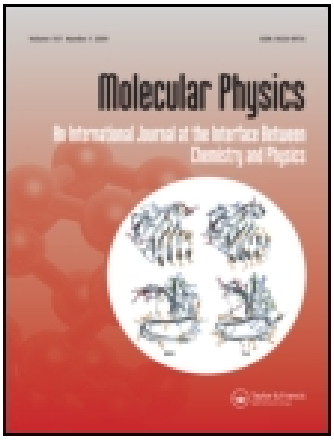

Molecular Physics: An International Journal at the Interface Between Chemistry and Physics

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/tmph20

Some investigations in the theory of open-shell ions

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Published online: 23 Aug 2006.

To cite this article: J.S. Griffith (1960) Some investigations in the theory of open-shell ions, Molecular Physics: An International Journal at the Interface Between Chemistry and Physics, 3:5, 457-475, DOI: 10.1080/00268976000100501

To link to this article: http://dx.doi.org/10.1080/00268976000100501

Some investigations in the theory of open-shell ions Part III. The calculation of matrix elements

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(*Received* 3 *March* 1960)

The use of V, W and X coefficients in calculations of matrix elements is shown. General formulae for all two-electron spin–orbit coupling matrices in an octahedral strong-field coupling scheme are deduced. The parametrization of the electrostatic energy in ligand field theory is discussed and the number of parameters required is given in various cases. The configuration f^2 in an octahedral strong-field scheme is treated in some detail and reasons for the anomalously low paramagnetism of PuF_6 are exposed, largely in contradiction to earlier views [13, 14]. Finally it is shown that expressions involving recoupling matrix elements, which occur in a scheme for calculating matrix elements of one-electron operators given by Tanabe and Kamimura [3], are proportional to W and X coefficients, thus considerably extending the scope of the latter work.

1. Reduced matrix elements

In Part II we defined and investigated the properties of V, W and X coefficients for certain finite groups and gave tables of their values for the octahedral group [1]. In this and a subsequent paper the use of these coefficients in actual calculations will be shown. The applications invariably depend on the following proposition. Let a, b, c be irreducible representations of a group G with components α, β, γ. Suppose the standard choice for their matrices to be real and that the direct product abc contains the unit representation at most once. Then if $|a\alpha\rangle$, $T_\beta{}^b$, $|c\gamma\rangle$ are kets and operators transforming according to these representations we have

$$\langle a\alpha \,|\, T_\beta{}^b \,|\, c\gamma\rangle = \langle a \,||\, T^b \,||\, c\rangle \, V\begin{pmatrix} a & b & c \\ \alpha & \beta & \gamma \end{pmatrix}, \tag{1}$$

with the reduced matrix element $\langle a \,||\, T^b \,||\, c\rangle$ independent of α, β and γ. This equation is the expression in our new notation of one which has already been used in ligand field theory [2, 3] and is the form which the Wigner–Eckart theorem (see, e.g. Fano and Racah [4], henceforward referred to as FR, chapter 14) takes in this case. The order of the representations in the V symbol is important and will always be taken as in equation (1). I adopt the double-barred notation for the reduced matrix element [3, 4] rather than Condon and Shortley's four dots notation [5] which I have used previously [2, 6, 7]. It follows from equation (1) that

$$\langle c \,||\, T^b \,||\, a\rangle = (-1)^{a+b+c}\overline{\langle a \,||\, T^b \,||\, c\rangle} \tag{2}$$

for Hermitian T^b, where $(-1)^a$ is -1 for $a = A_2$ or T_1 and is $+1$ otherwise (see Part II). Our definitions do not apply only for G the octahedral group but we consider only that case in the present paper.

2. Irreducible products and their matrix elements

Given two sets of operators $T_\eta^{\,g}$ and $U_\theta^{\,h}$ transforming according to the irreducible representations g and h we define the irreducible products

$$(T^g \times U^h)_\kappa^{\,k} = \sum_{\eta\theta} \langle gh\eta\theta | ghk\kappa \rangle T_\eta^{\,g} U_\theta^{\,h}$$
$$= \lambda(k)^{1/2} \sum_{\eta\theta} V \begin{pmatrix} g & h & k \\ \eta & \theta & \kappa \end{pmatrix} T_\eta^{\,g} U_\theta^{\,h}. \tag{3}$$

Suppose now we have two independent systems with states $|a\alpha\rangle$, $|a'\alpha'\rangle \ldots$ and $|b\beta\rangle$, $|b'\beta'\rangle \ldots$, etc., and that $T_\eta^{\,g}$ operates only on states of the first system and $U_\theta^{\,h}$ only on those of the second. It then follows that the matrices of T^g and U^h between states which are products of those of the two systems can easily be simplified by equations such as

$$\langle a\alpha | \langle b\beta | T_\eta^{\,g} U_\theta^{\,h} | a'\alpha' \rangle | b'\beta' \rangle = \langle a\alpha | T_\eta^{\,g} | a'\alpha' \rangle \langle b\beta | U_\theta^{\,h} | b'\beta' \rangle.$$

Using this we can simplify the matrix of an irreducible product $T^g \times U^h$ within the coupled states

$$|abc\gamma\rangle = \sum_{\alpha\beta} \langle ab\alpha\beta | abc\gamma \rangle |a\alpha\rangle |b\beta\rangle.$$

In fact we have

$$\langle abc\gamma | (T^g \times U^h)_\kappa^{\,k} | a'b'c'\gamma' \rangle$$
$$= \sum_{\alpha\beta\alpha'\beta'\eta\theta} \langle abc\gamma | ab\alpha\beta \rangle \langle gh\eta\theta | ghk\kappa \rangle \langle a'b'\alpha'\beta' | a'b'c'\gamma' \rangle, \tag{4}$$
$$\langle a\alpha | T_\eta^{\,g} | a'\alpha' \rangle \langle b\beta | U_\theta^{\,h} | b'\beta' \rangle$$
$$= \lambda(c)^{1/2} \lambda(c')^{1/2} \lambda(k)^{1/2} \langle a || T^g || a' \rangle \langle b || U^h || b' \rangle X \begin{bmatrix} a & b & c \\ g & h & k \\ a' & b' & c' \end{bmatrix} V \begin{pmatrix} c & k & c' \\ \gamma & \kappa & \gamma' \end{pmatrix}$$

where we used equation (1) and also equation (31) of Part II. Equation (4) can be rewritten in terms of the reduced matrix element of the irreducible product as

$$\langle abc || (T^g \times U^h)^k || a'b'c' \rangle = \lambda(c)^{1/2} \lambda(c')^{1/2} \lambda(k)^{1/2} \langle a || T^g || a' \rangle$$
$$\langle b || U^h || b' \rangle X \begin{bmatrix} a & b & c \\ g & h & k \\ a' & b' & c' \end{bmatrix} \tag{5}$$

when it corresponds to FR, equation (15.4).

An important special case occurs when $g = h = T_1$. Dropping the superscripts, we can regard T_η and U_θ as vectors with components x, y and z and find

$$(T \times U)^{A_1} = \frac{1}{\sqrt{3}} \mathbf{T} \cdot \mathbf{U}. \tag{6}$$

Equation (4) then simplifies to

$$\langle abc\gamma | \mathbf{T} \cdot \mathbf{U} | a'b'c'\gamma' \rangle = (-1)^{a+b'+c+T_1} \delta_{cc'} \delta_{\gamma\gamma'} \langle a || T || a' \rangle$$
$$\langle b || U || b' \rangle W \begin{pmatrix} a' & b' & c \\ b & a & T_1 \end{pmatrix}. \tag{7}$$

3. Spin–orbit coupling in two-electron systems

In the particular case of two-electron systems the eigenstates of $\mathbf{S}^2$ which span irreducible representations of the covering group of the three-dimensional

rotation group also do so for the octahedral group O. We can then use equation (7) by taking the kets $|a\alpha\rangle, \ldots$ to refer to spin and $|b\beta\rangle, \ldots$ to refer to space and $\mathbf{T}.\mathbf{U}$ as a part $\mathbf{s}_i.\mathbf{u}_i$ of the spin–orbit coupling energy.

The first application is to determine the form of the matrix of spin–orbit coupling between a pair of triplet terms, ^3b and $^3b'$ for the various possible representations c which they have in common. Equation (7) shows this matrix to be a multiple of

$$(-1)^c\delta_{cc'}\delta_{\gamma\gamma'}W\begin{pmatrix} T_1 & b' & c \\ b & T_1 & T_1 \end{pmatrix} = \delta_{cc'}\delta_{\gamma\gamma'}P(c), \quad \text{say.}$$

As an example consider $^3b = {}^3T_1$ and $^3b' = {}^3T_2$. Then

$$P(c) = (-1)^c W\begin{pmatrix} T_1 & T_2 & c \\ T_1 & T_1 & T_1 \end{pmatrix}$$

whence from table 3 of Part II we find $P(E):P(T_1):P(T_2) = \sqrt{3}:1:-1$. Thus for triplet terms we have a new method of calculating the ratios of the c-numbers given in reference [6]. The phases of the coupling coefficients in the latter are the same as in the present series except for coupling of T_2T_1 to E, T_1E to T_2 and ET_2 to T_1, but not the same as in references [3, 7 or 8]. I did not realize when I wrote that paper [6] that I could choose my phases so that W is invariant to odd permutations of its columns.

Next we calculate the complete matrix of spin–orbit coupling in a scheme in which the basic states are built up by coupling together one-electron functions which form bases for irreducible spin and space representations. These states are simple products of a symmetric (antisymmetric) spin function with an antisymmetric (or symmetric) space function. The forms of the spin functions are well known and we readily obtain the reduced matrix elements of the spin vectors $\mathbf{s}(1)$ and $\mathbf{s}(2)$ for the two electrons as follows:

$$\begin{aligned}
\langle 0||s(1)||0\rangle &= \quad \langle 0||s(2)||0\rangle = 0 \\
\langle 1||s(1)||1\rangle &= \quad \langle 1||s(2)||1\rangle = -\tfrac{1}{2}i\sqrt{6} \\
\langle 0||s(1)||1\rangle &= -\langle 0||s(2)||1\rangle = -\tfrac{1}{2}i\sqrt{3} \\
\langle 1||s(1)||0\rangle &= -\langle 1||s(2)||0\rangle = \tfrac{1}{2}i\sqrt{3}.
\end{aligned} \tag{8}$$

Here 0 and 1 in the kets and bras give the value of S and the phases are chosen in accordance with those of references [1 and 6]. Note that the reduced matrix elements here derive from equation (1) and use real spin functions behaving like x, y, z under rotation rather than the usual ones quantized with respect to S_z.

Because of the antisymmetry of our total functions we can take the spin–orbit coupling in the form

$$\mathscr{H}_s = 2\mathbf{s}(1).\mathbf{u}(1). \tag{9}$$

Equations (8) for $s(1)$ can be contracted into the formula

$$\langle S||s(1)||S'\rangle = \frac{\sqrt{3}}{2}i(S+S')^{1/2}(-1)^{S'}. \tag{10}$$

Introducing (9) and (10) into (7) and setting $c=c'$ and $\gamma=\gamma'$ yields

$$\begin{aligned}
&\langle {}^{2S+1}bc\gamma|\mathscr{H}_s|{}^{2S'+1}b'c\gamma\rangle \\
&= (-1)^{S+S'+b'+c+T_1}i\sqrt{3}(S+S')^{1/2}\langle b||u(1)||b'\rangle W\begin{pmatrix} S' & b' & c \\ b & S & T_1 \end{pmatrix}
\end{aligned} \tag{11}$$

where we interpret S and S' as the numbers 0 or 1 or as A_1 or T_1 depending on their context. When $S=0$, $S'=1$, the right-hand side simplifies to

$$-i\lambda(b)^{-1/2}\delta_{bc}\langle b||u(1)||b'\rangle.$$

We now determine $\langle b||u(1)||b'\rangle$ in terms of reduced one-electron matrix elements for $\mathbf{u}$. Both $|b\beta\rangle$ and $|b'\beta'\rangle$ are built up by coupling together a pair of one-electron representations and a number of cases arise depending on the extent to which the four sets of one-electron functions concerned are distinct. For $|b\beta\rangle$ itself there are two possibilities, either the two constituent sets are the same or different. If they are both the one-electron set $|e\epsilon\rangle$, say, then a typical product set is

$$|e^2b\beta\rangle=\lambda(b)^{1/2}\sum_{\epsilon\phi}V\begin{pmatrix}e & e & b\\ \epsilon & \phi & \beta\end{pmatrix}|e\epsilon(1)\rangle|e\phi(2)\rangle \tag{12}$$

and forms part of a singlet or triplet spin state according to whether b is contained in the symmetrized or antisymmetrized square of e. If b is composed of two different one-electron sets, $|e\epsilon\rangle$ and $|f\phi\rangle$ say, then

$$|efb\beta\rangle=\frac{1}{\sqrt{2}}\lambda(b)^{1/2}\sum_{\epsilon\phi}V\begin{pmatrix}e & f & b\\ \epsilon & \phi & \beta\end{pmatrix}\{|e\epsilon(1)\rangle|f\phi(2)\rangle+(-1)^S|f\phi(1)\rangle|e\epsilon(2)\rangle\} \tag{13}$$

where S is the spin.

Using (12) and (13) we can immediately obtain $\langle b||u(1)||b'\rangle$ in terms of one-electron elements. As an example consider matrix elements between e^2 and ef. We have

$$\langle e^2b||u(1)||efb'\rangle V\begin{pmatrix}b & T_1 & b'\\ \beta & \theta & \beta'\end{pmatrix}=\langle e^2b\beta|u_0(1)|efb'\beta'\rangle$$

$$=\frac{1}{\sqrt{2}}\lambda(b)^{1/2}\lambda(b')^{1/2}\sum_{\epsilon\phi\epsilon'\phi'}V\begin{pmatrix}e & e & b\\ \epsilon' & \phi' & \beta\end{pmatrix}V\begin{pmatrix}e & f & b'\\ \epsilon & \phi & \beta'\end{pmatrix}(-1)^{S'}\delta_{\phi'\epsilon}\langle e\epsilon'|u_0|f\phi\rangle$$

$$=\frac{1}{\sqrt{2}}\lambda(b)^{1/2}\lambda(b')^{1/2}(-1)^{S'}\langle e||u||f\rangle\sum_{\epsilon\epsilon'\phi}V\begin{pmatrix}b & e & e\\ \beta & \epsilon' & \epsilon\end{pmatrix}V\begin{pmatrix}b' & e & f\\ \beta' & \epsilon & \phi\end{pmatrix}V\begin{pmatrix}T_1 & f & e\\ \theta & \phi & \epsilon'\end{pmatrix}$$

$$=\frac{1}{\sqrt{2}}\lambda(b)^{1/2}\lambda(b')^{1/2}(-1)^{S'}\langle e||u||f\rangle W\begin{pmatrix}b & b' & T_1\\ f & e & e\end{pmatrix}V\begin{pmatrix}b & b' & T_1\\ \beta & \beta' & \theta\end{pmatrix}$$

where we have used equation (18) of Part II. Hence we have to insert

$$\langle b||u(1)||b'\rangle=\frac{1}{\sqrt{2}}\lambda(b)^{1/2}\lambda(b')^{1/2}(-1)^{S'+b+b'+T_1}\langle e||u||f\rangle W\begin{pmatrix}b & b' & T_1\\ f & e & e\end{pmatrix} \tag{14}$$

into equation (11). The other cases are dealt with in a precisely analogous way and we obtain the following four formulae which give a complete set of matrices of spin–orbit coupling for two-electron systems in terms of the reduced elements for one-electron functions:

$$\langle e^{2\,2S+1}bc|\mathscr{H}_s|e^{2\,2S'+1}b'c\rangle$$

$$=(-1)^{S+S'+b+b'+c}i\sqrt{3}(S+S')^{1/2}\lambda(b)^{1/2}\lambda(b')^{1/2}\langle e||u||e\rangle W\begin{pmatrix}b & b' & T_1\\ e & e & e\end{pmatrix}W\begin{pmatrix}S' & b' & c\\ b & S & T_1\end{pmatrix},$$

$$\langle e^{2\,2S+1}bc|\mathscr{H}_s|ef^{2S'+1}b'c\rangle$$

$$=\tfrac{1}{2}(-1)^{S+b+c}i\sqrt{6}(S+S')^{1/2}\lambda(b)^{1/2}\lambda(b')^{1/2}\langle e||u||f\rangle W\begin{pmatrix}b & b' & T_1\\ f & e & e\end{pmatrix}W\begin{pmatrix}S' & b' & c\\ b & S & T_1\end{pmatrix},$$

$$\langle ef^{2S+1}bc|\mathscr{H}_s|ef^{2S'+1}b'c\rangle$$
$$= \tfrac{1}{2}(-1)^{c+e+f}i\sqrt{3}(S+S')^{1/2}\lambda(b)^{1/2}\lambda(b')^{1/2}W\begin{pmatrix} S' & b' & c \\ b & S & T_1 \end{pmatrix}$$
$$\left[(-1)^{S+S'+b+b'}\langle e||u||e\rangle W\begin{pmatrix} b & b' & T_1 \\ e & e & f \end{pmatrix} + \langle f||u||f\rangle W\begin{pmatrix} b & b' & T_1 \\ f & f & e \end{pmatrix}\right],$$
$$\langle ef^{2S+1}bc|\mathscr{H}_s|eg^{2S'+1}b'c\rangle$$
$$= \tfrac{1}{2}(-1)^{S+S'+c+e+f}i\sqrt{3}(S+S')^{1/2}\lambda(b)^{1/2}\lambda(b')^{1/2}\langle f||u||g\rangle$$
$$W\begin{pmatrix} b & b' & T_1 \\ g & f & e \end{pmatrix}W\begin{pmatrix} S' & b' & c \\ b & S & T_1 \end{pmatrix}. \qquad (15)$$

The reduced matrix elements for $\mathbf{u}=\xi(r)\mathbf{l}$ are given in table 1 for p, d and f atomic orbitals and that table together with equations (15) give the spin–orbit matrices for any set of two-electron coupled states built up from s, p, d and f atomic orbitals. The resulting matrix for d^2 is identical with that derived from table 4 of reference [6], except for the consequences of the phase change mentioned earlier. In making this comparison remember that a change of order of coupling in equations (15) can sometimes produce a change of sign of the matrix element.

p	T_1
T_1	$-i\sqrt{6}$

d	E	T_2
E	0	$-2i\sqrt{3}$
T_2	$-2i\sqrt{3}$	$i\sqrt{6}$

f	A_2	T_1	T_2
A_2	0	0	$-2i\sqrt{3}$
T_1	0	$\frac{3}{2}i\sqrt{6}$	$-\frac{3}{2}i\sqrt{10}$
T_2	$2i\sqrt{3}$	$\frac{3}{2}i\sqrt{10}$	$-\frac{1}{2}i\sqrt{6}$

Table 1. Reduced matrix elements of **l** for p, d and f orbitals.

4. Electrostatic matrix elements

It is convenient at this stage to interpose a discussion of the electrostatic energy. In the theory for spherical symmetry this two-electron operator is usually expanded as a sum of scalar products of irreducible one-electron tensor operators [9]. However, under the octahedral group these latter are no longer usually irreducible. We start by considering a set of atomic orbitals, using the same kind of treatment as in § 4 of Part I [10] and then as in that section pass on later to functions classified according to the representations of a finite group.

We first discuss the expansion of the electrostatic energy as a sum of products of one-electron operators. First we suppose we have a set of $(2l+1)$ states $|m\rangle$ which are eigenstates of $\mathbf{l}^2$ and l_z and ask what is an operator equivalent suitable to represent a general two-electron operator ρ within the set of simple product states $|m_1m_2\rangle=|m_1\rangle|m_2\rangle$. Here the first ket in the product refers to

particle one and the second to particle two. An answer is an immediate generalization of equation (22) of Part I. We may use

$$X=\sum_{cc'\gamma\gamma'} Q_{\gamma\gamma'}^{cc'}\mathscr{L}_{-\gamma}^{(c)}(1)\mathscr{L}_{-\gamma'}^{(c')}(2) \tag{16}$$

where $\mathscr{L}_0^{(0)}=1$ and otherwise $\mathscr{L}^{(c)}(i)$ is the irreducible product of degree c of c orbital angular momentum vectors for the ith electron.

Assume now that $\rho=\bar{\rho}=\rho^*$ and $\rho(12)=\rho(21)$. Then using

$$\overline{\mathscr{L}_\gamma^{(c)}}=(-1)^c\mathscr{L}_\gamma^{(c)*}=(-1)^\gamma\mathscr{L}_{-\gamma}^{(c)}$$

we deduce that

$$Q_{\gamma\gamma'}^{cc'}=Q_{\gamma'\gamma}^{c'c},\quad \overline{Q_{\gamma\gamma'}^{cc'}}=(-1)^{\gamma+\gamma'}Q_{-\gamma-\gamma'}^{cc'}$$

where $Q_{\gamma\gamma'}^{cc'}=0$ when $c+c'$ is odd. If ρ is simply a function of the position of the two electrons, such as the electrostatic energy, we see by expressing our matrix elements in the Schrödinger representation that

$$\langle M_1M_2|\rho|M_3M_4\rangle=(-1)^{M_3-M_1}\langle M_3M_2|\rho|M_1M_4\rangle.$$

The same equation holds for the matrix elements of X. We derive a condition on the Q by expanding the latter equation in terms of the reduced matrix elements of the $\mathscr{L}_\gamma^{(c)}$ and the $\bar{V}$ coefficients. The orthogonality relations for the $\bar{V}$ then enable us to deduce that $Q_{\gamma\gamma'}^{cc'}=(-1)^cQ_{\gamma\gamma'}^{ec'}$, so the $Q_{\gamma\gamma'}^{cc'}$ are zero unless both c and c' are even. It follows also that ρ determines the $Q_{\gamma\gamma'}^{cc'}$ uniquely.

Suppose now that ρ transforms as the unit representation Γ_1 of a symmetry group G, i.e. is an invariant of G. Write $h=X-\rho$. Then h has zero matrix elements within all our product states. Therefore so also has gh for g any element of G. This means that as $g\rho=\rho$, gX and X have the same matrix elements. But as the set of matrix elements of a quantity of the kind in equation (16) determine the $Q_{\gamma\gamma'}^{cc'}$ uniquely it follows that $gX=X$. So X is an invariant of G. As c and c' in (16) must both be even and $Q_{\gamma\gamma'}^{cc'}=Q_{\gamma'\gamma}^{c'c}$ we can deduce that the number of parameters necessary to specify a general invariant ρ within our product states is the number of times Γ_1 occurs in the symmetrized square of the symmetrized square of a set of functions transforming as $|lm\rangle$. We can write this $[[l]^2]^2$. For example if $l=2$ we have $[d]^2=S+D+G$ and $[[d]^2]^2=3S+4D+F+4G+H+2I+L$. If our symmetry group is the three-dimensional rotation group R_3 then $\Gamma_1=S$ and we need three parameters. These are of course the Slater–Condon F_0, F_2 and F_4 when ρ is the electrostatic energy. If it is the octahedral group, $\Gamma_1=A_1$ and we need 10 parameters. For the latter group and $l=3$ we need 26 parameters.

A problem which is closely related to the preceding one and of much more interest is the following which we introduce via an example. We consider that d electrons in an octahedral complex are not in true d orbitals but merely in orbitals having the same transformation properties under the octahedral group. This may be made precise and more general by writing the transformation from lm to $l\Gamma_1M_1$ quantization† as

$$|l\beta_1\Gamma_1M_1\rangle=\sum_m\langle lm|l\beta_1\Gamma_1M_1\rangle|lm\rangle$$

where β_1 is introduced when necessary for large l to distinguish repeated Γ_1. For simplicity the $|l\beta_1\Gamma_1M_1\rangle$ are taken to be real and we modify them by

† Here Γ_1 is no longer necessarily the unit representation.

multiplying them by a real invariant $a(\beta_1\Gamma_1)$ which is independent of M_1:

$$|l\beta_1\Gamma_1 M_1\rangle' = a(\beta_1\Gamma_1)|l\beta_1\Gamma_1 M_1\rangle.$$

For $l=2$ this is what is meant by saying that d orbitals in an octahedral complex are not true d orbitals. We now show that it is formally equivalent to replacing the electrostatic energy V, which is an invariant of R_3, by a corresponding operator V' which is only an invariant of the restricted symmetry group and to leaving the states $|lm\rangle$ unchanged.

The problem is to replace the multiplication of the kets $|l\beta_1\Gamma_1 M_1\rangle$ by the quantities $a(\beta_1\Gamma_1)$ which depend on β_1 and Γ_1 by multiplication by an invariant operator which is independent of them. We can then transform back to the lm scheme and will have established our result. To do this define

$$p(\beta\Gamma M)|l\beta'\Gamma'M'\rangle = \delta(\beta\beta')\delta(\Gamma\Gamma')\delta(MM')|l\beta'\Gamma'M'\rangle.$$

The $p(\beta\Gamma M)$ are projection operators and satisfy $\bar{p}=p^*=p$. Then we have

$$|l\beta_1\Gamma_1 M_1\rangle' = A|l\beta_1\Gamma_1 M_1\rangle,$$

where

$$A = \sum_{\beta\Gamma M} a(\beta\Gamma)p(\beta\Gamma M), \tag{17}$$

and $V' = A_1A_2VA_1A_2$ is an invariant of the symmetry group, where A_i is the sum in (17) taken over projection operators operating only on kets for the ith electron. By expanding $\langle m_1m_2|V'|m_3m_4\rangle$ in the $l\Gamma_1M_1$ scheme we easily deduce that V' possesses all the properties which gave us our restrictions on the $Q_{\gamma\gamma'}^{cc'}$ of equation (16). Therefore V' has an operator equivalent (16) with the same restrictions.

We next consider how our analysis is modified when we work entirely within the scheme provided by a finite group G for which V symbols are defined. Given an operator $f(\Gamma_1M_1)$ which transforms as the M_1 component of a representation Γ_1 we have

$$\langle\alpha\Gamma M|f(\Gamma_1M_1)|\alpha'\Gamma'M'\rangle = \langle\alpha||f||\alpha'\rangle V\begin{pmatrix}\Gamma & \Gamma_1 & \Gamma_1'\\ M & M_1 & M'\end{pmatrix}. \tag{18}$$

Equation (18) gives us exactly the same computational apparatus for G as we used for R_3 earlier in this section. Therefore the same results hold. In place of the $\mathscr{L}_\gamma^{(c)}$ we can, if we wish, take unit operators $n(\Gamma_1M_1)$ defined, for fixed α, α', Γ, Γ', by $\langle\alpha||n||\alpha'\rangle=\delta_{\alpha\alpha'}$. As a simple example, for the octahedral group $[t_2]^2 = A_1+E+T_2$ and hence we need three parameters for a general t_2^n configuration as pointed out by Stevens [11].

Our treatment is easily extended to cover the case when we have interactions amongst product states based on a set $\sum$ of irreducible representations. Here we simply need a number of parameters equal to the number of times that the unit representation occurs in $[[\sum]^2]^2$. It is a consequence of this that the number of parameters needed to specify the electrostatic energy amongst products based on $2l+1$ orbitals which transform like $|lm\rangle$ under G but not necessarily under R_3 is the same as the number necessary to specify a general invariant, of the type considered earlier in the section, within the $|lm\rangle$. Therefore to specify the electrostatic interaction within a general $t_{2g}^m e_g^n$ set of configurations we need 10 parameters. Similarly for $a_{1u}^m t_{1u}^n t_{2u}^p$ we need 26. For d functions which are not 'true' d functions we need 23 and 26 for D_4 and D_3 respectively.

5. Off-diagonal matrix elements for the octahedral group

In actual calculations we may need matrix elements of the electrostatic energy of the general type $\langle m_1 m_2|V|m_3 m_4\rangle$. We now obtain all of these for d and for f configurations both without and with the assumption that the constituent orbitals are 'true' d and f orbitals. This could be done via a sum of products of one-electron functions but it is actually easier just to determine the restrictions on the matrix elements directly by applying rotations and permutations of the constituent orbitals. We define real orbitals satisfying

$$\left.\begin{aligned}\theta &= |20\rangle \\ \epsilon &= \tfrac{1}{2}\sqrt{2}(|22\rangle + |2-2\rangle)\end{aligned}\right\} \subseteq E \qquad \left.\begin{aligned}\xi &= \tfrac{1}{2}i\sqrt{2}(|21\rangle + |2-1\rangle) \\ \eta &= \tfrac{1}{2}\sqrt{2}(|2-1\rangle - |21\rangle) \\ \zeta &= -\tfrac{1}{2}i\sqrt{2}(|22\rangle - |2-2\rangle)\end{aligned}\right\} \subseteq T_2$$

for d electrons and

$$\left.\begin{aligned}x &= \tfrac{1}{4}(\sqrt{3}|31\rangle - \sqrt{3}|3-1\rangle - \sqrt{5}|33\rangle + \sqrt{5}|3-3\rangle) \\ y &= -\tfrac{1}{4}i(\sqrt{3}|31\rangle + \sqrt{3}|3-1\rangle + \sqrt{5}|33\rangle + \sqrt{5}|3-3\rangle) \\ z &= |30\rangle,\end{aligned}\right\} \subseteq T_1,$$

$$\chi = \tfrac{1}{2}i\sqrt{2}(|3-2\rangle - |32\rangle) \subseteq A_2,$$

$$\left.\begin{aligned}\xi &= \tfrac{1}{4}(\sqrt{5}|31\rangle - \sqrt{5}|3-1\rangle + \sqrt{3}|33\rangle - \sqrt{3}|3-3\rangle), \\ \eta &= \tfrac{1}{4}i(\sqrt{5}|31\rangle + \sqrt{5}|3-1\rangle - \sqrt{3}|33\rangle - \sqrt{3}|3-3\rangle), \\ \zeta &= \tfrac{1}{2}\sqrt{2}(|32\rangle + |3-2\rangle)\end{aligned}\right\} \subseteq T_2,$$

for f electrons. All the functions in the $l\Gamma_1 M_1$ scheme are real. For convenience of tabulation we also define

$$(ac;bd) \equiv \langle ab|V|cd\rangle$$

and have $(ac;bd)$ invariant to interchange of a with c, b with d or ac with bd. The calculation is now straightforward, but, at least for f electrons, a little lengthy. I illustrate it for d electrons.

First we derive some selection rules by classifying the orbitals by their behaviour under the group D_4 about OZ. ξ, η, ζ, θ, ϵ behave as ex, $-ey$, b_2, a_1, b_1, respectively under that group. Hence the 15 different products ac for the first electron form bases for representations of D_4 as follows:

$$\begin{aligned}&\frac{1}{\sqrt{2}}(\xi^2+\eta^2),\ \zeta^2,\ \theta^2,\ \epsilon^2 \subseteq A_1, \\ &\zeta\epsilon \subseteq A_2, \\ &\frac{1}{\sqrt{2}}(\xi^2-\eta^2),\ \theta\epsilon \subseteq B_1, \\ &\xi\eta,\ \zeta\theta \subseteq B_2, \\ &\xi\theta,\ \eta\zeta,\ \xi\epsilon \subseteq Ex, \\ &\eta\theta,\ \zeta\xi,\ \eta\epsilon \subseteq Ey. \end{aligned} \tag{19}$$

We have omitted minus signs for Ex and Ey. The products bd for the second electron are classified in the same way and then because V belongs to the unit representation of D_4 we have $(ac;bd)=0$ unless ac occurs in the same set as bd in (19). So the matrix of V breaks up into five completely non-interacting sub-matrices. We can also deduce relationships of the kind

$$(\xi^2;\ \theta^2) = (\eta^2;\theta^2), \quad (\xi^2,\ \theta\epsilon) = -(\eta^2, \theta\epsilon)$$

because $\xi^2+\eta^2$ and θ^2 are A_1 but $\xi^2-\eta^2$ and $\theta\epsilon$ are B_1.

A_1, B_1	ξ^2	η^2	ζ^2	θ^2	ϵ^2	$\theta\epsilon$
ξ^2	$a=A+4B+3C$	$b=A-2B+C$	$b=A-2B+C$	$d+\frac{2}{\sqrt{3}}c=A+2B+C$	$d=A-2B+C$	$c=2B\sqrt{3}$
η^2	$b=A-2B+C$	$a=A+4B+3C$	$b=A-2B+C$	$d+\frac{2}{\sqrt{3}}c=A+2B+C$	$d=A-2B+C$	$-c=-2B\sqrt{3}$
ζ^2	$b=A-2B+C$	$b=A-2B+C$	$a=A+4B+3C$	$d-\frac{1}{\sqrt{3}}c=A-4B+C$	$d+\sqrt{3}c=A+4B+C$	0
θ^2	$d+\frac{2}{\sqrt{3}}c=A+2B+C$	$d+\frac{2}{\sqrt{3}}c=A+2B+C$	$d-\frac{1}{\sqrt{3}}c=A-4B+C$	$e=A+4B+3C$	$e-2f=A-4B+C$	0
ϵ^2	$d=A-2B+C$	$d=A-2B+C$	$d+\sqrt{3}c=A+4B+C$	$e-2f=A-4B+C$	$e=A+4B+3C$	0
$\theta\epsilon$	$c=2B\sqrt{3}$	$-c=-2B\sqrt{3}$	0	0	0	$f=4B+C$

Table 2.

B_2	$\theta\zeta$	$\xi\eta$
$\theta\zeta$	$g+\sqrt{3}h=4B+C$	$-2i=-2B\sqrt{3}$
$\xi\eta$	$-2i=-2B\sqrt{3}$	$j=3B+C$

A_2	$\epsilon\zeta$
$\epsilon\zeta$	$g-\frac{1}{\sqrt{3}}h=C$

Ex	$\theta\xi$	$\epsilon\xi$	$\eta\zeta$
$\theta\xi$	$g=B+C$	$-h=-B\sqrt{3}$	$i=B\sqrt{3}$
$\epsilon\xi$	$-h=-B\sqrt{3}$	$g+\frac{2}{\sqrt{3}}h=3B+C$	$-\sqrt{3}i=-3B$
$\eta\zeta$	$i=B\sqrt{3}$	$-\sqrt{3}i=-3B$	$j=3B+C$

Ey	$\theta\eta$	$\epsilon\eta$	$\zeta\xi$
$\theta\eta$	$g=B+C$	$h=B\sqrt{3}$	$i=B\sqrt{3}$
$\epsilon\eta$	$h=B\sqrt{3}$	$g+\frac{2}{\sqrt{3}}h=3B+C$	$\sqrt{3}i=3B$
$\zeta\xi$	$i=B\sqrt{3}$	$\sqrt{3}i=3B$	$j=3B+C$

Table 2 (continued). The expressions for the non-zero $(ab;cd)\equiv\langle ac|V|bd\rangle$ for d electrons, classified according to the representation of D_4.

After this we progress by applying elements of O to matrix elements. For example

$$(\xi^2;\theta^2) = C_4{}^x(\xi^2;\theta^2)$$
$$= \tfrac{1}{4}(\xi^2;\theta^2) + \tfrac{3}{4}(\epsilon^2;\xi^2) + \tfrac{1}{2}\sqrt{3}(\xi^2;\theta\epsilon),$$

i.e. $(\xi^2;\theta^2) = (\xi^2;\epsilon^2) + \frac{2}{3}\sqrt{3}(\xi^2;\theta\epsilon)$. Having determined sufficient relations of this type we then express the entire set of matrix elements in terms of 10 chosen parameters. This is shown in table 2, together with the expressions in terms of the Racah parameters A, B and C for the case in which the orbitals are actually d orbitals (largely as in reference [8]).

A_1, B_1	χ^2	z^2	ζ^2	x^2	y^2	ξ^2	η^2	$x\xi$	$y\eta$	$z\zeta$
χ^2	a	b	c	b	b	c	c	0	0	0
z^2	b	d	i	g	g	j	j	$-l$	l	0
ζ^2	c	i	e	j	j	h	h	$-k$	k	0
x^2	b	g	j	d	g	i	j	0	$-l$	l
y^2	b	g	j	g	d	j	i	l	0	$-l$
ξ^2	c	j	h	i	j	e	h	0	$-k$	k
η^2	c	j	h	j	i	h	e	k	0	$-k$
$x\xi$	0	$-l$	$-k$	0	l	0	k	f	m	m
$y\eta$	0	l	k	$-l$	0	$-k$	0	m	f	m
$z\zeta$	0	0	0	l	$-l$	k	$-k$	m	m	f

(Ey) Ex	$(-\chi y)$ χx	$(\chi\eta)$ $\chi\xi$	$(-zx)$ yz	$(-\zeta\xi)$ $\eta\zeta$	$(x\zeta)$ $y\zeta$	$(z\xi)$ $z\eta$
$(-\chi y)\chi x$	n	0	s	t	u	$-u$
$(\chi\eta)\chi\xi$	0	o	0	0	v	v
$(-zx)yz$	s	0	p	w	x	$-x$
$(-\zeta\xi)\eta\zeta$	t	0	w	q	y	$-y$
$(x\zeta)y\zeta$	u	v	x	y	r	z
$(z\xi)z\eta$	$-u$	v	$-x$	$-y$	z	r

A_2, B_2	$\chi\zeta$	$x\eta$	$y\xi$	χz	xy	$\xi\eta$
$\chi\zeta$	o	v	v	0	0	0
$x\eta$	v	r	z	u	x	y
$y\xi$	v	z	r	$-u$	$-x$	$-y$
χz	0	u	$-u$	n	s	t
xy	0	x	$-x$	s	p	w
$\xi\eta$	0	y	$-y$	t	w	q

Table 3. The non-zero $(ab;cd)$ for f electrons in terms of generalized parameters.

The calculation for f orbitals follows exactly the same course. Table 3 gives the matrix elements in terms of the 26 parameters and table 4 gives those parameters in terms of the quantities

$$E^0 = F_0 - 10F_2 - 33F_4 - 286F_6,$$
$$E^1 = \tfrac{1}{9}(70F_2 + 231F_4 + 2002F_6),$$
$$E^2 = \tfrac{1}{9}(F_2 - 3F_4 + 7F_6),$$
$$E^3 = \tfrac{1}{3}(5F_2 + 6F_4 - 91F_6),$$

introduced by Racah [12] for f electron configurations.

$$a = E^0 + 3E^1 - 120E^2,$$
$$b = E^0 + E^1 + 80E^2 - 4E^3,$$
$$c = E^0 + E^1 - 40E^2 + 4E^3,$$
$$d = E^0 + 3E^1 + 24E^2,$$
$$e = E^0 + 3E^1 - 120E^2,$$
$$f = E^1 + 80E^2 + 2E^3,$$
$$g = E^0 + E^1 - 59\tfrac{1}{2}E^2 + \tfrac{1}{2}E^3,$$
$$h = E^0 + E^1 + 72\tfrac{1}{2}E^2 - 3\tfrac{1}{2}E^3,$$
$$i = E^0 + E^1 + 80E^2 - 4E^3,$$
$$j = E^0 + E^1 - 32\tfrac{1}{2}E^2 + 3\tfrac{1}{2}E^3,$$
$$k = \frac{\sqrt{15}}{2}(15E^2 - E^3),$$
$$l = -\frac{3\sqrt{15}}{2}(9E^2 + E^3),$$
$$m = -22\tfrac{1}{2}E^2 - 4\tfrac{1}{2}E^3,$$
$$n = E^1 + 80E^2 + 2E^3,$$
$$o = E^1 - 40E^2 - 2E^3,$$
$$p = E^1 - 59\tfrac{1}{2}E^2 - \tfrac{1}{4}E^3,$$
$$q = E^1 + 72\tfrac{1}{2}E^2 + \tfrac{7}{4}E^3$$
$$r = E^1 - 32\tfrac{1}{2}E^2 - \tfrac{7}{4}E^3,$$
$$s = 9\sqrt{15}E^2,$$
$$t = \sqrt{15}\,(15E^2 + 2E^3),$$
$$u = 3E^3,$$
$$v = \sqrt{15}(15E^2 - E^3),$$
$$w = -22\tfrac{1}{2}E^2 + 3\tfrac{3}{4}E^3,$$
$$x = \frac{3\sqrt{15}}{2}(9E^2 - \tfrac{1}{2}E^3),$$
$$y = \frac{\sqrt{15}}{2}(15E^2 + \tfrac{1}{2}E^3),$$
$$z = -22\tfrac{1}{2}E^2 + \tfrac{3}{4}E^3.$$

Table 4. The generalized parameters for f electrons expressed in terms of Racah's parameters E^i.

6. The f^2 configuration

Using the matrix elements in table 3 it is a straightforward matter to calculate the matrix of electrostatic energy for f^2 in terms of the 26 generalized parameters or the E^i. The results are given in table 5. They were checked by solving the associated secular equations in terms of the E^i and comparing with Racah [12]. The table, together with formulae (15) and table 1, give the complete matrices of electrostatic and spin–orbit coupling energies for f^2. Part of the latter matrix is written out in table 6 and will now be used to discuss the magnetic properties of the f^2 configuration in an octahedral field.

$^1A_1$	a_2^2	t_2^2	t_1^2
a_2^2	$E^0+3E^1-120E^2$ [a]	$\sqrt{3}(E^1-40E^2-2E^3)$ [$o\sqrt{3}$]	$\sqrt{3}(E^1+80E^2+2E^3)$ [$n\sqrt{3}$]
t_2^2	$\sqrt{3}(E^1-40E^2-2E^3)$ [$o\sqrt{3}$]	$E^0+5E^1+25E^2+3\frac{1}{2}E^3$ [$e+2q$]	$3E^1+15E^2-1\frac{1}{2}E^3$ [$f+2r$]
t_1^2	$\sqrt{3}(E^1+80E^2+2E^3)$ [$n\sqrt{3}$]	$3E^1+15E^2-1\frac{1}{2}E^3$ [$f+2r$]	$E^0+5E^1-95E^2-\frac{1}{2}E^3$ [$d+2p$]

$^1A_2=E^0+2E^1+70E^2+7E^3$ [$i+f+2w+2z$] ^1I

^1E	t_1^2	t_2^2	t_1t_2
t_1^2	$E^0+2E^1+83\frac{1}{2}E^2+\frac{1}{4}E^3$ [$d-p$]	$112\frac{1}{2}E^2+3\frac{3}{4}E^3$ [$i+f$]	$\frac{9}{2}\sqrt{10}(9E^2-\frac{1}{2}E^3)$ [$x\sqrt{6}$]
t_2^2	$112\frac{1}{2}E^2+3\frac{3}{4}E^3$ [$i+f$]	$E^0+2E^1-192\frac{1}{2}E^2-1\frac{3}{4}E^3$ [$e-q$]	$-\frac{3}{2}\sqrt{10}(15E^2+\frac{1}{2}E^3)$ [$-y\sqrt{6}$]
t_1t_2	$\frac{9}{2}\sqrt{10}(9E^2-\frac{1}{2}E^3)$ [$x\sqrt{6}$]	$-\frac{3}{2}\sqrt{10}(15E^2+\frac{1}{2}E^3)$ [$-y\sqrt{6}$]	$E^0+2E^1+205E^2-6\frac{1}{2}E^3$ [$i+f-w-z$]

$^1T_1$	a_2t_2	t_1t_2
a_2t_2	$E^0+2E^1-80E^2+2E^3$ [$c+o$]	$-\sqrt{30}(30E^2+E^3)$ [$-(t+v)\sqrt{2}$]
t_1t_2	$-\sqrt{30}(30E^2+E^3)$ [$-(t+v)\sqrt{2}$]	$E^0+2E^1-110E^2+E^3$ [$j+r+w+m$]

Table 5.

$^1T_2$	a_2t_1	t_1^2	t_2^2	t_1t_2
a_2t_1	$E^0+2E^1+160E^2-2E^3$ $[b+n]$	$-18\sqrt{15}E^2$ $[-2s]$	$-2\sqrt{15}(15E^2-E^3)$ $[-2v]$	$3\sqrt{2}E^3$ $[u\sqrt{2}]$
t_1^2	$-18\sqrt{15}E^2$ $[-2s]$	$E^0+2E^1-119E^2+\frac{1}{4}E^3$ $[g+p]$	$-45E^2-3\frac{3}{4}E^3$ $[m+z]$	$\frac{3\sqrt{30}}{2}(18E^2+\frac{1}{2}E^3)$ $[(x-l)\sqrt{2}]$
t_2^2	$-2\sqrt{15}(15E^2-E^3)$ $[-2v]$	$-45E^2-3\frac{3}{4}E^3$ $[m+z]$	$E^0+2E^1+145E^2-1\frac{3}{4}E^3$ $[h+q]$	$\frac{\sqrt{30}}{2}(30E^2-\frac{1}{2}E^3)$ $[(y+k)\sqrt{2}]$
t_1t_2	$3\sqrt{2}E^3$ $[u\sqrt{2}]$	$\frac{3\sqrt{30}}{2}(18E^2+\frac{1}{2}E^3)$ $[(x-l)\sqrt{2}]$	$\frac{\sqrt{30}}{2}(30E^2-\frac{1}{2}E^3)$ $[(y+k)\sqrt{2}]$	$E^0+2E^1-20E^2+2\frac{1}{2}E^3$ $[j+r-w-m]$

$^3A_2=E^0$ $[i-f+2w-2z]$ ^3F
$^3E=E^0-9E^3$ $[i-f-w+z]$ ^3H

$^3T_2$	a_2t_1	t_1t_2
a_2t_1	E^0-6E^3 $[b-n]$	$3\sqrt{2}E^3$ $[u\sqrt{2}]$
t_1t_2	$3\sqrt{2}E^3$ $[u\sqrt{2}]$	E^0-3E^3 $[j-r-w+m]$

Table 5 (*continued*).

$^3T_1$	a_2t_2	t_1^2	t_2^2	t_1t_2
a_2t_2	E^0+6E^3 $[c-o]$	$-6E^3$ $[-2u]$	0 $[0]$	$-3\sqrt{30}E^3$ $[(v-t)\sqrt{2}]$
t_1^2	$-6E^3$ $[-2u]$	$E^0+\frac{3}{4}E^3$ $[g-p]$	$-5\frac{1}{4}E^3$ $[m-z]$	$\frac{9}{4}\sqrt{30}E^3$ $[-(x+l)\sqrt{2}]$
t_2^2	0 $[0]$	$-5\frac{1}{4}E^3$ $[m-z]$	$E^0-5\frac{1}{4}E^3$ $[h-q]$	$-\frac{3}{4}\sqrt{30}E^3$ $[(k-y)\sqrt{2}]$
t_1t_2	$-3\sqrt{30}E^3$ $[(v-t)\sqrt{2}]$	$\frac{9}{4}\sqrt{30}E^3$ $[-(x+l)\sqrt{2}]$	$-\frac{3}{4}\sqrt{30}E^3$ $[(k-y)\sqrt{2}]$	$E^0+13\frac{1}{2}E^3$ $[j-r+w-m]$

Table 5 (*continued*). The complete electrostatic matrix for f^2 in terms of the E^i and (in square brackets) in terms of generalized parameters.

Plutonium hexafluoride presumably has two f electrons [13]. The orbital energies are likely to be such that the t_1 orbitals lie far above the a_2 or t_2 orbitals [14]. It is rather obvious from tables 5 and 6 that whatever the value of $\Delta = E(t_2) - E(a_2)$ the lowest state will be of A_1 symmetry. It is probable that Δ is positive [14].

A_1	a_2^2 $^1A_1$	a_2t_2 $^3T_1$	t_2^2 $^3T_1$	t_2^2 $^1A_1$
a_2^2 $^1A_1$	0	$\sqrt{6}$	0	0
a_2t_2 $^3T_1$	$\sqrt{6}$	$-\frac{1}{2}$	-2	$-\sqrt{2}$
t_2^2 $^3T_1$	0	-2	$-\frac{1}{2}$	$-\frac{1}{2}\sqrt{2}$
t_2^2 $^1A_1$	0	$-\sqrt{2}$	$-\frac{1}{2}\sqrt{2}$	0

E	a_2t_2 $^3T_1$	t_2^2 $^3T_1$	t_2^2 ^1E
a_2t_2 $^3T_1$	$\frac{1}{4}$	1	$-\sqrt{2}$
t_2^2 $^3T_1$	1	$\frac{1}{4}$	$\frac{1}{4}\sqrt{2}$
t_2^2 ^1E	$-\sqrt{2}$	$\frac{1}{4}\sqrt{2}$	0

T_1	a_2t_2 $^3T_1$	a_2t_2 $^1T_1$	t_2^2 $^3T_1$
a_2t_2 $^3T_1$	$-\frac{1}{4}$	$\frac{1}{4}\sqrt{2}$	-1
a_2t_2 $^1T_1$	$\frac{1}{4}\sqrt{2}$	0	$-\sqrt{2}$
t_2^2 $^3T_1$	-1	$-\sqrt{2}$	$-\frac{1}{4}$

T_2	a_2t_2 $^3T_1$	t_2^2 $^3T_1$	t_2^2 $^1T_2$
a_2t_2 $^3T_1$	$\frac{1}{4}$	1	$-\sqrt{2}$
t_2^2 $^3T_1$	1	$\frac{1}{4}$	$\frac{1}{4}\sqrt{2}$
t_2^2 $^1T_2$	$-\sqrt{2}$	$\frac{1}{4}\sqrt{2}$	0

Table 6. Spin–orbit coupling matrices for the three lowest octahedral strong-field configurations contained in f^2.

We now assume that only this A_1 state is thermally occupied and obtain an expression for its temperature-independent paramagnetic susceptibility. In terms of reduced matrix elements this is

$$\chi = \tfrac{8}{3} N\beta^2 \sum E_n^{-1} |\langle 0 \| \{l(1) + 2s(1)\} \| n \rangle|^2 \qquad (20)$$

where n runs over all T_1 levels. The matrix elements of $l(1)+2s(1)$ are easily worked out using the methods of §3 and are given in table 7. $|0\rangle$ is, to a good approximation a sum over the four A_1 states appearing in table 7. So apart from assuming values for E^i, ζ and Δ and obtaining a numerical value for χ, this completes the calculation.

A_1 \ T_1	a_2t_2 $^3T_1$	a_2t_2 $^1T_1$	t_2^2 $^3T_1$
a_2^2 $^1A_1$	0	$i\sqrt{6}$	0
a_2t_2 $^3T_1$	$-\frac{3}{4}i\sqrt{2}$	0	$i\sqrt{2}$
t_2^2 $^3T_1$	$i\sqrt{2}$	0	$-\frac{3}{4}i\sqrt{2}$
t_2^2 $^1A_1$	0	$-i\sqrt{2}$	0

Table 7. Reduced matrix elements $\langle A_1 \| \{l(1)+2s(1)\} \| T_1 \rangle$ for the lowest states of f^2 in an octahedral field.

The observed susceptibility of PuF_6 is temperature-independent and corresponds to $\chi = 130 \times 10^{-6}$ for the two f electrons. The interpretation of this was discussed before (Griffith and Orgel [14]) using an inadmissably simple model. The main defect was the neglect of the matrix element of spin–orbit coupling energy between $a_2^{\,2}\,{}^1A_1$ and $a_2t_2\,{}^3T_1$. The ground state was regarded as either $a_2^{\,2}\,{}^1A_1$ or $a_2t_2\,{}^3T_1A_1$ and in neither case was it possible to obtain as low a χ as 130×10^{-6} although the former state had the lower χ and it was concluded that it was in fact the ground state. It seems clear now that that view was incorrect and that the true ground state is a mixture, almost certainly containing substantial amounts of both $a_2^{\,2}\,{}^1A_1$ and $a_2t_2\,{}^3T_1$ and quite likely also $t_2^{\,2}\,{}^3T_1$. As an example if one neglects the upper $^1A_1$ and assumes these three A_1 states to have the same diagonal energies one finds

$$|0\rangle = \frac{\sqrt{3}}{\sqrt{10}}|a_2^{\,2}\,{}^1A_1\rangle - \frac{1}{\sqrt{2}}|a_2t_2\,{}^3T_1A_1\rangle - \frac{1}{\sqrt{5}}|t_2^{\,2}\,{}^3T_1A_1\rangle \qquad (21)$$

with a calculated susceptibility of about 150×10^{-6}. Using the same parameters as in our previous paper the $t_2^{\,2}\,{}^3T_1$ does in fact only lie about 4000 cm^{-1} above $a_2^{\,2}$.

However, not knowing the parameters at all accurately, all we can usefully say is that a suitable mixture can give the low observed susceptibility whilst the pure $a_2^{\,2}\,{}^1A_1$ or pure $a_2t_2\,{}^3T_1A_1$ can not without unreasonable values of the parameters. There is no suggestion that (21) is necessarily at all close to the actual ground state. Qualitatively, however, we can say that the low value of χ appears to arise partly from the large repulsion between these two low-lying A_1 states and partly to the fact that the matrix elements of $l(1)+2s(1)$ to excited states partially cancel.

It is interesting to mention here calculations which have been made in the octahedral weak-field scheme on the f^2 configuration. They were restricted to the lowest level, $^3H_4$ [15, 16], of the configuration or at most the lowest term, ^3H [17], but with either of those approximations the ground state still has A_1 symmetry.

7. Tanabe and Kamimura's scheme of calculation

Tanabe and Kamimura ([3], hereafter referred to as *TK*) have given a discussion of the calculation by tensorial methods of matrix elements of one-electron operators between states of $t_2^{\,m}e^n$ configurations, closely following Racah's treatment of atomic $l^m l'^p$ configurations [18]. The matrix elements are shown to be proportional to recoupling coefficients or to sums of products of recoupling coefficients. In each case, however, they are also proportional to W or X coefficients as we see now.

First put $U^h = 1$, $h = A_1$, $g = k$ in equation (5). As $\langle b||U^h||b'\rangle$ is then equal to $\delta_{bb'}\lambda(b)^{1/2}$ we find

$$\langle abc||T^g||a'b'c'\rangle = (-1)^{a'+b+c+g}\delta_{bb'}\lambda(c)^{1/2}\lambda(c')^{1/2}\langle a||T^g||a'\rangle \, W\begin{pmatrix} a' & b' & c' \\ c & g & a \end{pmatrix}. \qquad (22)$$

Because of the connection of W with recoupling coefficients (Part II, equation (16)), equation (22) is the same as TK 2.21 and 2.23. Equations TK 2.22

and 2.24 come similarly from (5) on putting $T^g = 1$. Actually the bracketted expressions defined in TK 2.23 and 2.24 satisfy

$$(dec[b]fea) = (-1)^{a+b+d+e}\lambda(c)^{1/2}\lambda(a)^{1/2}W\begin{pmatrix} a & b & c \\ d & e & f \end{pmatrix},$$
$$(edc[b]efa) = (-1)^{a+c+d+f}(dec[b]fea), \tag{23}$$

with our choice of phases for the constituent coupling coefficients.

In the evaluation of off-diagonal elements, more complicated recoupling coefficients appear (TK 2.37 and 2.39). These are easily shown to satisfy

$$[fde[b]kgh] = \lambda(e)^{1/2}\lambda(h)^{1/2}X\begin{bmatrix} E & b & T_2 \\ d & e & f \\ g & h & k \end{bmatrix} \tag{24}$$

for the octahedral group representations (TK 2.37) and

$$[S_1S_2S[1]S_3S_4S'] = (2S+1)(2S'+1)X\begin{bmatrix} S_4 & S_2 & \frac{1}{2} \\ S_3 & S_1 & \frac{1}{2} \\ S' & S & 1 \end{bmatrix} \tag{25}$$

for the spins (TK 2.39), the X of equation (24) being my X of Part II and of equation (25) being Racah's X. Incidentally the equation

$$\langle k, ab(c)(f)de|k, ad(g)(h)be\rangle = \lambda(c)^{1/2}\lambda(f)^{1/2}\lambda(g)^{1/2}\lambda(h)^{1/2}X\begin{bmatrix} a & b & c \\ d & e & f \\ g & h & k \end{bmatrix} \tag{26}$$

holds for the recoupling of k, a, b, d, four of our finite group representations. Equation (28) of Part II then connects the first and last forms of TK 2.37. (There are misprints: the last line of TK 2.37 lacks a Γ_2 and of TK 2.39 a tilda in the last W.)

The expression of Tanabe and Kamimura's symbols in terms of W and X has the advantage of revealing inherent symmetries which are otherwise hidden. From the point of view of applications it also greatly extends the scope of their paper for their tables only enable one to calculate within $t_2^m e^n$ configurations. However, configurations $c^m a^n$ for orbitals belonging to any pair of irreducible representations c and a can now be dealt with by simply replacing T_2 and E in (24) by c and a respectively, because we already calculated essentially all the X in Part II.

Finally note that Tanabe and Kamimura treat the spin–orbit coupling as a double tensor rather than, as in the present paper, an irreducible product. A double tensor $T_{\alpha\beta}{}^{ab}$ is defined with respect to two groups, G_1 and G_2 say, which are such that each element of G_1 commutes with each element of G_2. a and b are irreducible representations of G_1 and G_2 respectively with components α and β. Then for fixed β, $T_{\alpha\beta}{}^{ab}$ is an irreducible tensor operator belonging to the representation a when operated on by elements of G_1. A similar remark applies to G_2. Suppose V symbols are defined for both G_1 and G_2. Further suppose we have a system whose states are linearly dependent on simple products $|cd\gamma\delta\rangle = |c\gamma\rangle|d\delta\rangle$ of states for independent systems such that the elements of G_1 operate only on the $|c\gamma\rangle$ and those of G_2 only on the $|d\delta\rangle$. Then equation (1) is clearly generalizable to

$$\langle cd\gamma\delta|T_{\alpha\beta}{}^{ab}|c'd'\gamma'\delta'\rangle = \langle cd||T^{ab}||c'd'\rangle V\begin{pmatrix} c & a & c' \\ \gamma & \alpha & \gamma' \end{pmatrix} V\begin{pmatrix} d & b & d' \\ \delta & \beta & \delta' \end{pmatrix}, \tag{27}$$

and could be generalized further to deal with n mutually commuting groups $G_1 \ldots G_n$ if one wished. The spin–orbit coupling can be treated as a linear form in the components of the double tensor

$$T_{\alpha\beta}^{1T_1} = \sum_i s_\alpha(i) u_\beta(i)$$

with G_1 the unitary unimodular group U_2 and G_2 the octahedral group which is, in effect, what Tanabe and Kamimura do. Equation (27) serves the same purpose as TK 2.13.

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