonic terms. With such a restricted potential, the energies of T_1, T_2, and A_2 levels would be $6x$, $-2x$, and $-12x$, respectively. The octahedral splittings of F-terms of many d-electron configurations, however, can be obtained by setting $x = -Dq$ (^{3}F of d^2 and ^{4}F of d^7) and $x = +Dq$ (^{3}F of d^8 and ^{4}F of d^3), i.e., $(7/66)\langle\varrho_4(r)\rangle_{\mathrm{f}} = \mp Dq$. The splitting of f-orbitals or of an F-term is depicted in Figure 1.

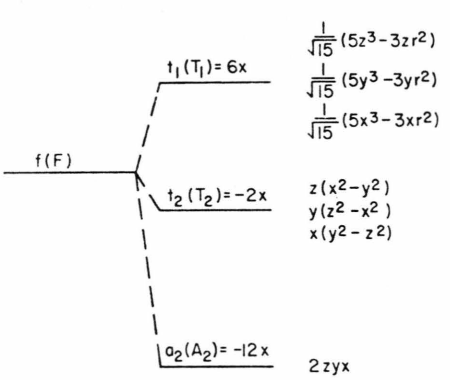

Fig. 1. Splitting of f-orbitals or of an F-term in an octahedral ligand field. With $x = (7/66)\langle\varrho_4(r)\rangle_{\mathrm{f}}$ and $\langle\varrho_6(r)\rangle_{\mathrm{f}} = 0$, these are the energies of the split levels of f-orbitals. With $x = -Dq$ and $+Dq$, the energies of the split levels of ^{3}F term of d^2 (or ^{4}F of d^7) and ^{4}F term of d^3 (or ^{3}F of d^8) configurations are produced, respectively.

Splitting of g-orbitals and of a G-term

We will use the restricted potential to show the splitting of a G-term. (A complete potential for one-electron 5 g orbitals of superactinides should include eighth degree spherical harmonic terms Y_8^0, $Y_8^{\pm4}$ and $Y_8^{\pm8}$ which will give rise to a third ligand field radial parameter $\langle\varrho_8(r)\rangle$.) Since we are using only the Y_4^0 and $Y_4^{\pm4}$ terms of the potential, it is necessary to know only the coefficients of these terms in the expansions of the products of the fourth degree spherical harmonics. The required products are given in Table 4. The calculated ligand field matrix elements are as follows:

$$\langle Y_4^0 \,|\, V_{\mathrm{O_h}}^{\mathrm{LF}} \,|\, Y_4^0 \rangle = (81/143)\langle\varrho_4(r)\rangle = 18x\,,$$
$$\langle Y_4^0 \,|\, V_{\mathrm{O_h}}^{\mathrm{LF}} \,|\, Y_4^{\pm4} \rangle = (9\sqrt{70}/286)\langle\varrho_4(r)\rangle = \sqrt{70}\,x\,,$$
$$\langle Y_4^{\pm4} \,|\, V_{\mathrm{O_h}}^{\mathrm{LF}} \,|\, Y_4^{\pm4} \rangle = (63/143)\langle\varrho_4(r)\rangle = 14x\,,$$
$$\langle Y_4^{\pm1} \,|\, V_{\mathrm{O_h}}^{\mathrm{LF}} \,|\, Y_4^{\pm1} \rangle = (81/286)\langle\varrho_4(r)\rangle = 9x\,,$$
$$\langle Y_4^{\pm1} \,|\, V_{\mathrm{O_h}}^{\mathrm{LF}} \,|\, Y_4^{\mp3} \rangle = (45\sqrt{7}/286)\langle\varrho_4(r) = 5\sqrt{7}\,x\,,$$
$$\langle Y_4^{\pm3} \,|\, V_{\mathrm{O_h}}^{\mathrm{LF}} \,|\, Y_4^{\pm3} \rangle = -(189/286)\langle\varrho_4(r)\rangle = -21x\,,$$
$$\langle Y_4^{\pm2} \,|\, V_{\mathrm{O_h}}^{\mathrm{LF}} \,|\, Y_4^{\pm2} \rangle = -(9/26)\langle\varrho_4(r)\rangle = -11x\,,$$
$$\langle Y_4^{\pm2} \,|\, V_{\mathrm{O_h}}^{\mathrm{LF}} \,|\, Y_4^{\mp2} \rangle = (135/286)\langle\varrho_4(r)\rangle = -15x\,,$$

where $x = (9/286)\langle\varrho_4(r)\rangle$ and

$$\langle\varrho_4(r)\rangle = \langle\varrho_4(r)\rangle_{\mathrm{g}} = ez\int_0^\infty (r_<^4/r_>^5)\,R_{\mathrm{g}}(r)^2 r^2\,\mathrm{d}r\,.$$

Since the $\langle Y_4^{\pm4} \,|\, V_{\mathrm{O_h}}^{\mathrm{LF}} \,|\, Y_4^{\mp4} \rangle = 0$, we can form

$$Y_4^{4\mathrm{c}} = (1/\sqrt{2})\,(Y_4^4 + Y_4^{-4}) \quad \text{and}$$
$$Y_4^{4\mathrm{s}} = -(i/\sqrt{2})\,(Y_4^4 - Y_4^{-4})$$

combinations such that

$$\langle Y_4^{4\mathrm{c}} \,|\, V_{\mathrm{O_h}}^{\mathrm{LF}} \,|\, Y_4^{4\mathrm{c}} \rangle = \langle Y_4^{4\mathrm{s}} \,|\, V_{\mathrm{O_h}}^{\mathrm{LF}} \,|\, Y_4^{4\mathrm{s}} \rangle = 14x\,,$$
$$\langle Y_4^0 \,|\, V_{\mathrm{O_h}}^{\mathrm{LF}} \,|\, Y_4^{4\mathrm{c}} \rangle = 2\sqrt{35}\,x\,, \quad \text{and}$$
$$\langle Y_4^0 \,|\, V_{\mathrm{O_h}}^{\mathrm{LF}} \,|\, Y_4^{4\mathrm{s}} \rangle = 0$$

which implies that $Y_4^{4\mathrm{s}}$ is a pure energy level by itself with an energy of $14x$.

The solution of the secular determinant of Y_4^0 and $Y_4^{4\mathrm{c}}$ gives the results:

$$E_+ = 28x\,,$$
$$\Psi_+ = \sqrt{7/12}\,Y_4^0 + \sqrt{5/12}\,[(1/\sqrt{2})\,(Y_4^4 + Y_4^{-4})]$$

Table 4. Coefficients of $Y_4{}^0$ and $Y_4{}^{\pm4*}$ Terms in the Expansions of the Products of Spherical Harmonics of Fourth Degree.

	Coefficient of	
	$Y_4{}^0$	$Y_4{}^{\pm4*}$
$Y_4{}^0 \cdot Y_4{}^0$	$243/1001\sqrt{\pi}$	0
$Y_4{}^{\pm1*} \cdot Y_4{}^{\pm1}$	$243/2002\sqrt{\pi}$	0
$Y_4{}^{\pm2*} \cdot Y_4{}^{\pm2}$	$-27/182\sqrt{\pi}$	0
$Y_4{}^{\pm3*} \cdot Y_4{}^{\pm3}$	$-81/286\sqrt{\pi}$	0
$Y_4{}^{\pm4*} \cdot Y_4{}^{\pm4}$	$27/143\sqrt{\pi}$	0
$Y_4{}^0 \cdot Y_4{}^{\mp4}$	0	$27/143\sqrt{\pi}$
$Y_4{}^{\pm1*} \cdot Y_4{}^{\mp3}$	0	$27\sqrt{10}/286\sqrt{\pi}$
$Y_4{}^{\pm2*} \cdot Y_4{}^{\mp2}$	0	$81\sqrt{70}/2002\sqrt{\pi}$

and

$$E_- = 4x,$$
$$\Psi_- = \sqrt{5/12}\,Y_4^0 - \sqrt{7/12}\,[(1/\sqrt{2})(Y_4^4 + Y_4^{-4})].$$

The solution of the determinant of Y_4^2 and Y_4^{-2} yields the results:

$$E_+ = 4x, \qquad \Psi_+ = (1/\sqrt{2})(Y_4^2 + Y_4^{-2})$$

and

$$E_- = -26x, \quad \Psi_- = -(i/\sqrt{2})(Y_4^2 - Y_4^{-2}).$$

Finally, the doubly degenerate determinant of $Y_4^{\pm 1}$ and $Y_4^{\mp 3}$ produces the results:

$$E_+ = -26x, \quad \Psi_+ = \sqrt{1/8}\,Y_4^{\pm 1} - \sqrt{7/8}\,Y_4^{\mp 3}$$

and

$$E_- = 14x, \qquad \Psi_- = \sqrt{7/8}\,Y_4^{\pm 1} + \sqrt{1/8}\,Y_4^{\mp 3}.$$

These imaginary wave functions can be combined, as in the case of the f-orbitals, to obtain the real forms. Thus, for the energy $-26x$:

$$\begin{aligned}
&-\sqrt{1/8}[(1/\sqrt{2})(-Y_4^1 + Y_4^{-1})]\\
&-\sqrt{7/8}[(1/\sqrt{2})(-Y_4^3 + Y_4^{-3})],\\
&-\sqrt{1/8}[(i/\sqrt{2})(Y_4^1 + Y_4^{-1})]\\
&+\sqrt{7/8}[(i/\sqrt{2})(Y_4^3 + Y_4^{-3})],
\end{aligned}$$

and for the energy $14x$:

$$\begin{aligned}
&\sqrt{7/8}[(1/\sqrt{2})(-Y_4^1 + Y_4^{-1})]\\
&-\sqrt{1/8}[(1/\sqrt{2})(-Y_4^3 + Y_4^{-3})],\\
&-\sqrt{7/8}[(i/\sqrt{2})(Y_4^1 + Y_4^{-1})]\\
&-\sqrt{1/8}[(i/\sqrt{2})(Y_4^3 + Y_4^{-3})].
\end{aligned}$$

The energies and the wave functions are summarized below. (A common factor of $3\sqrt{5}/4\sqrt{\pi}\,r^4$ has been taken out of the cartesian forms and the usual notation of cosine and sine combinations of spherical harmonics has been employed.)

$E = 28x$:

$$\begin{aligned}
&(\sqrt{7/12})\,Y_4^0 + (\sqrt{5/12})\,Y_4^{4\mathrm{c}}\\
&= (\sqrt{105}/6)(x^4 + y^4 + z^4 - 3r^4/5);
\end{aligned}$$

$E = 14x$:

$$\begin{aligned}
&Y_4^{4\mathrm{s}} = \sqrt{7}(x^2 - y^2)xy,\\
&(\sqrt{7/8})\,Y_4^{1\mathrm{c}} - (\sqrt{1/8})\,Y_4^{3\mathrm{c}} = \sqrt{7}(z^2 - x^2)zx,\\
&-(\sqrt{7/8})\,Y_4^{1\mathrm{s}} - (\sqrt{1/8})\,Y_4^{3\mathrm{s}} = \sqrt{7}(y^2 - z^2)yz;
\end{aligned}$$

$E = 4x$:

$$\begin{aligned}
&(\sqrt{5/12})\,Y_4^0 - (\sqrt{7/12})\,Y_4^{4\mathrm{c}}\\
&\quad = (1/2\sqrt{3})[(7x^2 - r^2)(y^2 - z^2)\\
&\qquad - (7y^2 - r^2)(z^2 - x^2)],\\
&Y_4^{2\mathrm{c}} = (1/2)[(7z^2 - r^2)(x^2 - y^2)];
\end{aligned}$$

$E = -26x$:

$$\begin{aligned}
&Y_4^{2\mathrm{s}} = (7z^2 - r^2)xy,\\
&-(\sqrt{1/8})\,Y_4^{1\mathrm{c}} - (\sqrt{7/8})\,Y_4^{3\mathrm{c}} = (7y^2 - r^2)zx,\\
&-(\sqrt{1/8})\,Y_4^{1\mathrm{s}} + (\sqrt{7/8})\,Y_4^{3\mathrm{c}} = (7x^2 - r^2)yz.
\end{aligned}$$

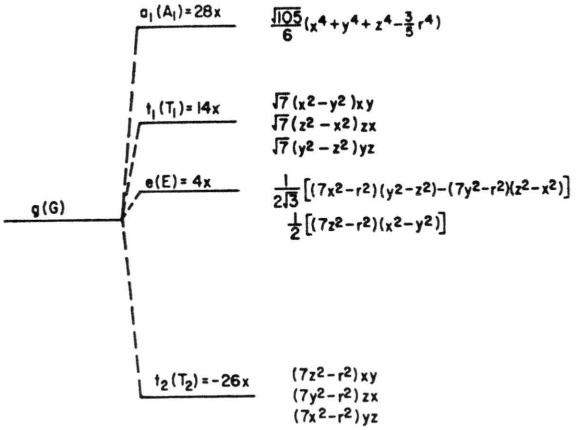

Fig. 2. Splitting of g-orbitals or of a G-term in an octahedral ligand field. With $x = (9/286)\langle\varrho_4(r)\rangle_{\mathrm{g}}$ and $\langle\varrho_6(r)\rangle_{\mathrm{g}} = \langle\varrho_8(r)\rangle_{\mathrm{g}} = 0$, these are the energies of the split levels of g-orbitals. With $x = (1/7)\,Dq$ or $x = -(1/14)\,Dq$, the energies of the split levels of ^{1}G term of d^2 configuration or of ^{2}G term of d^3 configuration are produced, respectively.

Table 5. Symmetry Transformation Properties of Cubic Oriented g-Orbitals in O Symmetry Point Group. [A common factor of $(3\sqrt{5}/4\sqrt{\pi}\,r^4)$ has been excluded from the orbitals.]

	E	$6C_4$	$3C_4^2$	$8C_3$	$6C_2'$
$(\sqrt{105}/6)(x^4 + y^4 + z^4 - 3r^4/5)$	1	1	1	1	1
$(1/2)(7z^2 - r^2)(x^2 - y^2) = \varepsilon$	1	-1	1	$-\varepsilon/2 - \sqrt{3}\,\theta/2$	-1
$(1/2\sqrt{3})[(7x^2 - r^2)(y^2 - z^2) - (7y^2 - r^2)(z^2 - x^2)] = \theta$	1	1	1	$-\theta/2 + \sqrt{3}\,\varepsilon/2$	1
$\sqrt{7}(x^2 - y^2)xy = a$	1	1	1	b	-1
$\sqrt{7}(z^2 - x^2)zx = b$	1	c	-1	c	c
$\sqrt{7}(y^2 - z^2)yz = c$	1	$-b$	-1	a	b
$(7z^2 - r^2)xy = \alpha$	1	-1	1	β	1
$(7y^2 - r^2)zx = \beta$	1	$-\gamma$	-1	γ	$-\gamma$
$(7x^2 - r^2)yz = \gamma$	1	β	-1	α	$-\beta$

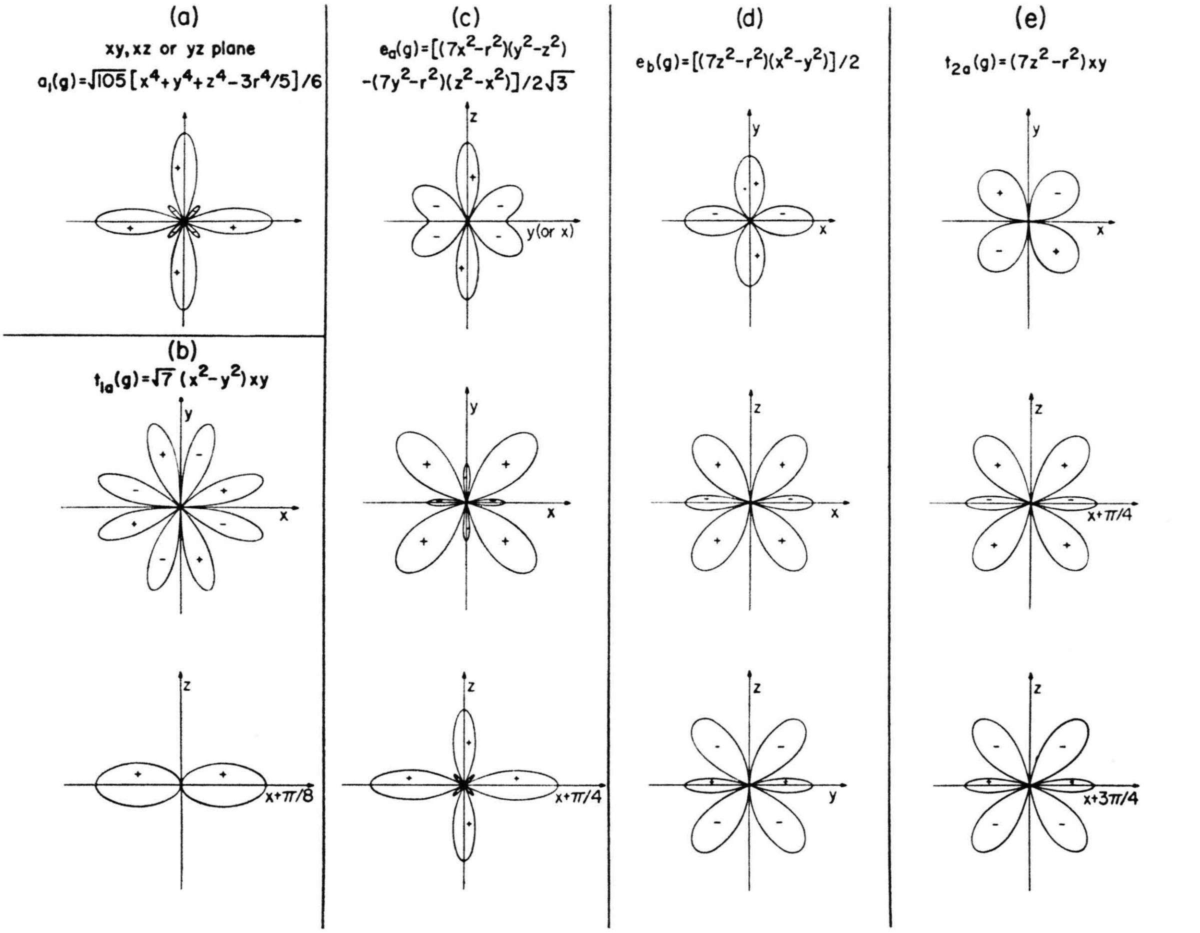

Fig. 3. Polar plots of the cubic oriented g-orbitals: (a) a_1 orbital. (b) t_{1a} orbital. The t_{1b} and t_{1c} orbitals are similar to t_{1a} except they are in the *zx* and *yz* planes, respectively. (c) e_a orbital. (d) e_b orbital. (e) t_{2a} orbital. The t_{2b} and t_{2c} orbitals are similar to t_{2a} in that they are obtained by replacing the *xy* plane by *zx* and *yz* planes, respectively, and the *z* axis by *y* and *x* axes, respectively.

The actual designations of representations that these are a_1, t_1, e and t_2, of course, are obtained from the symmetry transformation properties of the orbitals presented in Table 5.

The energies of the split levels of the ^1G term of the d^2 configuration are obtained by setting $x = (1/7)Dq$, i.e., $(63/286)\langle \varrho_4(r)\rangle_g = Dq$. However, the octahedral splittings of the ^2G term of d^3 configuration are given by $x = -(1/14)Dq$ or

$$(63/143)\langle \varrho_4(r)\rangle_g = -Dq^5.$$

The splitting of the g-orbitals or of a G-term is shown in Figure 2. The plots of the g-orbitals are shown in Figure 3[6].

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[5] It should be noted that only in the case of the terms of highest spin-multiplicity, the same ratio (within sign) of $\langle \varrho_4(r)\rangle_l/Dq$ gives the energies of split levels of terms of different configurations. Thus, just as the splittings of F-terms are obtained by $(7/66)\langle \varrho_4(r)_f\rangle = \mp Dq$, the splittings of D-terms can be obtained by equating $(1/6)\langle \varrho_4(r)\rangle_d = +Dq$ (^2D of d^1 and ^5D of d^6) and $-Dq$ (^2D of d^9 and ^5D of d^4). However, the $\langle \varrho_4(r)\rangle_l/Dq$ ratio will be different for splittings of terms that are not of highest spin-multiplicity, whether they are of different configurations or even of the same configuration. For instance, the energies of split levels of the ^2F term of d^3 configuration are given by $(7/11)\langle \varrho_4(r)\rangle_f = +Dq$.

[6] The author wishes to thank Mr. John Collins for constructing these plots.

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