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LOW-LYING LEVELS IN CERTAIN ACTINIDE ATOMS

B. R. Judd

July 6, 1961

ABSTRACT

The problem of calculating the ordering and properties of low-lying levels in configurations of the type $5f^n6d$ falls into four parts: (a) the choice of a coupling scheme to define the basic eigenfunctions; (b) the evaluation of the matrix elements of the spin-orbit interaction and of the Coulomb interaction in the form of linear combinations of certain radial integrals; (c) the estimation of the radial integrals; (d) the diagonalization of the energy matrices. With regard to (a), the Jj coupling scheme is considered to be the most appropriate; this implies that the Coulomb interaction between the core, comprising the equivalent f electrons, and the d electron (to whose levels the respective symbols J and j refer) is weak compared with the interactions within the two systems. Part (b) is carried out by applying the tensor operator and group theoretical methods of Racah. For (c), values of the Slater integrals $F_k(5f, 6d)$ and $G_k(5f, 6d)$ are estimated for various atoms by assuming that they maintain the ratios one to another as they do in ThIII, and that their variation along the actinide series parallels the variation of $G^3(5f, 7s)$. The last parameter is known for ThIII, and analyses of UII, PuII, and AmII show that it decreases as one advances along the actinide series. This decline is interpreted as being due to the collapse of the 5f shell, and the internal nature of the 5f electrons allows some general statements to be made about

the spin-orbit coupling constants. Additional information on the parameters is provided by an analysis of the properties of the four lowest levels of CmI. Part (d) is accomplished for the very lowest levels of f^2d, f^3d, f^4d, f^8d and $f^{10}d$ by the simple expedient of neglecting all off-diagonal elements; for UI f^3d, where extensive spectroscopic information is available, the interaction of the levels deriving from the Jj coupling of $^4I_{9/2}$ to $^2D_{5/2}$ with those deriving from the coupling of $^4I_{11/2}$ to $^2D_{3/2}$ is included. Where experimental data are available, agreement with the theory, both in respect to the positions of the levels and to their Landé g values, is good — often surprisingly so in view of the approximations made.

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1. COUPLING SCHEMES

It is now well established that the ground configurations of PaI,[1] UI,[2,3] NpI,[4] PuI,[5] AmI,[6] and CmI[7] are $5f^2 6d$, $5f^3 6d$, $5f^4 6d$, $5f^6$, $5f^7$, and $5f^7 6d$ respectively. The presence of a number of f electrons makes these configurations very complex; nevertheless, the ordering and the properties of the lowest levels of $5f^6$ and $5f^7$ are understood tolerably well. This is not the case with configurations of the type $f^n d$; indeed, even the question of the ordering of the lowest levels is by no means easy to answer. The special problems connected with the addition of a d electron to a configuration of the type f^n form the subject of this paper.

The central problem can be stated very simply. Taking the states of a configuration $f^n d$ as a basis, we have to diagonalize the matrix of H_1+H_2, where H_1 is the Coulomb interaction between the electrons, and H_2 represents the spin-orbit coupling. In detail,

$$H_1 = \sum_{i>j} e^2/r_{ij}$$

and

$$H_2 = \sum_i \zeta(r_i)\underset{\sim}{s}_i \cdot \underset{\sim}{\ell}_i .$$

The symbol r_{ij} stands for the distance between electrons i and j; $\underset{\sim}{s}_i$ and $\underset{\sim}{\ell}_i$ denote the spin and orbital angular momentum respectively of electron i. The function $\zeta(r_i)$ depends on

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the central field potential and has the same significance here as in the book by Condon and Shortley.[8] The complete matrix of H_1+H_2 breaks up into a number of smaller matrices, each characterized by the quantum number J_2 of the total angular momentum of the electron system. (The reason for the subscript 2 will soon be apparent.) Even so, the number of rows and columns possessed by these matrices increases very rapidly with n, and an exact diagonalization is often extremely tedious. A more profitable approach, and one that has a greater physical significance, is to choose the basis states in such a way that the largest entries in the matrix of H_1+H_2 form an extended string of tiny matrices running along the main diagonal. Provided the coupling between these tiny matrices is not too large, each one can be diagonalized separately.

In treating configurations of the type $f^n d$, it is advantageous to consider the f electrons as forming a central core, not only because they spend most of their time well within the orbit of the d electron, but also because the techniques for dealing with n equivalent f electrons have been extensively developed. Within the 5f shell, Russell-Saunders (LS) coupling, although not perfectly fulfilled by any means, is certainly a better approximation than jj coupling. If the Coulomb interaction between the d electron and an electron of the core is energetically more important than the spin-orbit coupling of the d electron, then LS coupling is a reasonable approximation for the entire configuration $f^n d$; in this coupling scheme the basic states are of the type

$$|f^n \gamma_1 S_1 L_1, d, S_2 L_2 J_2 M_2). \quad (1)$$

The quantum numbers have their usual meanings, and are subscripted to denote the groups of electrons to which they refer. Odd subscripts are always used to label states of the core, whereas quantum numbers that refer to the entire electron system have even subscripts.

In view of the different spatial distributions of the 5f and 6d electrons, it is not unlikely that the energy associated with the spin-orbit coupling of the d electron exceeds the Coulomb energy of interaction between the d electron and an f electron. It is now more appropriate to treat the core and the d electron as two separate systems, whose total angular momenta J_1 and j are weakly coupled to form J_2. We refer to this type of coupling as Jj coupling; the corresponding basic states are

$$|f^n \gamma_1 S_1 L_1 J_1, s d j, J_2 M_2). \quad (2)$$

The energy-level pattern to which this coupling scheme corresponds is shown in Fig.1 for the case of n = 4.

In order to discover which of the two coupling schemes more nearly approximates to the actual coupling scheme of the actinides, we consider the Zeeman splittings of the ground levels of PaI, UI, NpI, and CmI. For LS coupling, the Landé g value for a level characterized by the quantum numbers S_2, L_2, and J_2 is given simply by

$$g = g(S_2 L_2 J_2), \quad (3)$$

where

$$g(S\ L\ J) = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} . \tag{4}$$

On the other hand, for Jj coupling, it can be shown by elementary tensor operator techniques that

$$g = g(S_1\ L_1\ J_1)\ \frac{J_2(J_2+1) + J_1(J_1+1) - j(j+1)}{2J_2(J_2+1)}$$

$$+ g(s\ d\ j)\ \frac{J_2(J_2+1) + j(j+1) - J_1(J_1+1)}{2J_2(J_2+1)} . \tag{5}$$

The quantum numbers S_2, L_2, and J_2 for the ground level in LS coupling can be found by applying Hund's rule to the entire configuration $f^n d$; the quantum numbers S_1, L_1, J_1, and j which label the ground level in Jj coupling can be found by applying Hund's rule separately to the core and to the d electron. The results of the calculation are given in Table I. Remarkably good agreement is obtained between the experimentally observed g values and those calculated on the assumption of Jj coupling. We conclude that the states (2) form a more suitable basis than the states (1). The superiority of Jj coupling has been stressed by members of the atomic-beam group at Berkeley in their experimental papers, though we reject their explanation that deviations between the last two columns of Table I are due to configuration interaction.[7]

2. MATRIX ELEMENTS

Although our main interest lies in configurations of the type $f^n d$, it is scarcely any more trouble to develop the theory for the general configuration $\ell^n \ell'$. Accordingly, the specialization to $f^n d$ is dropped. It is particularly easy to evaluate matrix elements of H_2 in the Jj coupling scheme, since this operator does not couple the electron ℓ' to the core ℓ^n. On making the abbreviation

$$\psi_i \equiv \ell^n \gamma_i S_i L_i,$$

we can write

$$(\psi_1 J_1, s \ell' j', J_2 M_2 \mid H_2 \mid \psi_3 J_3, s \ell' j'', J_4 M_4)$$

$$= \delta(J_1, J_3)\, \delta(j', j'')\, \delta(J_2, J_4)\, \delta(M_2, M_4)$$
$$\times \Big[\delta(\psi_1, \psi_3)\, \zeta_{\ell'} (s \ell' j' \mid \underset{\sim}{s} \cdot \underset{\sim}{\ell} \mid s \ell' j')$$
$$+ \zeta_\ell (\psi_1 J_1 \mid \Sigma\, \underset{\sim}{s} \cdot \underset{\sim}{\ell} \mid \psi_3 J_3) \Big], \qquad (6)$$

where the summation runs over the n electrons forming the core. The spin-orbit coupling constants ζ_ℓ and $\zeta_{\ell'}$ are given by equations of the type

$$\zeta_\ell = \int_0^\infty R_\ell^2(r)\, \xi(r)\, dr,$$

where R_ℓ is the appropriate radial eigenfunction. The matrix

elements on the right-hand side of Eq. (6) can be found by the usual techniques for handling configurations of equivalent electrons.[9] Thus

$$(s\ \ell'\ j' \mid \underset{\sim}{s}\cdot\underset{\sim}{\ell} \mid s\ \ell'\ j')$$

$$= (-1)^{\ell'+j'+\frac{1}{2}} \left[3\ell'(\ell'+1)(2\ell'+1)/2\right]^{\frac{1}{2}} \begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & 1 \\ \ell' & \ell' & j' \end{Bmatrix}$$

and

$$(\psi_1\ J_1 \mid \sum \underset{\sim}{s}\cdot\underset{\sim}{\ell} \mid \psi_3\ J_3)$$

$$= n\left[3\ell(\ell+1)(2\ell+1)(2L_1+1)(2L_3+1)(2S_1+1)(2S_3+1)/2\right]^{\frac{1}{2}}$$

$$\times (-1)^{J_1+S_1+S_3+\ell+\frac{1}{2}} \begin{Bmatrix} S_1 & S_3 & 1 \\ L_3 & L_1 & J_1 \end{Bmatrix}$$

$$\times \sum_{\bar{\psi}} (\psi_1\{|\ \bar{\psi})(\psi_3\{|\ \bar{\psi})(-1)^{\bar{S}+\bar{L}} \begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & 1 \\ S_3 & S_1 & \bar{S} \end{Bmatrix} \begin{Bmatrix} \ell & \ell & 1 \\ L_3 & L_1 & \bar{L} \end{Bmatrix}.$$

Quantities of the type $(\psi_1\{|\ \bar{\psi})$ are fractional parentage coefficients: $\bar{\psi}$ defines a term of ℓ^{n-1}.

The ease of calculating matrix elements of H_2 in the Jj coupling scheme is offset by the difficulty of treating H_1. Even in LS coupling the resultant expressions are quite cumbersome. Thus, using the standard methods of tensor operators,[10] we find that the contribution to

$$(\psi_1,\ \ell',\ S_2\ L_2 \mid H_1 \mid \psi_3,\ \ell',\ S_4\ L_4) \tag{7}$$

coming from the Coulomb interaction of the electron ℓ' with the electrons in the core is equal to

$$\sum_k \Big[D_k(n;\ S_1\ L_1\ L_3;\ L_2)\ F^k(n'\ell,\ n''\ \ell') + E_k(n;\ S_1\ L_1,\ S_3\ L_3;\ S_2\ L_2)\ G^k(n'\ \ell,\ n''\ \ell') \Big]. \tag{8}$$

In this expression, $F^k(n'\ \ell,\ n''\ \ell')$ and $G^k(n'\ \ell,\ n''\ \ell')$ are the usual Slater integrals (see Condon and Shortley[8]), the symbols n' and n" denoting the principal quantum numbers attaching to electrons ℓ and ℓ' respectively. The quantities D_k and E_k are given by

$$\begin{aligned} D_k(n;\ S_1\ L_1\ L_3;\ L_2) &= (2\ell+1)(2\ell'+1)\,\delta(S_2,\ S_4)\,\delta(L_2,\ L_4)\,\delta(S_1,\ S_3) \\ &\times (-1)^{L_2+\ell+L_3} \begin{pmatrix} \ell & k & \ell \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell' & k & \ell' \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} \ell' & k & \ell' \\ L_1 & L_2 & L_3 \end{Bmatrix} \\ &\times (\psi_1 \parallel U^{(k)} \parallel \psi_3), \end{aligned} \tag{9}$$

and

$$E_k(n;\ S_1\ L_1,\ S_3\ L_3;\ S_2\ L_2)$$

$$= \quad n(2\ell+1)(2\ell'+1)\,\delta(S_2,\ S_4)\,\delta(L_2,\ L_4)$$

$$\times \left[(2S_1+1)(2L_1+1)(2S_3+1)(2L_3+1)\right]^{\frac{1}{2}} (-1)^{S_1+S_3} \begin{pmatrix} \ell' & k & \ell \\ 0 & 0 & 0 \end{pmatrix}^2$$

$$\times \sum_{\bar{\psi}} (\psi_1 \{| \bar{\psi})(\psi_3 \{| \bar{\psi}) \begin{Bmatrix} s & \bar{S} & S_3 \\ s & S_2 & S_1 \end{Bmatrix} \begin{Bmatrix} \bar{L} & \ell & L_3 \\ \ell & k & \ell' \\ L_1 & \ell' & L_2 \end{Bmatrix} . \qquad (10)$$

The tensor $\underset{\sim}{U}^{(k)}$ is the sum of the unit tensors $\underset{\sim}{u}_i^{(k)}$ for the electrons i of the core; the reduced matrix element occurring in Eq. (9) is given by

$$(\psi_1 \| U^{(k)} \| \psi_3)$$

$$= n \sum_{\bar{\psi}} (\psi_1 \{| \bar{\psi})(\psi_3 \{| \bar{\psi})(-1)^{\bar{L}+k+\ell+L_1} \begin{Bmatrix} \ell & L_1 & \bar{L} \\ L_3 & \ell & k \end{Bmatrix} . \qquad (11)$$

In order to find the matrix elements of H_1 in the Jj coupling scheme, we write

$$|(S_3\ L_3)J_3,\ (s\ \ell')j'',\ J_4)$$

$$= \sum_{S_4,\ L_4} ((S_3\ s)S_4,\ (L_3\ \ell')L_4,\ J_4\,|\,(S_3\ L_3)J_3,\ (s\ \ell')j'',\ J_4)$$

$$\times\ |(S_3\ s)S_4,\ (L_1\ \ell')L_4,\ J_4);$$

as is well known,[11]

$$((S_3\ s)S_4,\ (L_3\ \ell')L_4,\ J_4 \mid (S_3\ L_3)J_3,\ (s\ \ell')j'',\ J_4)$$

$$= \left[(2S_4+1)(2L_4+1)(2J_3+1)(2j''+1)\right]^{\frac{1}{2}} \begin{Bmatrix} S_3 & s & S_4 \\ L_3 & \ell' & L_4 \\ J_3 & j'' & J_4 \end{Bmatrix} .$$

Hence

$$(\psi_1\ J_1,\ s\ \ell'\ j',\ J_2 \mid H_1 \mid \psi_3\ J_3,\ s\ \ell'\ j'',\ J_4)$$

$$= \delta(J_2,\ J_4)\left[(2J_1+1)(2J_3+1)(2j'+1)(2j''+1)\right]^{\frac{1}{2}}$$

$$\times \sum_{S_2,\ L_2} (2S_2+1)(2L_2+1) \begin{Bmatrix} S_1 & s & S_2 \\ L_1 & \ell' & L_2 \\ J_1 & j' & J_2 \end{Bmatrix} \begin{Bmatrix} S_3 & s & S_2 \\ L_3 & \ell' & L_2 \\ J_3 & j'' & J_2 \end{Bmatrix}$$

$$\times (\psi_1,\ \ell',\ S_2\ L_2 \mid H_1 \mid \psi_3,\ \ell',\ S_2\ L_2). \tag{12}$$

It might be hoped that when the expression (8) is substituted for the matrix element under the summation in Eq.(12), the detailed forms of D_k and E_k would permit the sums over S_2 and L_2 to be carried out. We can examine the feasibility of this simplification by drawing out the coupling diagrams for the sums. This is done in Fig.2 for the sum involving D_k and in Fig.3 for that involving E_k. Every triangular condition in the sums, save those involving the running indices S_2 and L_2,

is replaced by the junction of three branches labelled by the corresponding quantum numbers of angular momentum. The figure for D_k is quite simple; in fact, if the branch labelled J_2 were eliminated, it would be identical to the figure for the Biedenharn-Elliott sum rule.[11] The effect of the extra branch is to produce an additional 6-j symbol when the sums over S_2 and L_2 are carried out. Instead of the product of two 6-j symbols, which the Biedenharn-Elliott sum gives rise to, we obtain the triple product

$$\begin{Bmatrix} j' & k & j'' \\ \ell' & s & \ell' \end{Bmatrix} \begin{Bmatrix} j' & k & j'' \\ J_3 & J_2 & J_1 \end{Bmatrix} \begin{Bmatrix} J_1 & k & J_3 \\ L_3 & S_1 & L_1 \end{Bmatrix}$$

together with some associated factors. The situation for E_k is more complex, however. The intricate connectivity of the coupling diagram suggests that in this case the sums over S_2 and L_2 cannot be carried out so simply. Indeed, we have a species of 18-j symbol to contend with. Faced with this difficulty, the best approach seems to be to construct the 9-j symbols and the matrix element on the right hand side of Eq. (12), and then explicitly perform the sum. When $\ell' = 2$, the sum comprises at most tem terms.

3. SIMPLIFICATIONS

Prior to the insertion of the matrix elements (7) into

the sum of Eq. (12), the quantities D_k and E_k of Eqs. (9) and (10) must be evaluated. If we are interested solely in the lowest groups of levels for configurations of the type $\ell^n \ell'$, then only the lowest terms of the core ℓ^n are relevant in the first approximation. For these, $S_1 = S_3 = S_m$, the maximum spin for ℓ^n: in detail,

$$S_m = \tfrac{1}{2}n \qquad \text{for } 0 \leq n \leq 2\ell+1$$

or

$$S_m = \tfrac{1}{2}(4\ell+2-n) \qquad \text{for } 2\ell+1 \leq n \leq 4\ell+2.$$

In the following we shall assume that the quantum number L_1 is sufficient to define a term of maximum multiplicity of the core; the symbols γ_i can therefore be dropped.

We first confine our attention to the case for which $0 \leq n \leq 2\ell+1$, that is, to the first half of the shell. As is well known, the terms of maximum multiplicity exhibit a certain symmetry about the quarter-filled shell: for example, the terms of f^2 are ^3P, ^3F, and ^3H, while those of f^5 are ^6P, ^6F, and ^6H. This is a reflection of the fact that irreducible representations of $U_{2\ell+1}$ (the unitary group in $2\ell+1$ dimensions) of the type

$$[\underbrace{111\cdots 1}_{n}] \qquad \text{and} \qquad [\underbrace{111\cdots 1}_{2\ell+1-n}] \tag{13}$$

decompose into the same set of irreducible representations of R_3 (see, for example, Jahn[12]). The branching rules for the reduction $U_{2\ell+1} \rightarrow R_{2\ell+1}$ are particularly simple to describe for representations of $U_{2\ell+1}$ comprising a succession of ones: if $n \leq \ell$, we simply replace the square brackets by parentheses,

adding zeros to make the total number of enclosed digits up to ℓ; if $\ell+1 \leq n \leq 2\ell+1$, we write down $2\ell+1-n$ ones and add $n-\ell-1$ zeros, again enclosing the resulting set of ℓ digits in parentheses. Both representations (13) decompose into the same representation of $R_{2\ell+1}$, and we denote it by $(11\cdots10\cdots0)$. Under the reduction $R_{2\ell+1} \rightarrow R_3$, this simple representation decomposes into precisely those irreducible representations $\mathcal{D}_L$ of R_3 for which L is a term label. For $\ell = 3$, $n = 2$,

$$(110) \rightarrow \mathcal{D}_1 + \mathcal{D}_3 + \mathcal{D}_5.$$

Now the tensors $\underset{\sim}{U}^{(k)}(2k+1)^{\frac{1}{2}}$ for $k = 1, 3, \cdots, 2\ell-1$ form the $\ell(2\ell-1)$ components of a single generalized tensor that transforms according to the representation $(110\cdots0)$ of $R_{2\ell+1}$, while for $k = 2, 4, \cdots, 2\ell$, the tensors form the $\ell(2\ell+3)$ components of a single generalized tensor that transforms according to the representation $(20\cdots0)$ of $R_{2\ell+1}$. (These results are due to Racah.[13]) By means of the theory of groups, it is possible to show that $(11\cdots10\cdots0)$ occurs not more than once in the decomposition of the Kronecker products

$$(110\cdots0) \times (11\cdots10\cdots0)$$

and

$$(20\cdots0) \times (11\cdots10\cdots0).$$

An application of the Wigner-Eckart theorem gives at once

$$(\ell^n\, S_m\, L_1 \,\|\, U^{(\lambda)} \,\|\, \ell^n\, S_m\, L_3)$$

$$= A_\lambda\, (\ell^{2\ell+1-n}\, S'_m\, L_1 \,\|\, U^{(\lambda)} \,\|\, \ell^{2\ell+1-n}\, S'_m\, L_3), \qquad (14)$$

where A_λ is independent of L_1 and L_3, and has at most one value for odd λ and another for even λ (excluding zero). The symbol S'_m stands for the maximum spin of $\ell^{2\ell+1-n}$, and is equal to $\frac{1}{2}(2\ell+1)-S_m$.

To find the first value of A_λ, we set $\lambda = 1$ and $L_1 = L_3$. The tensor $\underset{\sim}{U}^{(1)}$ is proportional to $\underset{\sim}{L}$, and we obtain

$$A_\lambda = 1 \qquad \text{for odd } \lambda .$$

The second is a little more difficult to arrive at. If $L_1 = L_3 = L_m$, the maximum value for the given S_m, then a state of the type $|\ell^n\, S_m\, L_m\, M_S\, M_L)$ can be expressed as a single determinantal product state if M_S and M_L also have their maximum values. In this case, it is straightforward to derive the equation

$$(\ell^n\, S_m\, L_m \,\|\, U^{(2)} \,\|\, \ell^n\, S_m\, L_m)$$

$$= \frac{2\ell-2n+1}{2L_m-1} \left[\frac{(2L_m+3)!\,(2\ell-2)!}{(2L_m-2)!\,(2\ell+3)!} \right]^{\frac{1}{2}} .$$

On setting $L_1 = L_3 = L_m$ and $\lambda = 2$ in Eq.(14), we find

$$A_\lambda = -1 \qquad \text{for even } \lambda .$$

Both results, and also the trivial case of $\lambda = 0$, can be summarized in the equation

$$(\ell^n\, S_m\, L_1 \,\|\, U^{(\lambda)} \,\|\, \ell^n\, S_m\, L_3)$$
$$= (-1)^{\lambda+1}\, (\ell^{2\ell+1-n}\, S'_m\, L_1 \,\|\, U^{(\lambda)} \,\|\, \ell^{2\ell+1-n}\, S'_m\, L_3)$$
$$+ \delta(\lambda, 0)\, \delta(L_1, L_3)\, [(2\ell+1)(2L_1+1)]^{\frac{1}{2}}. \qquad (15)$$

The value of Eq.(15) is soon apparent. If the 3-j symbols of Eq.(9) are not to vanish, k must be even. Hence, for $k > 0$,

$$D_k(n;\, S_m\, L_1\, L_3;\, L_2) = -\, D_k(2\ell+1-n;\, S'_m\, L_1\, L_3;\, L_2). \qquad (16)$$

Again, for $S_1 = S_3 = S_m$ (with the condition $n \leq 2\ell+1$ maintained), the parental spin $\bar{S}$ can assume only the value $S_m - \frac{1}{2}$ in Eq.(10). We may therefore place the 6-j symbol before the summation sign. If we expand the 9-j symbol, after a single interchange of its first and third columns, the summation over $\bar{\psi}$ becomes identical to that of Eq.(11). We may now use Eq.(15) and reverse the sequence of operations: the new reduced matrix element is expanded by means of Eq.(11) and then the sum over the product of three 6-j symbols is carried out. The point of this manoeuvre is that the phase factor $(-1)^{\lambda+1}$ in Eq.(15) prevents a 9-j symbol's being formed, and we get instead a product of two 6-j symbols. The final result is

$$E_k(n;\ S_m\ L_1,\ S_m\ L_3;\ S_2\ L_2)$$

$$= (-1)^{2S_m}(2S_m+1)(2\ell+1)\begin{pmatrix}\ell & k & \ell' \\ 0 & 0 & 0\end{pmatrix}^2 \begin{Bmatrix} s & S_m-\frac{1}{2} & S_m \\ s & S_2 & S_m\end{Bmatrix}$$

$$\times\Bigg[\delta(L_1,\ L_3) - (2\ell+1-n)(2\ell'+1)\left[(2L_1+1)(2L_3+1)\right]^{\frac{1}{2}}$$

$$\times\sum_{\bar{\psi}'}(\psi_1'\{|\bar{\psi}')(\psi_3'\{|\bar{\psi}')\begin{Bmatrix}\ell & k & \ell' \\ L_2 & L_3 & \bar{L}'\end{Bmatrix}\begin{Bmatrix}\ell & k & \ell' \\ L_2 & L_1 & \bar{L}'\end{Bmatrix}\Bigg]. \qquad (17)$$

In this expression,

$$\psi_i' \equiv \ell^{2\ell+1-n}\ S_m'\ L_i,$$

and $\bar{\psi}'$ defines a term of the configuration $\ell^{2\ell-n}$. The advantage of Eq. (17) over Eq. (10) is that the 9-j symbol is replaced by a pair of 6-j symbols. These can be rapidly found from the tables of Bivins, Metropolis, Rotenberg, and Wooton[14], whereas the arguments of many of the 9-j symbols occurring in Eq. (10) are too large for existing tables of 9-j symbols to be of use.

Similar techniques to those described above can be used to derive expressions for configurations in the second half of the shell, that is, for configurations $\ell^n\ell'$ for which $2\ell+1 < n \leq 4\ell+2$. The equation

$$(\ell^n\, S_m\, L_1 \,\|\, U^{(\lambda)} \,\|\, \ell^n\, S_m\, L_3)$$
$$= (\ell^{n-2\ell-1}\, S'_m\, L_1 \,\|\, U^{(\lambda)} \,\|\, \ell^{n-2\ell-1}\, S'_m\, L_3)$$
$$+ \delta(\lambda, 0)\, \delta(L_1, L_3)\, [(2\ell+1)(2L_1+1)]^{\frac{1}{2}}$$

can be used in place of Eq.(15). The extension of Eq.(16) is

$$D_k(n;\, S_m\, L_1\, L_3;\, L_2) = -D_k(6\ell+3-n;\, S'_m\, L_1\, L_3;\, L_2)$$
$$= D_k(n-2\ell-1;\, S'_m\, L_1\, L_3;\, L_2) = -D_k(4\ell+2-n;\, S_m\, L_1\, L_3;\, L_2). \tag{18}$$

Maintaining the condition $n > 2\ell+1$, we can also prove

$$E_k(n;\, S_m\, L_1,\, S_m\, L_3;\, S_m+\tfrac{1}{2},\, L_2)$$
$$= -(2\ell+1)\, \delta(L_1, L_3) \begin{pmatrix} \ell & k & \ell' \\ 0 & 0 & 0 \end{pmatrix}^2 \tag{19}$$

and

$$E_k(n;\, S_m\, L_1,\, S_m\, L_3;\, S_m-\tfrac{1}{2},\, L_2)$$
$$= \frac{2\ell+1}{2S_m} \begin{pmatrix} \ell & k & \ell' \\ 0 & 0 & 0 \end{pmatrix}^2 \delta(L_1, L_3)$$
$$+ \frac{2S_m+1}{2S_m}\, E\,(n-2\ell-1;\, S'_m\, L_1,\, S'_m\, L_3;\, \ell+1-S_m,\, L_2). \tag{20}$$

The striking invariance of $E_k(n;\, S_m\, L_1,\, S_m\, L_1;\, S_m+\tfrac{1}{2},\, L_2)$ with respect to L_1 and L_2 can be seen in a direct way by expressing the states as linear combinations of determinantal

product states and using the conventional techniques of Condon and Shortley.[8] Many of the formulae given above can be checked by using the tables of matrix elements of H_1 for configurations of the type $d^n p$; it is to be noted, however, that in the collected tables of Slater,[15] all diagonal matrix elements are given relative to the average energy of the configuration. The formulae of this section require some elaboration for configurations $\ell^n \ell'$ with $\ell \geq 4$, since the symbols γ_i are sometimes necessary to distinguish terms of maximum multiplicity of ℓ^n.

4. THE CONFIGURATIONS $\ell^n s$

On setting $\ell' = 0$ in Eqs. (9) and (10), and dropping the delta functions $\delta(S_2, S_4)$ and $\delta(L_2, L_4)$, we get

$$D_k(n;\ S_1\ L_1\ L_3;\ L_2) = n\,\delta(k, 0)\,\delta(\psi_1, \psi_3)\,\delta(L_1, L_2) \tag{21}$$

and

$$E_k(n;\ S_1\ L_1,\ S_3\ L_3;\ S_2\ L_2)$$

$$= n\,\delta(k, \ell)\,\delta(L_1, L_2)\,\delta(L_1, L_3)\,[(2S_1+1)(2S_3+1)]^{\frac{1}{2}}\,(2\ell+1)^{-1}$$

$$\times\ (-1)^{S_1+S_3} \sum_{\bar{\psi}} (\psi_1 \{| \bar{\psi})(\psi_3 \{| \bar{\psi}) \begin{Bmatrix} s & \bar{S} & S_3 \\ s & S_2 & S_1 \end{Bmatrix}.$$

If $S_1 \neq S_3$, the parental spin $\bar{S}$ is limited to the value $\frac{1}{2}(S_1+S_3)$. The 6-j symbol can be placed before the sigma and the sum over $\bar{\psi}$ gives $\delta(\psi_1, \psi_3)$. But according to the initial hypothesis, $S_1 \neq S_3$; hence E_k is zero. For $S_1 = S_3$, the dependence of the fractional parentage coefficients on $\bar{S}$, given explicitly by Racah,[13] allows the sum over $\bar{\psi}$ to be carried out. With some manipulation, we obtain

$$E_k(n;\ S_1\ L_1,\ S_3\ L_3;\ S_1+\tfrac{1}{2},\ L_2)$$

$$= -\ \delta(k,\ell)\,\delta(L_1,\ L_2)\,\delta(\psi_1,\ \psi_3)(S_1+\tfrac{1}{2}n)/(2\ell+1) \qquad (22)$$

and

$$E_k(n;\ S_1\ L_1,\ S_3\ L_3;\ S_1-\tfrac{1}{2},\ L_2)$$

$$= \delta(k,\ell)\,\delta(L_1,\ L_2)\,\delta(\psi_1,\ \psi_3)(S_1+1-\tfrac{1}{2}n)/(2\ell+1). \qquad (23)$$

These results are equivalent to those previously obtained by van Vleck[16] (see also Slater[15]).

The extreme simplicity of Eqs. (21), (22), and (23) enables the summation in Eq. (12) to be carried out. If we are interested solely in the relative energies of the terms, we may disregard D_k and also the symbols $\frac{1}{2}n$ in Eqs. (22) and (23). For $J_1 = J_3$, we get

$$(\psi_1\ J_1,\ {}^2S_{\frac{1}{2}},\ J_2 \mid H_1 \mid \psi_3\ J_3,\ {}^2S_{\frac{1}{2}},\ J_2)$$

$$= \pm\ \delta(\psi_1, \psi_3)\ G^{\ell}\ (2\ell+1)^{-1}\ (2J_2+1)^{-1}$$

$$\times \left[L_1(L_1+1) - S_1(S_1+1) - J_1(J_1+1)\right], \qquad (24)$$

where the plus sign is taken for $J_2 = J_1+\frac{1}{2}$, the minus sign for $J_2 = J_1-\frac{1}{2}$. If $J_1 \neq J_3$, then we may take $J_1 = J_2\pm\frac{1}{2}$, $J_3 = J_2\mp\frac{1}{2}$. The result of the calculation is

$$(\psi_1\ J_2\pm\tfrac{1}{2},\ {}^2S_{\frac{1}{2}},\ J_2\ |\ H_1\ |\ \psi_3\ J_2\mp\tfrac{1}{2},\ {}^2S_{\frac{1}{2}},\ J_2)$$
$$= \delta(\psi_1, \psi_3)\ G^{\ell}\ (2\ell+1)^{-1}\ (2J_2+1)^{-1}$$
$$\times \left[(S_1+L_1+J_2+3/2)(S_1+L_1+\tfrac{1}{2}-J_2)(L_1+J_2+\tfrac{1}{2}-S_1)(S_1+J_2+\tfrac{1}{2}-L_1)\right]^{\frac{1}{2}} \tag{25}$$

It is understood that Eq.(24) includes only the contribution coming from the interaction of the s electron with the core; to obtain the complete matrix element we must add

$$(\psi_1\ J_1\ |\ H_1|\ \psi_3\ J_1).$$

5. PARAMETERS

Eq.(6) permits a matrix element of H_2 to be expressed as a linear combination of the spin-orbit coupling constants ζ_ℓ and $\zeta_{\ell'}$. By substituting (8) into Eq.(12), we can express the contribution to a matrix element of H_1 arising from the Coulomb interaction of the electron n" ℓ' with the core $(n'\ell)^n$ as a linear combination of the Slater integrals $F^k(n'\ell,\ n''\ell')$ and $G^k(n'\ell,\ n''\ell')$. Only those integrals need be considered for which the associated quantities D_k and E_k

are nonzero; an inspection of the 3-j symbols in Eqs. (9) and (10) indicates that for configurations of the type $5f^n6d$ we may restrict our attention to F^0, F^2, F^4, G^1, G^3, and G^5. The interactions within the core introduce the additional integrals $F^k(5f, 5f)$, where $k = 0, 2, 4$, and 6; however, the lowest levels in a configuration of the type $5f^n6d$ derive from the Hund term of the corresponding core configuration $5f^n$ (see Fig. 1), and hence these integrals do not enter into the calculations. Since only the relative energies of terms are of interest to us, $F^0(5f, 6d)$ can be dropped. Following Condon and Shortley,[8] we introduce

$$\begin{aligned} F_2(5f, 6d) &= F^2(5f, 6d)/105, \\ F_4(5f, 6d) &= F^4(5f, 6d)/693, \\ G_1(5f, 6d) &= G^1(5f, 6d)/35, \\ G_3(5f, 6d) &= G^3(5f, 6d)/315, \\ G_5(5f, 6d) &= G^5(5f, 6d)/1524.6, \end{aligned} \tag{26}$$

to avoid the occurrence of large denominators in the calculations.

From the considerations above, we see that the energies of the levels of $5f^n6d$ deriving from the ground term of the core $5f^n$ depend on the seven quantities

$$\zeta_f, \quad \zeta_d, \quad F_2, \quad F_4, \quad G_1, \quad G_3, \quad G_5.$$

If accurate 5f and 6d radial eigenfunctions were available for atoms of interest to us, then these quantities could, in principle,

be calculated. In the absence of such calculations for PaI, NpI, and CmI, we are obliged to treat them as parameters, to be adjusted to fit the data. However, in order to make the comparisons meaningful, it is important to impose some restrictions on the values that it is supposed they can assume. Corresponding parameters in different actinide atoms should vary in a systematic way along the actinide series: for example, we expect

$$\zeta_f(\mathrm{PaI};\ 5f^2 6d) < \zeta_f(\mathrm{UI};\ 5f^3 6d) < \zeta_f(\mathrm{NpI};\ 5f^4 6d) < \zeta_f(\mathrm{CmI};\ 5f^7 6d).$$

The ratios of the Slater integrals G^k and F^k, one to another for a given atom, are characteristic of the nature of the two-particle interaction (in this case Coulombic), and are comparatively insensitive to the shapes of the radial eigenfunctions. We may greatly reduce the number of disposable parameters by assuming that the ratios are not merely insensitive but actually invariant; Racah's values (in cm^{-1}) for ThIII[10], namely

$$\begin{aligned} F_2(5f,\ 6d) &= 190, \\ F_4(5f,\ 6d) &= 22.6, \\ G_1(5f,\ 6d) &= 423, \\ G_3(5f,\ 6d) &= 43, \\ G_5(5f,\ 6d) &= 5.9, \end{aligned}$$

can then be used as a basis for calculations throughout the entire actinide series. For a neutral atom AI, the matrix

elements of H_1 now depend on the single parameter Ω(AI) that satisfies

$$F_k(\mathrm{AI};\ 5f,\ 6d) = \Omega(\mathrm{AI})\ F_k(\mathrm{ThIII};\ 5f,\ 6d)$$
$$\text{and} \quad G_k(\mathrm{AI};\ 5f,\ 6d) = \Omega(\mathrm{AI})\ G_k(\mathrm{ThIII};\ 5f,\ 6d). \tag{27}$$

The insertion of AI and ThIII in the parentheses makes clear the atom to which the Slater integrals refer.

The internal character of the 5f electrons has already been mentioned. Evidence for the contraction of the 5f shell at the onset of the actinide series is presented in the next section; at this point we wish merely to indicate how the assumption that the core of 5f electrons lies near the nucleus can be used to obtain information about the parameters ζ_f and ζ_d. The properties of the f electrons should be largely independent of the presence of the outer electrons; consequently we expect equations of the type

$$\zeta_f(\mathrm{UI};\ 5f^3 6d 7s^2) = \zeta_f(\mathrm{UII};\ 5f^3 7s^2)$$
$$= \zeta_f(\mathrm{UIII};\ 5f^3 7s) = \zeta_f(\mathrm{UIV};\ 5f^3)$$

to be fairly well fulfilled. The sequence of values (in cm^{-1})

$$\zeta_f(\mathrm{ThII};\ 5f6d7s) = 1195$$
$$\zeta_f(\mathrm{ThIII};\ 5f6d) = 1240 \tag{28}$$
$$\text{and} \quad \zeta_f(\mathrm{ThIV};\ 5f) = 1236$$

obtained by Kessler[18] and Racah[17] supports this hypothesis.

Furthermore, the properties of the outer electrons should be unaffected if an f electron is removed and at the same time the nuclear charge is reduced by one unit. This statement is exemplified by

$$\zeta_d(\text{ThIII; 5f6d}) = 1430$$
$$\text{and} \quad \zeta_d(\text{AcIII; 6d}) = 1361, \tag{29}$$

which can be obtained from Racah's paper and the observed[19] separation of $^2D_{5/2}$ and $^2D_{3/2}$ in AcIII. Since the 5f shell has not collapsed to its typical transuranic radius for as early a member of the actinide series as thorium, we may expect the consequences of the assumption of a highly contracted 5f shell to be even better fulfilled for the atoms further along the series.

Cohen[20] has carried out a relativistic self-consistent calculation for the normal uranium atom, and it might be thought that the accurate 5f and 6d radial eigenfunctions that he obtains could be used to check Eqs. (27) and, if necessary, supplant them. A set of Slater integrals has been calculated by Winocur[21] from Cohen's eigenfunctions, and used, with other sets, in an examination of the properties of the lowest levels in PaI.[1] In spite of the indisputable accuracy of the eigenfunctions, the notorious unreliability of analogous calculations for other atoms is a strong reason for treating the set of Slater integrals with a good deal of reserve. Slater[15] has commented on the discrepancies between the experimental and theoretical values of

$F^k(3d, 3d)$; corresponding values of $F^k(4f, 4f)$ are given in Table II for PrIV. The discrepancies are popularly ascribed to configuration interaction; more precisely, they can be visualized as due primarily to an internal screening effect,[22] produced by the closed shells of electrons, which prevents the full Coulomb field of one 4f electron from being felt by the other. The orbits of the two 4f electrons in PrIV correspond to the same radial eigenfunction and overlap strongly; even so, discrepancies of up to 20% are to be noted in Table II. For the integrals $F^k(5f, 6d)$ and $G^k(5f, 6d)$, we may expect the disagreement to be much more severe, since the 6d electron is essentially an outer electron, whereas the 5f electrons are located deep inside the atom. From these considerations, it seems best to follow the traditional approach and take the radial integrals as variable parameters; owing to Eqs. (27), these are effectively only three, namely Ω, ζ_f and ζ_d.

6. COLLAPSE OF THE 5f SHELL

The term analyses that have been performed to date on the spectra of members of the actinide series are fragmentary in character. It is therefore important to take advantage of such data as are available. Like the rare-earth series, a common feature of singly ionized atoms of the actinide series

is a low-lying configuration of the type $f^n s$. Such configurations are easy to analyze, since, according to Eqs. (24) and (25), the interaction of the s electron with the core depends, for members of the actinide series, on the single Slater integral $G^3(5f, 7s)$. The orbit of the 7s electron lies mainly in the outer shells of the ion, and hence should not change very much if simultaneously a 5f electron is added to the core and the nuclear charge is increased by one unit. The variation of $G^3(5f, 7s)$ along the actinide series therefore reflects the behaviour of the 5f electrons in the core, and bears directly on the parameter Ω, since the latter represents the analogous variation of $G^k(5f, 6d)$ and $F^k(5f, 6d)$.

It is convenient to begin with the typical case of UII $5f^4 7s$. Schuurmans, van den Bosch, and Dijkwel[3] have observed four levels corresponding to J = 7/2, 9/2, 11/2, and 9/2 at energies 0, 1052.65, 3683.82, and 3759.55 cm^{-1} relative to the lowest energy of the four. On the assumption that LS coupling is a good approximation for the four 5f electrons, the lowest levels of the core are the pure levels $^5I_4$, $^5I_5, \cdots$, $^5I_8$. The functions $\delta(\psi_1, \psi_3)$ in Eqs. (24) and (25) indicate that within this approximation, the interaction between the s electron and the core can be treated exactly without the necessity of considering perturbations from levels deriving from excited terms of the core. If we suppose $^5I_5$ lies an energy A above $^5I_4$, then $^5I_6$ must lie 11A/5 above $^5I_4$ for the Landé interval

rule to be obeyed. From Eqs.(24) and (25), we find that the energies $\epsilon(J_2)$ of levels of $5f^4 7s$ are given by the solutions to the equations

$$-2G^3/7 - \epsilon(7/2) = 0,$$

$$\begin{vmatrix} A - 3G^3/35 - \epsilon(9/2) & 3G^3(14)^{\frac{1}{2}}/35 \\ 3G^3(14)^{\frac{1}{2}}/35 & 8G^3/35 - \epsilon(9/2) \end{vmatrix} = 0,$$

$$\begin{vmatrix} 11A/5 + G^3/14 - \epsilon(11/2) & 5G^3/14 \\ 5G^3/14 & A + G^3/14 - \epsilon(11/2) \end{vmatrix} = 0,$$

etc. The limits $A \gg G^3$ and $G^3 \gg A$ correspond to Jj and LS coupling respectively; the equations given above enable intermediate coupling schemes to be studied. To plot out $\epsilon(J_2)$ in a convenient way, we define

$$\eta = [\epsilon(J_2) - 14A] / [(26A)^2 + (5G^3/7)^2]^{\frac{1}{2}}$$

and

$$\xi = \chi/(1 + \chi),$$

where

$$\chi = (5G^3/7)/(26A).$$

The curves of η against ξ are drawn out in Fig.4. They possess the following properties: (i) The Jj and LS coupling extremes correspond to $\xi = 0$ and 1 respectively; (ii) For a given value of ξ, the various values of η determined by

the curves represent the values of $\epsilon(J_2)$ to scale; (iii) For both $\xi = 0$ and $\xi = 1$, the maximum and minimum values of η differ by 1; (iv) For all ξ, the center of gravity of the energy level system lies on the line $\eta = 0$. A similar co-ordinate scheme has been used in other contexts by Condon and Shortley.[8] For UII, we find that quite a good fit can be obtained between experiment and theory if we take $G^3 = 2600$ and $A = 2850 cm^{-1}$. In detail,

$$\epsilon(J_2) + 804 = 61, \quad 1100, \quad 3604, \quad 3730$$

for $J_2 = 7/2$, $9/2$, $11/2$, and $9/2$ respectively. The number 804 is added to $\epsilon(J_2)$ so that a direct comparison can be made with the experimental results quoted at the beginning of this paragraph. The quality of the fit can be seen from Fig.4. The data of Albertson, Harrison, and McNally[23] on NdII, for which $4f^4 6s$ is the ground configuration, is also included in this figure. The agreement with the theoretical curves could in this case be very much improved by relaxing the Landé interval rule with respect to J_1 in the limit $\xi = 0$.

We may carry out a similar analysis with the data of McNally and Griffin[24] for PuII $5f^6 7s$. The positions of the core levels ^7F_J deviate so much from the Landé interval rule that it is essential to treat them and G^3 as variable parameters. The results of the calculation are given in Table III; with $G^3(5f, 7s) = 2240 cm^{-1}$ and the energies of the core levels

given in the second column of the table, we obtain the energies $\epsilon(J_2) + 403$ in the fifth column. It is interesting to notice how closely the calculated positions of the levels of the core agree with the levels of PuI $5f^6 7s^2$ as found by Bovey and Gerstenkorn[25] (see column 3 of Table III), thus substantiating the hypothesis of the internal nature of the 5f electrons. The Landé g value of the level corresponding to the linear combination

$$\cos\theta \mid f^6\ {}^7F\ J_2-\tfrac{1}{2},\ {}^2S_{\frac{1}{2}},\ J_2) + \sin\theta \mid f^6\ {}^7F\ J_2+\tfrac{1}{2},\ {}^2S_{\frac{1}{2}},\ J_2)$$

is easily found to be given by

$$g = 3/2 + \left[\tfrac{1}{2} + \tfrac{1}{2}(2J_2+1)\cos\theta + (195/4 - J_2^2 - J_2)^{\frac{1}{2}}\sin\theta\right]/4J_2(J_2+1),$$

from Eqs. (3), (4), and (5). The calculated values of $|g|$ are compared to experiment in the seventh and eighth columns of Table III. Discrepancies are to be ascribed largely to the impurity of the core levels ${}^7F_J$, which undoubtedly contain large admixtures of ${}^5D_J$, ${}^5F_J$ and ${}^5G_J$.

Fred and Tomkins[26] have found that the level ${}^7S_3$ lies 2598.32cm^{-1} above ${}^9S_4$ in AmII $5f^7 7s$, and this datum leads at once to a value of 2274cm^{-1} for $G^3(5f, 7s)$.

From the results of Meggers, Fred, and Tomkins[19], it is easy to show that the level ${}^1F_3$ in AcII 5f7s lies 5341cm^{-1} above the center of gravity of the multiplet ${}^3F$. LS coupling is fairly well fulfilled, and we find $G^3(5f, 7s) = 18690\text{cm}^{-1}$ for this configuration. The various values of $G^3(5f, 7s)$

are collected in Table IV; the result of a calculation by Racah[17] for ThIII 5f7s is included. The striking features of this table are the sharp drop of $G^3(5f, 7s)$ in passing from AcII to ThIII, and the levelling off in the decline of this parameter for later members of the actinide series. The reduction of $G^3(5f, 7s)$ must be mainly ascribed to the collapse of the 5f shell. Mayer[27] has shown that with the onset of the actinide series a deep potential well for 5f electrons develops near the nucleus; when Z is large enough, a 5f electron is drawn from the outer shells of the atom into the interior. As Z increases, the internal 5f orbits become well established and change little with Z. Similar effects can be observed with the singly ionized rare earth atoms; for LaII, $G^3(4f, 6s)$ is $3100 cm^{-1}$, while for CeII it is approximately $1450 cm^{-1}$. The integral remains quite close to this value throughout the entire rare earth series.

7. CmI

The low-lying levels in the configuration f^7d are particularly easy to treat. The lowest term of f^7 is ^8S, and is well separated (probably by as much as $20\ 000 cm^{-1}$) from the first excited level. Furthermore, Eqs. (9) and (10) simplify considerably on setting $L_l = 0$, and it is straightforward

to plot out the arrangements of the energy levels for points intermediate between LS and Jj coupling. This is done in Fig.5; an analogous system of co-ordinates to that of Fig.4 is adopted. The configuration f^7d has been observed in the spectrum of GdI as well as in that of CmI; the experimental data[28] for the former are included in Fig.5, and lie quite close to the LS extreme. The contraction of the multiplet ^7D relative to the theoretical scheme is due mainly to an excited term ^7D of f^7d, deriving from the level ^6P of the core; its effect is to reduce ζ_d for ^7D to

$$\zeta_d - 32\,\zeta_f(2G_1 + 3G_3 - 33G_5)/3\Delta\,,$$

where Δ is the energy of ^6P above ^8S.

It can be seen from Fig.5 that the ratios of the spacings between the lowest four levels change only slightly from LS to Jj coupling; indeed, the Landé interval rule is obeyed in both limits. Fortunately, the abscissa corresponding to CmI can be quite accurately found by making use of the observed[7] g values for the lowest levels, and fitting them to a theoretical scheme. The high accuracy of the atomic beam results makes it desirable to improve the simple methods that led to the entries in Table 1. In the first place, the operator $\underset{\sim}{L} + 2\underset{\sim}{S}$ is replaced by $\underset{\sim}{L} + g_s\underset{\sim}{S}$, where $g_s = 2.0023$. For electrons of the core, this correction is small compared with the effects of the deviations from perfect LS coupling. Marrus et al.[6] find

that the g value of $^8S_{7/2}$ in AmI $5f^7$ is not exactly 2.002, but instead 1.937. The admixture of $^6P_{7/2}$ in the level $^8S_{7/2}$ that produces this discrepancy is presumably slightly different from the admixture of $^6P_{7/2}$ in the core level $^8S_{7/2}$ of CmI $5f^7 6d$; but in the absence of further information we shall suppose they are the same. The Slater integrals enter the calculation through the single parameter

$$G = 24G_1 + 96G_3 + 528G_5,$$

which represents the energy separation of ^9D and ^7D in the LS limit. Denoting the g value of the impure core level $^8S_{7/2}$ by g(7/2), we find

$$\begin{aligned} g = {} & \left[J_2(J_2+1) + 12\right] g(7/2)/2J_2(J_2+1) \\ & + (6-g_s)\left[J_2(J_2+1) - 12\right]/10J_2(J_2+1) \\ & + \sin^2\phi \left[(g_s-1)\left\{10J_2(J_2+1) - 19\right\}^{\frac{1}{2}}\right. \\ & \qquad \left. - 25\left\{g(7/2) - 1\right\}\right]/10J_2(J_2+1) \\ & + \sin 2\phi\, (g_s-1)\left[(J_2+7)(6-J_2)(J_2+2)(J_2-1)\right]^{\frac{1}{2}}/10J_2(J_2+1) \end{aligned} \tag{30}$$

for the g value of a level of total angular momentum J_2, where ϕ satisfies

$$\tan\phi = \frac{\left[(J_2+7)(6-J_2)(J_2+2)(J_2-1)\right]^{\frac{1}{2}}}{22 - J_2(J_2+1) + 50\zeta_d/G}.$$

When two levels with the same value of J_2 occur, the root for

which $\sin 2\phi > 0$ must be selected to give the g value of the lower level. With $50\,\zeta_d/G = 17$ and $g(7/2) = 1.937$, we obtain the numbers in the second column in Table V. In view of the neglect of diamagnetic and relativistic corrections in the calculations, the agreement is as good as can be expected. The ratio ζ_d/G fixes the position of the vertical line marked CmI in Fig. 5; rather surprisingly, it does not lie as close to the Jj extreme as the discussion of Sec. 1 leads us to expect. The populations of the various levels in the beam of curium atoms permits approximate energies of the lowest four levels to be found, and thereby determines the magnitude of ζ_d and G. With $\zeta_d = 2200$ and $G = 6471$, the calculated positions of the lowest four levels are 0, 490, 1230, and 2380cm^{-1} relative to the ground level. As can be seen in Fig. 5, the agreement with experiment is good.

For the Slater integrals G_k(ThIII; 5f, 6d), we find $G = 17395$. The contraction factor Ω(CmI), defined in Eqs. (27), is thus 0.372. From Table IV, it is clear that the corresponding reduction factor for G^3(5f, 7s) is approximately 2250/5341 = 0.421. The similarity between these two factors suggests that the variation of G^3(5f, 7s) along the actinide series can be taken to represent the variation of Ω. More precisely, it suggests the validity of the equation

$$G^3(\text{AII; 5f, 7s}) = \Omega(\text{AI})\, G^3(\text{ThIII; 5f, 7s}). \qquad (31)$$

This equation, which at best can only be a crude approximation, enables us to make use of Table IV to estimate the Slater integrals $F_k(5f, 6d)$ and $G_k(5f, 6d)$ for a number of actinide atoms.

8. UI

Of the spectra of all atoms beyond thorium, that of uranium has received the greatest attention. Kiess, Humphreys, and Laun[2] obtained the positions of 18 low odd levels of UI, several of which could be confidently assigned to the ground configuration $5f^3 6d$. Blaise[29] has recently extended this list of levels by taking advantage of the isotope shift $U^{235} - U^{238}$, and has also corrected some assignments made by Kiess et al.

At the outset of the analysis we confine our attention to those levels of $5f^3 6d$ that derive from the term ^4I of the core $5f^3$. From the tables[30] of the reduced matrix elements of $U^{(k)}$, the coefficients D_k may be rapidly found by using Eq. (9). It can be seen from Eq. (17) that the evaluation of the coefficients E_k requires the construction of certain coefficients of fractional parentage connecting the configurations f^4 and f^3. With the aid of Racah's tables[13] we obtain

$$(f^4\ {}^5I \{|\ f^3\ {}^4F) = -(1/8)^{\frac{1}{2}},$$

$$(f^4\ {}^5I \{|\ f^3\ {}^4G) = (21/88)^{\frac{1}{2}},$$

and

$$(f^4\ {}^5I \{|\ f^3\ {}^4I) = (7/11)^{\frac{1}{2}}.$$

On putting the quantities D_k and E_k into Expression (8), we arrive at the following energies for the terms of $5f^3 6d$ deriving from the core term ^4I:

$$^3G,\ ^5G: \quad (210F_2 - 476F_4)/33 + (1/3, -1)(17G_1 - 142G_3 + 14486G_5)/33,$$

$$^3H,\ ^5H: \quad (-5F_2 + 408F_4)/11 + (1/3, -1)(-21G_1 + 496G_3 + 3997G_5)/11,$$

$$^3I,\ ^5I: \quad (-51F_2 - 408F_4)/11 + (1/3, -1)(-9G_1 + 334G_3 + 2581G_5)/11,$$

$$^3K,\ ^5K: \quad -4F_2 + 17F_4 + (1/3, -1)(17G_1 + 38G_3 + 101G_5),$$

$$^3L,\ ^5L: \quad 4F_2 - 3F_4 + (1/3, -1)(21G_1 + 54G_3 + 21G_5).$$

The factor multiplying the linear combination of the integrals G_k is 1/3 for triplets and -1 for quintets. A constant term has been omitted from these expressions. Owing to Eqs. (27), we may conveniently postpone choosing a value for Ω(UI) and simply insert the Slater integrals for ThIII into these expressions. The resulting energies are included in Table VI. As is to be expected, the Hund term ^5L is lowest.

The next step is to perform the sum of Eq. (12). The 9-j symbols are not too tedious to evaluate, since one of their arguments is $\frac{1}{2}$. The resulting matrix elements between states in Jj coupling have to be multiplied by Ω(UI) to allow for the reduction in the Slater integrals F_k(5f, 6d) and G_k(5f, 6d) in passing from ThIII to UI. From Table IV and Eq. (31) we immediately obtain

$$\Omega(\mathrm{UI}) = 2600/5341 = 0.487.$$

In view of the approximate character of this calculation, it seems preferable to round off this figure to 0.5. The Slater integrals for UI can now be obtained by simply dividing the corresponding integrals for ThIII by 2.

If we were interested solely in the four lowest levels of $5f^3 6d$, that is, in those deriving from the coupling of the ground level $^4I_{9/2}$ with the level $^2D_{3/2}$ of the d electron, then the fixing of Ω(UI) would eliminate all disposable parameters, and the calculation could be completed. However, the observation of higher levels prompts a study of those levels deriving from the couplings of $^4I_{11/2}$ with $^2D_{3/2}$ and of $^4I_{9/2}$ with $^2D_{5/2}$. To place the structures that derive from these three coupling schemes relative to one another, we need to know the energies of $^4I_{11/2}$ above $^4I_{9/2}$ and $^2D_{5/2}$ above $^2D_{3/2}$. These two energy separations depend on ζ_f and ζ_d respectively. For the former, we can improve on the elementary approach,

which involves estimating ζ_f and then assuming perfect LS coupling in the core to find the energy gap between $^4I_{11/2}$ and $^4I_{9/2}$. Schuurmans et al.[3] have observed that for UII $5f^3$, $^4I_{11/2}$ lies 4421cm^{-1} above $^4I_{9/2}$; the hypothesis of an internal 5f shell allows us to assume that this figure also represents the corresponding energy separation for the core levels of UI $5f^36d$. At the same time, we automatically make some allowance for deviations from perfect LS coupling in the core; for it is known[31] that similar deviations in configurations of the type $4f^n$ have the effect of increasing the separation of the two lowest levels above the value that would be calculated on the assumption of perfect LS coupling.

The spacing between $^2D_{5/2}$ and $^2D_{3/2}$ is a little more difficult to estimate. It would be unrealistic to suppose that Eqs. (29) could be reliably extended to give

$$\zeta_d(\text{UI};\ 5f^36d) \quad = \quad \zeta_d(\text{CmI};\ 5f^76d),$$

since the atomic number changes by as much as 4 in going from U to Cm. However, we can be fairly sure that ζ_d for UI lies between the limits of 1430 and 2200, corresponding to ThIII and CmI respectively. The spacing between $^2D_{5/2}$ and $^2D_{3/2}$ is $5\zeta_d/2$, and for ζ_d of about 2000cm^{-1}, this spacing is very similar to the value of 4421cm^{-1} given above for the energy separation of the two lowest levels of the core. In the absence of more precise information, we assume that the energies

are not just similar, but actually identical; this makes the computational work slightly easier, and corresponds to a value of 1768cm^{-1} for ζ_d(UI; 5f^{3}6d). Levels for which J_2 = 4, 5, 6, and 7 occur in the coupling of $^4I_{11/2}$ to $^2D_{3/2}$ as well as in that of $^4I_{9/2}$ to $^2D_{5/2}$; the calculated energies are therefore the roots of quadratic equations.

The results of the calculation are given in Table VII and are drawn out in Fig.6. It can be seen that the theory accounts extremely well for the general grouping and overall pattern of the observed levels; the g values are reproduced reasonably well too. The most noticeable discrepancies occur for the two lowest levels for which J_2 = 4. The two levels at 7645.6 and 7326.1cm^{-1} possess J_2 values of 7 and 8; presumably they arise from the combined coupling of $^4I_{13/2}$ to $^2D_{3/2}$ and $^4I_{11/2}$ to $^2D_{5/2}$, just as the levels at 4275.7 and 3800.8cm^{-1}, with J_2 values of 6 and 7, arise from the combined coupling of $^4I_{11/2}$ to $^2D_{3/2}$ and $^4I_{9/2}$ to $^2D_{5/2}$, and lie much lower than their companions with smaller J_2.

It is not difficult to show that a model based on LS coupling gives a less satisfactory account of the experimental results. Within states of a given S and L, the replacement

$$\sum_i \xi(r_i)\, \underset{\sim}{s}_i \cdot \underset{\sim}{\ell}_i \rightarrow \lambda\, \underset{\sim}{S} \cdot \underset{\sim}{L}$$

is valid; the values of λ for all terms deriving from the core term ^4I of 5f^3 are given in Table VIII. It is now straightforward to calculate the multiplet splittings: their

centers of gravity are simply the term energies of $5f^3 6d$ in Table VI, corrected by including the factor Ω(UI). Taking Ω(UI) to be 0.5, and treating ζ_f and ζ_d as variable parameters, we soon find that it is impossible to get even a moderate agreement with experiment. The occurrence of a low-lying level for which $J_2 = 3$ is particularly difficult to understand on a model based on LS coupling, in contrast to the natural explanation it receives if the Jj coupling scheme is adopted. The latter model also gives better agreement with almost all the g values, a result that must be regarded as quite remarkable when it is recalled that the g values of atoms approximating to Jj (or jj) coupling are subject to first order corrections, whereas small deviations from perfect LS coupling produce no changes in the g values.

9. OTHER ACTINIDE ATOMS

The analysis of the previous section can be extended to other configurations of the type $f^n d$. The Coulomb energies of the terms deriving from the Hund term of the core have been calculated for n = 2, 4, 8, and 10 with the aid of Eqs. (17), (18), (19), and (20); the results are included in Table VI beside the analogous calculation for $f^3 d$. Since no spectroscopic analyses are yet available for PaI, NpI, BkI, or EI, the sums (12)

have been carried out only for j' and j" both equal to 3/2, with values of J_1 and J_3 appropriate to the lowest level of the ground multiplet of the core configuration. The results are given in Table IX; the corresponding results for UI $5f^3 6d$ are included for purposes of comparison. The calculations for PaI were performed in collaboration with Dr. J. Winocur, who has also considered the perturbing effects of other levels deriving from the core multiplet ^3H (see refs. 1 and 21).

A number of generalizations can be drawn from Table IX. For configurations $5f^n 6d$ with $n < 7$, the ordering of the levels is inverted with respect to J_2: that is, the energies of the levels increase as J_2 decreases. If $n > 7$, however, no special ordering can be discerned. It is interesting to notice that in the first case, the J_2 value of the lowest level agrees with that calculated on applying Hund's rule to the configuration $5f^n 6d$ as a whole; indeed, the expansion of the lowest Jj coupled state in terms of LS eigenfunctions reveals a very strong component corresponding to the Hund term. For example, for UI, we find

$$|\,^4I_{9/2},\ ^2D_{3/2},\ 6) = [2(34)^{\frac{1}{2}}/13]\,|\,^5L_6) + [(30)^{\frac{1}{2}}/13]\,|\,^3K_6) - \ldots$$
$$\ldots - [3(2)^{\frac{1}{2}}/1430]\,|\,^5G_6),$$

showing that over 80% of the Jj coupled state comprises $|\,^5L_6)$. In the second case, namely that for which $n > 7$, an analogous correspondence between the lowest Jj coupled state and that

deduced on the basis of Hund's rule no longer obtains. Thus for $5f^8 6d$, the Hund term is ^8H; if $3\zeta_f > 2\zeta_d$ (as seems virtually certain), the lowest level deriving from this term is $^8H_{17/2}$. However, no level for which $J_2 = 17/2$ appears under the column for BkI in Table IX. If $5f^8 6d$ turns out to be the ground configuration for BkI, we shall almost certainly be confronted with a situation where the ground level of a free atom cannot be correctly predicted from Hund's rule.

10. CONCLUSION

Although much of the foregoing has been taken up with discussing the advantages of the Jj coupling scheme, there should be no mistaking its essentially approximate character. Strictly, we have already abandoned it in the treatment of eight excited levels in UI $5f^3 6d$; for by including the interaction of the levels deriving from the coupling of $^4I_{9/2}$ to $^2D_{5/2}$ with those deriving from the coupling of $^4I_{11/2}$ to $^2D_{3/2}$, we force J_1 and j to lose their status as good quantum numbers.

A more complete calculation would take into account the interactions of all levels of the same value of J_2 deriving from the lowest core multiplet. For UI $5f^3 6d$, this would involve diagonalizing matrices as large as 8×8 (for $J_2 = 6$). Until such a program is undertaken, there appears to be no

virtue in adjusting the Slater integrals to improve what is already a satisfactory fit; for the neglected interactions are almost certainly large enough to render such adjustments meaningless.

A program of much greater magnitude is that of considering the entire configuration $5f^3 6d$; there are 42 terms for which $J_2 = 6$, and finding their energies involves diagonalizing a matrix with that many rows and columns. Even if this were done, a really excellent fit might still elude us. The ground level $^7M_6$ of the configuration $5f^3 6d^2 7s$ has been observed[2] to lie only $6249 cm^{-1}$ above the ground level of $5f^3 6d 7s^2$, and the interaction between these two configurations could be significant.

ACKNOWLEDGEMENTS

The initial impetus to analyze actinide spectra was provided by the atomic beam group at Berkeley; to the members of this team, and in particular to Professor W. A. Nierenberg, my thanks are due. I am also grateful to Dr. J. Blaise for allowing me to quote his experimental results on UI prior to publication.

Table I

g values

Atom	LS coupling		Jj coupling		
	Ground level	g	Ground level $(J_1, j)J_2$	g	Experimental g
PaI	$^4K_{11/2}$	0.769	(4, 3/2)11/2	0.800	0.8141±0.0004
UI	$^5L_6$	0.714	(9/2, 3/2)6	0.745	0.75
NpI	$^6L_{11/2}$	0.615	(4, 3/2)11/2	0.655	0.6551±0.0006
CmI	$^9D_2$	2.667	(7/2, 3/2)2	2.600	2.561±0.003

Table II

Parameters for PrIV $4f^2$

Parameter	Theory[a]	Expt.[b]
$F_2(4f, 4f)$	395.6	306.6
$F_4(4f, 4f)$	50.93	51.51
$F_6(4f, 4f)$	5.405	5.286

All values are in cm^{-1}

[a] E. C. Ridley, Proc.Cam.Phil.Soc. 56, 41 (1960).

[b] W. A. Runciman and B. G. Wybourne, J.Chem.Phys. 31, 1149 (1959)

Table III

Data for PuII $5f^6 7s$

Core levels	Energies of core levels	Energies of corresponding levels in PuI	J_2	$\epsilon(J_2) + 403$	Energies of observed levels	|g| Theory	|g| Expt.
$^7F_4$	7691						
$^7F_3$	6061	6144.2	5/2	7437	7498.5	1.34	1.304
			7/2	5718	5718.0	1.61	1.579
$^7F_2$	4281	4299.6	3/2	5527	5502.1	1.16	1.168
			5/2	4031	3969.9	1.69	1.670
$^7F_1$	2110	2203.6	1/2	3263	3235.8	0.13	0.304
			3/2	1990	2015.0	1.91	1.883
$^7F_0$	0	0.0	1/2	- 27	0.0	3.47	3.139

All energies are in cm^{-1}

Table IV

The Integrals $G^3(5f, 7s)$ (in cm^{-1})

Z	Atom	Configuration	$G^3(5f, 7s)$
89	AcII	5f7s	18690
90	ThIII	5f7s	5341
92	UII	$5f^4 7s$	2600
94	PuII	$5f^6 7s$	2240
95	AmII	$5f^7 7s$	2274

Table V

g values for CmI

J_2	g Theory	g Experiment
5	1.6672	1.671±0.003
4	1.7798	1.776±0.002
3	2.0030	2.000±0.003
2	2.5590	2.561±0.003

Table VI

Energies of low-lying terms of several configurations $5f^n6d$

(Slater integrals as for ThIII)

$5f^26d$		$5f^36d$		$5f^46d$		$5f^86d$		$5f^{10}6d$	
^2K	6702.3	^3L	4468.5	^4I	4040.4	^6P	4619.4	^4G	1409.8
^2F	3460.5	^3K	2764.5	^4K	3251.2	^6D	3819.2	^4H	463.1
^2G	3286.8	^3H	1843.6	^4L	2406.7	^6G	2293.1	^4I	- 843.9
^4F	1196.3	^3G	1757.3	^4G	82.7	^6F	- 2354.3	^4K	- 8346.7
^2I	788.4	^3I	- 937.9	^4H	- 146.7	^6H	- 3406.4	^4L	- 9663.7
^4H	- 2265.8	^5G	- 1739.7	^6H	- 3172.7	^8P	- 9169.2	^6G	- 14337.7
^4G	- 2460.4	^5H	- 2523.3	^6G	- 4746.3	^8H	-13253.0	^6H	- 14468.9
^2H	- 4090.5	^5I	- 4063.1	^6I	- 7565.8	^8F	- 15819.2	^6L	- 14528.6
^4I	- 6219.5	^5K	- 9796.7	^6K	-11125.6	^8D	- 16318.2	^6K	- 15596.6
^4K	- 7975.8	^5L	- 10636.7	^6L	- 13087.6	^8G	- 18568.0	^6I	- 16940.0

All values are in cm^{-1}

Table VII

Comparison between experiment and theory for UI

J_2	Energy (in cm^{-1})		g value	
	Theory	Expt.	Theory	Expt.
7	10222	10069.1	0.906	
4	8181		1.007	
6	7931	7005.5	0.898	0.97
2	7600		0.333	
5	7539	7864.1	0.969	
7		7645.6		
8		7326.1		
3	7504	7103.9	0.648	
4	7308	5991.3	0.781	0.86
5	6285	5762.0	0.839	0.82
6	4330	4275.7	0.921	0.93
3	4119	3868.4	0.700	
7	3711	3800.8	0.920	0.91
4	3510	4453.4	0.725	0.66
5	818	620.3	0.738	0.73
6	0	0.0	0.745	0.75

Table VIII

Spin-orbit parameters λ for UI

Term	λ
^3G	$(35\zeta_f + 6\zeta_d)/60$
^5G	$(7\zeta_f - 2\zeta_d)/20$
^3H	$(55\zeta_f + 3\zeta_d)/120$
^5H	$(11\zeta_f - \zeta_d)/40$
^3I	$(65\zeta_f - 3\zeta_d)/168$
^5I	$(13\zeta_f + \zeta_d)/56$
^3K	$5(23\zeta_f - 3\zeta_d)/336$
^5K	$(23\zeta_f + 5\zeta_d)/112$
^3L	$(5\zeta_f - \zeta_d)/16$
^5L	$(3\zeta_f + \zeta_d)/16$

Table IX

Energies of low-lying levels in several actinide atoms

Atom and configuration	PaI $5f^2 6d$		UI $5f^3 6d$		NpI $5f^4 6d$		BkI $5f^8 6d$		EI $5f^{10} 6d$	
Assumed Ω	0.6		0.5		0.45		0.3		0.3	
Energies of levels with specified J (in cm^{-1})	5/2	4657	3	4119	5/2	3794	15/2	1459	15/2	394
	7/2	4031	4	3510	7/2	2743	13/2	1103	19/2	350
	9/2	699	5	818	9/2	1899	9/2	364	13/2	70
	11/2	0	6	0	11/2	0	11/2	0	17/2	0

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Captions to figures

Fig. 1. Schematic representation of the energy levels for f^4d in Jj coupling. In the absence of any interaction between the core and the d electron, the combined energy level system can be found by superposing the multiplet comprising the levels $^2D_{3/2}$ and $^2D_{5/2}$ on every level of the core. When the interaction is included, the degeneracy is lifted, as shown on the far right.

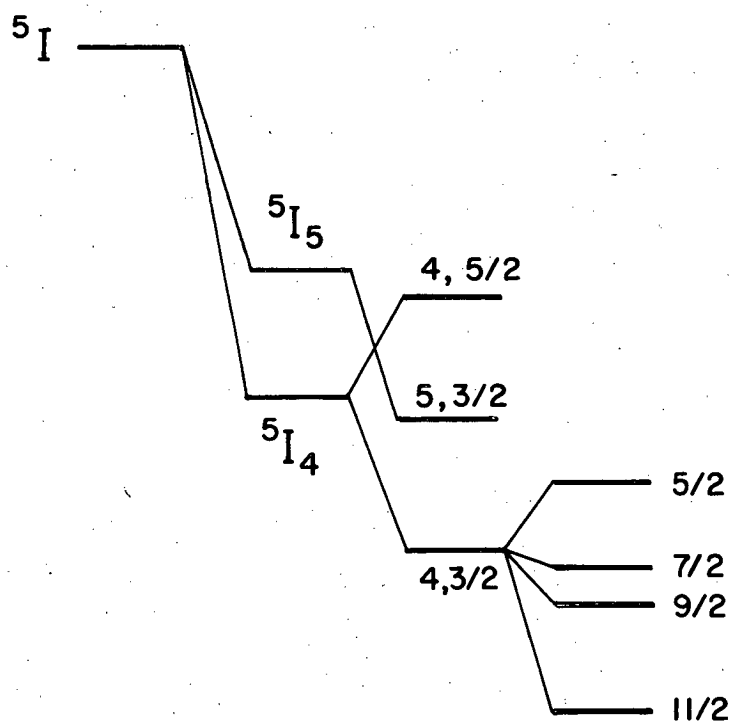
Fig. 2. The coupling diagram for D_k.

Fig. 3. The coupling diagram for E_k.

Fig . 4. Levels of the configuration f^4s that derive from the core multiplet ^5I. The Jj limit is on the left, the LS limit on the right.

Fig. 5. On adding a d electron to the term ^8S, the two terms ^9D and ^7D are formed. This LS coupled scheme is shown on the left. If, on the other hand, the ^8S term is regarded as a level with $J_1 = 7/2$, and the orbital angular momentum of the d electron is coupled to its spin to give $j = 3/2$ and $5/2$, the energy level scheme on the right is obtained.

Fig. 6. Levels of UI: a comparison between theory and experiment.



Schematic arrangement of Energy Levels in J j coupling

MU-23509

Fig. 1

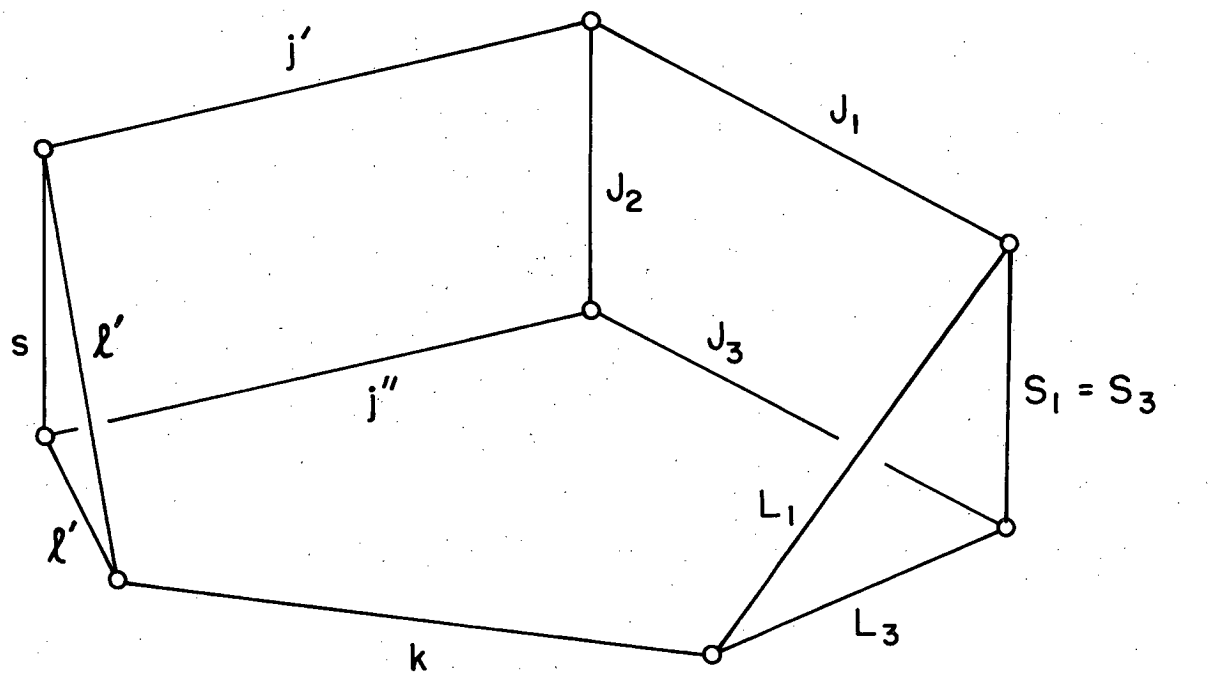


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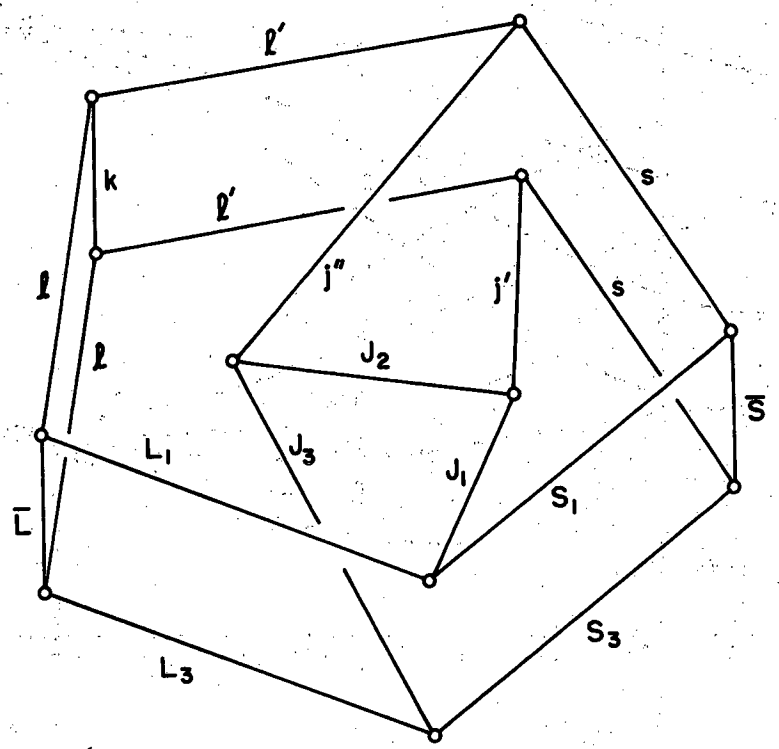
Fig. 2



MU-24160

Fig. 3

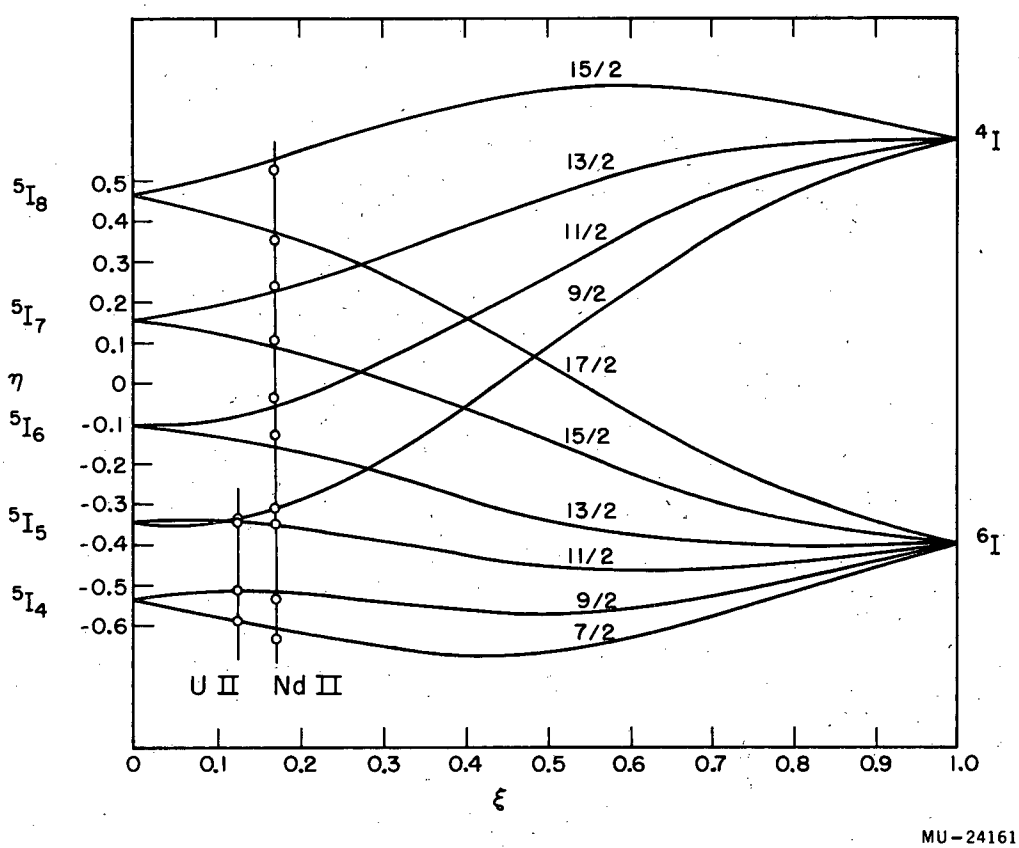

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Fig. 4

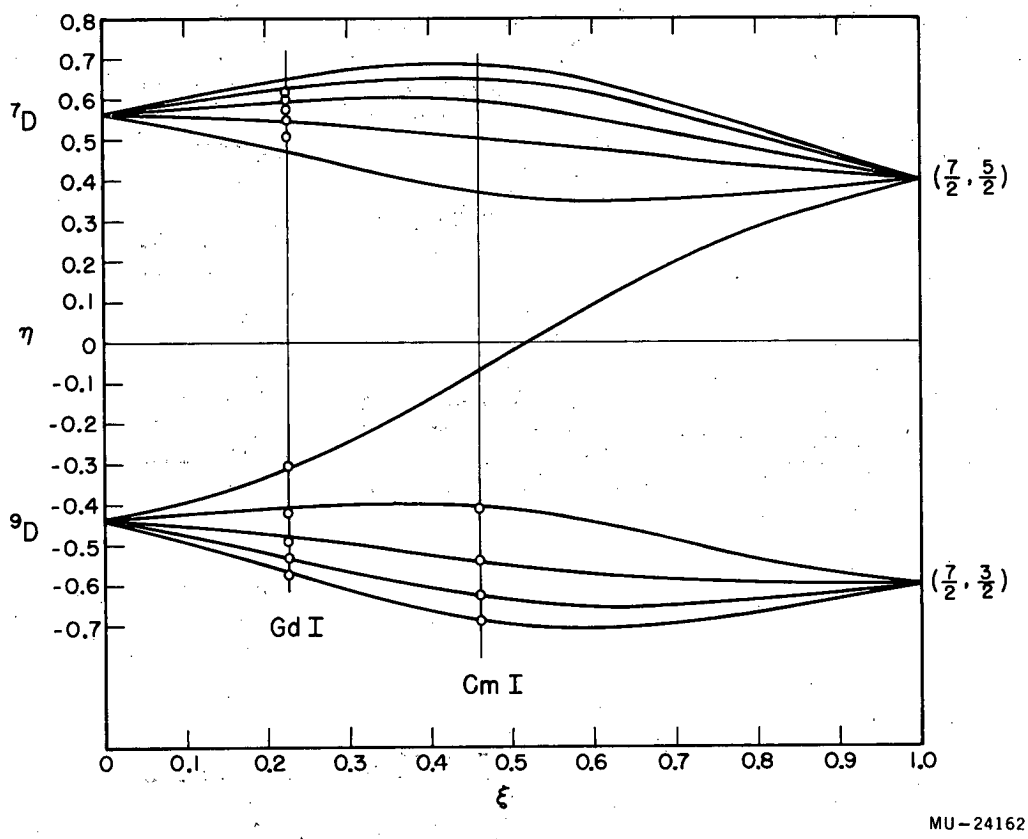
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Fig. 5

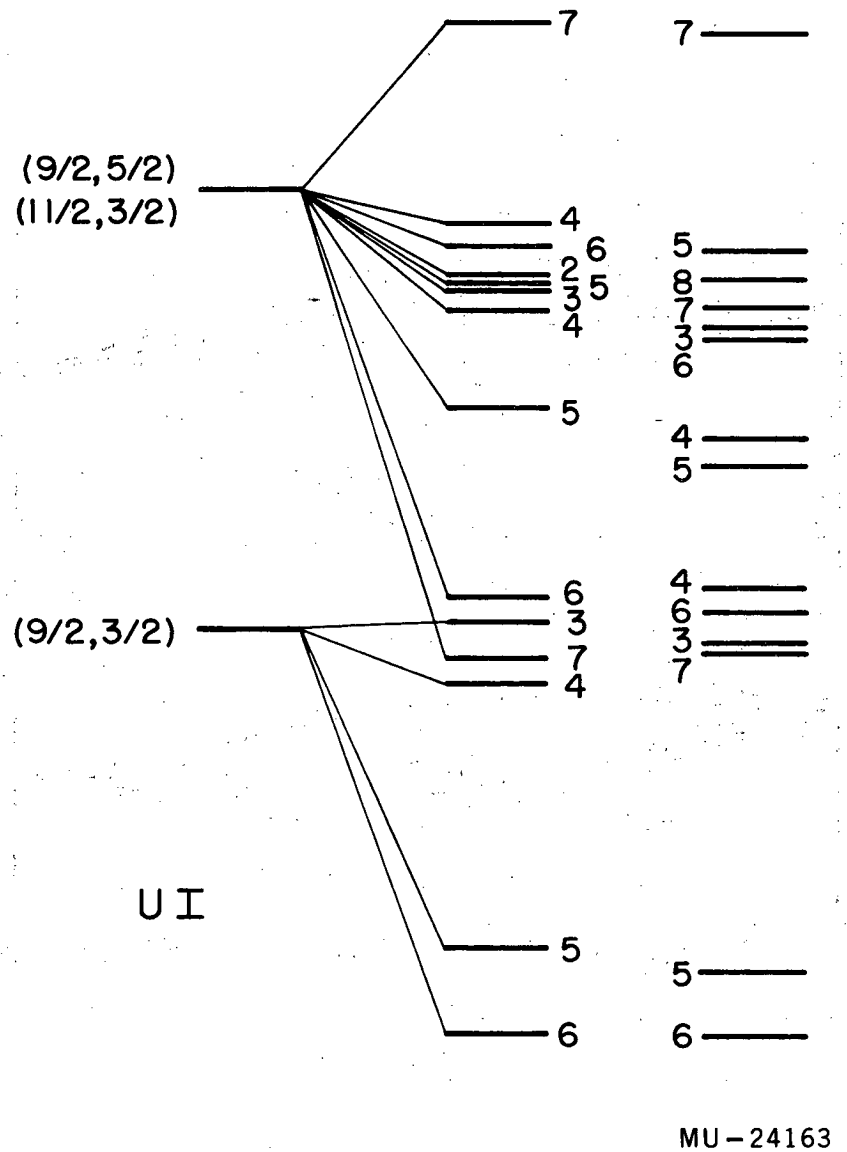
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Fig. 6

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